A feasibility study in the use of domestic water treatment residuals to remove phosphorus from wastewater

By

Ben Gersten

BEng (Hons) MSc

This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD)

School of Engineering, Cardiff University
Cardiff, Wales, UK

2017

DECLARATION

This work has not been submitted in substance for any other degree or award at this or any other university or place of learning, nor is being submitted concurrently in candidature for any degree or other award.

Signed .... (candidate) Date 14/07/17..................

STATEMENT 1

This thesis is being submitted in partial fulfillment of the requirements for the degree of PhD (insert MCh, MD, MPhil, PhD etc, as appropriate)

Signed .... (candidate) Date 14/07/17..................

STATEMENT 2

This thesis is the result of my own independent work/investigation, except where otherwise stated, and the thesis has not been edited by a third party beyond what is permitted by Cardiff University's Policy on the Use of Third Party Editors by Research Degree Students. Other sources are acknowledged by explicit references. The views expressed are my own.

Signed .... (candidate) Date 14/07/17..................

STATEMENT 3

I hereby give consent for my thesis, if accepted, to be available online in the University's Open Access repository and for inter-library loan, and for the title and summary to be made available to outside organisations.

Signed .... (candidate) Date 14/07/17..................

STATEMENT 4: PREVIOUSLY APPROVED BAR ON ACCESS

I hereby give consent for my thesis, if accepted, to be available online in the University's Open Access repository and for inter-library loans **after expiry of a bar on access previously approved by the Academic Standards & Quality Committee.**

Signed .... (candidate) Date 14/07/17..................

ABSTRACT

There is growing evidence that even low levels of phosphorus ($<0.1mgL^{-1}$) entering natural water systems can cause eutrophication. Waste water treatment plants discharge over 23kT of phosphorus into UK surface waters per year. The Water Framework Directive requires that this be greatly reduced. Although many processes have been developed, they are often complex and energy intensive. This thesis aimed to assess how a novel process using dewatered water treatment works residuals (DWTR) could be engineered to maximize phosphorus removal from waste water treatment plant effluents while minimising system complexity and energy use.

An extensive yearlong experiment was operated at two sites to investigate how phosphorus removal rates varied over time in relation to DWTR type, phosphorus concentration, hydraulic retention time (HRT) and scale. DWTR from eight different water treatment works were used in 35 experimental models of dimensions 0.1Ø x 1m and two meso scale beds 1x1x0.8m.

The most significant factors effecting P removal rate were found to be DWTR type and media particle size. Total P removal varied between 58-95% for the 8 different DWTR over the year. Increasing particle size from 0.6-2 to 6-20mm reduced P adsorption capacity by 30% on average with 6 hours HRT and $5mgL^{-1}$ TP input.

The key physical and chemical properties of the DWTR were measured to assess the effect of the parameters on the P removal ability of the media. No significant relationship ($p<0.05$) between the amount of Al, Fe, Ca or Mg in the media and its P removal ability were found.

An idealised adsorption system using DWTR as the media would operate with 2 to 3 beds in series with a minimum HRT of 6 hours and maximum particle size of 6mm and depth of 1m. Computer models of such a system predict >95% TP removal for over two years of operation.

Acknowledgements

Firstly I would like to thank all the people who helped me with the practical stuff. Jeff Rowlands and Marko Santonasaso in the CLEER Labs who analysed over 2000 samples for me. Steffan Jones and Harry Lane in the Civils labs who could not have been more helpful when I was building my experimental rigs and Richard Rogers in the electronics lab who designed, made and soldered a lot of PCBs' for me.

All the staff in the postgraduate office and the staff in the finance office who were always incredibly helpful and kind.

I would like to thank Dr Akin Babatunde for all the great papers he published which a lot of the work in this thesis is based upon; Northumbrian Water and Cardiff University for funding my PhD and allowing access to their sites and providing lots of useful information; Dr Bettina Bockelmann-Evans for reading my thesis and providing some really useful feedback.

A huge thanks must go to my parents in law who let me set up my experimental rigs on their land, and let me install a complex control system in their garage. They also gave me access to all the lovely stuff they and their neighbours flush down the toilet!

And of course I need to thank my beautiful partner Barbara who always told me how well I was doing when we both really knew that wasn't true, and for the hours of time she has spent reading my work.

Lastly, I want to thank my gorgeous black dog Lyra who took me for many long and thought provoking walks in the beautiful Black mountains where I live. Things always seem to make so much more sense when you have been for a long walk.

Table of Contents

Chapter 6 Further chemical results from the column and meso scale experiments..184

Nomenclature

A = Area
C_e = Equilibrium concentration of adsorbate in solution
C_0 = Initial concentration of P in solution
C_t = Concentration of P in solution at time t
e = Voids ratio
H = Height (hydraulic head difference)
K = Hydraulic Conductivity
K_L = Langmuir constant (L mg^{-1})
K_F = Freundlich constant (mg $^{1-1/n}$L $^{1/n}$ g^{-1})
K_H = Henrys Law constant
k_1 = First order rate constant (min^{-1})
k_2 = Second order rate constant
k_p = Intraparticle rate constant
L = Length
m_m = Mass of media
n = Freundlich heterogeneity factor,
NSD = Normalised Standard deviation
P_s = Particle size
q_{ad} = Mass of P adsorbed per cycle per mass of media
q_e = Amount of solute adsorbed on the adsorbent at equilibrium.
q_{in} = Mass of P input to the system per mass of media
q_m = Maximum monolayer adsorption capacity
q_t = Amount of solute adsorbed on the adsorbent at time (t)
S_r = Degree of saturation (%)
SSE = Sum of the square of the errors
V = Volume
W_a = Weight of EGME retained by sample
W_s = Weight of soil added
w = Water content expressed as a percentage
ρ = Bulk density

ρ_D = Dry density

ρ_S = Particle density

ρ_{sat} = Saturated density

ρ_w = Density of water (assumed 1g cm^{-3})

$\%P_{rem}$ = Average percentage of P removed

Abbreviations

BOD	Biological Oxygen Demand
BOF	Basic Oxygen Furnace Steel Slag
BPR	Biological Phosphorus Removal
COD	Chemical Oxygen Demand
DOP	Dissolved Organic Phosphorus
DWTR	Domestic Water Treatment Residuals
Al-DWTR	Domestic Water Treatment Residuals with Alum as coagulant
Fe-DWTR	Domestic water Treatment Residual with Ferric as coagulant
EBCT	Empty Bed Contact Time
EGME	Ethylene Glycol Monomethyl Ether
GHG	Green House Gas
GUI	Graphical User Interface
HC	Hydraulic conductivity
HLR	Hydraulic Loading Rate
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
MTZ	Mass Transfer Zone
NOM	Natural Organic Matter
OC	Organic Carbon
P	Phosphorus
PAO	Phosphorus Accumulating Organism
p.e.	Population Equivalent
PFO	Pseudo-first-order equation
PP	Particulate Phosphorus
PSO	Pseudo-second-order equation
RWW	Real Waste Water
SWW	Synthetic Waste water
SRP	Soluble Reactive Phosphorus
SSA	Specific Surface Area
SS	Suspended solids
STP	Soluble Total Phosphorus
SOP	Soluble Organic Phosphorus

TC	Total Carbon
TSS	Total suspended solids
TP	Total Phosphorus
TDP	Total Dissolved Phosphorus
TDP(ICP)	Total Dissolved Phosphorus(measured with ICP)
WFD	Water Framework Directive
WWTW	Waste Water Treatment Works

Chapter 1. Introduction

‘Life can multiply until all the phosphorus has gone and then there is an inexorable halt which nothing can prevent…..We may be able to substitute nuclear power for coal power, and plastics for wood, and yeast for meat and friendliness for isolation-but for phosphorus there is neither substitute nor replacement’ (Asimov, 1975, Emsley, 2001) .

The words above written by Isaac Asimov in 1975 were quite prophetic, as the way humanity uses its finite resource of phosphorus has only come to the fore in the last 20 years. Not only is phosphorus being consumed in an unsustainable way (Neset and Cordell, 2012), but as with many other of our natural resources the careless and inefficient way it is used results in much of the carefully mined and processed phosphorus simply being lost into the environment. Once in the biosphere it disrupts the natural balance often with devastating results (Smith et al., 1999).

Phosphorus is critical to all living things as it is a key structural component of DNA and RNA. Phosphorus must be present in soil to allow plants to grow. Phosphorus is also used in large quantities by many industries, particularly in the water industry for plumbosolvency control and in cleaning products for use in washing machines and dishwashers. There is no known chemical or technological substitute for phosphorus in either natural ecosystems or in the agro-ecosystem that produce food and commodities (Childers et al., 2011).

Over 20 000 tonnes of phosphorus is thought to be passing straight through the UK’s water treatment systems and entering directly into rivers and the sea (Cooper and Carliell-Marquet, 2013). This phosphorus is not only lost to humanity for millions of years but causes eutrophication before it finally settles to the bottom of the ocean (Smil, 2000). Legislation and environmental pressure is forcing the water companies to try to capture more of this phosphorus as it passes through their treatment works (Mainstone et al., 2000).

The removal of phosphorus from waste water presents many technical challenges, especially as energy and resource use become a more critical component of the treatment process (Neethling et al., 2011, Shaw et al., 2011). The 'holy grail' of phosphorus removal would be a process that completely removes phosphorus from waste water while using minimal amounts of energy and resources (chemicals, materials, process plant and labour); linked with a cost effective method to recycle and reuse the captured phosphorus.

The use of domestic water treatment residuals (DWTR) to remove phosphorus may not represent the Holy Grail of a phosphorus removal process, but it has the potential to offer a low energy and chemical free way of removing phosphorus from waste water.

Although the use of DWTR to remove phosphorus from waste water has been researched for over twenty years (Dharmappa et al., 1997, Huang and Chiswell, 2000), it has still never been used in any large scale system. This may be because there are still many gaps in our understanding of how a DWTR system could be constructed and operated successfully. There has been very little research on how the production processes of DWTR may affect its ability to remove phosphorus and there is still much debate as to the key chemical and physical properties of the media that allow it to remove phosphorus. There has been almost no research undertaken on optimising hydraulic retention time or analysis of how the kinetics of removal change over the long term. The majority of studies undertaken have used synthetic waste water with very small amounts of DWTR. Using real waste water and larger scale systems will inevitably change how much phosphorus the DWTR can remove.

These identified gaps in the knowledge led to the key aims and objectives for this PhD.

Thesis Aims

The aim of this research was to deliver engineering design advice to enable the construction of a novel chemical-free and sustainable water treatment process capable of reducing phosphorus levels in waste water streams to discharge levels required by the statutory authorities. The process should utilise unadulterated domestic water treatment residuals (DWTR) generated in water treatment processing as a media for achieving this goal. The finished process should have as small an energy demand, maintenance requirement and footprint as possible.

The objectives to achieve this aim were

- To design and conduct experiments to assess the key variables that effect the performance of DWTR, in relation to phosphorus removal from waste water; retention time, inlet concentration, media type, scale and the effect of real waste water.
- To determine if any of the key chemical and biological parameters in the waste water affected phosphorus removal.
- To determine if DWTR leaches Fe or Al in quantities that could be toxic to the aquatic environment.
- To determine if any key operational parameters in the production of DWTR effect their ability to remove phosphorus. For example does high polymer dose result in DWTR that can reduce phosphorus more effectively?
- To provide design and operational information about how a phosphorus removal system using DWTR could be constructed to enable the scaling up of the system.

1.1 Structure of this thesis

This thesis has been split into 10 chapters.

Chapter 2 is a literature review which discusses how phosphorus cycles through the biosphere including the quantity and nature of the phosphorus that reaches water treatment works. The main processes currently used to remove phosphorus in treatment works and possible future processes. The majority of the review explores the history and use of DWTR to remove phosphorus and the relevant theory which has been used to assess the phosphorus removal pathways. The chapter finishes with a discussion on life cycle analysis that has been undertaken on current and future phosphorus removal pathways.

Chapter 3 outlines the more specific aims and objectives of the experimental work and details the materials and methods.

Chapter 4 assess the physical and chemical properties of the media. Experimental data from the raw water feeds into the 8 treatment works is presented. The type and quantities of chemicals dosed in the production of DWTR and the way the media is dewatered is also explored. The results from this section are used in Chapter 9 to try and find correlations between phosphorus removal and the physio chemical properties of the media.

Chapter 5 investigates how well all the experimental systems removed phosphorus. The results enabled observations and comparisons between:

- the 8 DWTR tested,
- 8 different hydraulic loading regimes
- three different phosphorus inlet concentrations
- real waste water and synthetic,
- column and meso scale

Chapter 6 investigates the other chemical and biological parameters that were monitored to show if phosphorus removal was mediated or assisted by other chemical or biological processes operating in the system, and to make sure that the DWTR was not leaching any chemicals that were toxic to the environment.

Chapter 7 details the results from the hydraulic conductivity analysis that was undertaken on the operational columns. The efficiency of the real waste water systems at removing the suspended solids is also assessed.

Chapter 8 details ancillary experimental work that was undertaken on how phosphorus removal is affected by particle size and presents results and analysis on how the kinetic removal of phosphorus by DWTR changed over the course of the year.

Chapter 9, the discussion, brings together all the findings and tries to synthesise it to inform our knowledge and understanding of the use of DWTR for phosphorus removal. It uses this to provide engineering design recommendations for the practical application of DWTR in a full scale phosphorus removal system.

Chapter 10 the conclusion provides a summary of the main research findings, and highlights areas that need further work.

Chapter 2 Literature review

2.1 Introduction

This chapter discusses how phosphorus (P) is cycled throughout the Earth, why it is needed by animals, plants and industry, and how excessive and inefficient use of phosphorus is causing problems to many eco systems.

Although phosphorus reaches water courses through both point and diffuse sources this review concentrates on technologies that can reduce the phosphorus outlet concentration of point sources produced by waste water treatment plants.

Many processes are currently in use to remove phosphorus at water treatment works and many new technologies are either at pilot or laboratory scale. This review provides a brief summary of the performance and processes involved in these technologies and the legislative drivers which are forcing their introduction. The current study focusses on the use of domestic water treatment residuals (DWTR) in an adsorption based removal process, and thus a more detailed description of adsorption theory and operation is discussed with particular reference to previous research on the use DWTR to remove phosphorus.

This chapter concludes with a brief summary of technologies that can be used to reduce phosphorus to very low levels and the possible environmental impacts that the phosphorus removal processes themselves may cause.

2.2 Phosphorus in the natural environment

2.2.1 The need for Phosphorus

Phosphorus is critical to all living things as it is a key structural component of DNA and RNA. The synthesis of all complex molecules of life is powered by energy released by the phosphate bond reversibly moving between adenosine diphosphate (ADP) and adenosine triphosphate (ATP). In the human body approximately 40kg of ATP are produced and reused each day (Valsami-Jones, 2004). Phosphorus is also vital for the production of bones and teeth in all vertebrates. Roughly 20% of the human skeleton and teeth are made of calcium phosphate, and the average human body contains about 650grams of phosphorus (Childers et al., 2011). Phosphorus must be present in soil to allow plants to grow. Phosphorus in plants increases their response to the uptake of nitrogen and potassium. This improves the rate of biofixation and maintains higher levels of soil organic matter, which in turn improves the water holding capacity of soils and reduces erosion (Smil, 2000).

Phosphorus is also used in large quantities by many industries, particularly in the water industry for plumbosolvency control and in cleaning products for use in washing machines and dishwashers (Environment Agency, 2012) .

There is no known chemical or technological substitute for phosphorus in either natural ecosystems or in the agro-ecosystem that produce food and commodities (Childers et al., 2011).

2.2.2 The phosphorus cycle, and the history and politics of phosphorus

Phosphorus is the 11th most common element found in the lithosphere, containing around 5-10 x 10^8 million tonnes (Scholz and Wellmer, 2013). However, only a tiny amount of this phosphorus is available to life at the earth's surface as most sedimentary rocks contain very small concentrations of phosphorus, typically 0.1%, and this phosphorus is present in poorly soluble forms (Cooper et al., 2011). Around 95% of phosphorus is found as a calcium phosphate mineral, known as Apatite. This Apatite is steadily eroded by the rain and wind which feeds phosphorus to the biosphere, where it is recycled through different life forms on land and in the ocean (Smil, 2000).

On timescales of a 1000 years or so, the natural phosphorus cycle is basically a one way flow, with minor adsorption of a small fraction of the element by the biota. Weathering, erosion, mineralisation and runoff transfer soluble and particulate phosphorus to the ocean where it eventually sinks into the sediments. Recycling of these sediments depends on the slow reshaping of the Earth's crust due to tectonic uplift. The phosphorus cycle is complete after a period of ten to a hundred million years as the phosphorus containing rocks are re-exposed to the surface (Ruttenberg, 2003). This very slow recycling of phosphorus through the lithosphere make phosphorus a non–renewable resource on human time scales.

In contrast, to the incredibly slow recycling of phosphorus in the lithosphere, the secondary land and water based cycling of phosphorus has a rapid turnover in periods of weeks and months (Emsley, 2001). Plants take in dissolved inorganic phosphorus and convert it to organic phosphorus as it becomes part of their tissue. Animals get the phosphorus they need by eating either plants, other animals or decomposing plant and animal material. As plants and animals excrete waste or die, the organic phosphorus they contain is converted back to inorganic phosphorus by bacterial decomposition. The inorganic phosphorus is either taken up by plant roots on land or returned to the water column. When the bottom sediment is stirred up by animals, human activity, chemical interactions or water currents, the phosphorus cycle begins again. The recycling of phosphorus has to be efficient for life to be sustained as any phosphorus that is lost can only be naturally replaced by the slow weathering of phosphorus bearing rocks (Smil, 2000).

Historically phosphorus was supplied for crop production in manure, human excreta, bone meal and to some extent through guano. During the 19thcentury, in the wake of industrialisation and population growth agricultural soils grew steadily less productive partly due to lack of phosphorus. If the commercial manufacturing process for phosphoric fertilizer had not been discovered in the 1840's life in industrialised countries would have become unstable due to a shortage of food (Dawson and Hilton, 2011).

The large scale production of phosphorus based fertilizer depends on the availability of rock with a high percentage of phosphorus known as phosphorites which typically contain between 10 and 20% phosphorus. These occur rarely over the earth's surface and much of this rock is inaccessible under the sea. However, there are a few places on the earth's crust where it is easily accessible on the surface or in mines (Cooper et al., 2011). This has already caused political problems. During the 2008 food crisis, fertiliser prices soared and the commodity price of phosphate rock increased by 800% over a period of 18 months Figure 2.1.

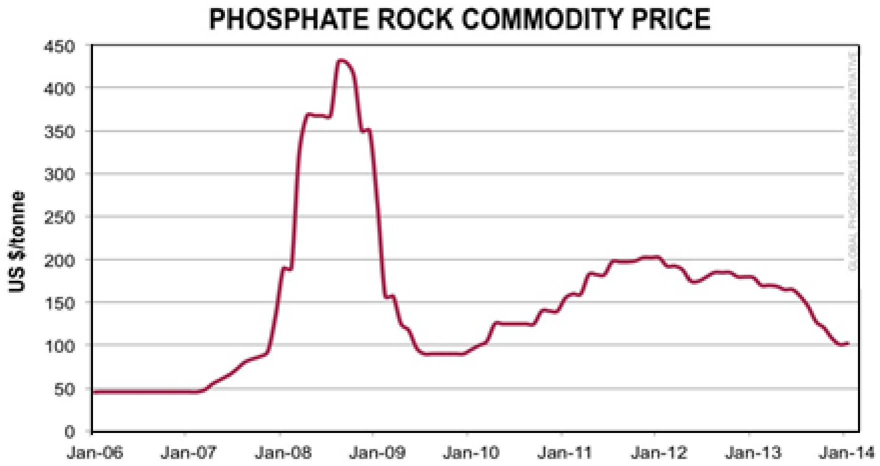


Figure 2.1 Price of phosphate rock Jan 2006 to Jan 2014
(phosphorusfutures.net, 2016)

There have been many papers written about the looming shortage of phosphorus rock, some predicting that we will reach peak phosphorus availability by 2030 (Cordell et al., 2011, Cordell, 2013). However, this has been rebutted by many other authors and by the phosphorus mining industry itself (Scholz and Wellmer, 2013). The U.S Geological Survey now estimate that there is enough phosphate rock to last around 370 years at current extraction rates (Jasinski, 2014). Nevertheless, there is little doubt that unless further large sources of phosphorus rock are discovered by 2050 over 80% of the world's phosphorus will be in Morocco (Cooper et al., 2011).

2.2.3 Phosphorus as a pollutant

On a world wide scale the current use of the mined phosphorus rock is very wasteful. While approximately 19 Mta^{-1} of phosphorus is mined specifically for food production, only a fifth of this actually reaches the food consumed by the global population (Cordell et al., 2011). The rest is lost to the environment causing pollution.

To show how phosphorus is consumed and wasted in the UK Cooper et al (2013) undertook a detailed substance flow analysis of phosphorus. The results provide a clear picture of how much phosphorus is imported, exported and ‘lost’ from the UK (Figure 2.2 and 2.3)

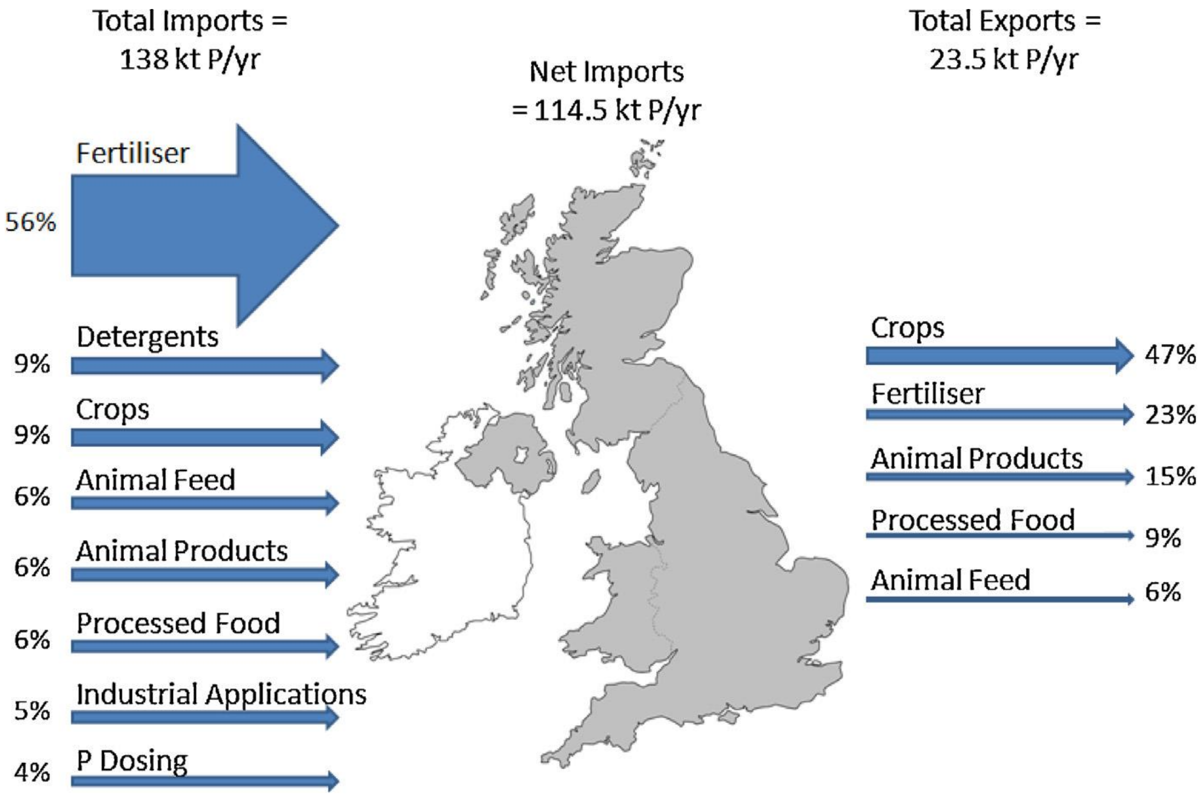


Figure 2.2 Phosphorus imports and exports in the UK(Cooper and Carliell-Marquet, 2013)

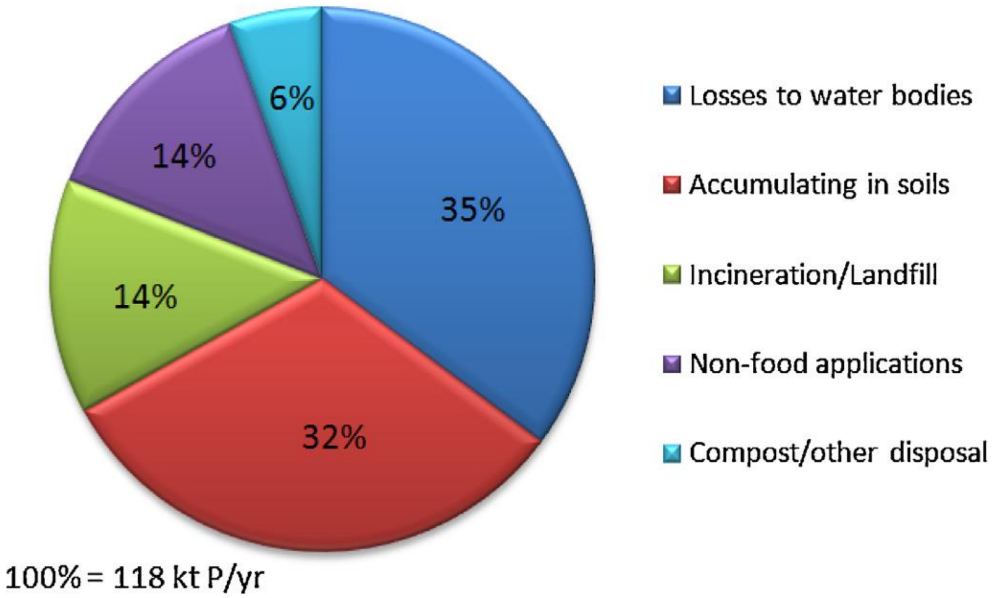


Figure 2.3 Accumulation and Losses of P imported to UK(Cooper and Carliell-Marquet, 2013)

For life to flourish there is an optimum ratio of carbon, nitrogen and phosphorus known as the Redfield ratio C:N:P = 106:16:1 on a molar ratio, (or 41:7:1 by mass) (Kadlec and Wallace, 2008, Correll, 1998). When any one of these elements is below the required quantity, plant growth is severely limited, this is known as Liebig's Law of the minimum (Smith et al., 1999). Since carbon and nitrogen are both readily available from the atmosphere, and phosphorus can only be obtained from the slow erosion of phosphate containing rock, it is very often the limiting nutrient in natural terrestrial and freshwater systems (Smil, 2000). The 35% loss of phosphorus to UK water bodies shown in Figure 2.3 represents approximately 41.5ktP yr^{-1} entering UK water bodies. This huge increase in phosphorus input to our water bodies greatly unbalances the natural order and causes plants and bacteria to grow in abundance in that water; this process is known as eutrophication.

Eutrophication is defined by the Environmental agency as:

"The enrichment of water by nutrients, stimulating an array of symptomatic changes including increased production of algae and/or higher plants, which can adversely affect the diversity of the biological system, the quality of the water and the uses to which the water may be put"

(Environment Agency., 2000)

"*Although the role of phosphorus cannot be unequivocally proven to be the main cause of eutrophication in our lakes, rivers and estuaries, without holding all other influencing factors constant. There is clear evidence that the impact of adding phosphorus to the natural environment is the most important underlying change upon which other anthropogenic factors can be superimposed*" (Mainstone and Parr, 2002).

Evidence of improvements to higher plant communities once phosphorus has been removed from effluents is building steadily, with some notable success stories in America and Italy (Smith et al., 1999).

2.2.4 Phosphorus in waste water in the UK.

Although much of the phosphorus entering the riverine system is running directly off the land and into rivers, due to excess and inappropriate fertiliser use; significant proportion comes from point sources primarily from waste water treatment works (WWTW)(Sharpley et al., 2013). There is evidence that point sources are responsible for a far greater proportion of river eutrophication than non-point sources (Jarvie et al., 2006). Cooper et al (2013) estimate that approximately 55kt Pyr^{-1} enter WWTW of which very close to 50% pass straight through without being treated. Figure 2.4a shows the relative amounts of imported phosphorus which end up at WWTW and how much of it is treated. Figure 2.4b further details how the phosphorus captured at WWTW is disposed of.

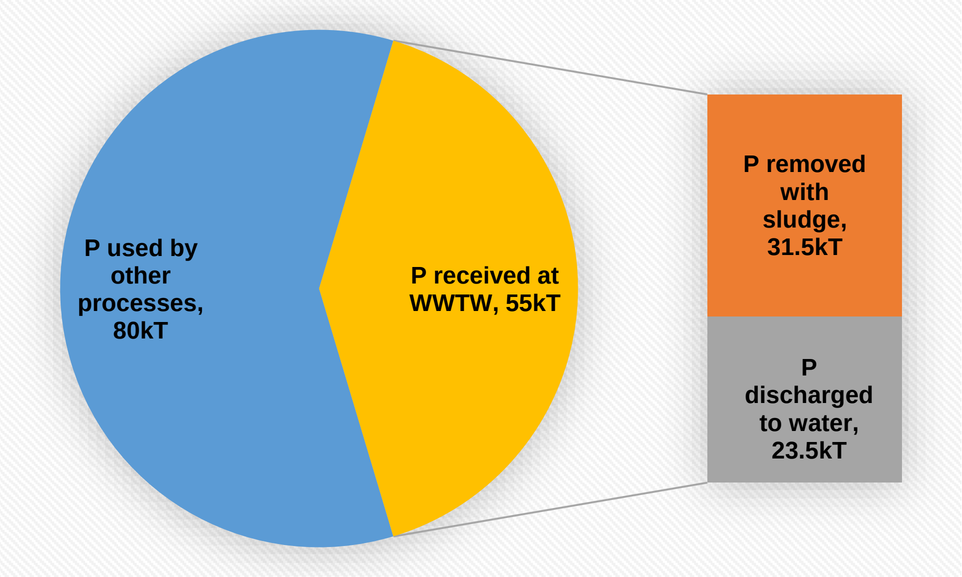


Figure 2.4a Relative amounts of imported phosphorus which end up at WWTW. Total P imported to UK 135kT

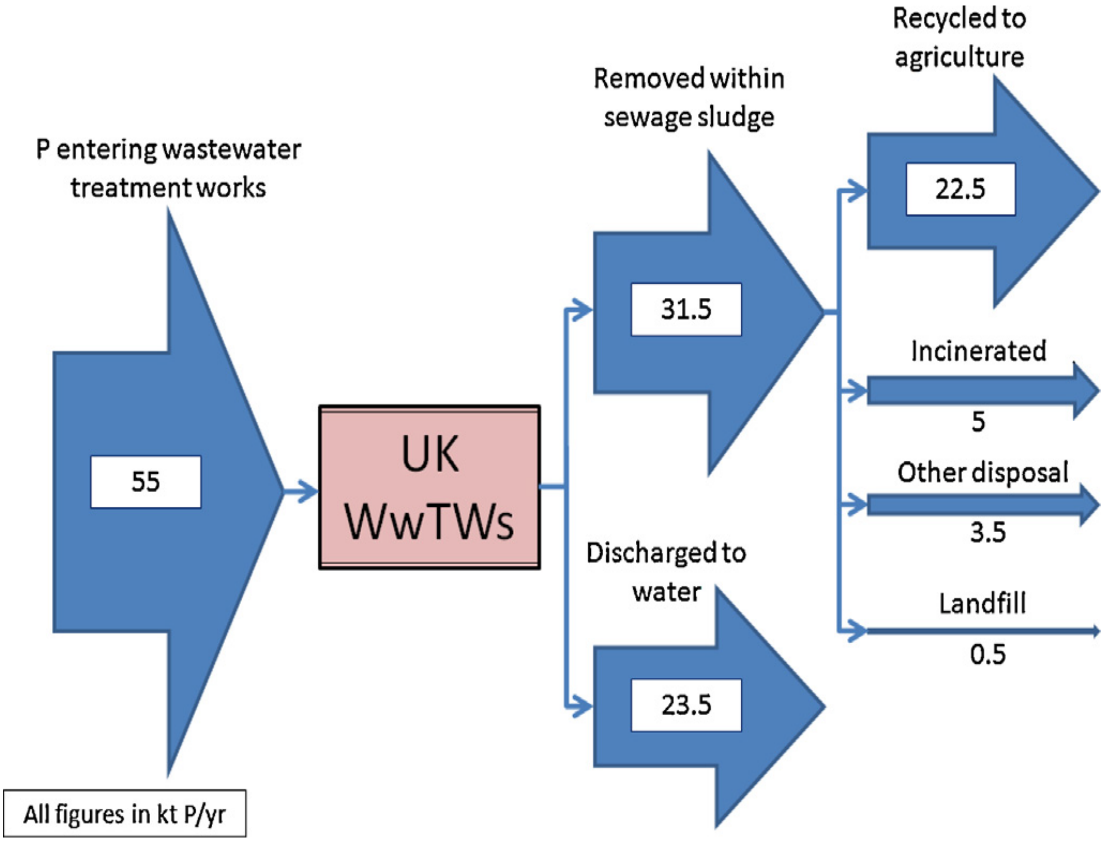


Figure 2.4b Quantities of P entering UK WWTW (Cooper and Carliell-Marquet, 2013)

The concentration of phosphorus in sewage entering waste water treatment works (WWTW) ranges from 3.7 to 11mgL^{-1} total phosphorus (TP), 2.1-6.3mgL^{-1}

organic phosphorus and 1.6-4.7mgL^{-1} inorganic phosphorus (Metcalf et al., 2014)[Note these are American values]. The United Kingdom Water Industry Research limited (UKWIR) estimate that 50kT of phosphorus a year are being received at UK WWTW (UKWIR, 2008) which is in close agreement with that found by Cooper et al (2013). Phosphorus arrives at WWTW in many forms and comes from many variable sources. A breakdown of the sources of phosphorus arriving at UK WWTW is shown in Figure 2.5.

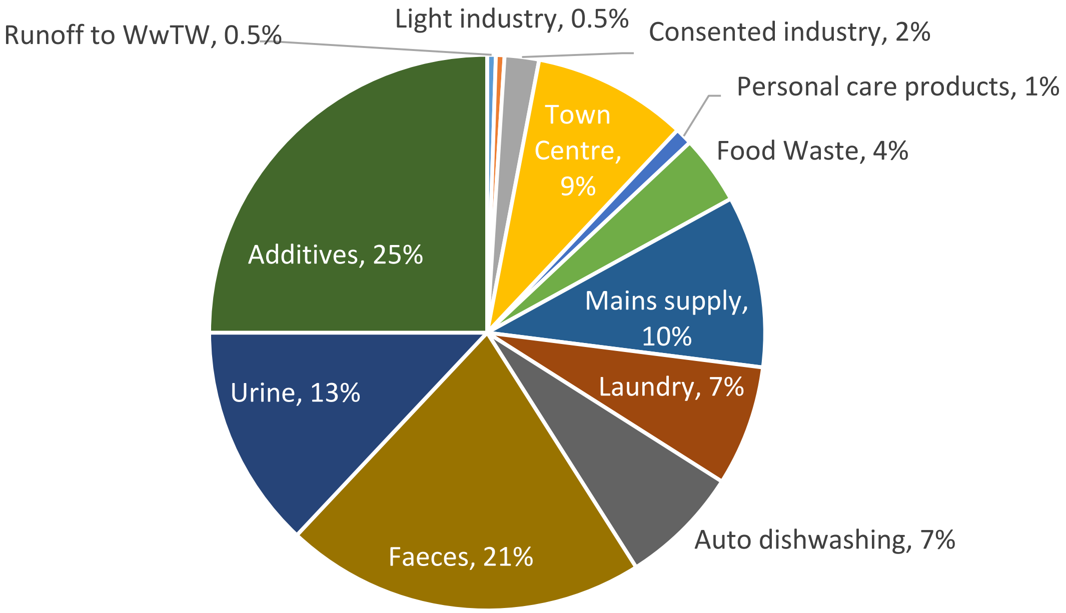


Figure 2.5 Proportion of Phosphorus Sources arriving at WWTW (UKWIR, 2008)

Inputs to WWTW are dominated by the human diet and approximately 59% of the total phosphorus load (i.e. additives, urine and faeces) arrive from this route (Environment Agency, 2012). The majority of phosphorus that we eat simply passes straight through our bodies, typically an individual excretes between 1.5-4.5g of phosphorus/day (Metcalf et al., 2014). It is interesting to note that many phosphorous food additives are present for aesthetic reasons particularly in processed meats, rather than for any health benefits (Uribarri and Calvo, 2003).

Drinking water is typically dosed with 1 to 2 mgL^{-1} of phosphorus to limit the amount of lead solubilised in older plumbing. This enables the water companies to comply with the standard of 10µg/l of lead in drinking water. Phosphorus dosing has been shown to be very cost effective compared with replacing lead piping and is unlikely to change unless the Water Framework Directive demands it (Environment Agency, 2012).

Procter and Gamble were the first company to use phosphates in detergents in 1946. The improvement in the cleaning power of the powders was so successful that within ten years all detergents contained phosphates (Emsley, 2001). During this period water treatment systems were in their infancy and high levels of phosphorus were discharged into the great lakes of America causing them to become eutrophic (Emsley, 2001). Although since the 1950’s the amount of phosphates in detergents has been greatly reduced, they still represent 14% of the phosphorus reaching WWTW. In 2012 the Council of European Union adopted a regulation on the restriction of phosphorus in detergents with a limit of 0.5mgP per dose of laundry detergent. The dose has also been reduced in dishwasher detergents and this will come into force in 2017, however, increasing use of dishwashers may limit the effect of this (Environment Agency, 2012).

Food scraps and personal care products complete the domestic sources of phosphorus reaching the WTWW which is estimated to be 88% of the total load (Environment Agency, 2012). The final 12% arrives from town centre runoff (food waste and washing detergents) and consented industrial wastes.

2.2.5 Phosphorus control legislation

It is now widely accepted that the large amount of phosphorus entering WWTW must be removed to levels which do not cause eutrophication in receiving waters. However, deciding what that level should be is complex, and has been the subject of an ongoing worldwide discussion for over twenty years. During this period many pieces of legislation have come into force to compel the water companies to remove phosphorus from waste water. Six of the key pieces of legislation affecting the discharge of phosphorus from WWTW are shown in Table 2.1.

Table 2.1 Key-obligations and pressure driving phosphorus control in rivers adapted from (Mainstone and Parr, 2002)

Obligation	Requirement
Water Framework Directive- EC directive establishing a framework for Community action in the field of water policy(2000)	To reach and or maintain at least 'good' ecological status in all surface waters. The assessment of ecological status includes specific consideration of nutrient status.
EC Directive 91/271/EEC concerning Urban Waste Water treatment-the Urban Waste Water Treatment (UWWT) Directive (1991)	To identify 'sensitive areas' and to install appropriate treatment facilities for phosphorus and or nitrogen removal at sewage treatment works serving more than 10 000 population equivalents.
EU Directive 92/43/EEC on the Conservation of Natural Habitats and of Wild Fauna and Flora-the Habitats Directive (1992)	To maintain or restore the 'favourable conservation status' of specified natural habitats and species of wild fauna and flora mainly through a network of Special Areas of Conservation
EU Directive 79/409/EEC on the conservation of Wild Birds- the Birds Directive (2009)	To protect and where necessary enhance the populations of specified bird species through a range of measures including the designation of Special Protection Areas and the control of pollution
The 1981 Wildlife and Countryside Act	To protect the national network of Sites of Special Scientific Interest as representative examples of the habitats flora and fauna of the UK.
The Rio Convention on Biological Diversity (1993)	Through the UK Biodiversity Action Plan, to conserve and where possible enhance populations and natural ranges of priority native species, the quality and range of priority habitats and the biodiversity of habitats where this has been degraded.

Of the legislation and directives the Urban Waste Water Treatment Directive and the Water Framework Directive (WFD) have the most direct impact on the water industry.

2.2.5.1 The Water Framework Directive (WFD)

The Water Framework Directive (WFD) was adopted in October 2000 (DEFRA, 2012). The WFD does not set defined effluent targets as it has been argued that source control alone could allow a cumulative pollution load to develop which could be severely detrimental to the environment. To this end, the WFD prescribes a requirement for general ecological protection. 'Good ecological status' is defined in terms of the quality of the biological community, the hydrological and the chemical characteristics of the receiving water. It is not possible to set absolute standards for biological quality which apply across the European Community because of ecological variability. The controls are, therefore specified as allowing only a slight departure from the biological community which would be expected in conditions of minimal anthropogenic impact (Mainstone et al., 2000).

The implication of the WFD to the UK water companies in regard to phosphorus are that phosphorus concentrations in effluents must not be higher than the levels that would have existed in the natural water courses they are discharging into. This can be very hard to define, as most waterways in the UK have had high levels of phosphorous discharging into them for many years, and the natural background levels are very hard to calculate (Mainstone and Parr, 2002). However, there has been a general agreement that pragmatic management targets for the discharge of soluble reactive phosphorus (SRP) into water courses should vary between 0.1 and 0.02mgL^{-1}, depending on river type, with an interim target of 0.2 mgL^{-1} for heavily enriched rivers (Mainstone et al., 2000, Correll, 1998). Target phosphorus concentrations for rivers in England and Wales are summarised in Table 2.2.

Table 2.2 Target soluble reactive phosphorus discharge levels (Environmental Agency, 2000)

Target	Mean SRP (mgL^{-1})	Suggested application
1	0.02	Upland watercourses and headwaters
2	0.06	Rivers on chalk, hard sandstone and limestone
3	0.1	Lowland rivers on clay alluvium
4	0.2	Interim target for heavily enriched rivers.

2.2.5.2 The Urban Waste Water Directive

The Urban waste water directive was adopted on the 21st of May 1991. Total phosphorus (TP) discharge limits were set at 1mgL^{-1} for works larger than

100,000 population equivalent (p.e.) and 2mgL^{-1} for works between 10,000 and 100,000 p.e. By the end of 2007 the UK was 99.9% compliant (DEFRA, 2012).

2.2.6 American legislation

America has had more stringent phosphorus removal targets in operation for many years. The United States Environmental Protection Agency (EPA) published a national nutrient criteria strategy in 1998. The ecoregion criteria set by the EPA results in very low in stream nitrogen and limits. For example ecoregion criteria for rivers and streams range from 0.010 to 0.076mg TP mgL^{-1} (Neethling et al., 2011). The early uptake of such high removal rates for phosphorus has meant that many of the technologies designed for phosphorus removal have now been well tested in the USA.

2.2.7 Summary

Phosphorus causes humanity two problems.

1. We need phosphorus to fertilise the soil to provide food to feed the world, but phosphorite is a finite resource that is going to run out sometime in the future.
2. Humanity uses the phosphorus resource available very inefficiently with perhaps as little as 1/5 of the phosphorus that is mined ending up in useful products, the remainder being washed into our rivers and oceans where it has caused severe environmental degradation to many of the world’s water systems (Cordell, 2013).

A high percentage of the phosphorus reaching the riverine systems and the sea arrives from point sources such as sewage treatment works (Cooper and Carliell-Marquet, 2013). There are many pieces of legislation that affect the discharge from sewage treatment works.

2.3 Current processes to remove phosphorus from waste water

As the WFD comes into force much more phosphorus will have to be removed from our waste water. If we can capture and recycle this currently wasted phosphorus it will have the triple benefit of cleaning our water bodies, reducing phosphorus imports and the reduction of the amount of energy used to mine and transport phosphorus. The majority of current treatment approaches are based on converting the soluble phosphorus in wastewater into insoluble forms. This is achieved by using metal based coagulants to precipitate the phosphorus (chemical removal) or by utilising a form of biological treatment to incorporate the phosphorus within biomass (biological removal) which can then be settled and removed as sludge.

2.3.1 Chemical Phosphorus removal

Chemical precipitation is a physio-chemical process in which the addition of a divalent or trivalent metal salt to wastewater causes the precipitation of an insoluble metal phosphate that is settled out by sedimentation, filtration or both (Morse et al., 1998). The principle chemicals used for removal of phosphorus from waste water are: aluminium(Al(III)), ferric iron(Fe(III)), ferrous iron(Fe(II)) and calcium(Ca(II)). The salts most commonly used are lime ($Ca(OH)_2$, alum $Al_2(SO_4)_3 \cdot 18H_2O$, sodium aluminate ($NaAlO_2$), ferric chloride ($FeCl_3$), ferric sulphate($Fe_2(SO_4)_3$), ferrous sulphate ($FeSO_4$) and ferrous chloride ($FeCl_2$) (Sedlak, 1991). The chemistry of phosphorus removal using aluminium and iron is quite different from calcium.

2.3.1.1 Phosphorus removal with Aluminium and Iron salts

Although chemically mediated phosphorus removal is widely used, the mechanisms of removal are poorly understood (Gilmore et al., 2011, Smith et al., 2007). Historically the reactions of Al and Fe salts have been summarised by the following two equations.

$$\boldsymbol{Al^{3+} + H_nPO_4^{3-n} \leftrightarrows AlPO_4 \downarrow + nH^+} \qquad \textbf{Equation 2.1}$$

$$\boldsymbol{Fe^{3+} + H_nPO_4^{3-n} \leftrightarrows FePO_4 \downarrow + nH^+} \qquad \textbf{Equation 2.2}$$

Although these reactions have been helpful to work out the stoichiometric ratio for salt additions, they are deceptively simple and the reality of the chemistry is much more complex.

Extensive work has been undertaken to model the addition of metal salts and it has been proposed that the reaction is better modelled by equation 2.3 (Sedlak, 1991).

$$rMe^{3+} + HPO_4^{-} + (3r-1)OH^{-} \rightarrow Me_r \cdot H_2PO_4(OH)_{3r-1}(s)$$ **Equation 2.3**

Where r =1.6 for Fe (III) and 0.8 for Al (III)

The removal of phosphate is thought to occur in a number of different ways including, the formation of ferric or aluminium oxides which serve as a substrate for phosphate adsorption, incorporation into the hydrous oxide structure, formation of mixed action phosphates and formation of ferric or aluminium phosphate (Metcalf et al., 2014). These reactions of the metal salts and phosphorus are greatly affected by the alkalinity, pH, trace elements and ligands found in the waste water (Metcalf et al., 2014). Although many more complex models of the reactions have been created the amount of chemical salt dosed at sewage treatment works has historically either been based on operator experience, or bench scale tests (Smith et al., 2007).

2.3.1.2 Phosphate removal with calcium.

Calcium is normally added in the form of lime $Ca(OH)_2$. When lime is added to water it reacts with the alkalinity to precipitate $CaCO_3$. As the pH increases above 10 the excess calcium ions react with the phosphate according to equation 2.4 to precipitate hydroxylapatite (Metcalf et al., 2014).

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^{-} \leftrightarrows Ca_{10}(PO_4)_6\ (OH)_2$$ **Equation 2.4**

The quantity of lime added depends primarily on the alkalinity and is usually around 1.4 to 1.5 times the total alkalinity expressed as $CaCO_3$. When lime is added to raw wastewater or to secondary effluent pH adjustment is usually required before subsequent treatment or disposal. Due to the additional costs of pH correction metal salts are more commonly used than lime (Metcalf et al., 2014).

2.3.1.3 *Kinetics*

The reaction of the metal salts with phosphorus is initially very fast and can occur in less than one minute as long as there is good mixing intensity (Smith et al., 2007). Thus metal salts are generally injected into a point in the plant that is well mixed. A smaller part of the total initial phosphate is removed by a consecutive slow kinetic reaction, this reaction can take hours or days to complete (Smith et al., 2007).

2.3.1.4 *Dosing points for chemical additions*

Three specific dose points are commonly used in wastewater treatment plants: primary clarifiers, secondary clarifiers and tertiary treatment. The effects of dosing at different points are summarised in Table 2.3. Multiple dose points using a combination of the above are also used (Sedlak, 1991).

Table 2.3 Common chemical dosing points for phosphorus removal and issues associated with them (Sedlak, 1991)

Dose Point	Anticipated Level of Effluent TP (mgL^{-1})	Issues
Primary Treatment	≥1	Enhances BOD and TSS removal efficiency , reduces phosphate loading on downstream processes , may require polymer for flocculation
Secondary Treatment	≥1	Less efficient chemical use. Additional solids in MLSS, phosphate carryover in effluent TSS.
Tertiary Treatment	≤ 0.5	Required to meet stringent standard, significant increased cost.

2.3.1.5 *Chemical phosphorus removal in the UK*

Chemical precipitation is the favoured option in UK WWTW as it is easy to retrofit into existing sewage works. It is relatively simple to control so can easily deal with shock loads and temperature changes. However, the reactions taking place are still not well understood so significant overdosing of chemicals takes place with costs associated with transport and the chemicals themselves. Chemical dosing also substantially increases the amount of sludge produced which is hard to dewater. Currently much of the sludge produced at treatment works is sent to land, in the future there are likely to be caps on the amount of iron and aluminium that can be applied to land thus making chemical precipitation as a phosphorus treatment option very expensive (Environment Agency, 2012). A summary of the advantages and disadvantage of chemical dosing are shown in Table 2.4.

Table 2.4 Pros and cons of chemical phosphorus removal (EU Directorate, 2002)

Advantages	Disadvantages
Reliable and a lot of detailed research.	Operating costs higher than for biological P removal.
Chemical costs can be greatly reduced if waste pickle liquors are available and can be used.	More sludge is produced than by biological processes.
Controls are relatively simple.	Tertiary filtration required to remove P in effluent.
Retrofitting into existing works is relatively simple.	Effluents may be coloured if iron salts are used.
Sludge can be processed in the same manner as in non-P removal systems.	Potential for toxicity to the biological process if the chemical loading is inefficient.
Primary clarifier chemical addition can reduce the organic load to secondary treatment by 25-35%.	Increase metal loads on agricultural land
	Phosphorus is not as available for agricultural use as compared to inorganic P fertilizer.

2.3.2 Biological Phosphorus removal (BPR)

Biological phosphorus removal is based on the activated sludge process. In the conventional activated sludge process bacteria only use enough phosphorus to satisfy their basic metabolic requirements. This results in maximum phosphorus removal rates of 50% or less (Fuhs and Chen, 1975). For biological phosphorus removal to take place the phosphorus in the waste water must be incorporated into phosphorus accumulating organisms (PAOs) and these must then be settled out and removed from the system as sludge. When PAOs grow they not only consume phosphorus for cellular components but also accumulate large quantities of polyphosphate within their cells (Sedlak, 1991).

The process works by selecting for PAOs by putting them under anaerobic conditions, then exposing the same microorganisms to aerobic conditions. Under anaerobic conditions the microorganisms obtain energy by partially oxidizing supplied organics while breaking up stored polyphosphate, thereby releasing some orthophosphate to the water. Under aerobic conditions the microorganisms take up orthophosphate and store it as polyphosphate, when the cells are wasted from the activated sludge process the phosphate is removed (Brett, 1997).

The presence of nitrate can be a complicating factor in BPR as when it is present in the anaerobic zone, it has an adverse effect on the competitive advantage PAOs have over other bacteria. In these conditions, heterotrophic bacteria will use nitrate to consume readily biodegradable chemical oxygen demand in the anaerobic zone, leaving less for PAOs, resulting in an overall decrease in phosphorus removal efficiency (Metcalf et al., 2014). If the nitrate concentration is too high in the influent stream an anoxic zone must be incorporated into the plant. In an anoxic environment biological denitrification is achieved by both NH_4-N oxidation and NO_3-N and NO_2-N reduction to nitrogen gas.

The performance of a biological phosphorus removal system is also dependent on readily biodegradable supply of chemical oxygen demand (COD) in the sewage, including volatile fatty acids such as acetate. The organic substrate is vital in order to create a biological demand for phosphorus. Many WWTW rely on an industrial source of carbon, which is often a waste product. However, even such waste products can be very costly to transport (Martin et al., 2009).

2.3.2.1 BPR in the UK

It was estimated that by the end of 2015 there were around 20 works employing BPR in the UK (Environment Agency, 2012). BPR systems work well in stable flow conditions and with relatively high temperatures. In the UK BPR processes can be very hard to control as flow rates and effluent concentration are greatly affected by rainfall events. In high rain fall, flows become high and diluted, causing starvation and washout of micro-organisms (Environment Agency, 2012).

2.3.2.2 Summary of Biological Phosphorus Removal Process

The reactor systems in BPR must be designed such that POAs are favoured over competing microorganisms, to achieve this there must be anaerobic and aerobic zones, a source of volatile fatty acids (VFA's) and denitrification must have occurred before phosphorus can be removed (usually in an anoxic zone). There are many process options for achieving BPR and there is continuing development of the system. Principal advantages and disadvantages of BPR are summarised in the Table 2.5 (Barnard et al., 2011).

Table 2.5 Advantages and disadvantages of BPR (EUDirectorate, 2002)

Advantages	Disadvantages
The amount of sludge generated is similar to conventional biological treatment.	P process removal is limited by the BOD: P ratio of influent wastewater (except for PhoStrip system). Requires low molecular weight substrates available in the influent.
Can be installed at existing 'plug flow' activated sludge plants with minimal new equipment requirements.	Secondary clarifier performance must be efficient to achieve effluent concentrations <1mgL^{-1}P
Existing sludge handling methods can be used provided the risk of phosphorus resolubilisation are controlled.	Cannot be readily used to retrofit fixed film processes
No chemical additive costs unless effluent polishing is included.	Potential for P release during sludge handling, which would then be released to the head of the treatment works.
Some process arrangements combine nitrogen and P removal at virtually no additional cost.	Standby chemical treatment equipment may be required in case of low performance or failure of the biological system.
Improved process control results in reduced risks of filamentous organisms	Sludge can have poor settling characteristics.
The enhanced P content of sludge is available for agricultural use.	Increased retention time required in activated sludge plants.

Chemical removal is a much easier process to control and retrofit into existing systems but is expensive to operate and may become untenable if the sludge produced is not allowed onto agricultural land. Biological systems are much more environmentally friendly but require very large capital expenditure and are hard to optimise in the UK.

2.4 Theory of phosphorus removal with adsorptive media

Before a discussion of the many materials that have been studied for use as phosphorus adsorbents the following section summarises basic adsorption theory.

2.4.1 Adsorption Theory

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. Irving Langmuir described the process very concisely in his paper on adsorption in 1918.

“When gas molecules impinge against any solid or liquid surface they do not in general rebound elastically, but condense on the surface, being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface. The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this” (Langmuir, 1918)

Two principal types of adsorption are recognized; physical and chemical adsorption. Physical adsorption is nonspecific rapid and reversible; the adsorbate being held at the interface only by the relatively weak dispersion and polarization forces. Chemisorption is simply the formation of a two dimensional compound in which the forces of attraction are much stronger chemical bonds. [A subsidiary type of chemisorption is ionic exchange adsorption] (Findlay and Levitt, 1972). A comparison between physical and chemical adsorption is shown in Table 2.6

Table 2.6 Comparison of Physical and Chemical adsorption adapted from (Crittenden et al., 2012)

Parameter	Physical Adsorption	Chemical Adsorption
Process speed	Limited by mass transfer	Variable
Type of bonding	Nonspecific bonding mechanisms such as van der Waals forces, vapour condensation	Specific exchange of electrons, chemical bond at surface
Type of reaction	Reversible, exothermic	Typical irreversible, exothermic
Heat of adsorption	4-40kJ/mol	>200kJ/mol

While physical adsorption and chemisorption can be distinguished easily, at their extremes some cases fall between the two as a highly unequal sharing of electrons may not be distinguishable from the high degree of distortion of an electron cloud that occurs with physical adsorption (Crittenden and Thomas, 1998).

2.4.2 Theories of adsorption equilibria

The amount of substance adsorbed at any surface decreases with a rise of temperature, since all adsorption processes are exothermic. At constant temperature the amount adsorbed increases with the concentration of the adsorbate and the relationship between the amount adsorbed and the concentration is known as the adsorption isotherm (Findlay and Levitt, 1972). The shape of the adsorption isotherm gives qualitative information about the adsorption process and the extent of the surface coverage by the adsorbate (Faust and Aly, 2013). Many mathematical models have been used to predict the shape of the isotherm curve enabling prediction of adsorptive capacity of a media in relation to the concentration of the compound of interest in the adsorbate. The curve can also help predict the volume of water that can be treated by a certain mass of adsorbent. The Henry's law, Langmuir and Freundlich isotherm models are the most commonly used (Crittenden and Thomas, 1998).

2.4.2.1 *Henry's law Isotherm*

This represents the simplest isotherm in which the amount of adsorbate adsorbed various directly with the equilibrium concentration of the solute. The isotherm is described by equation 2.5.

$$q_e = K_H C_e$$ **Equation 2.5**

where

K_H = Henrys Law constant
q_e = equilibrium adsorbent phase concentration (mg adsorbate/g adsorbent)
C_e = equilibrium concentration of adsorbate in solution (mgL^{-1})

This isotherm is obtained under conditions of low concentration, when the adsorbed layer is extremely dilute and the amount adsorbed is only a fraction of the monolayer capacity of the adsorbent. Usually the linear relationship is observed at the lower concentration levels of a total adsorption system (Faust and Aly, 2013).

2.4.2.2 *The Langmuir Isotherm*

Langmuir made some basic assumptions about adsorptive systems and produced a very elegant and simple equation that models many adsorption systems relatively well (Equation 2.6). Langmuir assumed that the surface of the adsorbent is covered by a large number of sites on each of which an adsorbed molecule may sit. The sites are all equivalent and the adsorbed molecules are assumed not to interact with each other or to jump from site to site. The fraction of all the sites is called ϴ. When each site is occupied ϴ=1 and the surface is covered and no more adsorption can occur.

The theory assumes that a molecule can stick to the surface only if it strikes an empty site; if it hits an occupied site it will be reflected back. The rate of condensation of the molecules on the surface is proportional to both the rate of bombardment of the surface (i.e. concentration in solution) and to the fraction of surface left uncovered (i.e. 1-ϴ)(Findlay and Levitt, 1972).

Using these key assumptions the Langmuir equation 2.6 can be derived. These assumptions result in an idealized adsorbent surface in contrast to the heterogeneity of actual media surfaces. However the Langmuir equation provides a very useful starting model for adsorption systems (Wu and Sansalone, 2013b).

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$$ **Equation 2.6**

K_L = Langmuir constant (L mg^{-1}) which is related to the energy of adsorption.
q_m = maximum monolayer adsorption capacity (mg g^{-1})

One of the very useful outputs from the Langmuir model is the value for q_m the predicted value of the maximum adsorption capacity of the media. This value provides a quick way to compare different media. However, it must also be used with caution as the q_m value is ascertained from experiments that generally use very high concentrations of the adsorbate of interest (Wu and Sansalone, 2013a).

2.4.2.3 The Freundlich Isotherm

In contrast to the Langmuir isotherm the Freundlich model was not produced from a theoretical basis but from empirical observation. The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems (Faust and Aly, 2013). The Freundlich model is generally shown in the form of equation 2.7 and is applicable to non-ideal adsorption on heterogeneous surfaces (Das et al., 2014). The Freundlich equation assumes that the heat of adsorption decreases in magnitude with increasing extent of adsorption and that this decline in the heat of adsorption is logarithmic, thus implying an exponential distribution of adsorption sites and energies (Crittenden and Thomas, 1998). There is much experimental evidence that real energy distributions, while perhaps not strictly exponential, are indeed roughly of this sort (Callery et al., 2016).

$$q_e = K_F C_e^{1/n}$$ **Equation 2.7**

Where

Kf = Freundlich constant (Lg^{-1}) related to bonding energy

1/n = Heterogeneity factor, ranging between 0 and 1, becoming more heterogeneous as its value becomes closer to zero.

2.4.2.4 Limitations of isotherm models.

The creation of isotherm curves provides both a very useful tool to assess the performance of an adsorbent in relation to a particular adsorbate and enables comparisons of different media (Crittenden and Thomas, 1998). However the isotherms are usually constructed from batch experiments, which generally involve shaking very small quantities of adsorbent for a set period of time with different concentrations of adsorbate at constant temperature. When the media is used in a full scale adsorption system it is not generally shaken and is used in large quantities at different temperatures in a continuous or semi-batch process (Crittenden and Thomas, 1998). Many papers have shown that using the Langmuir and Freundlich equations with such experimental data can lead to biased and unrealistic estimates of the adsorption parameters and should be used with caution for phosphorus adsorption. Maximum phosphorus adsorption capacity is generally underestimated at low input phosphorus concentrations and overestimated at high phosphorus concentration's (Drizo et al., 2002).

2.4.3 Kinetics of adsorption

Analysis of the kinetics of adsorption is important not only because it describes the uptake rate of the adsorbate, which controls the residence time required at the adsorbent solution interface, but it also provides valuable information about the reaction pathways and the mechanisms of sorption processes (Ho and McKay, 1999).

2.4.3.1 Kinetic Models

As for adsorption isotherms, it is very useful to model kinetic experimental data mathematically. The most common models used are the pseudo first order, pseudo second order and intraparticle diffusion models (Lin and Wang, 2009).

The pseudo first order (PFO) kinetic equation was proposed by Lagergren (Lin and Wang, 2009, Lagergren, 1898) and can be expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$ ***Equation 2.8***

Where k_1 = rate constant of model (min^{-1})
q_t = amount of solute adsorbed on the adsorbent at time (t).($mg\ g^{-1}$)

The pseudo second order model (PSO) proposed by (Blanchard et al., 1984) and can be expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$ **Equation 2.9**

Where k_2 = second order rate constant

Both the PFO and PSO are often used in their linear forms to determine which best fits the experimental data. The linear forms are discussed in Chapter 8. It is generally proposed that the PFO kinetic model indicates physisorption; whereas data fitting a PSO model implies chemisorption (Das et al., 2014). The PFO equation assumes that the removal of the adsorbate is not affected by the concentration of phosphorus on the adsorbent. Whereas the PSO model implies that the removal rate is proportional to both the concentration of the phosphorus in the adsorbate as well as the concentration in the adsorbent. In other words the process is slowed as both the concentration of phosphorus in solution falls and as the available adsorption sites are used up.

To elucidate if intraparticle diffusion is the rate limiting step Weber and Morris, (1963) proposed an intraparticle diffusion model.

$$q_t = k_p t^{0.5}$$ **Equation 2.10**

Where k_p = intraparticle rate constant (mg $g^{-1}min^{-1/2}$).

If the experimental data fits the intraparticle model it would suggest that intraparticle diffusion is the rate limiting step (Yang et al., 2006b).

Plots of the intraparticle diffusion model may present multi-linearity indicating that two or more adsorption steps take place. The first sharper portion represents the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is the rate controlling step (Özacar, 2003).

2.5 Manufactured media, natural media and waste products for the removal/adsorption/ion exchange of phosphorus

Although chemical and biological phosphorus removal are very effective at removing phosphorus both processes are sensitive to seasonal change, diurnal variations in temperature and changes in feed compositions (Zhao and Sengupta, 1998). They also rely on either a complex control system or a ready supply of chemicals. Conversely, processes using adsorbent media can consistently remove phosphorus to low concentrations, using relatively simple and maintainable machinery and the sludge generation is minimal (Martin et al., 2009).

In the past extensive studies have been undertaken to explore the effectiveness of fixed bed ion exchange processes for phosphate removal because of their operational simplicity and adaptability to changing wastewater flow rates and compositions. Ion exchange processes are also reversible which can enhance life expectancy of the media through regeneration and also provide a route to enable the recycling of the captured phosphorus (Martin, 2010). Commercial anion exchange materials such as alumina and zirconium oxides were well studied but had many shortcomings, including poor selectivity towards phosphorus over competing species such as sulphate, chloride and dissolved organics, very low capacity in neutral pH range and very poor regeneration capacity (Zhao and Sengupta, 1998). The poor ability of anion exchange resins has led to further research into new forms of manufactured adsorbent media that could preferentially adsorb phosphorus, but can still be easily regenerated (Martin, 2010, Blaney et al., 2007, Fitzpatrick et al., 2011). A selection of some of the manufactured ion exchange media studies are shown in Table 2.7.

Material	Average particle diameter (mm)	Feed Solution	Type of Study	Contact Time	Capacity/ removal efficiency	Key Findings	Challenges	Reference
Hybrid anion exchanger-ion exchange beads with a dispersion of ferric oxide nanoparticles	0.69	Synthetic 0.26mgPL^{-1}	Column	2min.	2.3mgPg^{-1}	Effluent of<.01.mgPL^{-1}for 11000 bed volumes. Selective removal of phosphate with small competitive effect from sulphate. Easy to regenerate and recover P	Optimising process for differing wastewater streams and regenerant regimes	(Blaney et al., 2007)
Metal oxide with ion exchange properties	0.55	Secondary sand filtered wastewater Ranging from 5 to 0.5mgP/l	Pilot and column	1.5min.	2.2-2.6 gPL$^{-1}_{media}$	Remove TP<01.mgL^{-1} 90% of time and orthoP to 0.01mgL^{-1} 90%	Although the removal rate per gram is very low the system has been thoroughly tested and works well	(Fitzpatrick et al., 2010)
Carbon-magnetite nanocomposite (tannin based carbon iron oxide and carbon magnetite)	Not stated	Model solutions	Batch	2 hrs	11.96 mgPg^{-1}	Carbon-magnetite was better than carbon iron based composites	The process to produce the resins is more environmentally friendly than most as based on a natural material, but still a lot of research to make into a commercial product	(Weinberg et al., 2011)
Polymeric ligand exchanger-Lanthanum bound to chelex resin	0.152-0.297	Seawater dosed with phosphorus 7.8mgPL^{-1}	Column	0.66 min	Effluent< 0.1mgPL^{-1}	Removal very good not influenced by chloride and sulphate, regenerated by removing sorbed P by eluting with 6M HCl	Only 16% of the potential La(111) sites available for binding P. Regeneration results in some loss of La(111) over time	(Wu et al., 2007)
Polymeric ligand exchanger-ion exchange beads loaded with copper	0.3-0.8	Secondary wastewater 2.2mgPL^{-1}	Column	8.8mins	99% removal	Effluent <0.1mgPL^{-1} for first 500 bed volumes. Selective phosphate removal and easy regeneration.	Commercial availability, optimising process for differing streams.	(Zhao and Sengupta, 1998)

Table 2.7 Synthetic materials used for phosphorus adsorption/ion exchange

There has also been a great deal of research undertaken into natural and waste materials which can adsorb phosphorus (Vohla et al., 2011). These products are attractive because they have no manufacturing cost and are the main focus of this thesis.

A suitable waste material for use as a phosphorus adsorbent needs to fit the following criteria (Crittenden and Thomas, 1998, Vohla et al., 2011):

- a high phosphorus adsorption capacity
- a high internal volume which is accessible to the phosphorus compounds being removed from the fluid. (These can be carbonaceous, inorganic, synthetic or naturally occurring).
- a high hydraulic conductivity
- good mechanical properties such as strength and resistance to attrition
- good kinetic properties (must be capable of transferring adsorbing molecules rapidly to adsorption sites).
- inexpensive (to compete successfully on economic grounds with other separation processes.)

Historically to assess the suitability of a natural media or a waste product to remove phosphorus initial analysis has been based on the physical and chemical characteristics of the media. Characteristics such as Fe, Al and Ca content, specific surface area (SSA), porosity, particle size distribution, hydraulic conductivity, and ‘pseudo–equilibrium’ batch experiments (isotherms); have all been shown to affect phosphorus adsorption capacity. This type of analysis is reasonably quick and easy to produce and enables initial screening of suitable media. However it does not reveal the long term phosphorus removal capacity of the media (Drizo et al., 2002).

Many methods have been used to assess the long term phosphorus adsorption capacity of different types of media. including continuous flow through experiments (Penn, 2011), desorption and dissolution tests (Pratt et al., 2007), phosphorus saturation potential (Drizo et al., 2002) and oxalate-extractable A l and Fe (Dayton and Basta, 2005). However, none of these methods have proved to be ideal, and the longevity of the sorption capacity of a particular media is still a main focus for research (Johansson Westholm, 2006, Vohla et al., 2011).

A summary of some of the waste materials tested in the laboratory under batch and flow through conditions is shown in Table 2.9-2.11. Larger pilot and full scale studies are summarised in Table 2.12. The type of media used can be classed as mineral aggregates, soils, marine sediment, man made and industrial by products. However comparing the materials ability to operate in an adsorption process directly from these tables is complex as many other factors have to be taken into account. A summary of these factors is shown in Table 2.8.

Table 2.8 Reasons why comparisons between different adsorbent media are hard to compare, table adapted from (Kadlec and Wallace, 2008)

Mineral properties of aggregate	Different substances show a huge difference in phosphorus absorbing ability, but this is primarily controlled by the amount of aluminium oxides, iron oxides and calcium carbonates. Comparisons between media are very difficult as most experiments are very different often involving different process steps and lengths of time.(Johansson Westholm, 2006)
Historical mineralogy	Phosphorus sorption is strongly influenced by surface chemistry, and as the material ages and weathers its properties can change (Hedström, 2006)
Size of aggregate	Finer materials provide more surface area for sorption but at the cost of lower hydraulic conductivity.(Rustige et al., 2003)
Batch flow vs continuous flow	There is no standard test , batch experiments often use very high phosphorous loadings which do not relate to the real world (320-10000mgLP^{-1} are common) also many batch experiments use shakers which produces a much higher mix that is possible on site.
Time scale of experiments	Short term batch tests usually greatly overestimate sorption capacities.(Stoner et al., 2012, Drizo et al., 2002)
Laboratory versus field conditions	Not too many field experiments have been done, (Drizo et al., 2008, Shilton et al., 2006) authors recommend a reduction of at least 50% when converting from bench to full scale tests.
Speciation of phosphorus	Usually in the lab (KH_2PO_4) is used, this is completely soluble and inorganic so is not a good representation of real waste water which can contain high levels of organic P and NRP.

To make the comparison between materials easier Tables 2.8 and 2.9 have been split between Calcium/Magnesium and Aluminium/Iron rich materials.

Material	Source	Max. P retention ($mgPg^{-1}$)	Particle diameter(mm)	pH	Material to solution ratio	Contact time (hours)	Initial P conc (mgL^{-1})	Estimation method for Max.P retention	Reference
Ca and Mg rich materials									
Red Mud	By-product of aluminium works	113.9	<0.149	11.7	1:200	4	0.31-3000	Langmuir isotherm	(Li et al., 2006)
Red mud+gypsum	By product of aluminium works	5	<2	8.5	1:5	25	0-800	Langmuir isotherm	(Cheung et al., 1994)
Utelite	Utelite Corp, Utah USA	3.5	<2	10.1	1:25	24	0-320	Langmuir isotherm	(Zhu et al., 2003)
Blast furnace slag	By-product of ironworks(Australian Steel Mills Ltd, Australia)	44.2	-	-	1:10	48	10-1000	Langmuir isotherm	(Sakadevan and Bavor, 1998)
Amorphous slag	By products of steel works, Czech republic	6.5	0-0.1	-	1:200	150	50-500	Langmuir isotherm	(Kostura et al., 2005)
Crystalline slag	By product of steel works ,Czech republic	18.9	0.0.1	-	1:200	150	50-500	Langmuir isotherm	(Kostura et al., 2005)
Shellsand	Natural material produced by shells(Norway)	9.6	8.8	8.8	1:30	24	0-480	Peak of the sorption isotherm	(Adam et al., 2007)

Table 2.9 Maximum phosphorus retention capacities and other parameters for Ca and Mg rich waste products according to batch experiments adapted from(Klimeski et al., 2012)

Material	*Source*	Max. P retention (mgPg^{-1})	Particle diameter (mm)	pH	Material to solution ratio	Contact time	Initial P conc. (mgL^{-1})	Estimation method	Reference
Al and Fe- rich materials									
Untreated biolite	Beneficiation process of apatite(Kemira biotite, Finland)	4.5	>0.2	9.6	1:50	7 days	0-5	Peak of sorption Isotherm	(Hartikainen and Helinä Hartikainen, 2008)
Acid-treated biotite	as above	10.9	>0.2	3.2	1:100	7 days	0-500	Peak of sorption Isotherm	(Hartikainen and Helinä Hartikainen, 2008)
Partly neutralised biotite	As above	15.4	>0.2	4.6	1:100	7 days	0-600	Peak of sorption Isotherm	(Hartikainen and Helinä Hartikainen, 2008)
Al-DWTR*	WTP, Melbourne, Fl,USA	10	<2	5.7	1:10	10 days	250-1000	Single point sorption	(Makris et al., 2005a)
Fe-WTR*	WTP,Tampa, Fl, USA	9.2	<2	6.3	1:10	10 days	250-1000	Single point sorption	(Makris et al., 2005a)
Fly ash	By-product of coal combustion process(China)	63.2	<0.149	9.4	1:200	4h	0.31-3100	Langmuir isotherm	(Li et al., 2006)
Furnace slag	By-product of combusted coal	8.9	0-5	12.3	1:20	4h	10-1000	Langmuir isotherm	(Xu et al., 2006)

Table 2.10 Maximum phosphorus retention capacities and other parameters for Al and Fe rich waste products according to batch experiments adapted from(Klimeski et al., 2012) *****DWTR are discussed in greater detail in section 2.6 and are shown here for comparison purposes.*

Material	Source	Max. P retention (mgPg^{-1})	Particle diameter (mm)	Test period (days)	P conc. (mgL^{-1})	Loading rate (Ld^{-1}g^{-1})	P removal efficiency (%)	Volume of material (cm^3)	Reference
Iron oxide tailings	Mineral processing industry Canada	-	0.069	44	20	0.00075	90(mass removal)	127	(Zeng et al., 2004)
Filtrate P	Saint-Gobian Weber, Norway	0.473	0.5-4	229	4.9	0.00048	91(conc. removal)	18800	(Adam et al., 2007)
Shellsand	Natural material from sheels,snails and algae,Norway	0.497	3-7	303	10	0.00027	92(conc. removal)	18300	(Adam et al., 2007)
Iron sludge	Wessman water treatment plant, The Netherlands	16.1	<2	238	3.95	0.05-0.5	10-30		(Klimeski et al., 2012)
Iron coated sand	Someren,water treatment plant (the Netherlands)	-	<2	238	3.95	0.0039	90		(Klimeski et al., 2012)
Electric arc furnace slag	Ispat Sidbec,Tracy,Canada	2.35	2.5-10	278	350-400	0.00074			(Drizo et al., 2002)
Fly ash	Yatagan, Turkey	-	0.063-0.125	3	140	0.56	80 conc.removal		(Ugurlu and Salman, 1998)
Electric arc furnace slag	Steel mill Ft,Smith,AR,USA	1.3	6.35-11	0.2	0.515			1.1	(Penn, 2011)

Table 2.11 Manufactured and waste products assessed in flow through column experiments (adapted from (Klimeski et al., 2012)

Material	Source	Particle diameter(mm)	Test period	P concentration (mgL^{-1})	P removal efficiency(%) or P retention	Volume (m^3)	Reference
Shellsand	Natural, shells and snails Norway	>1 pre filter <1 main filter	May1999-Mar 2000	7.7	2.85mg g^{-1}	0.7	(Suliman et al., 2006)
Slag	By product from steel works, Australia	10-20	11 years(1993-2003)	TP annual mean 8.2	77% (mass removal) in first five years	12,973	(Shilton et al., 2006)
Granular Ochre	Oxidation and precipitation of Fe from mine water, UK		Nov 2003-Mar 2005, Leitholm	TP 4-6	12% conc .removal	1.7	(Dobbie et al., 2009)
Ochre pellets	Oxidation and precipitation of Fe from mine water, United Kingdom	6.4-9.5	May-sept 2005, Nov 2005-Jan.2006	TP 4-6	May-Sept 2005. 12% Nov.2005-Jan 2006:66%	0.9	(Dobbie et al., 2009)
Electric Arc Furnace Slag	Sestao, Spain	20-40	96 weeks from Autumn 2010	TP 8.5±1.3	37%	6	(Barca et al., 2012)
Basic Oxygen Furnace Steel Slag	Fos Sur Mer , France	20-40	96 weeks from Autumn 2010	TP 8.5±1.3	64%	6	(Barca et al., 2012)
Al-DWTR	Drinking water sludge(Dublin)	1-10	Feb-Dec 2009	10.7-33.3	75-94%	≈4	(Zhao et al., 2011a)

Table 2.12 Phosphorus removal efficiencies obtained in larger scale applications of phosphorus sorbing materials adapted from(Klimeski et al., 2012)

2.5.1 Summary of the phosphorus removal performance of natural/manufactured media and waste products

The phosphorus retention capacities of the different materials in Table 2.9-2.12 show a large range from 0.473 to 113.9mgPg^{-1} for Filltralite P and red mud, respectively. It is also notable that the results of phosphorus retention capacity tend to be lower for the flow through experiments compared to the batch experiments. For example Shellsand has a phosphorus retention capacity of 9.6mgPg^{-1} in the batch experiments and only 0.497mgPg^{-1} in the flow through experiments. This result highlights the difficulty in choosing appropriate materials to use in full scale trials.

Many of the materials listed that have very good phosphorus removal characteristics also tend to increase the pH of the influent. Red mud, blast furnace slag and fly ash all increase the pH to>9 and the effluent would require pH adjustment before being discharged.

The particle diameters range from 0.069 to 20mm and it is generally the case that as particle size reduces phosphorus adsorption increases. However it must be noted that as particle size decreases the hydraulic conductivity of the media is likely to decrease and this has not been measured by most authors.

The manufactured ion exchange media tend to remove more of the phosphorus from the waste streams often reporting >99% removal. However the maximum adsorption capacity tends to be quite low when compared to the waste products, ranging from 0.1 to 11.96 mgPg^{-1}. As ion exchange media is designed to be regenerated the maximum adsorption capacity represents the time the system can run before regeneration rather than a finite limit to adsorption as is the case for waste products.

The only very long term and full scale experiment that has been undertaken with phosphorus adsorbent media is described in Shilton et al (2006). The full scale beds operated with approximately 13, 000 m^3 of steel slag for over 10 years. The beds worked very successfully with overall phosphorus removal of 77% by mass.

All other larger scale experiments still only represent pilot scale systems with a maximum of 4m^3 of media. As can be seen from Table 2.12 the performance of the ochre pellets was very poor in the pilot scale system with the majority of the time only 12% of the phosphorus being removed whereas 66% removal was achieved in laboratory the trials (Dobbie et al., 2009). This clearly demonstrates the need for work on the effects of scale in phosphorus adsorption process.

Due to the very variable nature of the results shown in the tables the choice of material to use as adsorbent media is still very much open to question and more experimental work is currently being undertaken by many research groups (Vohla et al., 2011).

The maximum phosphorus retention of the water treatment residuals shown in the tables sit towards the lower quartile of the materials tested in the batch experiments. However, in the longer running field scale tests DWTR appear to be one of the most promising media.

2.6 Using domestic water treatment residuals to remove phosphorus

For well over twenty years research has been undertaken into the potential of using DWTR for the removal of phosphorus from waste water (Dharmappa et al., 1997, Makris et al., 2004a, Babatunde et al., 2011a, Georgantas and Grigoropoulou, 2005, Yang et al., 2006b, Huang and Chiswell, 2000, Mortula and Gagnon, 2007, Makris et al., 2004b, Ippolito, 2015, Boyer et al., 2011). Many of these papers suggest phosphorus removal rates can be greater than 95% over a prolonged period of time. Some studies demonstrate that DWTR performs better than synthesised materials produced specifically for phosphorus removal (Boyer et al., 2011, Brennan et al., 2011).

The residuals have many properties that make them stand out as an ideal medium to use in phosphorus adsorption beds.

1. They have good phosphorus adsorbent properties.
2. They have reasonable hydraulic properties
3. They are a waste product produced by the water industry, so they provide a local product that is readily available at low cost.
4. The pollutants in the water that are treated by the DWTR are mostly turbidity, colour, suspended clays and humic substances therefore they are unlikely to contain substantial quantities of toxic substances or pathogens.
   (Babatunde et al., 2009, Makris et al., 2005a, Ippolito et al., 2011)

2.6.1 Production of DWTR

DWTR is the residue of the chemical coagulation, flocculation, filter backwash water, water softening, and settling process in the treatment of potable water (O'Kelly, 2008). For typical water treatment plants between 60 and 90% of the residuals are collected from coagulant sedimentation or flotation process with the remainder coming from backwashing and settlement (Crittenden et al., 2012).

Natural surface waters contain inorganic and organic particles. Inorganic particles include clay, silt and mineral oxides which typically enter surface waters through natural erosion processes. Organic particles can include viruses, bacteria, algae, protozoan cysts and oocysts as well as detritus that has fallen into the water. Surface waters also contain very fine particles such as humic acids, which are produced from the decay and leaching of organic debris (Crittenden et al., 2012). Natural waters also contain phosphorus which has run off from farmers’ fields and roads, this phosphorus also ends up in the DWTR (Cooper and Carliell-Marquet, 2013).

Coagulation and flocculation are used in most drinking water treatment plants to remove, both the organic and inorganic matter. Coagulation is the destabilizing of colloidal particles. The particles are essentially coated with a chemically sticky layer that allows them to flocculate and settle within a reasonable period of time (Droste, 1997). The chemicals most commonly used are salts of aluminium and iron generally alum $Al_2(SO_4)_3$ or ferric chloride ($FeCl_3$) (Oliver et al., 2011)

Aluminium sulphate is the most commonly used coagulant in the USA and Canada (Yang et al., 2006b, Ippolito et al., 2011). Lime is also used as a coagulating agent. However, due to the pH correction required it is rarely used, therefore is not discussed further.

As much as 3 to 5 percent of the volume of the raw water entering a conventional water treatment plant may end up as a solid , semisolid or liquid residual (Crittenden et al., 2012). The residuals once produced are between 94-99.5% water and if the residuals cannot be discharged to sewer they must be thickened and dewatered to reduce the costs of transportation. The sludges are thickened using mechanical gravity thickeners, they are often dosed with polymers which improve their dewatering characteristics. With the use of thickeners the solids content can be increased to 2-6%. In hot countries once the sludge has been thickened it is possible to increase the solids content further by drying it on filter beds. In the UK sludge drying beds are rarely used, so the sludge is generally dewatered by mechanic means. The most common forms of mechanical dewatering are plate and frame filter presses, gravity and pressure belt filters and centrifuges. The output from these mechanical dewatering processes are commonly known as domestic water treatment residuals. Typical parameters associated with the dewatering process are shown in Table 2.13.

Table 2.13 Typical characteristics of dewatering process producing DWTR (Crittenden et al., 2012)

		Dewatering process	
Parameter	Unit	Plate and frame press	Centrifuges
Feed Solids	%	4-30	1-6
Thickened Sludge Dry Solids	%	15-30	12-15
Solids recovery	%	95-99	90-96
Polymer dose	g kg^{-1}		1-2

There is no shortage of DWTR, Goldbold et al (2003) estimated there was >182,000 tonnes of sludge produced per annum in the UK as dry solids. Dharmappa et al., (1997) estimated that 10,000 tonnes of waterworks sludge were produced a day worldwide, and this has no doubt increased greatly. Li et al (2013) estimated 1.5-2.4 million tonnes of dry sludge are produced in China every year. A large amount of this sludge is distributed to land in the UK however the disposal roots for this huge quantity of sludge are not well documented.

2.6.2 Characteristics of DWTR

The elemental constituents of DWTR do not vary greatly in their composition however, the relative abundance of the elements is site specific and dependent on (Ippolito et al., 2011):

:

1. characteristics of the raw water source
2. coagulant type used and dosage applied
3. other relevant plant operating conditions.

Typical compositions of Al and Fe based DWTR are summarised in Table 2.14

In general some of the most efficient phosphorus-sorbing materials tend to be those that contain Fe or Al hydroxides which are present in large quantities in DWTR as can be seen from Table 2.14 (Stoner et al., 2012).

Table 2.14 Physicochemical properties of aluminium and iron-based water treatment residuals (Ippolito et al., 2011)

Parameter	Al-DWTR	Fe-DWTR
pH	6.5 ± 0.3	7.0 ± 1.3
EC,ds m^{-1}	1.6±0.9	0.2 ± 0.0
	%	
Sand	69 ± 8	85 ± 2
Silt	17 ± 5	14 ± 2
Clay	14 ± 3	1.0 ± 0.3
	mg kg^{-1}	
Total N	4 065 ± 740	10 000
NH_4-N	22 ± 14	nd
NO_3-N	298 ± 207	nd
SRP	23 ± 6	nd
Olsen P	28 ± 4	nd
Oxalate-extractable P	2 320 ± 451	610
Oxalate extractable Al	65 820 ±9 030	927 ± 498
Oxalate extractable Fe	13 930 ± 7 695	109 300 ± 32 200
Total P	2 157 ± 361	710
Total Al	118 700 ± 24 260	61 390 ± 35 920
Total Fe	37 000 ±19 740	220 900 ± 32 200
Total Ca	10 360 ± 4 299	nd
Total Mg	2 407 ± 572	nd
Total Na	355 ±142	nd
Total K	3 547 ± 582	nd
Total S	6 763 ± 2 955	nd
Total Mn	2 998 ± 1 122	1 088 ±178
Total Zn	98 ± 31	36 ± 4
Total Cu	624 ± 581	46 ± 12
Total Ni	28 ± 10	64 ± 14
Total Pb	22 ± 12	47 ± 1
Total Cr	20 ± 12	38 ± 4
Total Cd	0.12 ± 0.02	nd
Total Hg	0.46	nd
Total Mo	0.9 ± 0.5	nd

nd = Not determined

2.6.3 Phosphorus removal mechanisms in DWTR

Due to the high quantities of amorphous Fe and Al hydroxides present in DWTR the main mechanism for phosphorus removal in DWTR is thought to be via a ligand exchange reaction (Yang et al., 2006b). In ligand exchange the sorbing phosphate anion forms a covalent chemical bond with a metallic cation at the sorbent surface resulting in the release of other potential determining ions such as OH^-, Cl^- and SO_4^{2-} previously bonded to the metallic cation (Yang et al., 2006b). Thus phosphate is said to form an inner sphere complex at the sorbent surface (Loganathan et al., 2014). The phosphate ions can form either monodentate or bidentate complexes on the metal oxides as shown in Figure 2.6 and 2.7 (Sigg and Stumm, 1981). The formation of bidentate complexes takes place at low phosphorus saturation of the oxide surface, whereas at higher phosphorus saturation, monodentate complexes dominate. The phosphate once adsorbed is much less likely to be released if bidentate complexes are formed (Klimeski et al., 2012).

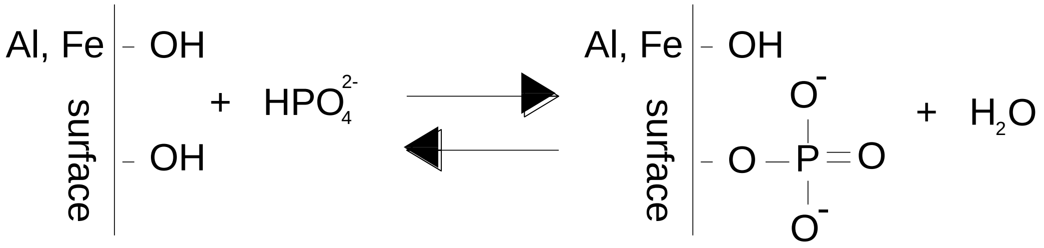


Figure 2.6. The formation of monodentate complexes on metal oxide surfaces

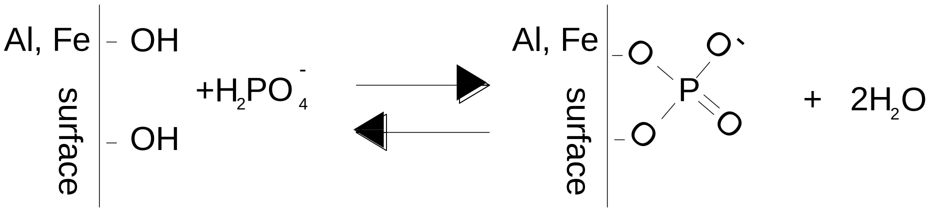


Figure 2.7 The formation of bidentate complexes on metal oxide surfaces

To further characterise the phosphorus removal mechanisms, many research groups have observed the phosphorus removal kinetics of DWTR. Phosphorus sorption kinetics by metal hydroxides are well characterized and generally show a fast sorption phase followed by a slower reaction rate where sorption may never reach true equilibrium. The fast reaction is ascribed to low energy external surface sites where ligand exchange is believed to be the main adsorption mechanism. The slower reaction between phosphorus and metal hydroxides can proceed for days or months and has been attributed to surface precipitation reactions or intraparticle diffusion into micro pores of the DWTR (Makris et al., 2004b, Loganathan et al., 2014).

Discerning when the reaction changes from adsorption to precipitation is not possible from analysis of the kinetics alone and requires more detailed analysis of the surface chemistry, (Li and Stanforth, 2000). This has not been undertaken in detail for DWTR. However research has been undertaken to assess the role of diffusion processes in the removal of phosphorus (Makris et al., 2004a, Makris et al., 2005b, Yang et al., 2006b). By using the intraparticle diffusion model Babatunde and Zhao (2010) concluded that phosphorus adsorption takes place via surface exchange reactions until the surface functional sites are fully occupied and thereafter the phosphorus molecules diffuse into the pores of the DWTR. Makris et al (2004a) postulates that phosphorus must be moving into the intraparticle pores of the media as measured micro pore volume decreased as more phosphorus was adsorbed. The same study also found that an intraparticle diffusion model fitted phosphorus removal data well (r^2= 0.83), and the maximum apparent phosphorus diffusion coefficient was calculated as $4 \times 10^{-15} cm^2 s^{-1}$ which agreed with published values for intraparticle diffusion in microporous sorbents. In an alternative study. Makris et al (2004b) further hypothesised that phosphorus bound in micropores should not be released in circumneutral pH aqueous media, which makes the phosphorus sorption process practically irreversible barring disintegration of the particles themselves.

2.6.3.1 First and second order kinetic studies of DWTR

Most studies on DWTR kinetics have used pseudo first and second order analysis (Makris et al., 2005a, Song et al., 2011, Babatunde and Zhao, 2010, Gao et al., 2013) the majority of authors find reasonable fits to fist order kinetics but very good fits (r^2>0.97) to second order kinetics.

The constants from the PFO and PSO analysis provide useful information to enable comparison of different media and show how the kinetics of removal vary with different inlet phosphorus concentrations. A summary of the PFO and PSO results from a number of studies is shown in Table 2.14.

The rate constants show great variation across the different experiments 0.011 to 11.6 min^{-1} for the PFO and 0.003 to 2.5 g mg^{-1} min^{-1} for the PSO constant. Both experiments that observed the affect of different inlet concentrations showed a marked decrease in both first and second order rate constants and an increase q_e as inlet phosphorus concentration is increased. This implies that the contact time necessary to achieve equilibrium might be affected by the initial phosphorus concentration with more time being required to reach equilibrium at higher values of initial phosphorus concentration (Babatunde and Zhao, 2010).

Makris et al. (2005a) used a different experimental and theoretical method to calculate PSO constants. This involved a very high initial dose of phosphorus and very long retetntion times of 80 days with no shaking thus the results are not directly comparabel with the other experiments listed on Table 2.15. Makris's experiments compare 7 DWTR taken from different treatment plants, and the PSO constants show a very large spread 1.3 x 10^{-4} to 1.24 x 10^{-9} (L s^{-1} mg^{-1}). These results clearly demonstrates the great heterogeneity of the different media in relation to phosphorus adsorption.

It is commonly reported that the kinetics of adsorption between Fe and Al based media is different with Al-DWTR exhibiting faster phosphorus sorbtion kinetics than Fe based media (Makris et al., 2004b).

				First order				Second order			
Coagulant Type	Mass (g)	Size (mm)	Initial Pconc. (mgL^{-1})	Measured q_e (mg g^{-1})	Calculated q_e (mg g^{-1})	K_1 (min^{-1})	r^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	r^2	Reference
Fe and Al	2.5g in 500ml	<0.18	30	3.59	3.22	.006	0.94	3.5	0.003	0.98	(Gao et al., 2013)
Fe	.15g in 250ml	<0.098	27.43	nr	21.98	11.16	nd	26.12	2.85	nr	(Song et al., 2011)
Al	1g in 100ml	<2	5	nr	0.11	0.05	.95	.51	0.83	.99	(Babatunde and Zhao, 2010)
Al			15	nr	0.44	0.02	.97	1.45	0.13	.99	“
Al			30	nr	1.06	0.014	.97	2.54	0.05	.99	“
Al			60	nr	2.3	0.011^{-2}	.92	4.47	0.02	.99	“
Fe and Al	0.5g in 50ml	<2	100	4.97	4.74	.78	.99	5.01	.33	.99	(Wang et al., 2011)
Fe and Al			500	18.01	16.51	.65	.97	17.79	.06	.99	“
Fe and Al			1000	23.74	21.38	.44	.88	23.86	.03	.94	“
									*(L s^{-1} mg^{-1})		
Al	nr	<2	1000	nr	nr	nr	.87	nr	2×10^{-7}	.98	(Makris et al., 2005a)
Al			“	nr	nr	nr	.86	nr	3.4×10^{-5}	.95	“
Al			“	nr	nr	nr	.84	nr	1.3×10^{-4}	.94	“
Al			“	nr	nr	nr	.89	nr	2.4×10^{-4}	.96	“
Fe	nr	<2	1000	nr	nr	nr	.8	nr	1.07×10^{-7}	.97	“
Fe			“	nr	nr	nr	.71	nr	5.8×10^{-9}	.77	“
Fe			“	nr	nr	nr	.12	nr	1.24×10^{-9}	.12	“

Table 2.15 Reported results of Pseudo first and second order kinetic analysis of various DWTR (All samples were air or oven dried)

2.6.3.2 *Specific Surface area (SSA)*

SSA is defined as the external surface area per weight of a dry particle and is usually measured in m^2g^{-1} (Crittenden et al., 2012). Logically the greater the SSA of a material the more surface area is available for adsorption, thus media with high SSA have been traditionally used for adsorption processes. However measuring SSA is a relatively complex process. The majority of SSA results reported for DWTR use the adsorption of nitrogen at low temperature, with the surface area being derived from adsorption isotherm data and the application of Brunauer Emmet Teller (BET) theory. However by analysing the maximum parking density of PO_4 molecules Makris et al (2004b) found that the amount of phosphorus adsorbed by the DWTR was greater than was possible when compared to the N_2-SSA results. The study suggested that this is because N_2 molecules do not have the necessary activation energy to overcome barriers associated with micropores that might be present in DWTR's. To overcome this problem Makris et al used CO_2 instead of N_2 and analysed the experimental data using the Dubinin Radushkevich method. Generally the CO_2-SSA calculations produces a much higher result than N_2-SSA see Table 2.16.

The adsorption of polar liquids is often used to measure the SSA of soils, but has not been applied in many cases to DWTR. This method involves wetting a sample with Ethylene Glycol Monoethyl Ether (EGME), equilibrating and then removing excess liquid through evacuation. The SSA is calculated under the assumption that a monomolecular layer of EGME is adsorbed on the surface (Cerato and Lutenegger, 2002). Values for all three methods measured by different research groups for various DWTR both before and after saturation with phosphorus are shown in Table 2.15.

Table 2.16 SSA measured for DWTR using three different methods.

Coagulant Type	SSA no P (m^2g^{-1})	SSA after P saturation (m^2g^{-1})	Method	Reference
Al	nd	525	BET- N_2	(Georgantas and Grigoropoulou, 2005)
Al Fe	nd nd	227 6.7	BET- N_2 BET- N_2	(Boyer et al., 2011) “
Al and Fe	45-55	nd	BET- N_2	(Wang et al., 2015)
Fe and Al	76.8	nd	BET- N_2	(Gao et al., 2013)
Fe and PAC PAC	74 52	nd nd	BET- N_2 BET- N_2	(Bai et al., 2014) “
Fe Fe Al Al Al Fe	30 150 45 130 110 30	15 140 50 130 80 18	BET- N_2 BET- N_2 BET- N_2 BET- N_2 BET- N_2 BET- N_2	(Makris et al., 2005b) “ “ “ “
Fe Al	3.9 [27.5] 36 [104.9]	2.9 [17.3] 27 [79.9]	BET-N_2 [DR-CO_2] BET-N_2 [DR-CO_2]	(Makris et al., 2004b) “
Fe	33	nd	EGME	(Park, 2009)
Al	28-41	nd	BET- N_2	(Babatunde et al., 2009)

PAM = Polyacrylamide, PAC= Polyaluminium chloride

The SSA measurements show a very large range from 7 to 525m^2g^{-1}. Al based media tend to have higher SSA with an average ≈90m^2/g compared with 50m^2g^{-1} for Fe based media. There is generally a small reduction in SSA measurement once the media has been saturated with phosphorus but this is not always the case. Although Makris measured low values for SSA using N_2 many other researchers report very high values using this method. This either points to a great heterogeneity of the media or a great variation in experimental procedure.

Typical SSA values for activated carbon vary from 400-1500m^2g^{-1} (Crittenden et al., 2012), and average values for typical low cost materials that have been analysed for phosphorus removal are between 1-10 m^2g^{-1} (Boyer et al., 2011). Thus it can be seen that although DWTR cannot compete with the adsorption capacity of activated carbon it compares very favourably with other waste and natural products.

2.6.3.3 DWTR Amorphous nature

High SSA values are generally associated with materials that are amorphous in nature, many studies have examined DWTR morphologically using scanning electron microscopes (SEM) and X-ray diffraction (XRD). All the studies report that DWTR is almost totally amorphous in nature having no distinct shape or form (Yang et al., 2006a, Boyer et al., 2011, Ahmad et al., 2016, Babatunde et al., 2009, Ippolito et al., 2011). The lack of crystallisation present in DWTR further adds to the hypothesis that adsorption is the main mechanism for phosphorus removal in DWTR.

2.6.3.4 Limits of phosphorus removal with adsorption

Although it is clear that adsorption processes represent the main removal mechanism of phosphorus by DWTR, it must be noted that once sorption sites are used up no more phosphorus can be removed and the media would have to be replaced. Generally only a small fraction of sorption capacity can actually be utilized under field conditions because of low incoming concentrations compared to those needed to fill the sorption sites (Vymazal, 2007).

2.6.4 Factors effecting phosphorus adsorption by DWTR

2.6.4.1 pH

Many studies have observed the effect of altering solution pH on DWTR's ability to adsorb phosphorus. Most authors report that optimal phosphorus removal occurs between pH 4-5 (Kim et al., 2003, Razali et al., 2007, Babatunde et al., 2009, Bai et al., 2014, Al-Tahmazi, 2016). An increase in phosphorus adsorption at low pH can be explained by competitive adsorption between phosphate and hydroxyl ions. The pH at the point of zero charge (pH_{pzc}) also plays an important role. pH_{pzc} for DWTR are commonly reported between 7.5-8.5 (Yang et al., 2006b). At pH below pH_{pzc} the surface would be positively charged. Therefore at low pH phosphate adsorption would be facilitated by electrostatic and chemical attraction onto the positively charged surface. As the pH rises above pH_{pzc} the surface becomes predominantly negatively charged due to competitive adsorption of OH^- and phosphate adsorption decreases (Babatunde et al., 2009).

2.6.4.2 Competition from other ions

Waste waters are known to contain cations and anions at various levels, (Metcalf et al (2014) report average concentrations for chlorides and sulphates of 59 and 39 mgL^{-1}, which is very high compared to 5.6mgL^{-1} for phosphates. Various studies have assessed how competing ions might interfere with the phosphorus adsorption process of DWTR. Georgantas and Grigoropoulou (2007) observed that there was little competition between phosphate ions and other common ions in waste water with aluminium hydroxide selectivity for phosphate >> sulphate > carbonate > nitrate > chloride. Al-Tahmazi and Babatund (2016) carried out extensive research into the competitive effect of both chloride and sulphate ions on phosphorus adsorption by 14 different DWTRs and found no significant ($p<0.05$) effect on the phosphorus selectivity for both Al and Fe based DWTR.

2.6.4.3 The effect of particle size

DWTR can have a very large range of particle sizes. Various groups have assessed how DWTR particle size affects phosphorus adsorption. Yang et al (2006a) graded Al-DWTR into six size ranges varying between 2.36 to <0.63mm and found a steady decrease in adsorption capacity from the larger to the smaller sizes. However after 50 hours size ranges of <0.25mm all had similar adsorption capacities, while the media of size 1 to 2.36mm adsorbed barely half of the dosed phosphorus. Lee et al (2015) used 4 size ranges of dried Al-DWTR (fine, 1.18-2.36, 2.36-4 and>4mm) dosed with 5mgL^{-1} TP. They found the fine media had removed all the phosphorus within 7 hours, media <4mm removed all phosphorus after 24 hours but particles >4mm had removed scarcely half the phosphorus after 50 hours. Lee et al also modelled the isotherms for the different particle sizes using the Freundlich equation and the derived constants are shown in Table 2.17.

Table 2.17 Freundlich isotherm K_f and n values for phosphorus adsorption by Al-DWTR with different particle size ranges (Lee et al., 2015).

Particle Size range	K_f	n	r^2
fine	15.57	6.41	.95
1.18-2.36	8.87	6.6	.84
2.36-4	4.72	7.15	.97
>4	3.05	7.34	.83

Interestingly Wang et al (2011) used 4 different particles size ranges of Al/Fe media 2-0.9, 0.9-0.6, 0.6-0.15 and <0.15mm and found that maximum phosphorus removal occurred for the size range 0.6 to 0.9mm They propose this may have been due to this size range having the highest total organic matter content of the samples tested, and crystallization of amorphous Fe and Al might be inhibited by organic matter providing more adsorption sites for phosphorus removal. However they also suggest that the 0.6-0.9mm range may have been more enriched with Fe and Al due to the heterogeneity of the samples.

2.6.4.4 Anaerobic / aerobic conditions

When DWTR is used in any kind of engineered adsorption process the redox status of the system will inevitably change. If the system has long retention times it will inevitably become anoxic or anaerobic. Under anaerobic conditions a release of phosphorus into soil solutions has commonly been observed in phosphorus bioretention systems (Roy-Poirier et al., 2010). This release of phosphorus has generally been explained as a result of the reduction and dissolution of (Fe^{3+}) (Oliver et al., 2011, Leader et al., 2008). There is significant evidence that in soils this process is actually mediated by soil microorganisms (Roy-Poirier et al., 2010).

Oliver et al. (2011) examined the capacity of Fe-DWTRs to retain sorbed phosphorus and sorb further additional phosphorus from aqueous solution under both aerobic and anaerobic conditions. The results showed that even in treatments with initial solution phosphorus concentrations of 100 mgL^{-1}, soluble reactive phosphorus concentrations rapidly fell to negligible levels (due to sorption by DWTRs). This equated to an added phosphorus retention rate of >98% regardless of anaerobic or aerobic status, indicating that DWTR are able to sorb and retain phosphorus in both aerobic and anaerobic conditions.

2.6.4.5 The ageing of DWTR

Several investigations have assessed the ability of DWTR to adsorb phosphorus as they age. A few authors suggest that as DWTR ages it may crystallise causing a reduction in the amount of non-structural OH^- at the expense of structural bridging OH^-. Since phosphorus removal is based on the ion exchange of the non-structural OH^- with phosphate ions a steady and significant decline in phosphorus sorption might be seen during the aging process (Georgantas and Grigoropoulou, 2007). However although both Berkowitz et al. (2006) and Georgantas and Grigoropoulou, (2007) found that phosphate sorption decreased by 15 to 50% with increased floc age and crystallinity for aluminium hydroxides over a six month period. Wang et al (2015) found very little difference in the phosphorus removal ability of media after incubating for 180 days before batch testing the media, although they did observe a 10% drop in SSA but this did not cause a change in the quantity of amorphous Fe or Al. Yang et al (2008) also observed no decrease in phosphorus removal performance after ageing Al-DWTR for 18 months in sealed buckets. Makris et al. (2005a) analysed two DWTR samples that had been air-dried for over 5 years and found that ageing under air-drying conditions did not influence the phosphorus sorption capacities of the two materials.

There is general agreement that pure aluminium hydroxides show a marked reduction in phosphorus adsorption as they age, but DWTR does not seem to suffer this effect. Makris et al (2005a) used thermogravimetric analysis to show that water was retained within the internal structure of air-dried DWTRs and postulates that, the number of sorption sites and particle rigidity should have therefore been maintained even under air-drying conditions (Makris et al., 2005a).

2.6.5 Results from Isotherm and flow through experimets using DWTR

2.6.5.1 Isotherm models

Although isotherm models do not provide explicate details of the long term phosphorus sorbing potential of the DWTR they are relativly easy models to produce from a simple and fast experimental procedure.Thus, it is often the first step in the analysis process of DWTRs and typical results for the isotherm models are shown in Table 2.18.

					Langmuir			Freundlich			
Media Type	**Drying**	**Size (mm)**	**Location**	**pH**	**q_m (mgP g^{-1})**	**K_L (l mg^{-1})**	**R^2**	**K_f (mg g^{-1})(L$mg^{1/n}$)**	**n**	**R^2**	Reference
Al-DWTR	Air 1 week	<2	Ireland	7	23	.025	.97	0.53	1.24	.93	(Babatunde and Zhao, 2010)
Al-DWTR	Air	<1.18	Ireland	7	3.12	1.24	.96	nd	nd	nd	(Babatunde et al., 2008)
Al-DWTR	Oven	<2	Korea	7	25	0.107	.98	nd	nd	nd	(Kim et al., 2003)
Fe-DWTR	Oven	<0.098	China	5.5	26.8	2.79	.98	18.03	2.95	.97	(Song et al., 2011)
Fe and Al	Air	<0.18	China	7	13.91	.0053	.97	0.59	2.28	.98	(Gao et al., 2013)
PAC	Oven	0.15-0.6	China	7	15.62	0.36	.98	0.37	1.29	.99	(Li et al., 2013)
PAC,PAM				7	4.2	0.57	.7	0.11	1.26	.97	
$Al_2(SO_4)_3$,PAM				7	60.9	0.03	.98	0.23	1.19	.98	
PAC				7	15.4	0.23	.95	0.255	1.44	.97	
PAC				7	20.4	.22	.95	0.349	1.28	.94	
Al	Oven	D_{60}=1.25	Canada	7-5.5	7.11 (OrthoP)	0.079	.72	1.36	0.63	.96	(Mortula and Gagnon, 2007)
Al	Oven	<1.18	Singapore	nd	nd	nd	nd	15.57	6.41	.95	(Lee et al., 2015)
		1.18-2.36						8.87	6.6	.84	
		2.36-4.00						4.72	7.15	.97	
		>4						3.05	7.34	.83	
PAC	Oven mixed with kaolin and humic acid	2-4	China	7	1.21	0.48	.98	0.36			(Wang et al., 2016b)

Table 2.18 Freundlich and Langmuir Isotherm constants from various DWTR

PAM = Polyacrylamide, PAC= Polyaluminium chloride

The Langmuir q_m in the studies shown in Table 2.18 varied between 1.21 and 60.9 mg g^{-1} of phosphorus adsorbed with an average and standard deviation of 18±16 mg g^{-1}. This is a high value when compared with the majority of materials shown in Table 2.9 and 2.10, but the large standard deviation implies that some DWTR will perform much better than others in terms of phosphorus removal and they should therefore be chosen carefully.

Most of the experiments fit both the Langmuir and Freundlech isotherms well, with r^2 generally above 0.95.

2.6.5.2 Flow through models

Although batch scale experiments provide useful information regarding the characteristics of the adsorption potential of the DWTR, flow through column experiments are more suitable in predicting the actual performance of the media because of their ability to simulate the constant application of a phosphorus solution that is continually being replenished while soluble reaction products are simultaneously being removed. Additionally, flow through experiments can be conducted to simulate a realistic retention time in which phosphorus solutions are in limited contact with the sorption material (Stoner et al., 2012).

Many studies have assessed the phosphorus removal of DWTR in a flow through setting using both synthetic and real waste water. The majority of the studies used columns of diameters from 2 to 10cm with continuous pumping forcing the phosphorus loaded water upwards through a bed of DWTR (Babatunde et al., 2008, Kim et al., 2003, Mortula and Gagnon, 2007, Razali et al., 2007). The tests have been run for varying lengths of time at many different phosphorus concentrations. Babatunde et al.(2008) ran a continuous column with Al-DWTR dried and ground to 1.18mm for over 100 days and varied the residence time from 3 to 0.5 hours. The comparative hydraulic loading rate varied from 2.32. to 9.28m^3/m^2day with a phosphorus loading rate from 3.9 to 16.5 gP/m^2/day. The phosphorus removal rate varied from 91% at start to 25% at finish. The system also performed well by removing 45% of phosphorus which was introduced as a shock load of 106.2g-P/m^2day towards the end of the experiment. The DWTR had a final operating capacity of 2.66mgPg^{-1} which was 83% of that predicted by the Langmuir equation. Razali et al (2007) operated a column using Al-DWTR of particle size <2.36mm for over 60 days with a very high loading rate of 210.5g $PO_4^{3-}m^{-2}d^{-1}$ and HLR of 2.79m^3/m^{2}d. The sludge bed remained stable and removed over 80% of the phosphorus input for the first 30 days and did not reach saturation for over 60 days. Kim et al (2003) used Al-DWTR ground to less than 2mm in upflow columns and found the columns could reduce orthoP from 30 to 1mgL^{-1} for over 250 pore volumes passed.

Some research has been undertaken using DWTR mixed with sand or gravel as a bio-retention media for controlling phosphorus in surface run off. O'Neill and Davis (2011) used columns amended with 5% dried DWTR and loaded them with simulated storm events and found 88.5% of total phosphorus by mass was still being removed after 12 weeks of operation. Lee et al (2015) used columns with mixtures of soil and DWTR. They found that soil mixes amended with 5 and 10% DWTR were able to consistently maintain 90% TP removal efficiency at TP loading of 6.45 gPm^{-3}.

2.6.5.3 Phosphorus species removal by DWTR

Only a few studies have analysed which species of phosphorus is best removed by DWTR both Razali et al (2007) and Kim et al (2003) found DWTR favourably adsorbed orthophosphate>polyphosphate>organic phosphate when the three species were simulated to their level in typical municipal waste water.

2.6.6 Predicting the long term phosphorus removal capacity of DWTR from their physio chemical properties.

Although it is likely that phosphorus adsorption is the key removal mechanism of DWTR. The research discussed in section 2.6.4 above clearly demonstrates that the adsorption capacity is not only highly dependent on the chemical properties of the media but is also affected by physical and process properties such as:

- particle size, porosity and shape
- equilibrium time

- initial phosphorus concentration
- ageing time of the sludge
- pH of the solid-solution system
- crystallographic properties
- properties of the waste water to be treated

(Yang et al., 2008, Klimeski et al., 2012, Dayton and Basta, 2005, Razali et al., 2007).

Many attempts have been made to correlate the physio-chemical properties of DWTR with its ability to remove phosphorus. The majority of this research has tried to correlate the chemical characteristics with the maximum amount of phosphorus adsorbed as calculated using the Langmuir equation. Dayton et al (2003) examined 21 Al-based water treatment sludges and found a significant relationship between maximum amount of phosphorus adsorbed and Al_{ox} ($r^2 =0.69, p<0.01$), but no relationship was found between soluble Ca or clay content and phosphorus adsorbed. Dayton and Basta (2005) studied a further 18 Al-DWTR in 2005 and found a stronger relationship between Al_{ox} and maximum phosphorus adsorbed ($r^2=0.916$, $p<0.01$) but the media was ground to <150µm and left to equilibrate for 6 days. Elliott et al (2002) found that the phosphorus sorbing ability of different types of DWTR when added to a sandy soil amended with biosolids could be predicated based on $Al_{ox}+Fe_{ox}$ but provides no correlation coefficients. However Makris et al (2005c) and Leader et al.(2008) found no significant correlation between oxalate extractable Fe+Al concentration and phosphorus sorption capacity or BET N_2-SSA but Makris did find a positive linear correlation ($p<0.001$) between the amount of phosphorus sorbed normalised to C, and the N_2:CO_2 SSA ratios of the DWTRs.

Both Bai et al (2014) and Al-Tahmazi and Babatunde (2016) used principle component analysis to compare the physio-chemical properties of DWTR , Bai et al found that Al_{ox} accounted for 35.5% of the variations in phosphorus adsorbed, and 28.5% was attributed to an integrated factor related to pH, Fe_{ox}, SSA and organic matter. They also found that desorption of phosphorus was limited but was significantly correlated to Fe_{ox} + Al_{ox}. Al-Tahmazi used three principal components and found that 42.75% of phosphorus adsorption could be related to Al,Fe,Al$_{ox,}$, Fe$_{ox}$ and SSA, 34.56% to Ca content (exchangable Ca),TC,, and TOC and 16.48% to $SO_4^{2-}$and the pH of the sludge. Both Bai and Al-Tahmazi's research demonstrate the complex relationship between competeting ions SSA and the metal content of the sludge.

It is intersting to note that many authors discuss a strong connection between phosphorus removal and the organic carbon content of the media (Oliver et al., 2011, Makris et al., 2005b, Al-Tahmazi, 2016, Bai et al., 2014). There is diagreement as to wether the presence of OC hinders or improves the phosphorus removal performance of the media as Bai et al.and Al-Tahmazi both show a positive correlation betwwen the presense of OC and phosphorus removal wheras Makris et al hypothises that OC inhibits the abilty of media to adsorb phosphorus. Oliver et al (2011) found that organic carbon concentrations in the outlet from their DWTR columns were significantly higher in their anaerobic systems and suggest that there was a strong possibility that the particulate or collodial phosphorus was at least partially associated with the OC. This kind of association is common in soils as particulate and collodial OC is known to be a transport vector of phosphorus (Gburek and Sharpley, 1998). As stated previously Wang et al (2011) postulates that the presence of organic carbon might inhibit the crystallization of amorphous Fe and Al, thus providing more adsorption sites for phosphorus.

2.6.7 Predicting the long term phosphorus removal capacity of DWTR from small scale flow through experiments.

A few studies have built mathematical models from the empirical results of small scale flow through experiments to aid in the prediction of life expectancy of the media.

Lyngsie et al (2015) and Stoner et al (2012) built a comprehensive model to estimate life expectancy of phosphorus adsorbing media given any retention time and inlet phosphorus concentration. The model was built from empirical data collected from many small scale flow through experiments. The model uses two empirical factors LSS and K which are the local sorption saturation and a coefficient determined from the slope of the relationship between cumulative sorbed phosphorus and cumulative phosphorus loaded. Once these factors are calculated it was found that there was a linear relationship between LSS, K and the retention time and inlet concentration. Therefore using multiple linear regression it was possible to predict the LSS and K factor given any input P and retention time. A very similar model was used by (Penn, 2011) to predict the performance of an operating steel slag flow through filter. This study found that the model slightly over predicted the cumulative phosphorus that was removed whereas the Langmuir model highly over predicted the media performance.

Another method of evaluating the long term performance of low cost adsorbents using small scale adsorption columns was proposed by Callery et al (2016). They hypothesised that an equation following the form of the Freundlich isotherm would describe the relationship between filter loading and media saturation; as the experimental results produced by plotting volume of effluent treated against mass of phosphorus adsorbed per unit mass of filter media strongly resembled the shape of the isotherm curve.

They propose the equation

$$\boldsymbol{q_e = AV^{\frac{1}{B}}}$$ ***Equation 2.11***

Where

B = a dimensionless constant of system heterogeneity, equivalent to n in the Freundlich equation
A = is a constant of proportionality with units mg g^{-1} $L^{-1/B}$
V = volume treated by filter (L)

The model was tested by analysing previously published data. The study found that the using data from small column experiments the model could predict the performance of a large scale adsorption filter for a period of three months with a high degree of accuracy (Callery et al., 2016).

In summary predicting the amount of phosphorus that a DWTR will adsorb is highly complex and is still unclear. However the magnitude and rate of phosphorus adsorption are related to Fe and Al content, DWTR internal structure (pore size) and SSA which in turn may be affected by organic carbon a major but variable component of DWTR's (Makris et al., 2005b). Using the Langmuir equation with batch experiments should be used with caution as it tends to lead to biased and unrealistic estimates of phosphorus adsorption parameters (Drizo et al., 2002) . However, empirical models proposed by Callery et al (2016) and Lyngsie et al (2015) using small scale column flow through data offer the potential for more accurate prediction of life expectancy.

2.6.8 Leachability studies

Although DWTR have been declared non-hazardous, according to the toxicity characteristic leaching procedure assessment method by the US EPA (Wang et al., 2014). DWTR contain many metals and contaminates that would cause problems if they were to leach from the media. There would be no point in removing phosphorus from the waste water only to increase levels of metals and other organic pollutants in the receiving waters. Much research has been undertaken to ascertain if DWTR leach Al, Fe and natural organic matter when the DWTR has been used in land application (Elliott et al., 1990a) and in waste water (Liu et al., 2016, Zhao et al., 2010, Babatunde et al., 2011a)

Because of strong adsorption and co precipitation by freshly formed Al and Fe hydroxides in the coagulation treatment step most heavy metals in DWTRs are predominantly bound in forms not readily released into solution (Elliott et al., 1990a). Therefore, in none of the studies assessed does leaching of metals appear to be a problem in either land or water based applications of DWTR. However in land applications, if the soil becomes acidic<5, there may be an issue with metal release (Elliott et al., 1990b). Both Thanalechumi et al (2015) and Babatunde et al (2011a) found that Al leaching was well below legislative limits as long as the first few bed volumes of water passing through the media were not discharged.

Natural organic matter (NOM) leakage from the media was studied by Liu et al (2016). Although this study found that DWTR leaches very low levels of NOM, they did find that NOM is released in greater quantities in alkaline conditions and with smaller particle sizes. Interestingly, they also found a positive relationship between NOM released and phosphorus adsorbed, this further demonstrates the complex relationship between phosphate, OH^- and organic substances.

It is the general conclusions of all the studies that leaching of either organic matter or metals is well below any legislative limits, and would therefore not be a limiting factor in the use of DWTR in a phosphorus adsorption system.

2.6.9 Using water treatment sludge for phosphorus removal before it is dewatered.

A few test have been undertaken using the raw sludge taken straight from the bottom of the clarifying tanks in the water treatment works and analysing its ability to remove phosphorus in waste water. Maher (2015) found the sludge to be very effective at removing phosphorus. The research found SRP removal of > 90% with 1 minute contact time. However, using the water works sludge in this way would require that the water treatment works are close to the waste water works as transporting raw sludge is likely be a huge expense, unless it could be pumped through existing pipework.

2.6.10 Recovering coagulant

Rather than using the sludge directly there is a case for trying to recover the coagulants from the sludge and using these for phosphorus removal. Re-solubilisation of coagulant metals with acid and re-use of the supernatants saw full scale use in the 1970’s but was withdrawn due to concern over its lack of specificity (Prakash and SenGupta, 2003). A detailed economic assessment of three methods of coagulant recovery was undertaken by Keeley et al.(2012); Donnan dialysis, electrodialysis and ultrafiltration. It was concluded that the economic viability of all these processes is dependent on a number of external prices, performance criteria and process practicalities. The current low value of ferric coagulants makes selective recovery of coagulant uncompetitive.

2.6.11 Making more complex phosphorus removal media by treating the DWTR.

A variety of research groups from around the world have tried to modify the DWTR to improve its phosphorus removal ability and longevity by either adding other components to the media and heating in an oven or grinding. Some of the experiments undertaken are summarised in Table 2.19.

Table 2.19 Performance and production of materials made from DWTR to remove phosphorus.

Process description	Performance	Reference
Mix DWTR with kaolin, humic acid and deionized water to make balls 2-4mm in diameter and baked at 200^0C	Average removal of SRP of 80%, q_m = 1.33mg g^{-1}	Wang et al., 2016c
DWTR treated in a nitrogen atmosphere at 350^0C for 4 hours then washed with deionized water and then oven drying at 50^0C.	Very poor P removal	Wang et al., 2016a
Dried and ground the DWTR , followed by high energy ball milling to produce particles from 45-96nm in diameter	The particles showed an increase in SSA from 53 to $129m^2g^{-1}$ and a 30 fold increase in P adsorption from $1.66mgg^{-1}$ to 50 mgg^{-1}	Elkhatib et al., 2015
The sludge was dried and then mixed with kaolin and deionized water making 20-30mm ball. The balls were then heated at 200 and 650^0C in a furnace	The balls were used in a column experiment that ran for one year fed with synthetic waste water with an inlet of $6.4mgL^{-1}$TP. The hyalite balls continually removed over 97% of the P applied	Wang et al., 2016b

Although the phosphorus removal performance of the media can be enhanced by altering its properties, particularly by high energy ball milling, the processes shown in Table 2.19 would demand a high energy cost and would therefore not be viable economically.

2.6.12 Summary of using DWTR for phosphorus removal

DWTR has the potential to be a relatively cheap and stable way of removing phosphorus from waste water. Many studies have shown that DWTR can remove over 90% of phosphorus from waste water for well over a year. DWTR has similar chemical constituents but can have very different quantities of the chemicals and particle sizes present and can therefore have very heterogeneous characteristics. The mechanism of adsorption is most likely to be a fast process of surface adsorption followed by a slow process of intraparticle diffusion. The characteristics that make the best DWTR for phosphorus removal are not well understood and there is still disagreement between research groups. However it is most probably related to the amount of Al, Fe, SSA, TC and particle size of the media and the pH of the waste water to be treated. The media is unlikely to leach any harmful contaminants and although altering the media by processing could enhance its phosphorus removal properties this is unlikely to be cost effective. No long term large scale studies using DWTR have been undertaken to date.

2.7 Constructed Wetlands for phosphorus removal

One of the aims of this research was to assess the possibility of using DWTR in a constructed wetland. Phosphorus removal in constructed wetlands has been studied by a variety of authors and is summarised below.

2.7.1 Types of constructed wetland

Constructed wetlands are man made systems that have been designed to emphasize specific characteristics of wetland processes found in nature. They can be broken down into two main groups in terms of the hydraulic flow regime:

- surface flow wetlands, which have an area of open water
- subsurface flow, where the flow is primarily underground

In the UK the majority of wetlands are subsurface flow, as surface flow wetlands tend to require much larger areas for the same level of treatment performance. Subsurface flow reed beds can be divided into horizontal and vertical systems.

- Horizontal subsurface flow wetlands typically use a gravel media planted with wetland vegetation. The water flows horizontally from the inlet to the outlet.
- Vertical flow wetlands generally have a distribution system that spreads the water over the surface until it is flooded. The effluent then slowly drains down through the media, with the contact time depending on the hydraulic conductivity of the media. The flow can also be in a tidal arrangement where the media is filled and then drained down. Less commonly vertical flow beds can be engineered with a continuous flow regime (Kadlec and Wallace, 2008).

2.7.2 Phosphorus forms and movement through wetlands

Phosphorus occurs as soluble and insoluble complexes in both organic and inorganic forms in wetlands. Inorganic forms include orthophosphates (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$) with the predominant form depending on pH. Phosphorus readily combines with dissolved organic materials within wetlands and as such is termed dissolved organic phosphate (DOP). DOP has been characterized in great detail for treatment wetland situations and found to consist of several kinds of organics, some of which are readily hydrolysed by soil enzymes. The hydrolysed organics and orthophosphate are classed as soluble reactive phosphorus (SRP). The organic components of SRP can move readily in soils and sediments (Anderson and Magdoff, 2005). Phosphorus also has an affinity for calcium, iron and aluminium; forming complexes if they are readily available (Mitsch and Gosselink, 2000). Phosphorus may also be associated with suspended particles in the reed bed matrix and this is classed as particulate phosphorus (PP). Wetlands provide an environment for the inter conversion of all these forms of phosphorus see Figure 2.8.

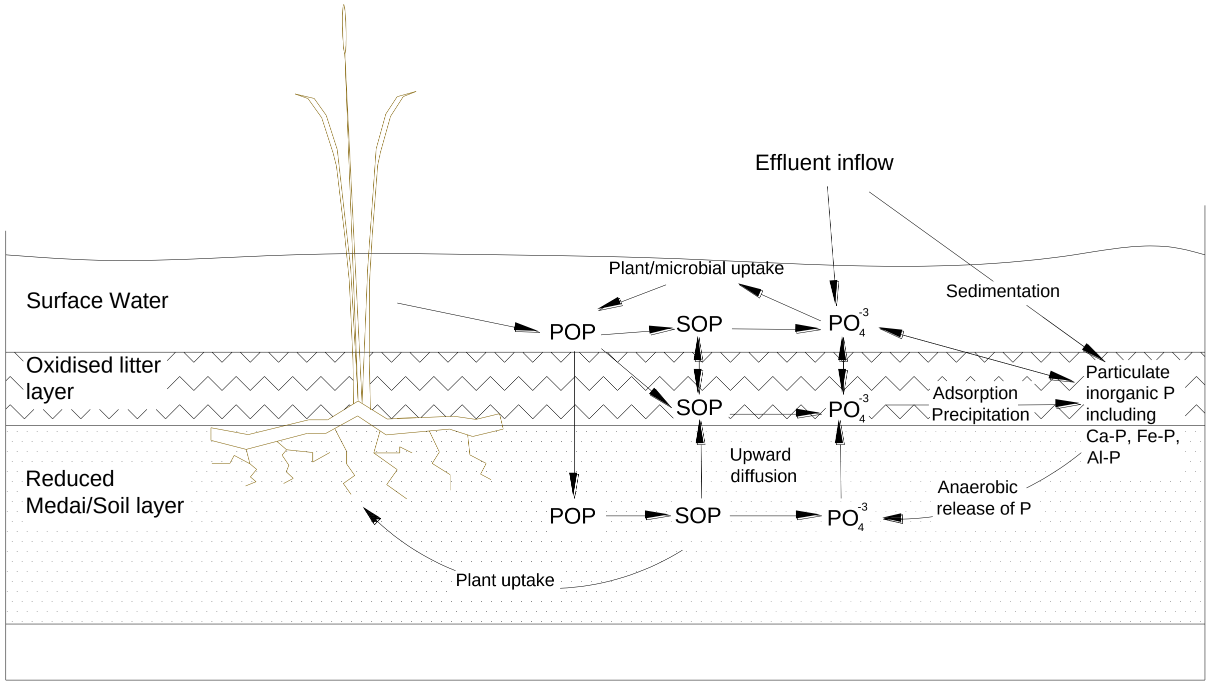


Figure 2.8 The phosphorus cycle through wetlands, adapted from Mitsch and Gosselink (2000).

Key

PO_4^{3-}: phosphates SOP: soluble organic phosphorus POP: particulate organic phosphorus

Trends for phosphorus movement in soils are as follows

- In acid soils, phosphorus may be fixed by aluminium and iron.
- In alkaline soils phosphorus may be fixed by calcium and magnesium if available.
- Reducing conditions may lead to solubilisation of iron minerals and release phosphorus co-precipitates.
  (Kadlec and Wallace, 2008).

2.7.3 Historical removal of phosphorus in wetlands

Constructed wetlands have been growing in popularity as both secondary and tertiary water treatment systems over the last few decades. There were over 1200 constructed wetlands in the UK in 2007 and this number has been steadily increasing (Cooper, 2009); of these 659 were being used as tertiary treatment beds, 86 as secondary treatment and 46 for combined sewage overflow and tertiary treatment. Although constructed wetlands are relatively simple to build and operate, the processes of treatment that occur within wetlands are very complex using a combination of biological, physical and chemical processes to remove contaminants from waste streams. Reed beds have proved to be very good at removing suspended solids and BOD. However, they have been historically very poor at removing phosphorus from waste water generally removing no greater than 50% TP and often less, (Brix et al., 2001, Martín et al., 2013, Vymazal, 2007).

Rustige (2003) analysed data from 50 constructed wetlands which had been operating for over 3 years and found that initially the beds removed 70 to 85% SRP but this fell to 50% after the third year and below 35% in the following years. Similar results were found by Tenner et al (1999) who loaded five gravel beds with dairy waste at various hydraulic loading rates. TP removal decreased over a 5 year period with all beds converging to removal rates of between 6-23% TP (Tanner et al., 1999).

2.7.4 Permanent Phosphorus removal and storage within constructed wetlands

Phosphorus retention within wetlands can be defined as the capacity of the system to remove water column phosphorus through physical (sedimentation), chemical (sorption and precipitation) and biological (plant and microbial uptake) processes, and retain it in a form that is not easily released under normal environmental conditions (Dunne and Reddy, 2005). The different methods of phosphorus storage within a constructed wetland represent many routes for the removal of phosphorus and are discussed in detail below.

2.7.4.1 Quantities of phosphorus in different components of wetland systems

Phosphorus compounds form a significant proportion of the living parts of a wetland including plants, detritus, microbes, wildlife and soils. The mass of these varies greatly in different wetland types and with the seasons (Kadlec and Wallace, 2008). An approximation of the relative masses of phosphorus in various components of a wetland are shown in Figure 2.9.

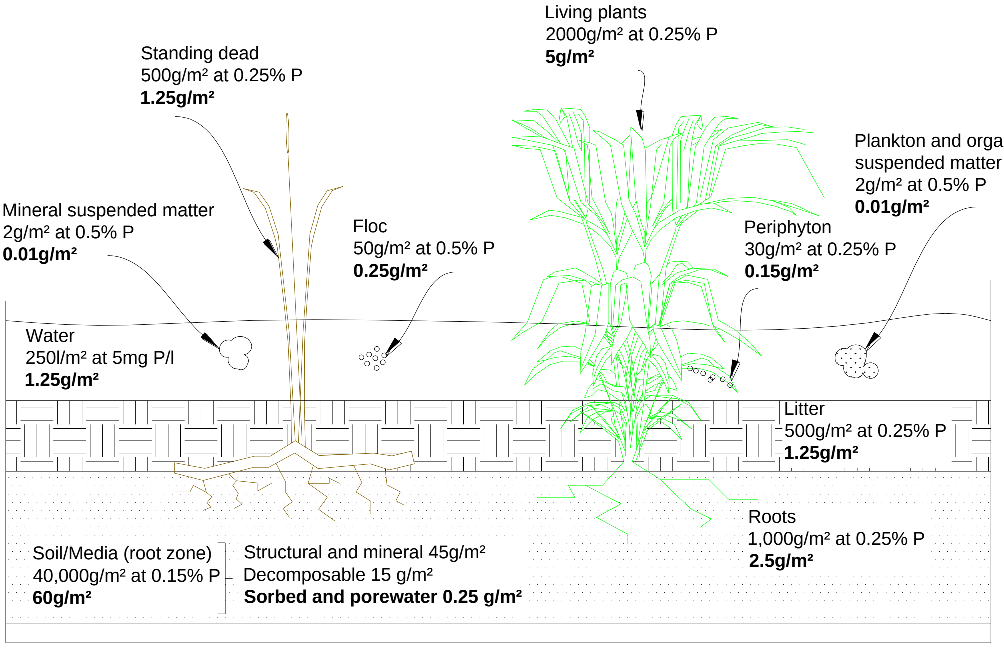


Figure 2.9 Approximate phosphorus storage levels in a constructed wetland adapted from Kadlec and Wallace (2008).

Phosphorus entering subsurface flow wetlands can be stored in plant biomass, the wetland media or accreted sediment. The largest proportion of phosphorus is found in the wetland soil/media and sediment. Plants and litter comprise most of the remainder, a very small amount being found in the microbes' algae and water (Kadlec and Wallace, 2008).

Soluble reactive phosphorus is taken up by plants or may become sorbed to the wetland media. Organic phosphorus may be released as soluble phosphorus if the organic matrix is oxidised. Insoluble precipitates form under some circumstances, but may redissolve under altered conditions. Organic phosphorus forms can generally be grouped into:

- Easily decomposable organic phosphorus (nucleic acids, phospholipids and sugar phosphates).
- Slowly decomposable organic phosphorus (inositol phosphates or phytin).

In general large quantities of organic phosphorus can be immobilised in wetland soils/media and only a small portion of this organic phosphorus is bioavailable. The relative recalcitrant nature of this phosphorus means this storage represents one of the key removal mechanisms for phosphorus from waste water in wetlands (Dunne and Reddy, 2005).

2.7.4.2 Plants

Plants can uptake a substantial amount of phosphorus but this varies greatly from season to season with the plant uptake reaching a maximum by the end of the growing season followed by a senescence season decrease to a minimum (Kadlec and Wallace, 2008).

Plants uptake phosphorus through their root system. The phosphorus is transported from the rhizosphere to the above ground components of the plant by diffusion and vertical movement driven by transpiration flux. Some of the new plant growth is taken from stores in the rhizomes and some is taken directly from internal pore water. It is possible that phosphorus rich pore water causes less withdrawal from the rhizomes (Tanner, 2001).

The process of growth, death, litter fall and decomposition operate all year round, and with different speed depending on climatic conditions and habitat. In cold climates the above ground standing crop changes once per year in hot climates this can be from 3.5 to 10 times (Bernard, 1999).

Various studies have been undertaken to assess the phosphorus uptake by plants (Meuleman et al., 2003, Browning and Greenway, 2003). In some instances the total phosphorus input has been shown to be taken up by the plants during summer months. However, unless the plants are cropped this phosphorus is returned to the water by leaching and decomposition as the plants senescence in winter, so the plants do not represent a net storage system for phosphorus (Kadlec and Wallace, 2008).

2.7.4.3 Removal of phosphorus by harvesting plants

The potential for phosphorus to be removed from a system by harvesting plants seems to be an attractive proposition. However, the literature contains conflicting views as to whether this is a good idea or not. Wang and Mitsch (2000) conclude that harvesting plants can provide a considerable contribution to the removal of phosphorus in wetlands whereas, Crites and Technobanoglous (1998) conclude that harvesting is not a practical option. Vymazal (2007) strikes a more balanced view concluding that the amount of phosphorus that can be removed by plant harvest is usually low but may be significant if inflow rates are $<20gPm^{-2}yr^{-1}$ (Vymazal, 2007).

Kadlec and Wallace (2008) conclude that the harvestable amount of above ground phosphorus is typically $1\text{-}5gPm^{-2}$, but inlet phosphorus loadings can be extremely variable spanning the range $1\text{-}10{,}000g\ Pm^{-2}yr^{-1}$. Thus the fraction of incoming load that may be harvested depends almost entirely on the inlet load. Furthermore harvesting is quite an involved operation requiring complex machines, and once the biomass is removed it must either by composted or digested for biogas. This involves lots of machinery movements and is generally very expensive and not viable when wetlands are being used at WWTP (Kadlec and Wallace, 2008).

2.7.4.4 Removal of phosphorus by accretion.

In traditional constructed wetlands (with soil, sand or gravel as media) the accretion of new sediments and soils represents the only permanently sustainable way that phosphorus can be removed from the influent water as all other forms of removal are saturable and therefore have finite limits, (unless plants are harvested)(Dunne and Reddy, 2005). The wetland environment can provide appropriate conditions for long term phosphorus build up. Historically accumulation in peat lands is of the order of a few millimetres per year or from 0.4 to 4 $gPm^{-2}yr^{-1}$ (Dunne and Reddy, 2005). The accretion of phosphorus in wetlands occurs because of the decaying plants and the settling of refectory solids. The (refractory) decay resistant portion of the plant biomass is generally in the range 10-15% of the overall biomass produced, this equates to an accretion of phosphorus in the top layers of reed beds of around $0.8\text{-}1.2gm^{-2}yr^{-1}$ (Kadlec and Wallace, 2008). Unfortunately, accretion of sediment in subsurface flow wetlands reduces porosity and hydraulic conductivity and represents a major problem to the long term operation of constructed wetlands.

Phosphorus accumulation rates are complex to calculate and are generally assessed either by using atmospheric deposition markers (such as radioactive caesium) or by a mass balance approach (Kadlec and Wallace, 2008). Reported rates of phosphorus accretion in wetlands are generally below 1g$m^{-2}yr^{-1}$ and usually average 0.5g $m^{-2}yr^{-1}$ (Vymazal, 2007).

2.7.4.5 Removal of phosphorus by particulate settling

The internal environment of traditionally designed HSF and VF subsurface flow wetlands are conducive to the removal of suspended solids. The solids are removed through particulate settling and interception mechanisms which result in the deposition of influent TSS in the inlet region of the bed (Kadlec and Wallace, 2008). Tanner (1999) reports of up to 50% of phosphorus removal occurring in the inlet area of their pilot scale gravel beds over a 5 year period, which represented 170 gm^{-2} of phosphorus retention. The accumulation of organic matter, and associated phosphorus, reduced bed porosity by 50% which caused hydraulic problems over the 5 year period.

2.7.4.6 Summary of permanent phosphorus removal

The removal of phosphorus by accretion, plant removal and particulate settling all represent long term removal capacities for phosphorus. However, none of these methods can provide long term viable removal of phosphorus at the loading rates required by WWTW.

2.7.5 Phosphorus removal by sorption processes in wetlands

The material used to construct the wetland is a reservoir of potential adsorption sites for the removal of phosphorus. The amount of phosphorus that can be sorbed is a function of the inlet phosphorus concentration and the material properties of the bed media (Kadlec and Wallace, 2008).

Although sorption process have a finite limit they represent the best way of removing phosphorus in the wetland environment. If the sorption capacity of the media can be made large enough the phosphorus removal efficiency can be sustained for a long period of time before the media will need replacing.

In a theoretical ideal plug flow system water will uniformly flow through the wetland cross section be it vertical or horizontal. Soluble phosphorus will be absorbed by the bed media. As the media sorbs the phosphorus the equilibrium phosphorus concentration increases. Eventually the equilibrium concentration is the same as the inlet concentration and the bed will absorb no more phosphorus as the driving force for the sorption process has stopped. This would of course change if the inlet concentration increases. However, there may be a reverse reaction if the inlet phosphorus concentration reduces (Kadlec and Wallace, 2008). Real constructed wetlands have many processes that complicate the idealized theoretical phosphorus removal these include plant uptake, the development of biological solids, and mineralization of phosphorus. All these processes may free up new sorption sites.

Adsorption materials that can be used in reed beds have previously be shown in Table 2.9 to 2.11.

2.7.6 Using DWTR in a wetland

To assess the suitability of DWTR for use in a reed beds two long term studies using meso scale constructed wetlands to assess phosphorus removal have been undertaken by Babatunde et al (2011b) ,Babatunde et al (2010) and Zhao et al (2010) Shorter trials using DWTR in pre and post filters have been undertaken by Park (2009) and Leader et al (2005).

Park (2009) used Al-DWTR as both pre and post filter beds before and after an oyster shell based meso scale wetland in a 240 day trial. The media was dried and ground to a particle size of 0.6-1.3mm and the overall HRT for the system was 3.5 days. This set the HLR at $0.13m^3m^{-2}day^{-1}$. Although the systems were fed with real waste water, the inlet phosphorus concentration was artificially increased from $3\text{-}5mgL^{-1}$ to between $10\text{-}27mgL^{-1}$. Both systems removed over 99% of the phosphorus input. When the Al-DWTR was used as a pre filter the input to the constructed wetland was reduced from 17.9 to $0.1mgL^{-1}$ when it was used as a post filter the phosphorus across the filter was reduced from 1.17 to

$0.04mgL^{-1.}$ Park reports that from previous experiments the maximum adsorption capacity of the Al-DWTR was 24.5gP kg^{-1} .Since the beds were adsorbing approximately 0.4g d^{-1} and there was 42kg of media, the estimated life expectancy for the system was approximately 3 years (this allows for a 50% reduction from the predicated maximum adsorption performance).

Leader et al (2005) used a similar approach to Park placing Fe and Ca-DWTR in pre-filter units before mesoscale reed beds. The DWTR was not dried but there is no mention of particle size. The experiments were operated for a year with inputs from secondary treated waste water and waste water from a dairy farm (SRP 0.44-1.8 and 3.8-15.6 mgL^{-1}), respectively and TP (0.47-2.5 and 33-49 mgL^{-1}) .The TSS of the dairy water was $2390mgL^{-1}$ compared to $<1mgL^{-1}$ for the secondary waste water. The total HRT of the complete system was 14 days with the water residing in the pre- filter and reed bed for 7 days each. The HLR to the pre-filter cells was $0.08m^3$ m^{-2} d^{-1}. Both systems removed phosphorus with SRP reduced from 0.7 to 0.01 mgL^{-1} (98% removal) and TP removed by 93% with secondary waste water, compared with SRP reduction from of 22% and TP by 53% with the dairy farm waste. After 52 weeks of operation the TP mass reduction was 60% for secondary water. Leader et al (2005) concluded that the dairy water filter was greatly affected by the high TSS and the DWTR was not suitable as a pre-filter. They therefore suggest that the TSS should be removed before entering filters as it has a negative effect on phosphorus removal performance and causes filter blockage.

Meso scale beds were studied by Babatunde et al. (2011b) consisting of two beds in series operated with an HLR of $0.56m^3$ m^{-2} d^{-1} and a HRT of 4 hr, the surface area of each system was $1.17m^2$ with a media depth of 65cm. The media was Al-DWTR with particle size range from 1.48±7.25cm. The system was planted with *Phragmitis australis* and was operated with a tidal flow regime for 46 weeks. The system was fed from a liquid farm waste which had very variable characteristics with PO_4-P from $2.8-60mgL^{-1}$, COD from 124-1644 and SS 25-633). The performance of the bed was variable with percentage removals of 14–84% for COD, 52–100% for TP, 54–100% for PO_4-P. The reed bed system demonstrated a gradual increase in treatment efficiency and except for periods when there were operational disruptions, most of the lower removal efficiencies were recorded during the start up. However, both TP and PO_4-P removal were relatively high and consistent throughout the monitoring period. The system achieved pollutant removal rates ranging from, 35.6–502.0 $gm^{-2}d^{-1}$ for COD and 2.7–14.6 $gm^{-2}d^{-1}$ for PO_4-P. This compares well with typical PO_4-P removal rates of other adsorption based reed bed trials of between 0.23–0.9 $gm^{-2}d^{-1}$ for PO_4-P (Lin et al., 2002). No correlation was found between the removal of TP or PO_4 with BOD, SS or COD, implying that the mechanism of removal was mostly adsorption (Babatunde et al., 2010).

Zhao et al (2010) carried out the largest experiment using raw Al-DWTR as a media in a four stage tidal flow wetland system operated for one year. The four beds were constructed from 1100 litre bins and operated in series with 4 hours load and 4 hours rest time, the influent was a diluted effluent from a farm. The total HLR of the system was $0.29m^3m^{-2}d^{-1}$. Average pH showed a slight decline between influent and effluent (from 7.6 to 7.3). Mean monthly removal rate of COD was 36-84%. The influent TP varied between 10.7 and 33.3 mgL^{-1} and removal rate varied between 75-94%. The first two stages of the system accounted for 75% of TP removal. The highest removal rates were found in the summer months. Generally the effluent concentrations mirrored the influent concentrations suggesting a mass loading limit.

The four trials mentioned above demonstrate that DWTR can be used as a media in a reed bed treatment system and the operation of the systems can sustain substantial phosphorus removal for prolonged periods.

2.7.6.1 Notes on Tidal flow systems and the importance of rest times

The pilot beds operated by Babatunde et al. (2011b) and Zhao et al (2011b) were both operated in tidal flow. Tidal flow systems have not been used extensivly in constructed wetands but offer the considerable advantage of providing capacity for oxygen tranfer to the media while providing substantial contact time and limited short circuiting when compared to horizontal flow beds (Babatunde et al., 2010, Sun et al., 1999).

Tidal flow systems also provide a time period when the media is ‘rested’ with no contact with the influent waste water. It has been noted by many authors that resting the media allows time for the diffusion of the adsorbate molecules further into the absorbent particles, thus resulting in a rejuvenation of the adsorbate surface prior to the next loading (Callery et al., 2016, Ouvrard et al., 2002, Sengupta and Pandit, 2011). Weber and Morris (1963) noted some rejuvenation in their activated carbon adsorption systems when they were left to rest. They concluded that the incompletely exhausted carbon has the ability to regain some of its immediately available surface on standing because of continuing diffusion of the adsorbed solute further and further into the capillaries due to intraparticle diffusion of the adsorbate.

Although the effect of rest time has not been well quantified, it is possible that it might have a significant effect on the ability of DWTR to remove phosphorus. Hu et al (2012) used tidal flow columns with contact times varying between 4 and 6 hours and rest time between 10 minutes and 2 hours. Although the experiments showed that rest time had a significant effect on biological nitrogen removal, the phosphorus removal of the systems stayed very consistent throughout the year long experiment with average TP removal of >95% for all rest times, implying a small effect on rest time. However, Drizo et al.(2008) found that resting previously phosphorus saturated columns consisting of electric arc furnace steel slag for 5 weeks increased their overall phosphorus retention capacity by >49%. It is therefore plausible that resting DWTR for a prolonged period may increase TP adsorption capacity.

2.7.7 Current studies using adsorptive media used in pilot scale wetland trials

Both Thames Water and Wessex Water have been running trials with constructed wetlands using adsorptive media to remove phosphorus. The results of the trials have not yet been published, and the size of the beds or flow rates have not been made available. However the experiment at Thames Water is trialling reed beds using three sizes of Basic Oxygen Furnace Steel Slag (BOF) (5,7 and 10mm) which is a waste product from the steel industry and Apatite which is a manufactured adsorbent. There are 4 beds operating in horizontal subsurface flow with an HRT of 24 hours and input TP of 3-4mgL^{-1}. The beds treat flows for approximately 200p.e. and have been placed after a trickling filter and settlement tanks. Currently the beds have been operational for a little over a year and the appetite is still removing >94% of the TP input and the BOF between 89 and 94% depending on the particle size (smaller particle size has higher removal rate). Although the phosphorous removal is very good the media all increase the outlet pH to above 9 and initially above 12. There has also been a problem with Vanadium leaching from the BOF (Fonseca, 2016a). Very little information has been published about the extensive Wessex water trial.

2.8 Phosphorus removal to ultra-low levels

The implementation of the WFD may require ultra-low levels of phosphorus removal from waste water (<0.05mgL^{-1}), which cannot be achieved by chemical or biological treatment alone. Thus in recent years, particularly in the USA many systems have been designed to remove phosphorus to these levels. All the systems are used as a tertiary treatment step generally after secondary clarification with some form of biological process as the secondary step (trickling filters, activated sludge, biodisc etc.). The majority of the systems used to achieve ultra-low levels of phosphorus in waste water rely on

- Combinations of chemical and biological treatment or
- Tertiary filtration with granular medium filters or
- Novel technologies, including membranes, mechanised deep bed filters, magnetic separation and ion exchange

The expected levels of phosphorus removal associated with these technologies are summarised in Table 2.20.

Table 2.20 Expected phosphorus removal performance of different processes(Benisch et al., 2011)

Effluent TP mgL^{-1}	Process
<1	BPR and good clarifiers
<0.5	BPR, good clarifiers and filtration
<0.1	BPR, filtration and chemicals
<0.05	BPR, Post chemical plus filtration
<0.01	BPR, Chemical , Adsorption, membranes

.

A brief summary of advanced technologies to remove phosphorus is presented in Table 2.21.

Technology Type	Operation	Best P removal results (mgL^{-1})	Companies	Reference
Continuous Upflow Moving Bed Filters	Effluent forced upward through a moving bed of sand after being dosed with Fe or Al salts. After adsorption the Fe and P are abraded on the sand and a wash box separates the sand from waste Fe and P particles.	0.02	Densadeg®, Parkson DynaSand® BluePRO®	(deBarbadillo et al., 2010) (Benisch, 2007)
Ballasted and Magnetic Flocculation/Settling Processes	The ACTIFLO is a compact process that operates with microsand as a seed for flock formation. The microsand ballasted flocs have enhanced settling characteristics which allow clarifier designs with very high overflow rates and short retention times. The process comprises coagulation, sand and polymer injection, floc maturation, lamella clarification and sand recovery	0.05	ACTIFLO® Turbo process BioMag/CoMag®	(O'Hare and Perry, 2010) (deBarbadillo et al., 2010) (Tozer et al., 2007) (Woodward and Andryszak, Ellis and Cathcart, 2008)
Ultrafiltration	A flocculation tank is normally used upstream, in which alum is dosed to precipitate the reactive P. The solids are then filtered out by outside-in hollow fibre modules immersed directly in the feed water, nominal membrane pore size is 0.02µm. Membranes typically operate in semi batch mode where filtration and backwashing are alternated in sequence	0.02	ZenonZeeWeed™500 and 1000Ultrafiltration	(deBarbadillo et al., 2010) (Benisch, 2007) (Benisch et al., 2011)
Membrane Bioreactor (MBR).	MBR's utilise ultrafiltration membranes in conjunction with biological phosphorus removal (BPR). Effectively an ultrafiltration membrane is placed in the aerobic tank of a BPR process. An MBR differs from an ultrafiltration system as microbial growth is encouraged on the membrane surface	0.036		(Benisch et al., 2011) (Hu et al., 2014, Monclús et al., 2010)

Table 2.21 Processes to achieve ultra low phosphorus levels

The processes shown in Table 2.20 have all been operational in full scale trials and some of the technologies are now fully operational. Although the technologies are very successful at removing phosphorus to a very low level they all rely on complex operational control systems and machinery. Many of the studies undertaken on the pilot scale systems show very poor results as soon as there is any equipment failure (deBarbadillo et al., 2010, Falconer et al., 2011). All the systems also require a large amount of energy to run the many pumps and valves which keep the processes operational (Barnard et al., 2011).

2.9 The environmental and financial cost of removing phosphorus from waste water.

2.9.1 The case for a more holistic view of water treatment

For over 100 years, drinking water and wastewater treatment have existed for the protection of human health. In more recent decades, regulatory authorities in industrial regions have endeavoured to improve local water quality by more advanced forms of wastewater treatment. However, increasingly sophisticated means of treatment come at a cost of higher resource consumption and elevated environmental emissions. To date these environmental burdens have gone largely ignored or have in the main not been taken into consideration (Foley et al., 2010).

Instead of the traditional approach, a sustainable water and wastewater decision-making process considers environmental, economic and social ramifications of decisions across spatial and temporal scales. Sustainability demands that we acknowledge wastewater as a renewable resource from which we can extract water, fertiliser, bio plastics and energy rather than a waste product (Guest et al., 2009, Wyant et al., 2013).

The World Commission on Environment and Development defines sustainable development as ‘development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs' (WCED, 1987, Balkema et al., 2002).

To assess the full effect of treatment pathway the process must be analysed in terms of the whole life cycle of all the components, inputs and outputs form the system. This type of analysis has been undertaken by several research groups for the process involved in phosphorus removal.

2.9.2 Life cycle assessment (LCA)

Life cycle assessment is a tool traditionally used to calculate the environmental impacts of processes from a holistic perspective. LCAs can help avoid a narrow outlook on environmental concerns by:

- Compiling an inventory of relevant energy and material inputs and environmental releases.
- Evaluating the potential impacts associated with identified inputs and releases.
- Interpreting the results to help make more informed decision.
  (Baumann and Tillman, 2004)

Many authors have analysed nutrient removal processes at WWTW using LCAs to try and assess the impacts of removing phosphorus relative to the benefit of cleaning water (Shaw et al., 2011, Neethling et al., 2011, Falk et al., 2011, Foley et al., 2010)

2.9.2.1 LCA data input

To make a comparative assessment of the environmental effects of nutrient removal Neethling et al (2011), Falk et al (2011) and Banerjee et al (2011), used LCAs on computerised models of WWTW with different levels of nutrient removal. The models start with a simple standard treatment system and increase in complexity to the most advanced systems that are currently available to remove phosphorus. A summary of the levels of treatment modelled by Neethling et al (2011) are shown in table 2.22.

Table 2.22 Treatment level objectives and unit processes to achieve them (table adapted from (Neethling et al., 2011)

Level	BOD and TSS (mgL^{-1})	TN ($mgN\ L^{-1}$)	TP ($mgP\ L^{-1}$)	Brief description of process
1	30	-	-	Primary Clarifier, Activated Sludge, Disinfection/Dechlorination
2	<30	8	1	All of above+ Alum dose
3	<30	4-8	0.1-0.3	All of above+Filtration/Polymer dose
4	<30	3	0.1	All of above+Enhanced Settling, Denitrifying filtration
5	<30	<2	<0.02	+Micro-filtration and Reverse Osmosis

2.9.2.2 LCA data output

The output of the LCA provides information on(Shaw et al., 2011):

- Global Warming Potential
- Eutrophication Potential(Nitrogen and Phosphorus load)
- Terrestrial Acidification
- Human Toxicity(Carcinogens and non-Carcinogens)
- Terrestrial Eco-Toxicity
- Photochemical Oxidation Potential
- Aquatic Eco-Toxicity
- Fossil Energy Depletion
- Ozone Layer Depletion
- Water Consumption

These categories provide a method of assessing the different impacts each process has on human health, ecosystem quality, climate change and resources. Many of these categories are hard to quantify in exact terms and work is still on going to define suitable comparative units which is beyond the scope of this document.

2.9.2.3 Green House Gas (GHG) Emissions

All the authors found that as treatment levels increase, GHG levels increase. The largest contribution to GHG emissions is the energy required for pumping mixing and aeration followed by deep well injection (used to remove brine from the reverse osmosis plants), miscellaneous energy used, chemicals and N_2O emissions.

Neethling et al (2011) modelled 5 facilities with nominal flows of 10mgd and found that GHG emissions increased by about 1000 CO_2 eq mt/yr with each treatment step until the transition between level 4 and 5, where there was a 70% increase (see figure 2.7) (Neethling et al., 2011). Foley et al (2010) found that basic secondary wastewater treatment appeared to produce the least GHG emissions as the ‘do nothing approach’ and purely primary treatment caused large CH_4 emissions in the receiving environment.

The GHG emissions are further increased if the impacts are expressed in terms of the incremental mass of phosphorus removed. The incremental GHG emissions for every extra 450g of phosphorus removed increased exponentially after level 3. Based on these calculations an argument could be made that above level 3 (TP 0.1-0.3mgL^{-1}), there is a point of diminishing returns, where the extra GHG emissions to remove the last few grams of phosphorus produce significantly higher levels of pollution in other parts of the biosphere (Neethling et al., 2011, Falk et al., 2011).

2.9.2.4 Eutrophication

The primary purpose of removing phosphorus from waste water is to stop excessive growth of algae downstream of a treatment plant. However, the benefit of nutrient removal is hard to quantify. The LCAs discussed used SimaPro software to calculate the impact of eutrophication on receiving waters. The results for the algae growth show the reverse trend to GHG, as the treatment level increases algae formation in the receiving water diminishes. The models show that nearly 95% of potential algal production is reduced by moving from level 1 to level 3 see Figure 2.10. This would further imply that treating phosphorus to levels lower than level 3 (TP 0.1-03 mgL^{-1}) produces very little benefit for either the receiving water or the biosphere.

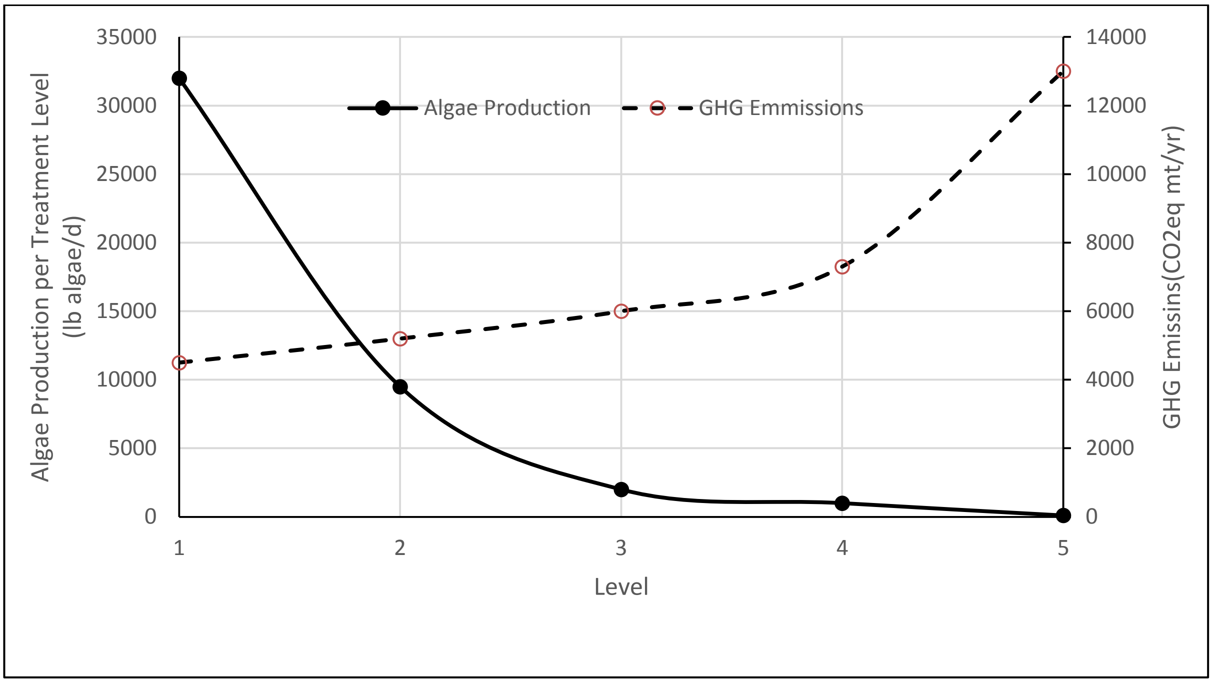


Figure 2.10 GHG Emissions and Potential Algal Production per Treatment Level (10mgd) adapted from (Neethling et al., 2011).

However, Shaw et al (2011) argues that comparing the data of GHG and algae growth is impossible without normalising the data sets. Normalising the LCA output provides a method for expressing the impacts in common units so they can be compared to each other and their relative significance assessed. Shaw et al(2011) uses normalization factors by taking the total environmental burden in each category and then calculating the 'person year' equivalent of the population exerting the burden. Using this system Shaw et al makes comparisons between the impacts of algal growth on local areas versus the effect on a global scale. The normalised data is represented in Figure 2.11 a and b.

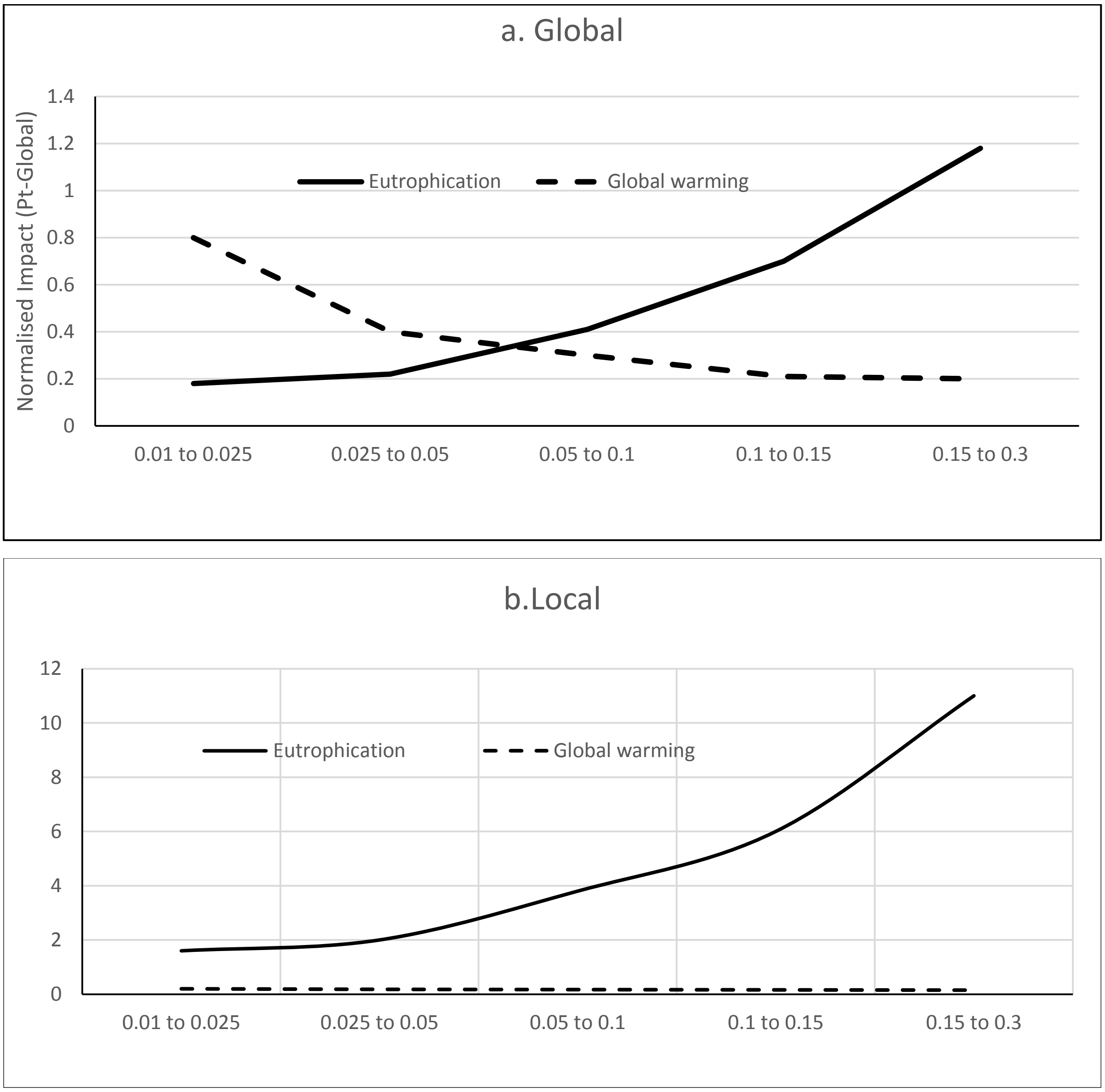


Figure 2.11 Eutrophication potential and global warming potential for different effluent phosphorus limits, using normalised impact sores based on a) local and b) global factors. Adapted from (Shaw et al., 2011).

As can clearly be seen from these two graphs the effect of eutrophication is always more important than global warming at a local level. Whereas on a global scale the impact of global warming is much greater than eutrophication when treating phosphorus to levels below 0.05 to 0.1mgL^{-1} (Shaw et al., 2011). In other words there is a key negative environmental trade-off between the improved quality of local receiving water that comes at the expense of higher resources needed to remove phosphorus from waste water. The increased resources include, the construction of advanced WWTP, higher electricity and chemical consumption and higher direct GHG emissions. These additional environmental burdens, albeit more widely dissipated may be carried by a much larger population of people than those that benefit directly from the improved receiving water quality (Foley et al., 2010).

2.9.3 Life cycle assessment of constructed wetlands for phosphorus removal.

Although there are many papers discussing the life cycle assessment of constructed wetlands (Dixon et al., 2003, Machado et al., 2007, Lopsik, 2013, Brix, 1999), the author can find no papers directly comparing phosphorus removal using wetlands and traditional treatment systems. However, Dixon et al (2003) found that constructed wetlands have less global warming potential (CO_2 emissions) and less energy use than conventional treatment. Machado et al (2007) found that wetlands also reduced aquatic toxicity and eutrophication compared to conventional activated sludge processes.

Lopsik et al (2013) compared the use of a manufactured light weight aggregate with standard gravel and sand which is used in the majority of reed beds. It was found that standard activated sludge plants had less environmental impact when compared to a constructed wetland using manufactured media, but more impact than gravel based reed beds. This result implies that using a manufactured media designed specifically for phosphorus treatment in wetlands may well not be a sustainable solution. However, the use of domestic water treatment residuals may provide a more sustainable alternative.

2.9.3.1 Conclusion of environmental considerations

There has been little assessment of the environmental impact of water treatment processes, and although there is no doubt that we must remove phosphorus from WWTP, reducing phosphorus levels to below $0.1 mgL^{-1}$ TP comes with high environmental impact unless more sustainable and low energy processes are used.

2.10 Conclusions and gaps in the knowledge

2.10.1 Conclusion

Phosphorus is a finite resource which is currently being used up at an unsustainable rate. Phosphorus is delivered to waste water treatment plants in large quantities mainly because of its in washing detergents and foods. Waste water treatment plants only remove around half of this phosphorus. New legislation is demanding that more of this phosphorus is removed. Traditional technologies using biological and chemical methods to remove phosphorus are expensive to install and operate. Using domestic water treatment residuals as a phosphorus adsorptive media offers a potential way to remove phosphorus at relatively low cost and causing minimal environmental harm.

2.10.2 Gaps in the knowledge

The use of DWTR for phosphorus removal has been widely reported in many papers (Makris et al., 2005b, Ippolito et al., 2011, Stoner et al., 2012, Razali et al., 2007, Babatunde et al., 2009). However, very few papers discuss the engineering principals that would be required to use the residuals in a full scale treatment process, or have analysed the use of the media at realistic scales with real waste water (Penn et al., 2014, Zhao et al., 2010).

Many papers have discussed the physio chemical mechanisms that enable the DWTR to remove phosphorus (Babatunde and Zhao, 2010, Bai et al., 2014) but few authors have suggested how this information may be used to optimise a treatment system or discuss the physical parameters of the media that may affect its ultimate phosphorus removal potential over an extended life (Lyngsie et al., 2015).

The water industry produces millions of tonnes of DWTR per year (Babatunde and Zhao, 2007) but each water treatment works produces residuals with different characteristics depending mainly on the inlet water quality, type of coagulant used (iron, aluminium or lime based) and the type of drying process used (press, belt press or centrifuge). Although there has been some work comparing the phosphorus adsorption capacity of the media using isotherms (Bai et al., 2014), the author can find no papers which directly compare different media in operational conditions.

The majority of experiments discussed in the literature analysed the performance of DWTR using a synthetic waste water dosed with phosphorus. Few report the use of real waste water, and none have undertaken experiments to compare the effect of using real and synthetic waste water.

The kinetics' of the phosphorus removal by DWTR has been analysed in many papers (Babatunde and Zhao, 2010, Razali et al., 2007), but few discuss how the kinetic rates may change over time as the media becomes more saturated with phosphorus. Although all the papers agree that phosphorus removal follows a biphasic process rate, few papers discuss the effect that changing the water/media contact time may have on these kinetic rates and how this may affect the long term phosphorus removal capacity of the media.

Nearly all papers studied use DWTR residuals that have been dried and crushed. No-one has investigates the optimum way to use the residuals in their raw untreated state.

The design of the experimental and analytical work discussed in the remainder of this thesis was driven by the gaps in the knowledge identified above.

Note: For the remainder of this thesis phosphorus is referred to as P (apart from in the titles)

Chapter 3 Materials and Methods

3.1 Introduction

This chapter details the design methodology, physical construction, operational principles, and methods of analysis used for all of the experiments, rigs and meso scale beds.

Most of the experimental work took place in two locations; at the University of Cardiff and at a site near Abergavenny in South Wales with access to real waste water. The experiments were operated from May 2015 to July 2016. In the University a large rig with 30 computer controlled column models was installed. The models were all 100mm in diameter, filled with 8 types of Domestic Water Treatment Residuals (DWTR), loaded for 8 different contact and rest periods in a tidal flow regime, and fed with P dosed tap water at two different concentrations. In the site near Abergavenny 5 similar computer controlled column models were installed but these were fed with real waste water (RWW) and used only two types of DWTR and two contact and resting periods. Two tidal flow meso scale beds with a surface area of approximately 1m^2 filled with two types of DWTR were also installed at this site and these were fed with the same real waste water supply.

In conjunction with the operation of the experimental columns and meso scale beds, analysis of many of the physical properties of the DWTR were undertaken. During the later stages of the column operation further investigations were designed to analyse some of the key variables arising from the results of the column experiments.

3.1.1 Aims of experimental work

The aims of the experimental work were:

- To design and conduct experiments to assess the key engineering variables that may affect the performance of DWTR as a media in a constructed wetland or passive system; primarily in relation to P removal from waste water.

- To determine if any key operational parameters in the production of DWTR effect their ability to remove P e.g. does the dewatering process affect the ability of DWTR to remove P more effectively?
- To determine if there are any negative environmental impacts from the use of DWTR for P removal in a constructed wetland or passive system.
- To provide design and operational information to enable the scaling up of the system.

3.1.2 Objectives of experimental work

To achieve these aims, the experiments were designed with the following objectives:

- To determine if there was a significant difference in P removal capacity between different DWTR.
- To find out what qualities of the DWTR physical or chemical affect the P removal ability of the media.
- To determine if increasing the contact time increases P adsorption capacity in the DWTR and whether this increase effects ferric and alum based media differently.
- To determine if increasing the rest time (i.e. time when the media is not in contact with the waste water) increases P adsorption capacity in the DWTR and whether that increase effects ferric and alum based media differently.
- To measure the differing effect of increasing contact and rest time when changing the inlet P concentration.
- To optimise the contact and rest time to provide maximum P adsorption capacity over the longest time period.
- To determine if increasing P inlet concentration increases P adsorption capacity in the DWTR.
- To find out how P adsorption capacity varies when using real waste water (RWW) as compared to synthetic waste water.

- To measure how P adsorption capacity is affected by scale.
- To determine how P adsorption is affected by time and how long a viable system should last.

3.2 Key system variables and experimental design

To meet the objectives outlined in 3.1.2, an assessment was made of the key variables associated with the performance of DWTR in an engineered wetland or passive system. From this analysis experiments were designed with factors and ranges which produced the maximum output impact within budgetary, time, equipment and space constraints.

3.2.1 DWTR type

Water treatment works generate a wide variety of DWTR's depending on the untreated water source, chemicals used for purification and types of unit operations used (Ippolito et al., 2011). In the majority of water treatment works salts of aluminium or iron are used as coagulants (Crittenden et al., 2012). The water is generally supplied to the works from either a river or reservoir and the sludge is dewatered by a press or centrifuge (Verrelli et al., 2009).

Eight types of DWTR were made available for these experiments obtained from 8 Northumbrian water treatment works. Although the DWTR provided did not cover all possible variations to allow a full factorial experimental design; the different treatment works were supplied from both rivers and reservoirs, used both ferric and alum as coagulants and were dewatered by either centrifuge or press (Table 3.1). The water inlet into the majority of the works was from reservoirs and all works that used a centrifuge as a dewatering process also used ferric as a coagulant. This was not ideal because it made it impossible to compare the effect of the dewatering process in relationship to the coagulant use.

The physical and chemical properties of the DWTR are detailed in chapter 4, and the results of media type experiments are detailed in section 5.5.

Table 3.1 Details of treatment works where DWTR was collected

Media	Coagulant	Inlet	Drying process
BS	Ferric	River	Centrifuge
FO	Ferric	Reservoir	Centrifuge
GU	Alum	Reservoir	Press
HH	Ferric	Reservoir	Centrifuge
HO	Alum and Ferric	River and reservoir	Press
LA	Ferric	Reservoir	Centrifuge
MO	Ferric	Reservoir	Centrifuge
WD	Alum	Reservoir	Press

3.2.2 Phosphorus concentration

The range of P concentrations entering sewage treatment plants is very variable depending on the size of works and location. Metcalf et al (2014) suggest average P concentrations of between 3.7 and 11mgL^{-1} TP (Metcalf et al., 2014). It is generally suggested that 50% of this P is removed by secondary treatment and up to 90% can be removed if a tertiary treatment step is included (Environment Agency, 2012). This provides a range of 1.85 to 5.5mgL^{-1}TP for secondary treatment and 0.37 to 1.1mgL^{-1} TP for tertiary treatment.

The experimental systems were designed with the view that the engineered system would be used to remove P after secondary or tertiary treatment, and therefore two levels of P concentrations were used in the inlet feeds to the University column models; 1mgL^{-1} and 5mgL^{-1} TP. These were at the higher ends of the ranges but it was felt for simplicity of measurement that these levels would provide a good indication of DWTR treatment performance. The waste water at the site near Abergavenny was pumped to the experiments after treatment from a package treatment plant and had an average and standard deviation TP of 9.37 ±4.96 mgL^{-1}.

The results of the experiments on inlet concentration are detailed in section 5.7

3.2.3 Contact and Rest time

Optimising the contact and rest time of a DWTR based tidal flow system requires a balance between using the media to its maximum P removal potential while keeping the physical footprint of the system to a minimum. When either the contact or rest time is increased the physical foot print or volume of the system must increase, if the flow into the system remains constant. The optimal contact time of the system depends on the kinetics of P removal and how that changes over time, whereas the optimal resting time depends on chemical changes that occur in the media while it is being ‘rested’.

The experiments were designed with 8 different load and rest times and 4 different load to rest time ratios (Table 3.2). The contact times ranged from 0.5 to 24hrs and rest times from 1 to 24 hours. The ranges were chosen in relation to previous investigations undertaken with DWTR and typical retention times used in reed bed treatment systems. The most extensive trial using DWTR in adsorption systems was undertaken by Zhao et al (2010), in which a retention and rest time of 4 hours were used; this trial showed very positive results with >90% P removal on average throughout the year. However, multiple studies on the kinetics of P removal (Makris et al., 2005a, Song et al., 2011, Babatunde and Zhao, 2010, Gao et al., 2013) all show that the majority of P is removed in the first 30 minutes to 1 hour. Fort (2013) provided details of 17 reed beds used by Seven Trent and the retention time for the reed beds varied between 15 and 59 hours. Therefore, in light of these studies and the availability of only 8 columns for the experiments it was decided to vary the contact time between 0.5 and 24 hours It was clear from the previous studies, that for any reasonable amount of P removal to occur a minimum contact time of 30 minutes would be required, whereas increasing the maximum contact time above 24 hours would lead to very few bed volumes being passed during the year long experiment. Although in a full scale system retention times up to 59 hours maybe possible, it was felt that if very positive P removal results were obtained from the 24 hour contact time experiments, future research could investigate increasing the contact time beyond 24 hours.

Table 3.2 Load and rest times used in experimental rig at the University

Load time(hrs)	Rest time(hrs)	Load:Rest ratio
0.5	1.5	0.33
1	1	1
1	3	0.33
3	1	3
6	2	3
6	6	1
12	6	2
24	24	1

The experiments were designed to operate at two scales, 100mm diameter columns with 500mm media depth using approximately 2.5kg of media and at meso scale with 1m^2 surface area and 250mm media depth and 80kg of media. The 100mm diameter columns were chosen as the minimum viable size that would enable the 35 column models to be constructed within the budgetary restrictions. The 1m^2 area of the meso scale beds was chosen as the maximum size of bed that could be supplied from the waste water source yet still provide useful scaling data.

The results of the experiments on contact and rest time are detailed in section 5.6.

3.2.4 Time Scale

Many column experiments have been undertaken using DWTR (O'Neill and Davis, 2011, Babatunde et al., 2008, Kim et al., 2003) but generally the column experiments are of short duration from one week to 60 days or the P concentration entering the columns has been very high >100mgL^{-1}TP, causing a bias to the results. The experimental rigs and beds for this study were all operated for a minimum of one year at low input P concentrations which provided a more realistic estimate of media performance and life expectancy under real operating conditions.

3.2.5 Flow regime

Constructed wetlands and passive systems can be run in many hydraulic modes. Traditionally sub surface flow constructed wetlands have been designed to run in continuous horizontal or batched vertical flow (Kadlec and Wallace, 2008). More recently systems have been operated in tidal flow where water is loaded into the system and left for a fixed contact time and then the system is drained leaving the media dry for a fixed rest time (Babatunde et al., 2011a). The use of a tidal flow regime alleviates the very short contact times of vertical flow systems and the short circuiting that is often associated with continuous flow horizontal beds especially at smaller scales (Kadlec and Wallace, 2008). Previous work has also proved the effectiveness of using DWTR in tidal flow beds (Babatunde et al., 2011b).

Ideally different flow regimes would have been tested. However, due to constraints on the number of columns available, it was thought that other variables were of greater consequence and hence more important to measure.

3.2.6 Reeds

Although it is proposed that the final system design may use DWTR as a media in a constructed wetland, it was felt that planting reeds in the model systems would provide a bias to the results. There are many reports that reeds can be effective at removing P from waste water during the first year of planting, but in subsequent years the P removal is greatly reduced (Kadlec and Wallace, 2008). The one year length of this experimental trial did not allow a realistic comparison to be made between systems running with or without plants.

3.2.7 Summary of key variables used in experiments

To answer the key questions posed for this thesis 37 experiments were designed using 35 column models and two meso scale beds. The experiments analysed the effect of media type, P concentration, loading regime and scale. The key factors and variable range are shown in Table 3.3.

Table 3.3 Summary of key design variables

Factors	Levels	Detail
Media Type	8	BS,FO,GU,HH,HO,LA,MO,WD
Phosphorus concentration	3	1 and 5 mgL^{-1} TP, RWW
Load times	6	0.5, 1, 3 ,6, 12, 24 hrs
Rest times	5	1, 1.5 ,2, 6 ,24 hrs
Scale	2	100mm Ø(2.6kg), 1m^2(80kg)

3.3 Experimental design details

The majority of the columns (30) were operated on an atrium with an open roof on the third floor of the department of Engineering at Cardiff University. The University columns were loaded with synthetic P dosed tap water while the remaining 5 columns and two meso scale beds were operated at a site near Abergavenny loaded with real waste water (RWW).

The 30 model experiments at the University were split into four experimental sections (Table 3.4).

1. Ten models compared 8 different types of DWTR. The loading and rest time were kept at a constant 6 hours per cycle and the inlet concentration was kept constant at 5mgL^{-1}TP. Two models were repeated to provide statistical significance to the results.
2. Sixteen models compared 8 different hydraulic loading rates and rest times, repeated with one alum and one ferric based DWTR. The inlet concentration was kept constant at 5mgL^{-1}TP. (The GU and BS media were chosen for comparison of alum and ferric based media, from the chemical analysis undertaken by Al-Tahmazi, with the GU media having the largest content of Al and the BS the largest content of Fe (Al-Tahmazi, 2016).
3. Four models operated at a lower inlet TP concentration of 1mgL^{-1}. These models ran at two different loading and rest times with both an alum and ferric based media.

4. Two control models were filled with 6mm gravel and were loaded with two inlet concentrations of 5 and 1mgL^{-1} TP. The load and rest time were kept constant at 6 hours.

The 5 model experiments that operated near Abergavenny were split into two groups. All of the models were loaded with real waste water (Table 3.5)

1. Three models ran with 6 hours contact and rest time repeated with ferric and alum media. One of the columns was repeated to give statistical significance to the results.
2. Two models operated with 12 hours contact and 6 hours rest time repeated with ferric and alum media.

The two meso scale beds were both operated with 6 hours contact and rest time loaded with real waste water from the same inlet tank as the columns above and were filled with two types of media (Table 3.6).

Model 0 to 10										
Experiment type	Comparison of different media								Replicates of 0&1	
Model Number	0	1	2	3	4	5	6	7	8	9
Media Type(Al=Alum,Fe=Ferric)	GU(Al)	BS(Fe)	MO(Fe)	HO(Fe Al)	LA(Fe)	WD(Al)	FO(Fe)	HH(Fe)	GU	BS
Influent P concentration (mgL^{-1} TP)	5	5	5	5	5	5	5	5	5	5
Contact Time (hrs)	6	6	6	6	6	6	6	6	6	6
Empty/Rest Time(hrs)	6	6	6	6	6	6	6	6	6	6
Cycles per day	2	2	2	2	2	2	2	2	2	2
HRT(days)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Volume of water per cycle(m^3)	0.00243	0.0015	0.0026	0.0019	0.0023	0.0027	0.0029	0.0026	0.0031	0.00217
Mass of media(kg)	2.741	2.79	2.776	3.147	2.762	2.525	2.754	3.475	2.754	2.748
HLR($m^3m^{-2}d^{-1}$)	0.62	0.38	0.66	0.48	0.59	0.69	0.74	0.66	0.79	0.55
Model 10 to 19										
Experiment type	Control	Comparison of different HRT								
Model Number	10	11	12	13	14	15	16	17	18	19
Media Type	Gravel	GU(Al)	GU(Al)	GU(Al)	GU(Al)	GU(Al)	GU(Al)	GU(Al)	BS(Fe)	BS(Fe)
Influent P concentration (mgL^{-1} TP)	5	5	5	5	5	5	5	5	5	5
Contact Time (hrs)	6	0.5	1	1	3	6	12	24	0.5	1
Empty/Rest Time(hrs)	6	1.5	1	3	1	2	6	24	1.5	1
Cycles per day	2	12	12	6	6	3	1	0.5	12	12
HRT(days)	0.25	0.021	0.042	0.042	0.125	0.250	0.500	1.000	0.021	0.042
Volume of water per cycle(m^3)	0.00228	0.00278	0.00272	0.0021	0.00222	0.00228	0.00218	0.002	0.00218	0.0022
Mass of media(kg)	9.299	2.635	2.61	2.677	2.454	2.561	2.712	2.552	2.705	2.792
HLR($m^3m^{-2}d^{-1}$)	0.58	4.25	4.16	1.60	1.70	0.87	0.37	0.13	3.33	3.36
Model 20 to 29										
Experiment type	Comparison of different HRT					Comparison of inlet P concentration				Control
Model Number	20	21	22	23	24	25	26	27	28	29
Media Type	BS(Fe)	BS(Fe)	BS(Fe)	BS(Fe)	BS(Fe)	GU(Al)	BS(Fe)	GU(Al)	BS(Fe)	Gravel
Influent P concentration (mgL^{-1} TP)	5	5	5	5	5	1	1	1	1	1
Contact Time (hrs)	1	3	6	12	24	6	6	12	12	6
Empty/Rest Time(hrs)	3	1	2	6	24	6	6	6	6	6
Cycles per day	6	6	3	1.3	0.5	2	2	1.3	1.3	2
HRT(days)	0.042	0.125	0.25	0.5	1.0	0.250	0.250	0.5	0.5	0.25
Volume of water per cycle(m^3)	0.0028	0.0022	0.00273	0.0022	0.00232	0.00275	0.00265	0.0028	0.00245	0.0027
Mass of media(kg)	2.89	2.854	3.073	2.939	2.854	2.396	2.908	2.625	2.864	9.575
HLR($m^3m^{-2}d^{-1}$)	2.14	1.68	1.04	0.37	0.15	0.70	0.67	0.48	0.42	0.69

Table 3.4 Column model design details and parameters for systems at the University loaded with synthetic waste water.

Model 30 to 35					
Experiment type	**Models with real waste water**				
Model Number	30	31	32	33	34
Media Type	GU(Al)	GU(Al)	BS(Fe)	BS(Fe)	GU Al
Influent P concentration (mgL^{-1} TP)	RWW	RWW	RWW	RWW	RWW
Contact Time (hrs)	6	6	6	12	12
Empty/Rest Time(hrs)	6	6	6	6	6
Cycles per day	2	2	2	1.3	1.3
HRT(days)	0.25	0.25	0.25	0.5	0.5
Volume of water per cycle(m^3)	0.003	0.0029	0.0014	0.0021	0.0029
Mass of media(kg)	2.9	2.9	5.2	3.9	5.1
HLR($m^3m^{-2}d^{-1}$)	0.76	0.74	0.36	0.36	0.49

Table 3.5 Column model design details and parameters for systems using real waste water

RWW=Real waste water TP≈2-12mgL^{-1}

Meso Scale Beds		
Experiment type	**Meso scale beds with real waste water**	
Model Number	Bed 1	Bed 2
Width,length,depth (mm)	860,1120,270	860,1120,220
Area (m^2)	0.96	0.96
Media Type	HO(Al and Fe)	GU Al
Influent P concentration (mgL^{-1} TP)	RWW	RWW
Contact Time (hrs)	6	6
Empty Time(hrs)	6	6
Cycles per day	2	2
HRT(days)	0.25	0.25
Volume of water per cycle(m^3)	0.089	0.07
Mass of media(kg)	98.2	75.9
HLR($m^3m^{-2}d^{-1}$)	0.18	0.14

Table 3.6 Model design details and parameters for Meso scale beds (RWW = 8 to 12mgl-TP)

Note although the HRT gives a measure of the length of time the waste water is in contact with the media it gives no indication of the relative rest and loading period. For this reason throughout the text I have used contact and resting times as the key parameters for comparison rather than HRT. The contact and resting rates have been abbreviated to C and R and the prefixing number is in hours. e.g. 6C12R implies a model running with 6 hours fully loaded with water and 12 hours fully drained down.

3.4 Design and Construction and collection of Experimental Components

3.4.1 Collection of DWTR

The DWTR were collected from 8 water treatment works on the 9-11 Feb 2015. The residuals were randomly dug from areas across the pile of DWTR at the end of the process conveyers or from the sludge storage bays (Figure 3.1). The samples were placed in sealed 20 litre buckets. Apart from the BS media none of the DWTR was older than three weeks. Of the 8 plants sampled 5 used ferric sulphate as a coagulant (BS,FO,LA,MO, HH), 2 use aluminium sulphate (WD and GU) and 1 used both alum and ferric(HO).

Figure 3.1 Collection of DWTR

3.4.2 Column models

3.4.2.1 Physical construction

The 35 column models were constructed in an identical manner Figure 3.2. Each model consisted of a 100mm internal diameter PVC pipe capped at the base with a 22mm outlet pipe connected to the centre. A rotary actuated valve was connected to the outlet pipe. A 100mm drainage layer of washed 20 to 40mm quartz gravel was placed above the pipe outlet on a PVC plastic net (5mm mesh). A 600mm layer of DWTR media was placed carefully on top of the gravel and a 50mm distribution layer of 6mm quartz gravel was placed on top of the media.

Each model had a surface area of 0.0079m^2 and a functional depth of 0.75m. The mass of each component loaded into the columns was weighed on scales with a tolerance of ±0.001kg.

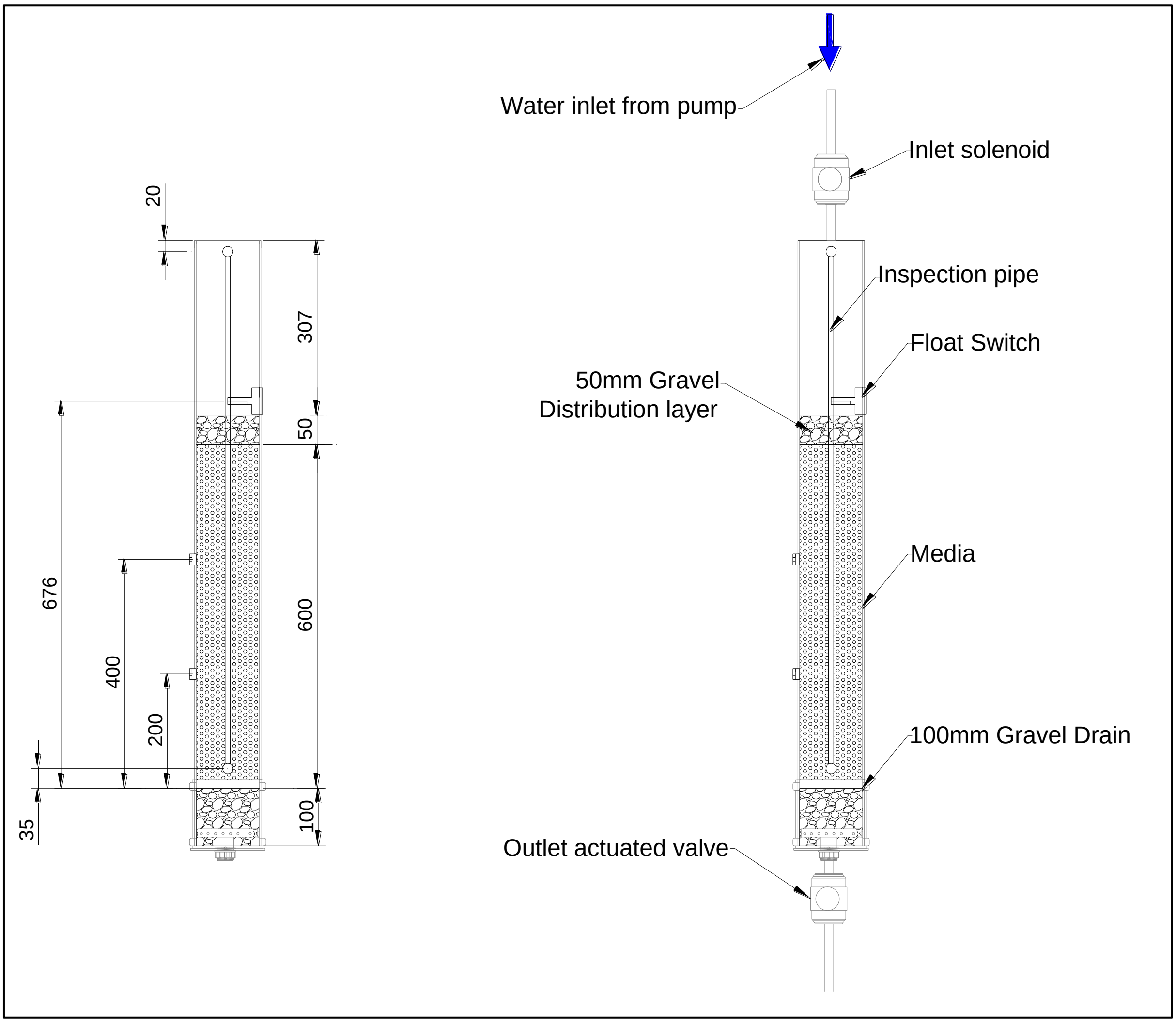


Figure 3.2 Dimensions and construction detail of column models

3.4.2.2 Engineering Design of the Column Rigs

Four rigs were constructed from 21 x 42mm galvanised steel unisturt. Three rigs held 10 columns (Figure 3.3) and were installed at the University a smaller rig with 5 columns was installed at the site near Abergavenny.

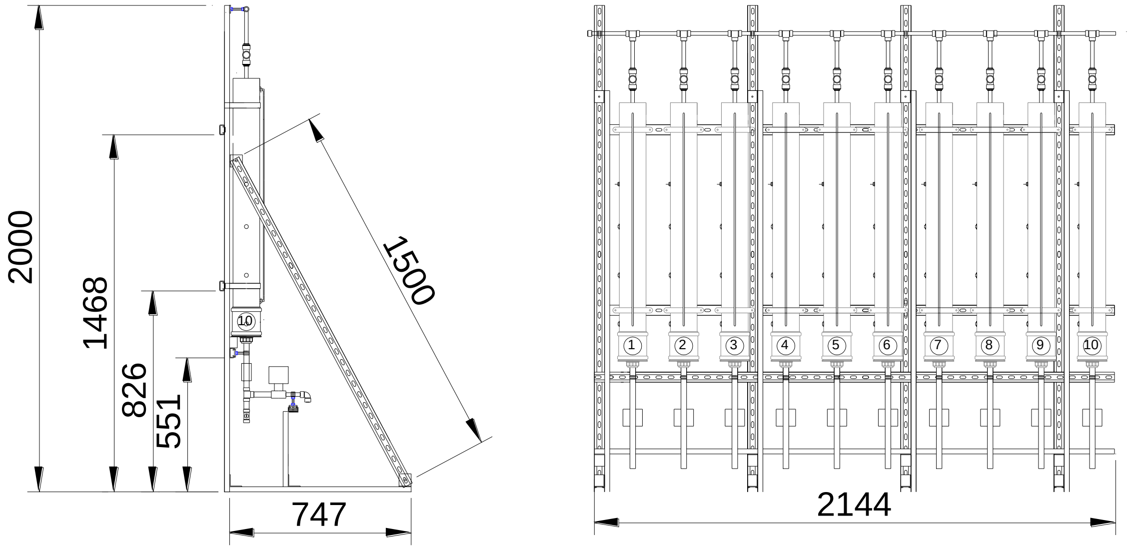


Figure 3.3 Dimensional and construction details of rig for 10 columns

3.4.2.3 Water flow control

The outlet and inlet arrangements for the system at the University and real waste water site were slightly different due to the nature of the control systems.

- At the University the outlet pipe could either discharge through a manual in line ball valve or through a 3 way 24v motorised ball valve supplied by Winner. The inlet to each column was controlled by a 12 volt servo assisted latching solenoid valve supplied by Beta Valve.
- At the real waste water site the outlet pipe could either discharge through a manually controlled ball valve or 110 volt ac ¼ turn actuated valve. The waste water was supplied to the columns via two 240volt submersible pumps (Titan TTB582PMP). The 5 columns were split into two inlet supply groups, one pump supplying column 1-3 and one supplying 4 and 5. The flow rate entering the column was controlled by a ball valve which was set on commissioning to provide the required volume of water into each column to just cover the gravel.

After two months of relatively consistent flow the ball valves blocked and it became very difficult to provide a consistent volume of water to the columns, the design of the system was therefore modified. A 15mm outlet was placed in each of the columns just above the surface of the gravel, and the control valves were opened fully. The pump run time was increased to allow for the columns to fill completely. Any excess flow was diverted into the overflow pipe Figure 3.4.

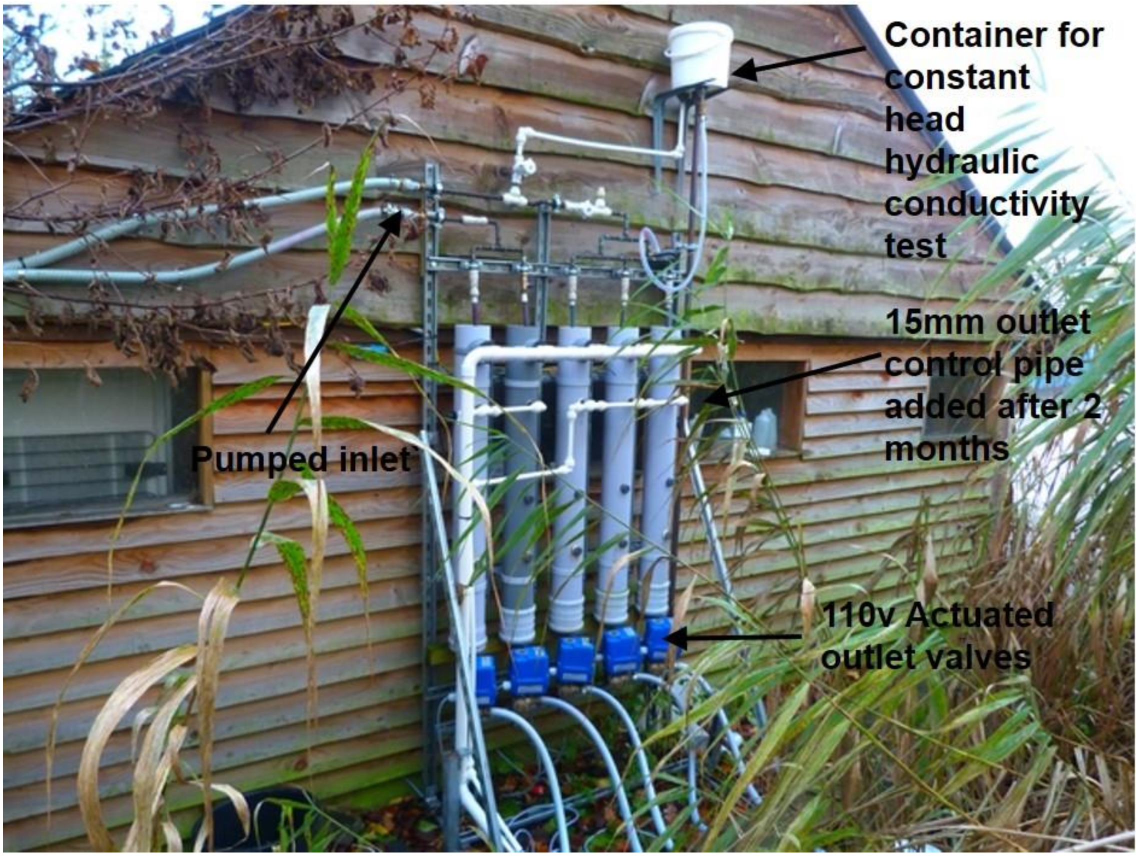


Figure 3.4 Model columns installed at site near Abergavenny

3.4.3 Design and construction of Meso Scale Beds

Two meso scale beds were constructed from treated pine planks with an 18mm sloping ply wood base dimensions 1120x860x320mm (length, width, depth) and 1:50 slope figure 3.5. The timber boxes were lined with a 0.3mm thick PVC damp proof membrane with a 22mm outlet in the lower corner of each bed. A 100mm predrilled drainage outlet pipe was placed in one corner along the length of the bed. The pipe was covered in gravel and surrounded by chicken wire to hold the gravel in place. A similar but narrower strip of gravel (50mm) was placed on the opposite side of the bed and the media was placed in between the gravel inlet and outlet. The bed was built up in 50mm layers. A 50mm diameter predrilled inlet distribution pipe was placed in the top layer of the inlet gravel connected to a 25mm feed pipe from the pump.

The beds were fed by a Titan submersible pump which could feed one bed at a time via a 110v three way actuated ball valve. The outlet was also controlled by similar ball valves.

Each bed had and effective area of 0.963m^2 the media depth was 0.27 and 0.22m in bed 1 and bed 2, respectively (Figure 3.6).

[Note although this is an unconventional way of building a constructed wetland , it was felt that if a larger system was built in this manner it would enable the changing of the media without too much disturbance to the rest of the system. In a conventional vertical flow system the media is sandwiched between a layer of gravel placed on the top and bottom of the system rather than at the sides]

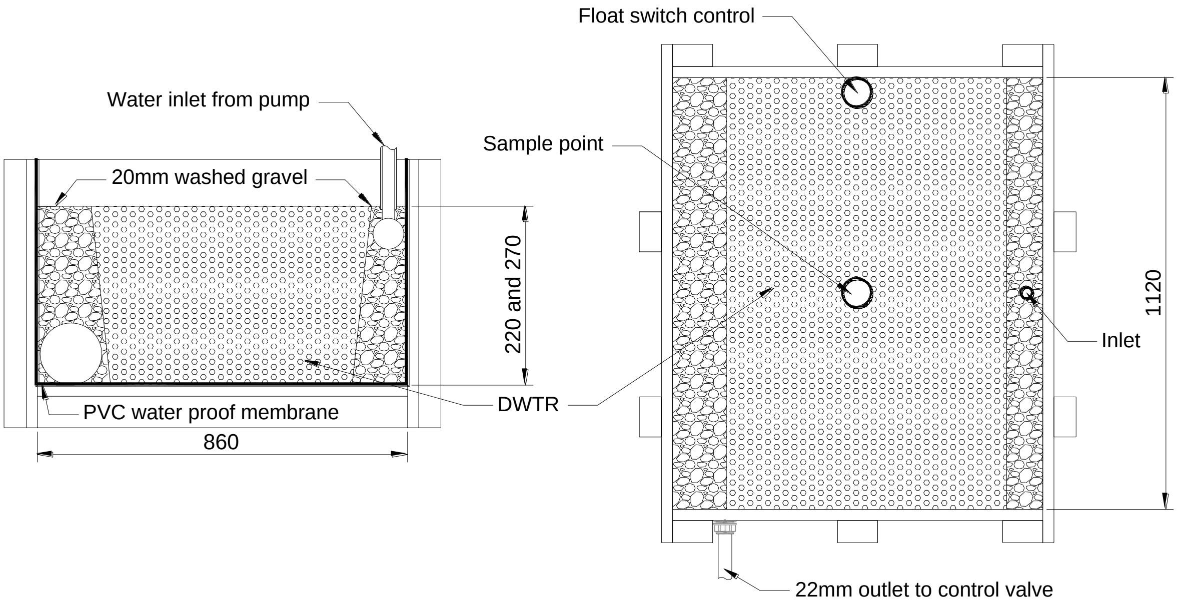


Figure 3.5 Cross section and plan view of meso scale beds

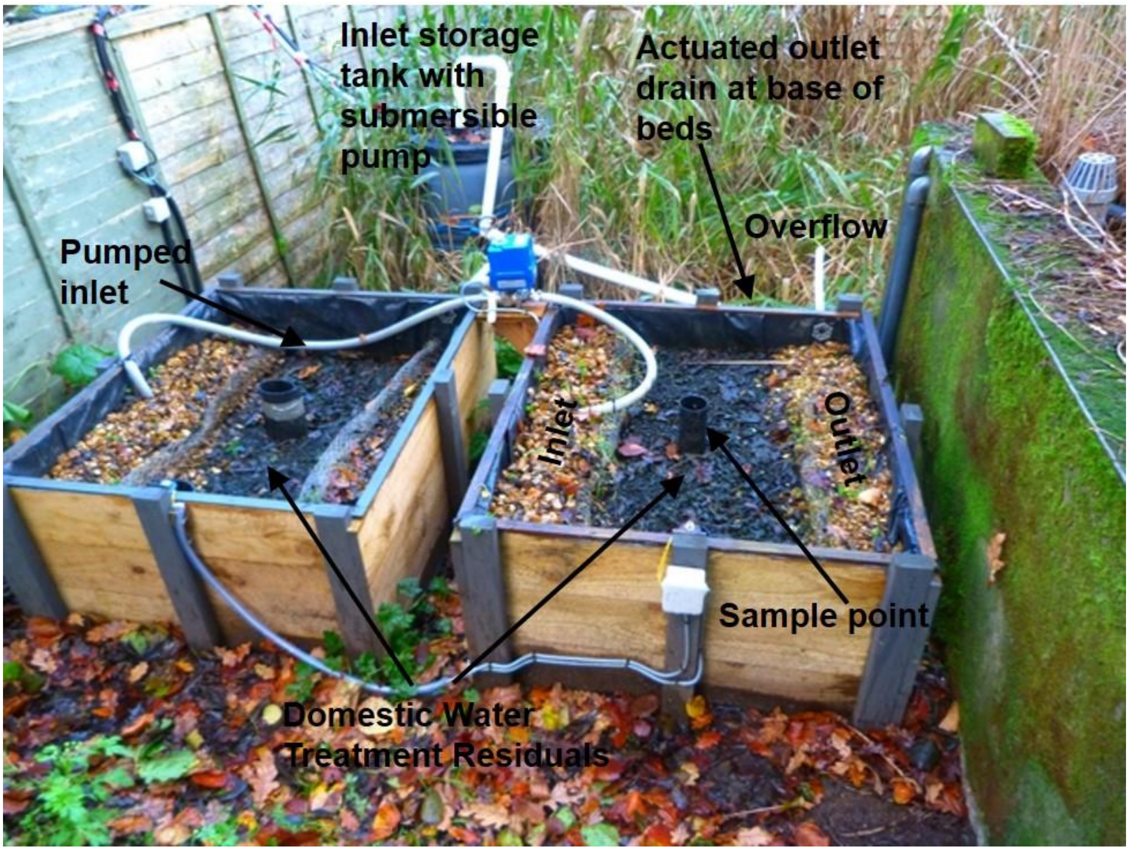


Figure 3.6 Meso Scale Beds installed at site near Abergavenny

3.4.4 University System site layout and control

The 30 columns at the university were fed from three water storage tanks. Two tanks of capacity 650 litres fed 25 models with an inlet concentration of 5mgL^{-1}TP and one tank with capacity 210 litres fed 5 column models with an inlet concentration of 1mgL^{-1}TP (Figure 3.7). The water was supplied to the columns through 3 Albin ALP peristaltic pumps (Figure 3.8), as the pumps were 3 phase and only a single phase supply was available ABB ACS55, 0.18kW, 230V 1ph to 3ph - AC Inverter Drive Speed Controllers were used to run the pumps. The inlet, outlet valves and pumps were all controlled by a programme written in LabVIEW which output to a 96 channel NI USB-6509 high density industrial digital I/O data acquisition device. The outputs from the USB-6509 controlled three circuit boards constructed at the university which operated the pumps and valves through a complex network of cabling (Figure 3.9.)

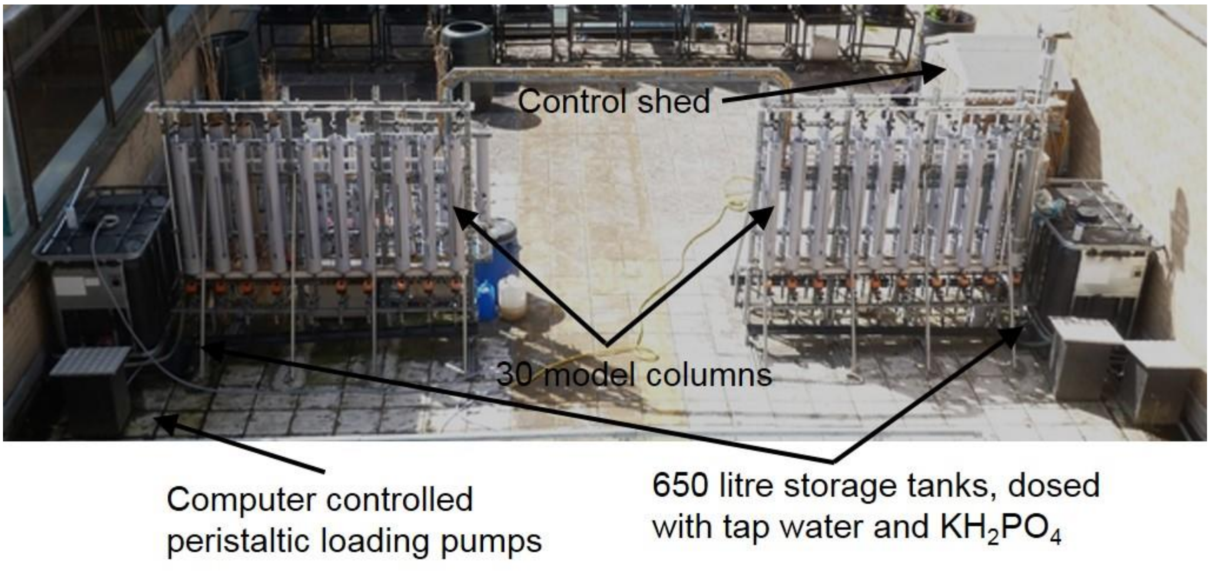


Figure 3.7 Site layout of university system

Figure 3.8 Peristatic loading pump at University system

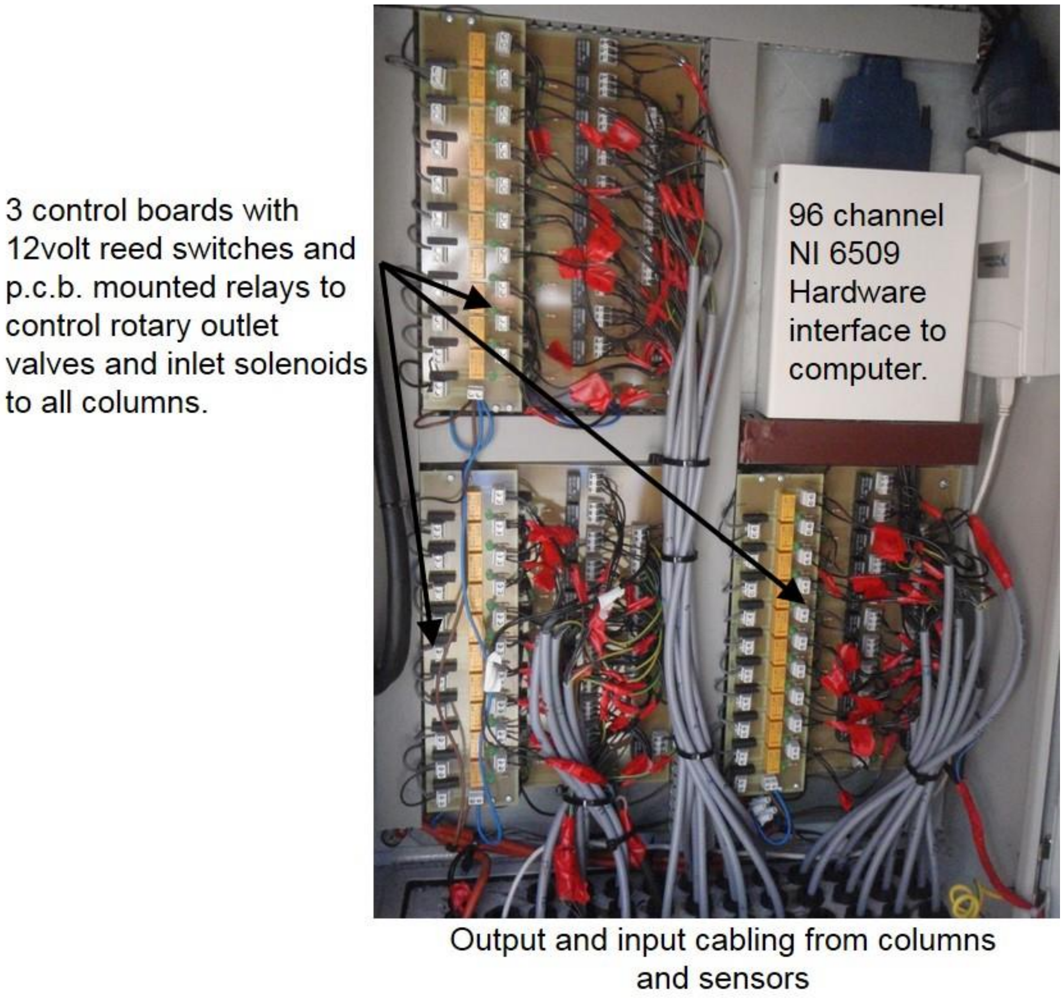


Figure 3.9 Control interface board between computer, valves and pumps

3.4.4.1 University control programme

The university rig was controlled by a programme written in LabVIEW. The programme had the following control parameters.

Column Control

Each column had individual settable loading time, empty time, valve run time and pumping time. Each column had manual overrides to enable pausing of the control system, opening of the solenoid loading valve and motorised outlet valve.

Sensor input

- A float valve in each column monitored water level in the columns. If a column was blocked after the emptying sequence the programme would wait 20 minutes and check the condition of the float valve before reloading.
- Float switches inside the loading tanks stopped column loading if the tanks were empty.
- Four temperature sensors were installed in the system one to measure external temperature and three were placed inside columns. The programme monitored external temperature and did not allow pumping or valve opening if the temperature fell below 1^0C.

Programme output

The programme displayed the state of each column on a screen which displayed time remaining on each cycle, number of completed cycles and the outside temperature (Figure 3.10). The programme wrote to a file once a day recording load, empty and pump time and the relevant temperature.

Figure 3.10 Display view from LabVIEW programme.

3.4.5 Real waste water site layout and control

The waste water used in column models 30 to 34 and the two meso scale beds was taken from the outlet of a small package treatment plant (Klargester) treating the waste from 20 domestic houses. The outlet from the plant was discharged into a chamber where it was pumped uphill into an existing reed bed system. The reed bed system consists of two vertical beds and one horizontal flow bed. The flow from one of the vertical flow beds was intercepted and diverted into two 210 litre storage tanks (Figure 3.11)

The outlet P concentration of the plant varied between 2-12 mgL^{-1} TP with an average $8.35 \pm 3.95 mgL^{-1}$. The very low levels of TP occurred during a few heavy rainfall events which diluted the flow. The main treatment tank was emptied three times during the course of the experiments which stopped flow to the experiments for a couple of days at each event.

.

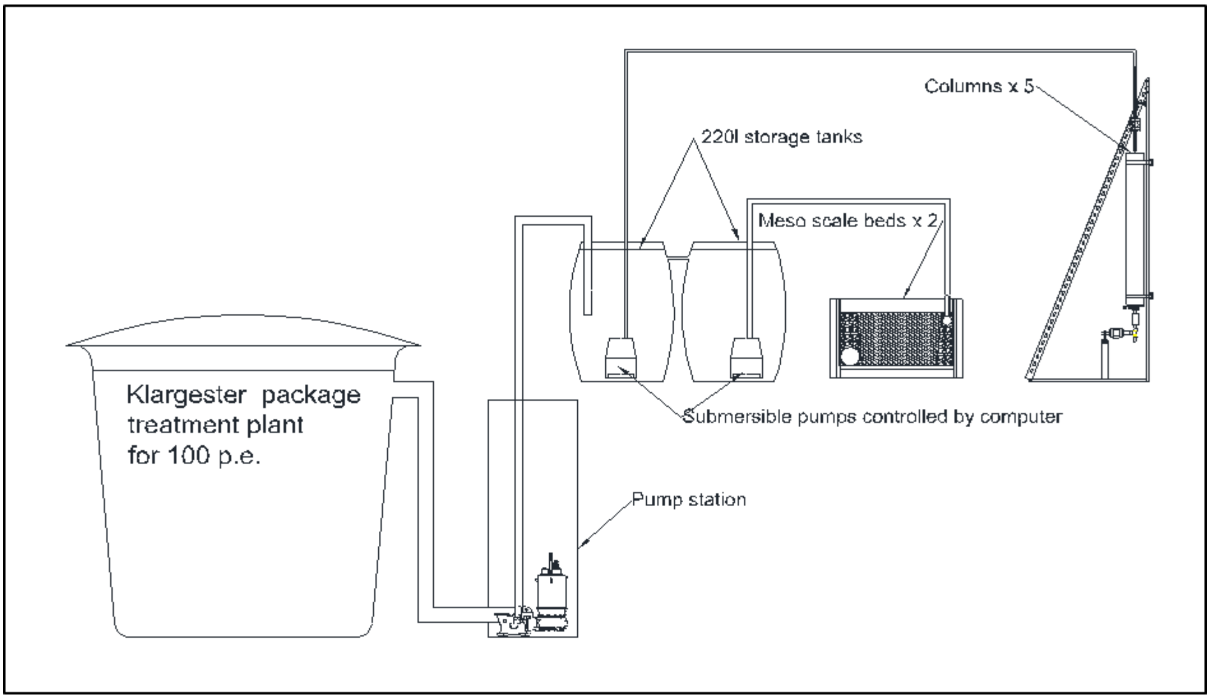


Figure 3.11 Simplified plan of waste water supply to Models (30 to 34 and the two meso scale beds)

Real waste water system control

The real waste water system was operated and controlled by a Schneider Zelio Logic Smart relay system which operated 110v relays for the actuated valves and 240v relays for the submersible pumps. The control programme was written in Zelio Soft 2 function block language. The programme controlled the pump and outlet valve timing. The system output the total number of cycles, load or rest time remaining to a display panel (Figure 3.12.)

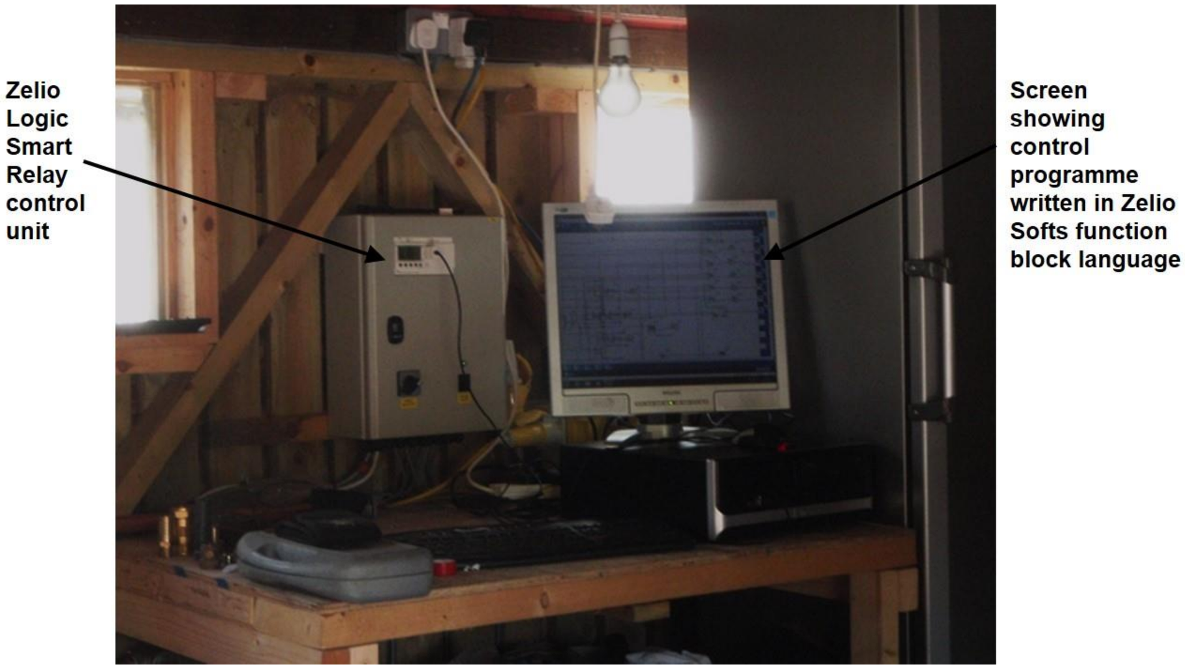


Figure 3.12 Control system for site with real waste water

3.4.6 System setup and calibration

3.4.6.1 Supply volume and porosity

Once all columns were mounted on the rig the volume of water to fill each column was calibrated by pouring a measured volume of water into the column until it was just visible at the surface. The systems were left for half an hour to make sure all air was removed from the system and the DWTR was fully saturated. The calibration was repeated three times for each column.

As the mass of the system components were known and the porosity of the gravel had been measured previously, the water volume also enabled the calculation of media porosity.

3.4.6.2 Pump Calibration University

The pump flow rate was calibrated at the input to each column, by measuring time to fill a calibrated 1 litre container. The pump run time was then set for each column in the LabVIEW control programme. Each column was filled so the water was just visible at the surface of the gravel.

3.4.6.3 Surface height measurement

The height of the gravel layer below the top of each column was measured on commissioning. The measurement was repeated every three months. As the gravel is effectively incompressible any movement measured was either due to media loss or media compression. If the media level fell the water volume entering the column was recalibrated.

3.5 System operation, and sampling procedure

3.5.1 Synthetic waste water production at the University

To keep the experimental rig at the university in continuous operation the 25 columns operating with an infeed of 5mgL^{-1} were supplied with approximately 200 litres of water per day and the 5 columns with 1mgL^{-1} required approximately 20 litres per day. The large quantities of water were supplied from two 650 litre and one 210 litre plastic tanks.

To produce the TP concentration of 5mgL^{-1} and 1mgL^{-1}, respectively two one litre stock solutions of concentrations 25 000 and 1 000 mgL^{-1} TP were prepared by mixing analytical grade KH_2PO_4 and deionised water with a magnetic stirrer. On commissioning the tanks were filled with tap water through a hose and a suitable quantity of stock solution was added to each tank to create the required P concentration. The stock solution was added while the hose was filling the tanks, which provided adequate mixing. After commissioning the tanks were topped up three times a week. The volume of water required to fill each tank was measured and a suitable quantity of stock solution was added. The stock solutions were kept in sealed glass containers and were replaced every month.

3.5.1.1 Inlet phosphorus levels at the University system

The experiments at the University were designed to be fed from three inlet tanks. Two of the tanks were to have a constant concentration of 5mgL^{-1} TP and one with a level of 1mgL^{-1} TP. Keeping the concentration at these levels was challenging as the STP measured in the tap water varied between 0.37 and 0.93 mgL^{-1} , see Figure 3.13. The effect of this was further confounded as the samples of tap water were obtained at the same time as the tanks were refilled for the next operating period. This meant that the concentration of STP in the tap water was only known a week after the tanks were filled. This did not produce a large effect in the tanks set at 5mgL^{-1} TP, with average and standard deviation STP levels of 5.19±0.74 and 5.04±0.61mgL^{-1} over the year for tank 1 and 2, respectively. However it was much harder to keep the levels of Tank 3 at 1mgL^{-1} and this resulted in a mean and standard deviation of 1.23±0.33mgL^{-1}STP over the year.

It is interesting to note the relatively high levels of P in the tap water. This P is primarily being dosed into the water by the water companies to alleviate plumbsolvency (Environment Agency, 2012).

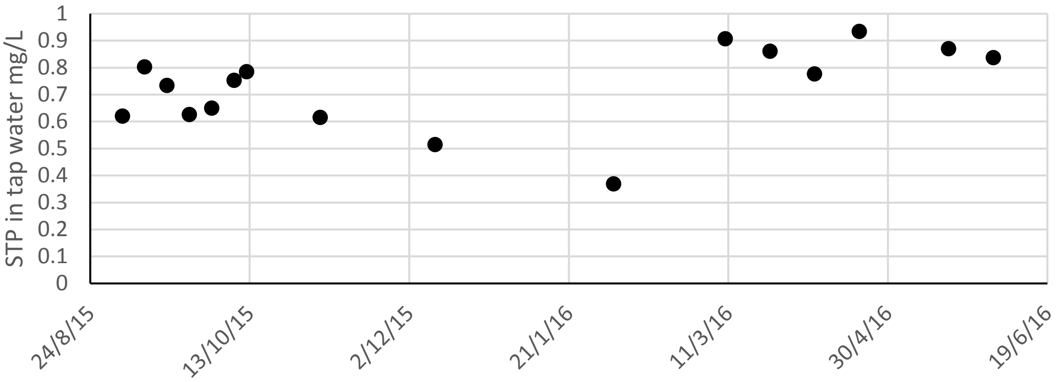


Figure 3.13 STP measured in the tap water used to fill the three feed tanks at the University

3.5.2 Operational problems with meso scale bed and column 32 at RWW site

Both column 32 (BS media with 12 hours contact) and meso scale bed 2(GU media) had substantial operational problems. Bed 2 was continually overloaded with inlet water due to a fault with the inlet float valve, and column 32 was under loaded for the first few months due to a balancing problem. Therefore, the results from bed 2 and column 32 have substantial experimental error associated with their results.

3.5.3 Sampling procedure university rig

The 30 columns at the University were sampled weekly over a one year period from May 2015 to May 2016. The outlet pipe from each column was left to discharge into a 200ml plastic sample bottle over a 24 hour period. The collected samples were therefore a composite of between one and 6 runs depending on the load/ rest time cycle length of the column. The samples were analysed for pH, Conductivity, SRP, Ca, S, Fe and initially for Al.

3.5.4 Sampling procedure real waste water site

Samples were collected weekly from the RWW site. The night before the samples were collected a 5 litre plastic bucket was positioned under the outlet for each column and a 20 litre bucket under the outlet of the meso scale beds. The samples were collected the following morning.

Each sample was analysed for pH, DO, TDS and conductivity on site using a Hanna HI-98194 Multiparameter meter. The samples were taken to the University and measurements for COD, TP, STP, PO_4, SO_4 and SS were undertaken within the next few hours. Samples for the Inductively Coupled Plasma-Atomic Emission Spectroscopy (IPC-AES) were stored in a fridge and analysis was completed within two days. (Note COD and TP were measured bi-weekly and then monthly as the experiments progressed.)

3.6 Chemical measurements

3.6.1 Overview of chemical measurements

The majority of the chemical analysis was undertaken using a benchtop spectrophotometer (Hach 3900) and the ICP-OES (Perkin Elmer Optima 2100 DV) in the CLEER laboratories of Cardiff University.

3.6.2 Overview of the measurement of Phosphorus concentrations in water

There is no standard analytical method for P analysis. However, one of the most common procedures is summarised graphically in Figure 3.14 (Gu et al., 2014).

The method generally requires that all forms of P species be decomposed to orthophosphate which can be measured using the phosphomolybdenum blue method. To achieve this certain fractions must be digested using acid and heat. However it is possible to measure Soluble Total Phosphorus (STP) using ICP-OES.(Jarvie et al., 1999, McKelvie et al., 1995).

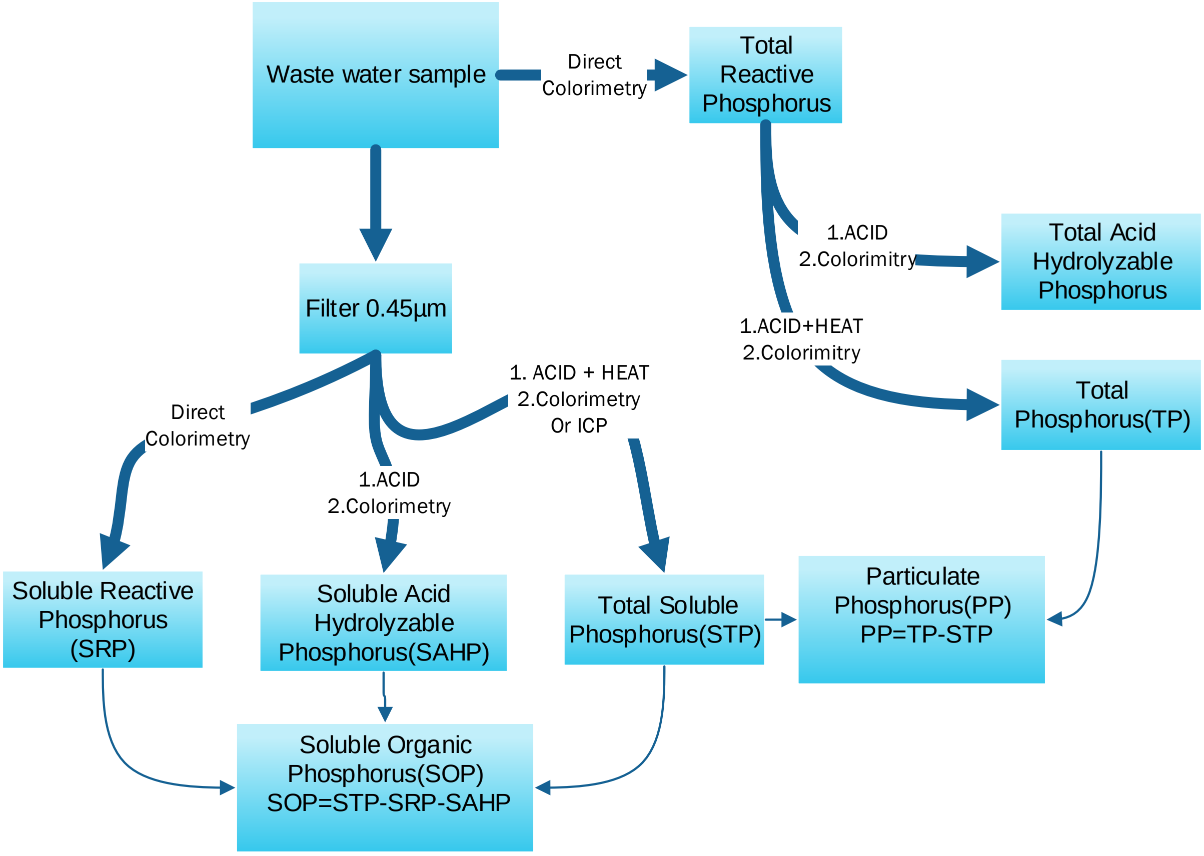


Figure 3.14 Phosphorus analysis adapted from Gu et al., 2011

3.6.2.1 Total Phosphorus (TP)

TP is the total of all filterable and particulate P forms. “Total" phosphorus is largely defined on the basis of how much P in its various forms will be oxidized into orthophosphate by a specific oxidant (Gu et al., 2011).

3.6.2.2 Soluble Reactive Phosphorus (SRP)

SRP consists largely of the inorganic orthophosphate (PO_4). Orthophosphate is the P form that is directly available for biological metabolism, and the concentration of this fraction constitutes an index of the amount of P immediately available for biological growth. However, the term "reactive" is used to indicate that the P in the SRP fraction is not solely inorganic P. It could include any form of P, including some organic forms that react with the reagents. There is a continuing debate as to what extent SRP represents solely the ortho form of P and how is biologically available it is.

3.6.2.3 Soluble Total Phosphorus (STP)

STP is measured after the filtration of the waste water with 0.45µm filtration, and the filtrate is either digested or analysed with ICP. The filtrate should contain all filterable forms of P, both organic and inorganic that are converted to orthophosphate by the digestion process.

3.6.2.4 Particulate Phosphorus (PP)

PP contains all material, inorganic and organic, particulate and colloidal, that was captured on the filter. Typically, particulate forms will contain bacteria, algae, detritus, and inorganic particulates such as clays, smaller zooplankton, and occasionally, larger zooplankton, sediments, or large plant material. Particulate P was obtained by subtraction of total soluble P (STP) from the total phosphorus concentration (TP).

In these experiments TP, STP and SRP were measured enabling the calculation of PP and SOP. The measurement methods are described in section 3.6.3 and 3.6.4.

3.6.2.5 Phosphorus measurement at the University site

All the P measurements at the University were undertaken by technicians using the ICP-OES. As has previously been discussed the resulting fraction of P measured has been classified as soluble total P (STP). During the first few months of operation 10 random samples were analysed to assess what proportion of the total P (TP) was STP. The results show that >97%±0.5% of the TP measured was STP. Thus within experimental bounds it can be assumed that STP and TP measurements at the University system are interchangeable.

However, throughout this document any measurements made by the ICP-OES are referred to as STP.

3.6.3 Measurement of Total Phosphorus (TP), Chemical Oxygen Demand (COD), Orthophosphate (PO_4), Sulphate (SO_4) and Suspended Solids (SS)

The concentrations of COD, TP, PO_4, and SO_4 were determined using a Benchtop Spectrophotometer (DR3900, *Hach-Lange*) and the relevant standard reagent assays (*Hach Lange*). In particular:

- COD, was measured using the LCI400 cuvette assays detection range of $0mgL^{-1} < COD < 1000mgL^{-1}$, The uncertainty to a 95% confidence interval was ±4.2 mgL^{-1}
- TP was measured using LCK348 and LCK349 cuvette assays detection range of $0.5 < TP < 5mgL^{-1}$ and $0.05 < TP < 1.5 mgL^{-1}$ and uncertainty to a 95% confidence interval of ±0.045 and 0.01mgL^{-1}, respectively.

Both COD and TP measurement required digesting at test specific temperatures and time periods, using a Thermostat (LT 200, *Hach Lange*)

- PO_4 was measured using Hach PhosVer® 3 Phosphate Reagent powder pillows, detection range $0.02 < PO_4 < 2.5 mgL^{-1}$. The uncertainty to a 95% confidence interval was 0.02 mgL^{-1} .The samples were all vacuum filtered through a 0.45µm filter paper and diluted by a factor of 10 with deionised water before analysis.
- SO_4 was measured using Hach Sulphate Reagent Powder Pillows, detection range $2 < SO_4 < 70mgL^{-1}$. The uncertainty to a 95% confidence interval was 0.7 mgL^{-1}. The samples were all vacuum filtered through a 0.45µm filter paper and diluted by a factor of 2 with deionised water before analysis.

- SS was measured directly using a pre-set programs in the DR3900 with a detection range $5 < SS < 750$ mgL^{-1}. 10ml samples were placed in the Hach sample bottles and shaken vigorously before analysis.

3.6.4 Measurement of Soluble Total Phosphorus (STP), Aluminium (Al), Iron (Fe), Calcium (Ca) and Sulphur(S)

Analysis for STP, Al, Fe, Ca and S was carried out on 30ml filtered water samples by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) by a University technician using a Perkin Elmer Optima 2100 DV ICP-OES.

3.6.5 Measurement of pH, Conductivity, Dissolved Oxygen and TDS Total Dissolved Solids (TDS)

3.6.5.1 pH and Conductivity in the laboratory

All samples from the rig at the University were analysed for pH and conductivity in the laboratory using a Mettler Toledo bench top meter with conductivity and pH probes installed with an accuracy of ±0.002 and 0.5%, respectively.

3.6.5.2 pH and Conductivity, DO, TDS in the field

Many of the waste water samples were analysed in the field using a Hanna HI-98194 Multiparameter meter which could measure pH, Conductivity, DO and TDS with an accuracy of (±0.02, 1µS/cm, ±0.1ppm, ±1mgL^{-1})

3.7 Measurement of Physical properties of DWTR

3.7.1 Measurement of moisture content, porosity, bulk density and particle density.

All the media were analysed for moisture content, porosity, bulk density and particle density. The moisture content was determined by placing a known mass of media in an oven at 105^{0}C until the mass remained constant. The porosity was determined from the amount of water required to saturate a known volume of media. The bulk density was calculated from the volume of water displaced by a known mass of media. The particle density was measured according to BS 1377-2:1990 using 50ml pyknometers and 5g media samples.

The physical properties of the media are reported in section 4.4.

3.7.2 Measurement of Hydraulic conductivity.

There is a great body of evidence that constructed wetlands can surfer from clogging due to the collection of suspended solids, chemical precipitates, formation of biofilms and the breakdown of the media (Kadlec and Wallace, 2008). Therefore, hydraulic conductivity was measured at the start and end of the experiments. The hydraulic conductivity was measured by two methods; in the laboratory and directly in the columns.

3.7.2.1 Measurement in the laboratory.

The hydraulic conductivity of all 8 media was measured in a constant head permeability cell according method BS 1377-5:1990 section 5 (Figure 3.15). Due to the compressible nature of the media all experiments were repeated three times.

Figure 3.15 Laboratory constant head hydraulic conductivity test

The results of the hydraulic conductivity measured in the laboratory are detailed in section 4.4.

3.7.2.2 Measurement on the test rigs

A high level header tank was added to the test rig and the system was plumbed to allow the feed pump to supply the header tank. An overflow pipe in the tank kept the head constant during the experiments. A removable water tight cap was manufactured which connected the column being measured to the header tank via a water tight 20mm tube (Figure 3.16). To complete the test the column and tank were first filled with water and all air was removed, the manual outlet valve at the base of the columns was then opened and the time to fill a 1 litre container was measured. All experiments were repeated three times. This design was adapted from (Liang, 2007). The results of hydraulic conductivity measurements made on the test rigs are detailed in section 7.3.

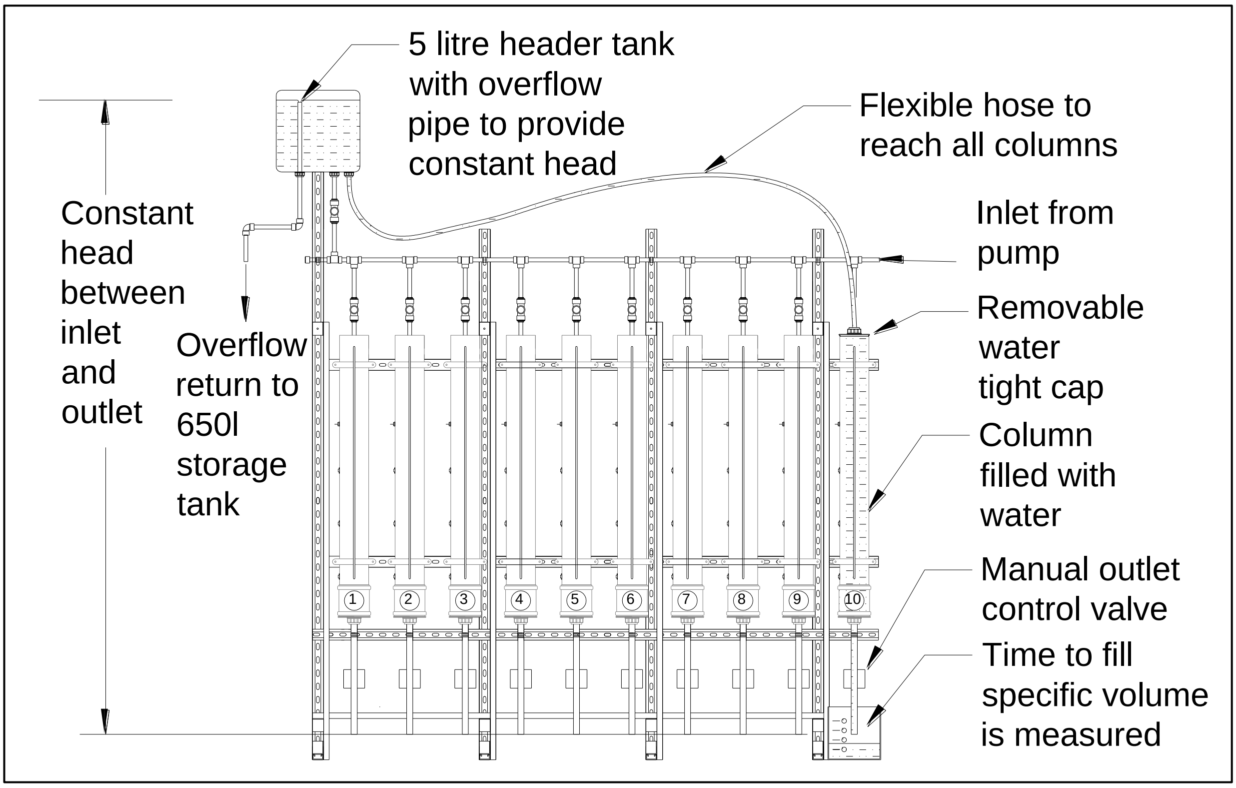


Figure 3.16 Components to measure hydraulic conductivity during rig operation.

The volume of water, V (mL), which passed through the sample in time, t (s), and the hydraulic head difference between the water surface and the bottom of the filter media, ΔH (cm) were measured. The hydraulic conductivity, K (cms^{-1}), was then calculated by

$$\boldsymbol{K = \frac{VL}{At\Delta H}}$$

Equation 3.1

Where A (cm^2) and L (cm) are the cross section area and the length of the media column, respectively.

3.7.3 Measurement of DWTR compressibility

The compaction test for soils is generally used to assess the relationship between dry density and moisture content for a given degree of compaction force (Head and Epps, 1986). However in this case the compaction tests provides a useful way of comparing the mechanical structure of the DWTR. The less compactable the DTWR the more structurally stable it is. The consolidation of each of the 8 DWTR was measured in an automatic computer controlled oedometer tester according to BS 1377-6:1990. The results of the consolidation tests are reported in section 4.4.1.

Figure 3.137 Automatic oedometer

3.7.4 Measurement of particle size distribution

The gross particle size of the media is critical to the adsorption process as the particle size is related to the surface area of the media available for adsorption. The DWTR was not amenable to either sieving or sedimentation tests which are the standard methods of measuring particle size distribution (Head and Epps, 1986). Sieving involves the drying of the media and then shaking vigorously in a stack of sieves. Both the drying and shaking of the media cause it to crumble and therefore reduces particle size. Sedimentation involves the complete dispersion of the media in water, this also irreconcilably changes the particle size of the media.

A nonstandard method of analysing particle size distribution uses digital image analysis. The process involved taking a random portion of the media and spreading it out over a white sheet of paper, making sure none of the particles were overlapping or touching. A digital photograph of the media was taken and the image was processed using the ImageJ software (Figure 3.18). Depending on quality of the images the *Dilate*, *Fill Holes* and *Erode* process in ImageJ were used to process the image. The number of steps of *Dilate* and *Erode* were kept constant to make sure the addition or removal of pixels was equal for all images. Once calibrated the software provided an output of the surface area of each particle analysed. The D_{50} particle size could then be calculated assuming that each particle is circular. The method is detailed in (Kumara et al., 2012). This procedure involves the use of many assumptions and could not be directly compared with standard methods, however it gave a valuable ability to compare the different media types.

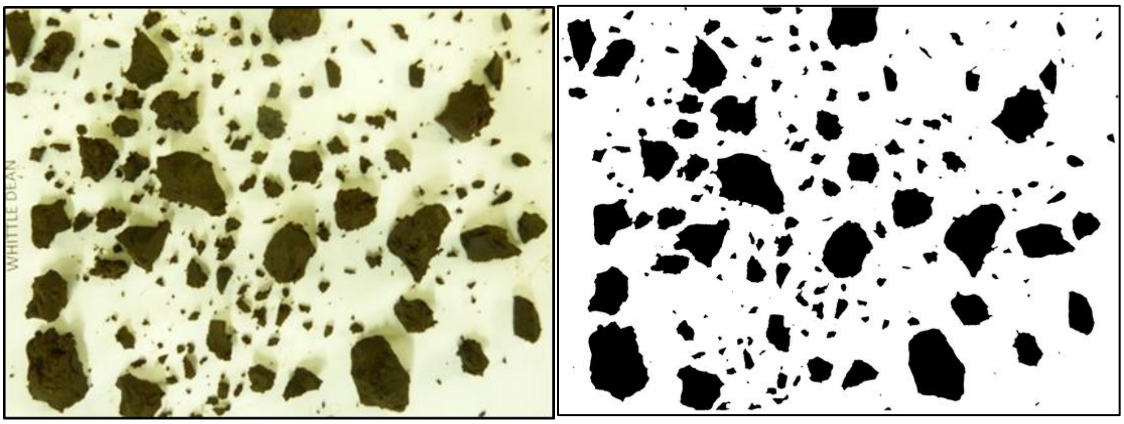


Figure 3.18 Raw and processed image of WD media

Once the area of each particle is known in mm^2 it is assumed that the particle is a perfect sphere so the approximate volume of each sphere is calculated. The cumulative frequency curve for the volumes was plotted in Matlab, and calculation for D_{10}, D_{50}, and D_{60}, were done using a shape preserving interplot and Matlabs curve fitting tools. The results of this analysis are reported in section 4.4.2.

3.8 Measurement of specific surface area (SSA)

The specific surface area is a property of solids defined as the total surface area of a material per unit of mass. As the removal of P by DWTR is thought to be primarily a surface phenomenon the measurement of SSA was of great importance.

Predominantly, two general approaches have been used to determine specific surface area of fine grain materials (Arnepalli et al., 2008): (1) the measurement of external surface areas by the adsorption of simple molecules, such as nitrogen at low temperatures, with surface areas being derived from adsorption isotherm data and the application of BET theory (Brunauer et al. 1938), and (2) the measurement of total surface area by the adsorption of polar liquids such as ethylene glycol monomethyl ether (EGME) (Carter et al., 1965).

Although the BET method has been the most commonly used to determine the SSA of DWTR (Makris et al., 2004b, Wang et al., 2015, Yang et al., 2008). It has been reported that polar sorbates such as EGME give higher estimates of SSA than non-polar substances such as N_2 due to the inability of N_2 to penetrate the "internal" surface area of any sample.(Jong, 1999). For comparison both the EGME and BET methods were used to analyse the SSA of the DWTR.

The measurements made by the gas sorption process were undertaken on the 8 raw media (which had been oven dried and ground to pass through a 0.5mm sieve). The tests were completed by a technician at the School of Chemistry at Cardiff University using a Quadrasorb-evo surface area analyser operating with nitrogen gas manufactured by Quantachrome.

16 samples of DWTR both before and after use in the experimental rigs were analysed using the EGME method. The procedure was completed by myself in the CLEER laboratories and the method is detailed below.

The results from both the BET and EGME measurements of SSA are shown in section 4.3.1.

3.8.1 EGME method

The EGME method used for the experiments is described by (Cerato and Lutenegger, 2002) and is summarised in brief. Approximately 1 gram of oven dried DWTR was crushed and passed through a 0.5mm sieve. This was placed in a clean dry aluminium tare 76mm in diameter and 10mm high. The mass of the DWTR was determined to the nearest 0.001g. Using a pipette approximately 2ml of laboratory grade EGME was gently placed over the sample. The solid and liquid were gently mixed using a slow swirling motion until a uniform slurry was formed. The tare was placed in a vacuum desiccator. A Plexiglas lid was placed over the tare leaving a 2mm air gap between tare and lid. The air was removed from the desiccator to a vacuum with a minimum of 635mm Hg. After 8 to 10 hours the tare was carefully removed and weighed. This was repeated after approximately 18 and 24 hours and in 4 hour steps after this until the weight of the tare did not vary by more than 0.001g.

The SSA of the media is then calculated using equation 3.2

$$\boldsymbol{SSA = \frac{W_a}{0.000286W_S}}$$

Equation 3.2

Where SSA = Specific surface area in m^2g^{-1}

W_a = weight of EGME retained by the sample in grams (final slurry weight-W_s)

W_s = weight of soli added initially (g)

0.000286 = weight of EGME required to form a monomolecular layer on a square meter of surface

3.9 Experiments to assess the change in P adsorption rate over time

The rate P is removed from the waste water with fresh dried DWTR has been studied by many authors (Babatunde and Zhao, 2010, Wang et al., 2011, Gao et al., 2013) . However the change in P adsorption kinetics as the media becomes saturated over a period of time has not been studied. Also all studies referenced above used a dried and crushed media for their experiments whereas the kinetic removal rates of the raw media is of key interest to this study.

The aim of these experiments was to compare the P removal rate of a ferric and alum based DWTR and monitor how the rate changed over a period of one year.

3.9.1 Method

Two of the columns operating with a 6 hour load and rest time had an additional outlet valve installed 200mm from the base of the media. The columns contained a ferric and alum based media (BS, GU, respectively). The additional valves were installed to make sure that water samples collected were directly in contact with the media rather than the gravel base. The results from these experiments are reported and discussed in section 8.3.

3.9.2 Sampling regime

As soon as the columns were loaded by the feed pump a 30ml sample of water was collected from the outlet, further 30ml samples were collected after 10, 20, 30, 60, 90,120,150,180,210, 240 and 270 minutes. The water was allowed to flow freely for 5 seconds before the samples were collected. The experiment was repeated every two months during the one year trial period.

3.10 Experiments to assess the effect of particle size on P adsorption

3.10.1 Background

The measurement of bulk particles size has been discussed in section 3.6.4. The results from these experiments showed a large difference in particle size distribution between the DWTR types particularly in relation to dewatering process (average D_{50} 12 and 20mm for centrifuged and pressed sludges, respectively.) It was hypothesized that the average particles size of the media would have a great effect on the P adsorption capacity, and an experiment was designed to assess this effect. The results from the experiments are reported in section 8.2

3.10.2 Method

Four particle sizes ranges of 20-6, 6.3-2, 2-0.6 and <0.6mm were chosen as representative of the particle size ranges that were used in these experiments and of those reported in the literature. 10 grams of each particle size range was placed in 500ml of deionised water dosed with different concentrations of P 1000, 500,100, 50, 10 and 5mgL^{-1} TP. A ferric and alum based (WD and BS) media were compared in the experiments making a total of 48 experimental solutions. 10 grams was chosen as this enabled the use of at least 10 particles of the larger media size.(The high levels of P concentration compared to those used on the test rigs were chosen because from earlier observations the P would have been removed from the synthetic solution almost instantaneously at levels below 5mgL^{-1}TP.) The mixtures were capped to avoid transpiration losses and shaken at 200rpm for 48 hours. 10ml Water samples were taken from the bottles after 0,10,20,30,60,120,180,250,1440 and 2880 minutes. The samples were all vacuum filtered through a 0.45µm filter and analysed for STP using the ICP.

3.10.3 Preparation of DWTR and experimental solutions

3 kg of ferric and alum based DWTR (BS and WD) were air dried for 5 days until the dry solids content was above 50% (The media had to be dried to enable sieving.). The dried media was placed in 500gramm batches into a stack of sieves

with apertures of 20, 6, 2 and 0.6mm. The stack was shaken for 3 minutes using a mechanical sieve shaker and the portions remaining on each sieve were carefully removed. To provide enough of the smaller particles size some of the media had to be ground using a hand grinder.

To make the different concentrations of synthetic P dosed water , a 1 litre of stock solution of concentration 10 000mgL^{-1} TP was mixed using analytical grade KH_2PO_4 and deionised water. Four litres of each of the synthetic P solutions was then made by mixing the stock solution with deionised water at the correct dilution factor. pH was adjusted to 7 in each solution using 0.1M NaOH.

3.11 Experiments to assess the formation of biofilm on P adsorption

During the operation of the experimental rigs it became apparent that the columns loaded with real waste water were removing significantly less P than those loaded with synthetic waste water. It was hypothesised that this may be due to the formation of a biofilm on the media which might inhibit available absorption sites. An experiment was designed to see if this effect could be quantified and the results are reported in section 6.9.

3.11.1 Growth of Biofilm

500 gram samples of a ferric and alum based DWTR (BS and WD) were taken from the storage containers and air dried for 5 days. The samples were sieved using a mechanical sieve shaker through a 2 and 0.6mm sieve. The samples on the 0.6mm sieve were used producing a particle size range from 0.6 to 2mm. Two 25g samples of each sieved DWTR were placed in 300ml sterile glass bottles. 100ml of Brain-heart infusion (BHI) broth was added to the samples which were then sterilised in an autoclave to remove all biofilm. 5ml of Streptococcus mutants were added to one of the alum and ferric samples (the 2 remaining samples were left untreated as controls) and all samples were incubated for 72hours at 45^{o}C. After 72 hours the samples were autoclaved again and centrifuged to remove the supernatant. Four sample media were produced two with forced biofilm growth and two controls.

This work was undertaken by Lucy Marsh in the dental bioscience laboratory in Cardiff University School of Dentistry under the supervision of Prof David Williams.

3.11.2 Confocal experiments

Before the biofilm experiments were undertaken some of the samples were analysed using the Leica TCS SP2 AOBS confocal system at the School of Biosciences Cardiff University. To analyse the samples for evidence of biofilm, small DWTR samples were removed from 2 of the columns loaded with real waster. The samples were spread very finely onto microscope slides and a few drops of live/dead stain (SYTO® 9 Green Fluorescent Nucleic Acid Stain) were added to the samples which were capped with a further microscope slide. The samples were left for 20 minutes and then placed under the confocal microscope. The live dead stain is adsorbed by any DNA present and causes the microbes to fluoresce, making any biofilm clearly visible. The results are discussed in section 6.9.

Chapter 4 Physical and chemical properties of the DWTR

4.1 Introduction

An objective of this research was to conduct experiments to assess which variables associated with the DWTR would optimise the removal of P. To achieve this a detailed investigation of both the physical and chemical properties of the 8 DWTR, and the processes involved in their production was undertaken.

Another objective was to provide design information about how a phosphorous removal system using DWTR could be constructed. The physical properties and amount of media produced at each works provide critical information as to both how big a system would have to be, and on what scale it could be constructed in light of the potential amounts of media available.

To achieve these objectives the experiments detailed in this chapter were designed to improve understanding of :

- the nature and chemical makeup of the raw water that entered the 8 treatment works where the DWTR were taken from.
- the amount and nature of the chemicals dosed and the dewatering processes used in the production processes of the DWTR.
- the quantities of DWTR produced at each treatment works.
- the chemical makeup of the DWTR.
- the physical properties of the DWTR.

This chapter reports the results of experimental work undertaken for this thesis. In addition data provided by Northumbrian Water was used along with chemical data relating to the chemical properties of the media which has been previously reported by Al-Tahmazi and Babatunde (2016). In Chapter 9 the physio chemical properties of the media are discussed in relation their ability to remove P, which is analysed in Chapter 5.

4.2 Inlet water quality parameters and DWTR production variables and quantities.

4.2.1 Inlet water quality parameters

Key parameters of the raw water from the 8 Northumbrian water treatment works that supplied the DWTR are shown in Table 4.1.

Table 4.1 Inlet water quality parameters (data from Northumbrian Water from Jan Dec 2014)

Media	Water Source	Inlet pH	Inlet turbidity (NTU)	TOC (mgL^{-1})	Alkalinity (mgL^{-1} as HCO_3)
BS	River	7.87 ±0.29	10.07±18	8.3±3.4	71± 20
FO	Reservoir	7.32±0.25	5.2±3.5	23±3.9	49± 12
GU	Reservoir	7.51±0.28	1.8±0.73	7.5±0.7	38± 11
HH	Mix of 3 Reservoirs	6.69±0.74	2.63±0.98	8.27±2.1	14±12
HO	River and Reservoir	7.70±0.28	5.47±6.5	9.34±2.3	75± 24
LA	Mix of 5 Reservoirs	7.39±0.41	2.75±0.08	10.25±2.9	35±13
MO	Reservoir	7.19±0.42	2.01	5.88±1.5	19±11
WD	Reservoir	7.89±0.27	3.47±0.91	7.57±2.9	124.±41

The values shown in Table 4.1 are calculated averages from data that was provided by Northumbrian water from the SCADA monitoring systems at the treatment works between Jan and Dec 2014. This is the previous year from the date of the experiments.

All the water supplies had circa neutral pH, all being slightly alkaline apart from HH which is slightly acidic. All the sites had relatively low levels of turbidity with a maximum of 10 NTU at BS which is unsurprising as it is the only site purely fed from a river. For seven of the sites the TOC levels varied between 5.8 and 10.25 mgL^{-1} , however FO stands out has having over twice as much TOC (23 mgL^{-1}) in the raw water. The alkalinity varied between 14 and 103 mgL^{-1} as HCO_3, with

HH and MO having much lower levels than the rest of the sites (14 and 19mgL^{-1}) compared with 124mgL^{-1} for WD being the highest. It must be noted that WD also had a very high standard deviation.

4.2.2 Coagulant and polymer doses for the 8 DWTR

Details of the type of coagulant used, drying process and amount of polymer dosed in the production of the DWTR are shown in Table 4.2. This data is an average of figures obtained between Jan 2014 and Dec 2014 and was supplied by Northumbrian Water.

Table 4.2 Type of coagulant used, polymer dose and drying process for the 8 DWTR (Data from Northumbrian Water)

Media	Coagulant	Coagulant dose (mgL^{-1})	Polymer dose (mgL^{-1})	Drying process
BS	Ferric	138±27	0.26±0.06*	Centrifuge
FO	Ferric	149±9	0.25±0.02*	Centrifuge
GU	Alum	89±20	nd	Press
HH	Ferric	61±29	#	Centrifuge
HO	Alum and Ferric	135±20	0.31±0.05*	Press
LA	Ferric	68±16	nd	Centrifuge
MO	Ferric	49±2	#	Centrifuge
WD	Alum	83±10	0.24±0.01*	Press

nd = not determined
\# = starch used as a polymer dosed between 1 to 2mg L^{-1}
* = polyelectrolyte used as polymer.

The coagulation dose varied between 49 and 138mgL^{-1} with MO receiving approximately 1/3 the dose of coagulant when compared to the BS, FO and HO sites. The three DWTR using alum as a coagulant also use a press to dry the media, therefore, any differences measured between the Al and Fe based media may be due to the drying process rather the chemical composition. The HO site receives water from both a reservoir and a river and is treated with both alum and ferric coagulants.

The polymer dose was very consistent across all sites that use polyelectrolyte as a coagulant at around 0.25mgL^{-1}. Although data was not available for the GU and

LA sites Northumbrian water confirm that the range of polymer dose is similar to the other sites. However the HH and MO sites are dosed with starch (which is made from potatoes) at a rate of 1-2mgL^{-1}.

4.2.3 Quantities of DWTR produced at the 8 treatment works

The amount of DWTR produced at the 8 sites of interest is shown in Table 4.3. The table also shows the amount of water each treatment works treats per day and the relative amount of sludge that was produced per m^3 of water treated.

Table 4.3 Quantities of sludge produced at the 8 different treatment works (Data from Northumbrian Water)

Site	Quantities of sludge produced per year (wet tonnes/yr)	Flow rate at treatment works (m^3/day)	Sludge produced per flow rate (Kg/m^3)
BS	12 500	68 216	0.50
FO	5 500	18 279	0.82
GU	580	9 559	0.17
HH	7 200	73 183	0.27
HO	4 400	37 725	0.32
LA	14 000	107 576	0.36
MO	8 750	132 981	0.18
WD	7 400	30 451	0.67

The data from this table reveals the very large quantities of sludge that are being produced at the treatment works. Collectively the 8 sites produce over 60 000 tonnes of wet sludge a year. The average moisture content was 20% so the total dry mass was approximately 12 000 tonnes a year. It is also interesting to note the difference between the relative efficiencies of the works at producing sludge with the rate of sludge production varying between 0.17 and 0.82 kg of sludge for every m^3 of water produced.

4.3 Chemical properties of the media

The quantities of the chemical constituent of the media are shown in Table 4.4. This data has been previously reported in Al-Tahmazi and Babatunde (2016).

Table 4.4 Chemical properties of 8 DWTR adapted from (Al-Tahmazi and Babatunde, 2016)

Media		BS	FO	GU	HH	HO	LA	MO	WD
Al	mg/g	4.59	21.16	112.81	5.16	65.35	6.8	3.89	104.22
Aloxa		1.14	17.36	110.12	1.36	58.63	1.02	1.85	95.28
Fe		298.1	241.69	17	193.85	143.29	255.46	257.8	9.75
Feoxa		143.08	121.33	13.35	121.38	72.41	144.48	149.52	3.68
P		0.61	0.43	0.24	0.44	0.65	0.29	0.39	0.7
Poxa		0.23	0.23	0.22	0.3	0.34	0.28	0.24	0.28
Ca		6.83	3.17	1.16	3.06	1.9	3.33	2.65	1.8
Mg		0.47	0.25	0.66	0.81	1.38	0.43	0.2	0.44
Mn		0.94	2.32	0.33	0.37	0.57	0.45	0.79	0.29
Zn		0.19	0.09	1.02	1.85	1.71	0.09	0.4	0.47
Cl-		0.22	0.3	0.11	0.33	0.16	0.21	0.16	0.24
SO_4		4.06	4.26	0.81	4.51	3.86	7.45	6.93	1.88
TC		110.8	137	119.6	161.9	105.2	115.9	117.4	119.6
OC		110.8	137	118.9	161.9	105.2	115.9	117.4	119.1
EC	µs/cm	522.8	378	455.5	375.8	665.7	410.7	488.3	723.1
pH	–	5.47	5.49	6.26	4.55	5.49	4.09	4.48	6.27

The DWTR have highly variable chemical properties, but have comparable values to those reported in the literature see Table 2.14 (Ippolito et al., 2011). The main constituent of the media by weight is either aluminium or iron. The GU and WD media contained the largest amount of Al (113 and 104 mg g $^{-1}$) as they were both dosed with alum. The Fe content of the remaining media ranged from 143 to 298 3mg g^{-1} for HO and BS, respectively. Apart from calcium, the content of the remaining metals is less than one hundredth the value of the Fe and Al content. All the media contain P that has been adsorbed from the receiving water with a range of 0.24 to 0.7mg g^{-1}. The TC and OC ranged from 105.2 to 161.9 mg g^{-1}, it can be seen that there is a negligible difference between TC and OC which implies that the content of inorganic carbon in the DWTR is negligible. It can further be deduced that most of the carbon in the DWTR is associated with natural organic matter entrained in the raw water as for the majority of the sludges the polymer dose is very small (>0.25mgL^{-1}). It is notable that HH had considerably more TC than all the other media which is surprising as the raw water feed to the treatment plant is no higher than the others, this might be explained by a higher dose of the starch based polymer. However it could also be because the sludge was taken on a day after cleaning maintenance had been undertaken at the plant (although this has not been qualified).

4.3.1 Specific Surface area

All of the raw media were analysed for SSA using both the EGME and the BET-N_2 method. The EGME method was detailed in Section 3.8. Analysis using the BET method (using N_2) was undertaken by the Chemistry department at Cardiff University. The results of the analysis shown in Table 4.5 in order from highest to lowest SSA (from the EGME method from this research). For comparative purposes results are also reported from Al-Tahmazi and Babatunde (2016) which assessed the SSA of identical media using the EGME method.

The results of all three tests show a huge difference both in range and order. However there is a significant correlation ($r=.79$, $p<.05$) between the EGME results produced by this research and Al-Tahmazi and Babatunde (2016). The correlation implies that there was possibly an error in the experimental procedure but that the error was relatively consistent between this study and Al-Tahmzi's experiments. The consequence of this difference is that the results are most useful as a relative measure when comparing the 8 different DWTR amongst themselves.

The results produced from the BET-N_2 analysis were lower in all cases than those produced from the EGME method apart from the HH media, in which all experimental results agree almost exactly. The lower results from the BET-N_2 method were also found by Makris et al (2005b) and the reasons for this were discussed in detail in 2.6.3.2.

Table 4.5 SSA measurements from this research compared with Al-Tahmazi and Babatunde (2016) and measurements made by chemistry department

SSA of Raw media				
Media	**EGME(This research)**		**EGME (Al-Tahmazi)**	**BET-N_2**
	No. of tests	**SSA(m^2) ± St Dev.**	**SSA(m^2)**	**SSA(m^2)**
HO	5	224 ±41	414	108
WD	3	214 ± 30	468	80
BS	3	200 ± 65	203	145
GU	2	190 ± 2	364	9
MO	3	148 ± 27	186	64
HH	3	132 ± 30	132	132
LA	4	97 ± 4	220	19
FO	3	86 ± 26	120	8
Max-Min		**224 - 86**	**468-120**	**145 - 8**

The results from both this research and Al-Tahmazi for the EGME experiments are generally higher than those reported in the literature, but the majority of analysis has been undertaken using the BET-N_2 method. As with the literature the average SSA of the media using, alum as a coagulant, was larger than those using ferric, 209 and 133m^2g^{-1}, respectively from this research, and 90 and 50m^2g^{-1} in the literature. However it is hard to draw conclusions from such a small data set with such high variability.

The results demonstrate the difficulty of measuring the SSA accurately. Nevertheless, it is clear that the DWTR has a very large SSA available for P adsorption when compared to the other waste products reported in the literature which is often between 1 and 10m^2g^{-1} (Johansson Westholm, 2006).

4.4 Physical properties of media

The bulk and particle density, dry solids content, porosity and hydraulic conductivity of all 8 media are shown in Table 4.5 (The hydraulic conductivity measurements were made in the laboratory with a constant head rig as shown in Figure 3.14. Further assessment of the hydraulic conductivity in the operational systems is discussed in section 4.4.3). The HH and FO media were too wet to be used in the model columns directly as in their raw state the hydraulic conductivity was below the measurable threshold of the hydraulic conductivity testing rig

($<0.0001ms^{-1}$) and would not have been viable for use in the experimental columns. Both media were therefore air dried for 5 days before being used in the columns. The resulting dry solids content was increased from 15 to 31% and 17 to 79%, for FO and HH, respectively. The bulk density decreased from 1264 to 655 and 1178 to 827kgm^{-3}, respectively. The results before and after drying of both media are shown in Table 4.6.

Table 4.6 Physical properties of the media

Media	Bulk density (kgm^{-3})	Particle density (kgm^{-3})	Dry solids (%)	Bulk Porosity	Hydarulic conductivity (ms^{-1})**
BS	828±237	2936±35	19	0.37	0.00057
FO	1264±13	2115±182	15		<0.0001
FO*	655±33	2115±182	31	0.49	0.0087
GU$^{\#}$	621±27	1848±17	19	0.41	0.014
HH	1178±77	2163±50	17		<.00001
HH*	827±25	2163±50	79	0.44	0.0034
HO$^{\#}$	639±23	2078±36	23	0.44	0.0063
LA	955±200	2143±37	19	0.39	0.0034
MO	963±173	2227±123	23	0.32	0.0085
WD$^{\#}$	680±53	1744±16	22	0.46	0.014
6mm Gravel	2213±43			0.39	0.014

FO and HH*.show results for media after being air dried for 5 days*
***Hydraulic conductivity results are accurate within limits of ±10%*
$^{\#}$ Media dewatered using a press

It is notable that the two alum based media have the lowest bulk density 621 and 680 kgm^{-3} and lowest particle density 1848 and 1744 kgm^{-3} for GU and WD, respectively. The pressed media generally have a higher dry solids content than the centrifuged media although this is not true in all cases. The porosity of the media was generally very high varying between 0.32 and 0.49 which compares well to the porosity of gravel (0.39) which is generally used in operational reed beds. The pressed media tended to have slightly higher hydraulic conductivities than those dewatered with a centrifuge.

4.4.1 Compression testing, calculation of degree of saturation and compression index.

All raw DTWR were compression tested in an automatic oedometer as detailed in section 3.7.3. The results for all the media are shown in Figure 4.1.

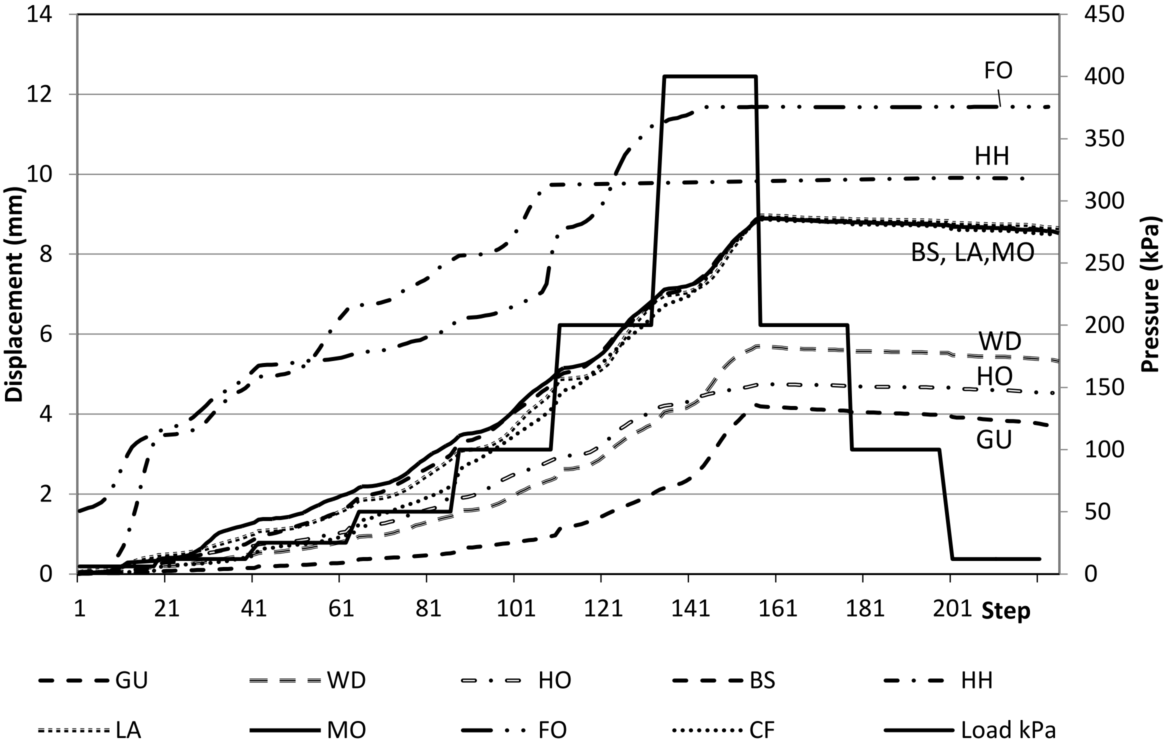


Figure 4.1 Comparative results of compression testing 8 DWTR

The results clearly demonstrate that media dewatered by a press (WD, HO and GU) were much less compressible than those that had have been dewatered by centrifuge. This implication of this observation is that the pore space between the media particles is smaller for pressed media. To assess the effect the compressibility of the media may have on water movement through the media a series of equations was used to calculate the wet and dry density, the pore volume, percentage saturation and the compression index of each of the media. The calculations were undertaken using Equations 4.1 to 4.6 adapted from (Head and Epps, 1986). The results from the analysis are shown in Table 4.7.

Dry Density ($\boldsymbol{\rho_D}$) is the mass of dry soil after drying at 105°C, contained in a unit volume of undried soil.

$$\boldsymbol{\rho_D = \frac{100}{100+w\%}\rho} \qquad \textbf{\textit{Equation 4.1}}$$

Where ρ = bulk density kg m^{-3}
ρ_D = dry density
w = water content expressed as a percentage

Voids ratio (e) is the ratio of the volume of voids (water and air) to the volume of the solid particles in a mass of media.

$$\boldsymbol{e = \left(\frac{\rho_s}{\rho_D}\right) - 1} \qquad \textbf{\textit{Equation 4.2}}$$

Where ρ_S = Particle density kg m^{-3}
e = voids ratio

Porosity (n) is the ratio of volume of voids to volume of solid.

$$\boldsymbol{n = \frac{e}{1+e}} \qquad \textbf{\textit{Equation 4.3}}$$

Saturated density, ($\boldsymbol{\rho_{sat}}$) is the bulk density of the media when it is fully submerged assuming all voids are filled with water

$$\boldsymbol{\rho_{sat} = \frac{\rho_s+e}{1+e}} \qquad \textbf{\textit{Equation 4.4}}$$

Where ρ_{sat} = saturated density

Degree of saturation (S_r) is the volume of water contained in the void spaces between media particles expressed as a percentage of total voids.

$$\boldsymbol{S_r = \frac{\rho_s\, w}{\rho_w e}}\ \% \qquad \textbf{\textit{Equation 4.5}}$$

Where S_r= degree of saturation (%)
ρ_w = density of water (assumed 1g cm^{-3})

Compression index (C_C) describes variation of the void ratio as a function of the change of effective stress plotted in the logarithmic scale. It therefore represents a deformation characteristic of consolidated soil. Numerically C_c is equal to the change in voids ratio for one log cycle of pressure change and is a dimensionless number.

C_C is calculated from the slope of the consolidation curve plotted to a logarithmic scale of pressure p, in the linear range. The straight line is represented by equation 4.5

$$e = e_0 - C_c \log_{10} \frac{p_0 + \delta p}{p_0} \qquad \textbf{\textit{Equation 4.6}}$$

Where δp = incremental pressure change
p_0 = pressure at start of cycle
e_0 = initial voids ratio

The results from this analysis further show the very porous nature of the media. The total calculated porosity which includes the voids within the media averaged 0.91 whereas the measured bulk free water porosity averaged 0.41, measured from the amount of water that filled a container full of media, this represents an effective doubling of porosity. Therefore there is a large potential for water to move both through the external bulk and within the particles of the media. However Makris and Harris (2006) used thermogravimetric methods to assess the nature of the water contained within the interstitial pores of the DWTR and concluded that the water was trapped within the pores when the particles were formed in the water treatment process and it is hard for this water to escape, as it would require increased kinetic energy to overcome the resistance due to pore size and path tortuosity.

By assessing the values of degree of saturation it can further be seen that the void spaces are between 56 and 86% filled with water but the pressed media shows markedly lower values than the centrifuged media (apart from the 2 that were air dried.) This implies that the pressing process forces more of the water from interstitial pores that the centrifuge process, which may in turn hinder P adsorption. This is discussed in section 8.3.

Media	Measured Bulk Density (ρ)	Measured Particle Density (ρ_s)	Measured Dry Solids	Measured Moisture Content (W)	Calculated Dry Density (ρ_d)	Calculated Voids Ratio (e)	Calculated Porosity (n)	Measured Bulk Free Water Porosity (n_f)	Calculated Degree of Saturation (S_r)	Calculated Compression Index (C_c)
	Mg m^{-3}	Mg m^{-3}	%	%	Mg m^{-3}				%	
BS	0.828	2.936	19	498	0.14	20.2	0.95	0.37	72	4.59
FO	1.264	2.115	15	627	0.17	11.2	0.92	nd	100	2.09
FO*	*0.655*	*2.115*	*31*	*335*	*0.15*	*13.0*	*0.93*	*0.49*	*54*	nd
HH	1.178	2.163	17	627	0.16	12.3	0.93	nd	100	4.27
HH*	*0.827*	*2.163*	*79*	*132*	*0.36*	*5.1*	*0.84*	*0.44*	*56*	nd
LA	0.955	2.143	19	512	0.16	12.7	0.93	0.39	86	2.73
MO	0.963	2.227	23	427	0.18	11.2	0.92	0.32	85	2.44
GU	0.621	1.848	19	513	0.10	17.2	0.95	0.41	55	0.82
HO	0.639	2.078	23	426	0.12	16.1	0.94	0.44	55	1.84
WD	0.68	1.744	22	439	0.13	12.8	0.93	0.46	60	1.43

Table 4.7 Measured and calculated physical parameters of 8 media.
Note: GU, HO and WD are dewatered by pressing shown at the bottom of the table for clarity
FO and HH* air dried for 5 days before being used in the columns. nd = not determined*

The calculated compression index generally followed the trend of the compression curves shown in Figure 4.1, with the three pressed media having the lowest C_c (0.82-1.84), the highest dry solids content and the lowest degree of saturation. However, the BS media has by far the highest C_c (4.59) which is not implied by the compression graph, and this anomaly is probably due to the very high measured particle density 2.9Mg m^{-3} compared to the average of the other media which was close to 2. The apparent high particle density reduces the degree of saturation of the media and hugely increase the voids ratio.

The compression index is a tool that is generally used in the assessment of foundations for buildings, although in the case of DWTR it does not relate directly to any meaningful parameter unless the media is used in very deep adsorption beds, and it is crushed under its own weight. The value of C_c provides another useful performance indicator which can be used in statistical analysis of the media to show if there is a difference between the pressed and centrifuged media and their ability to remove P.

To confirm if the results from this study were in a reasonably accepted range a review of the literature in relation to the value of C_c was undertaken. O'Kelly (2008) found the C_c index of 2.5 to 3.7 for pressed sludges from Ireland which is directly comparable with the results found in this study. However Yang et al (1992) found C_c values of 1.19 and 6.69 for centrifuged and bed dried DWTR respectively. These values imply that the centrifuged sludge used by Yang et al. was slightly less compressible than the results found in this study, but the bed dried media was much more compressible. It is unsurprising that bed dried media was more compressible as the media was dewatered by evaporation and gravity rather than mechanical means. There is a sparsity in studies that report the value of C_c for DWTR but the two studies listed above give confidence in the results produced by this work.

4.4.3 Particle size analysis

The bulk particle size of the media is of great importance to both P adsorption capacity and kinetics of P removal and was discussed in 2.6.4.3. The bulk particle size of the media was complex to measure and the process used was outlined in 3.7.3. There was only enough time to repeat the experiments three times although the data had very high margins of error (calculated at 20%). The bulk particle size measurement was further complicated by the fact the individual clumps and lumps were broken up by hand and spade as the media was originally placed in the buckets for transportation. To quantify the breaking up of the media would require a complex process of analysis which was beyond the time available for this thesis. The results of the particle size analysis are shown in Table 4.8.

Table 4.8 Calculated particle size distribution for 8 media

Media	Dewatering Process	D_{10} (mm)	D_{60} (mm)	Uniformity Coefficient (U)	Average (mm)
BS	Centrifuge	3.11	14.5	1.44	10.5
LA	Centrifuge	2.04	5.1	2.53	3.3
HH*	Centrifuge	2.36	5.3	2.27	4.9
MO	Centrifuge	2.61	7.6	2.80	2.9
WD	Press	3.62	10.5	2.88	5.1
GU	Press	3.88	10.97	2.82	6.2
HO	Press	4.23	11.6	2.73	6.6
FO*	Centrifuge	5.01	13.4	2.66	13.2

Note: average of 3 experimental runs, results ±20%. HH and FO had been dried before analysis

The average particle size ranged from 2.9 to 13.2mm, with the pressed media having slightly larger particle sizes on average. The centrifuged media tended to form clumps but these could be easily broken up by hand whereas the pressed media was in more solid lumps. All of the media had particle sizes and uniformity coefficients that were suitable for operation in a reed bed; with size d_{10} in the range of 0.3±2.0 mm, and d_{60} between 0.5 and 8 mm, and a uniformity coefficient of less than 4 as recommended by Brix et al (2001).

Apart from the FO media all the centrifuged media had a D_{50} less than the pressed media. Both the FO and the LA media had to be air dried for 4 days before the particle size tests could be undertaken even with the digital photo analysis system. It is therefore likely that the size of both the FO and LA media was overestimated. Compared to soils the uniformity coefficient values of between 1 and 4 would imply the media is very uniform in size (Head and Epps, 1986).

4.5 Summary

The physical and chemical properties of the DWTR and the nature of the water treatment processes that were used to make the media were assessed to find out if any of these properties were correlated to the ability of the media to remove P and to assist in the engineering design of a full scale system.

The 8 DWTR used in these experiments were taken from water treatment work sites that were fed from both rivers and reservoirs, used presses and centrifuges for dewatering, ferric or alum or both as coagulants and polyelectrolytes or starch as a polymer. The works produced between 580 and 14 400 tonnes of wet DWTR per year.

The major constituents of the media are Fe, Al and TOC The media using ferric as a coagulant contained much more Fe (≈200 mgg^{-1}), and those using alum had a much higher Al content (≈107 mgg^{-1}). The SSA of the alum media was higher on average than that of the ferric based media, although there is a very large uncertainty in the SSA results depending on the method of measurement.

The media had bulk densities varying between 621 and 1263kgm^{-3} and dry solids content between 15 and 23%. When the dry solids content was below 19% the media had to be dried before it had any viable hydraulic conductivity, which was the case for 2 of the media. The porosity varied between 0.32 and 0.44 and average particle size between 2.9 and 13.2mm.

Chapter 5. Phosphorus removal from the column and meso scale experiments.

5.1 Introduction

This chapter reports the key results relating directly to the P removal of the experimental systems discussed in Chapter 3, and tries to answer the following questions.

- Which of the 8 media tested is the best at removing P?
- Which contact and resting period provides the best P removal regime?
- How is the P removal affected by inlet P concentration?
- Is the removal potential of the media effected by using real waste water rather than synthetic P dosed tap water?
- Does the scale of the system affect P removal?
- How does the P removal vary over time?

This chapter begins with a description of the mass balance analysis that was used to enable relative comparisons between the columns. This is followed by an assessment of the 6 repeated sets of columns. The analysis of these repeated experiments shows whether the observed effects were statistically significant or not, and provides valuable information on the heterogeneity of the media.

The main section of this chapter provides a broad overview of the P removal results and concentrates on the strength of the various effects using a P mass balance approach.

The final section details three models of the data that were used to assess how the P removal rate changed over time.

5.2 Phosphorus mass balance analysis

Although the columns all contained similar volumes of media, each media had a different bulk density and porosity. Therefore, each column contained a specific mass of media and was loaded with a different volume of water depending on porosity (detailed in Tables 3.4. to 3.6). To enable relative comparisons between the columns a mass balance approach was used in which, the mass of P input to the system per kg of media and the mass of P removed by the system per kg of media per cycle period was calculated. The cumulative uptake of P for each system was then plotted against the cumulative P input per mass of media. Equations 5.1 to 5.4 were used for this analysis.

Note P represents either STP, TP or PO_4-P

% P removal

$$\%P_{rem} = \left(\frac{C_{in}-C_{out}}{C_{in}}\right) \times 100 \qquad \textbf{Equation 5.1}$$

Where

C_{in} = P inlet concentration (mgL^{-1})

C_{out} = P outlet concentration (mgL^{-1})

Volume of water passed through column per week (or recorded time period) **V_{week}**(L)

$$V_{week} = (C_{yi}-C_{yi-1})\, V_{cy} \qquad \textbf{Equation 5.2}$$

Where

C_{yi} = number of full cycles passed through column on day of measurement

C_{y-1} = number of full cycles passed through column at previous measurement period.

V_{cy} = Volume of water pumped per cycle (L) [porosity of media x media bulk volume]

Mass of P adsorbed per cycle per mass of media **q_{ad}** (g $kg^{-1}{}_{media}$)

$$q_{ad} = \frac{1000\,(C_{in}-C_{out})V_{week}}{M_m} \qquad \textbf{Equation 5.3}$$

Where

M_m = mass of media (kg)

Mass of P input per cycle per mass of media q_{in} (g kg^{-1}_{media})

$$q_{in} = \frac{C_{in} . V_{week}}{M_m} \qquad \textbf{\textit{Equation 5.4}}$$

Note mg g^{-1} = g kg^{-1}]

To enable comparison of effect size the majority of the graphs in the remainder of this chapter use mass balance plots. A further advantage of these plots is that the linear regression of the data provides a measure of the average percentage P removal of the system.

5.3 Results from the repeated columns

To validate the importance of any effect demonstrated from the P removal analysis, three repeated sets of columns were used in the experiments. The repeated columns contained similar media, were fed with the same inlet feed and had identical contact and rest times. Two repeated sets (columns 0,8 and 1,9) were operated at the University and one set (column 30,31) were run at the RWW site. The comparative results for the three columns are shown in different formats in Figure 5.1, 5.2 and 5.3.

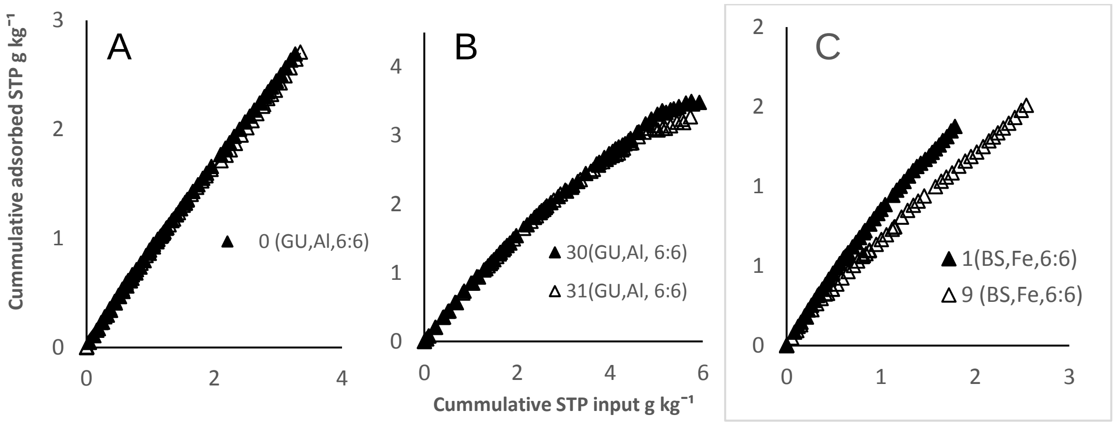


Figure 5.1 Cumulative STP adsorbed from the 3 sets of repeated columns A)GU media at University site, B)GU media at RWW site, C)BS media at University. Site.

Both at the RWW site and the University columns containing GU media (Fig 5.1 A and B) showed very good repetition. However the two columns using the BS media (Figure 5.1 C) were not so repeatable. It was not possible to assess the performance difference between the columns using a standard Tee test as regression analysis revealed r^2 values >0.999 for all the data, and therefore all the columns had significant differences between them at the 95% confidence levels. Therefore to make meaningful statistical comparisons between the columns, analysis of the weekly percentage STP removal data was undertaken. The results from the columns plotted as percentage STP removal against number of cycles passed are shown in Figure 5.2 A,B and C. As each cycle delivers a fixed volume of water to each system these plots also represent the volume of water treated plotted against percentage STP removal performance.

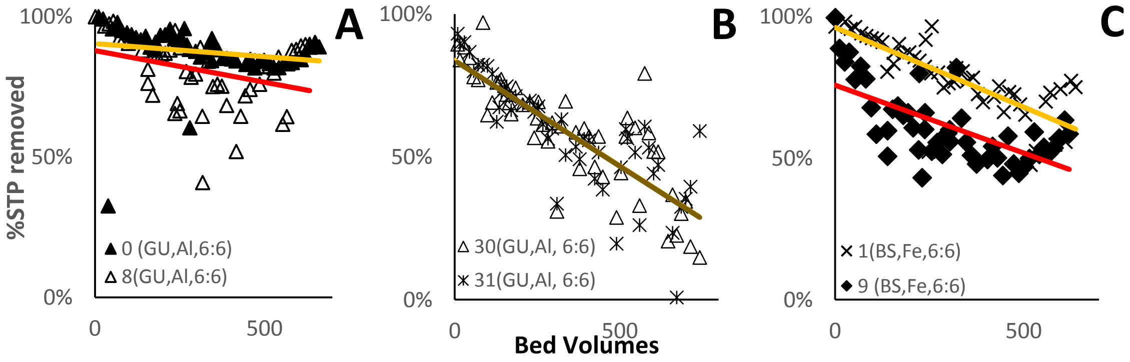


Figure 5.2 Comparison of the three sets of repeated columns, plotted percentage STP removal against system cycles. A) GU media at University, B) GU media at RWW site, C)-BS media at the University.

The linear regression models for these data sets can be compared statistically, using multiple regression analysis. The data was analysed using Statgraphics Centurion software (Relate, one factor, comparison of regression lines). The software compares both the slope and intercept of the regression models and provides p values with the null hypothesis being that the slopes and gradients are equal. In other words if p >0.05 there is no difference between the regression models. The results from the analysis are shown in Table 5.1 in which the predicted intercept and slope represent data from the linear regression lines produced from the graphs shown in Figure 5.2.

Table 5.1 Statistical analysis of the three repeated columns

Model	Predicted Intercept	Predicted slope (Rate of the fall in %STP removal per cycle)
0 8	0.960 0.887	-0.000207 -0.000208
P value for comparison	0.00	0.981*
30 31	0.842 0.827	-0.000736 -0.000687
P value for comparison	0.956*	0.626*
1 9	0.973 0.759	-0.000575 -0.000480
P value for comparison	0.000	0.321*

In all three sets of comparative columns there is no statistical difference (p>0.05) at the 95% confidence interval between the predicted slope of the graphs, however only the two columns at the RWW site show similar intercepts at p>0.05.

In physical terms the slope of the graphs indicates the rate at which the media is declining in its ability to remove P, and the intercept represents the predicted initial removal rate. Therefore, the P removal performance of all the comparative columns is similar at the 95% confidence level. However, the predicted initial performance of the 2 sets of repeats at the University was statistically different with the columns containing BS media having 21% difference(97.3 and 75.9%) in their ability to remove P but the two columns with GU having only a 7% difference (96.7 and 88.7%) The GU columns at the RWW site showed no significant difference between either the slope or intercept. Box plots of this data are shown Figure 5.3.

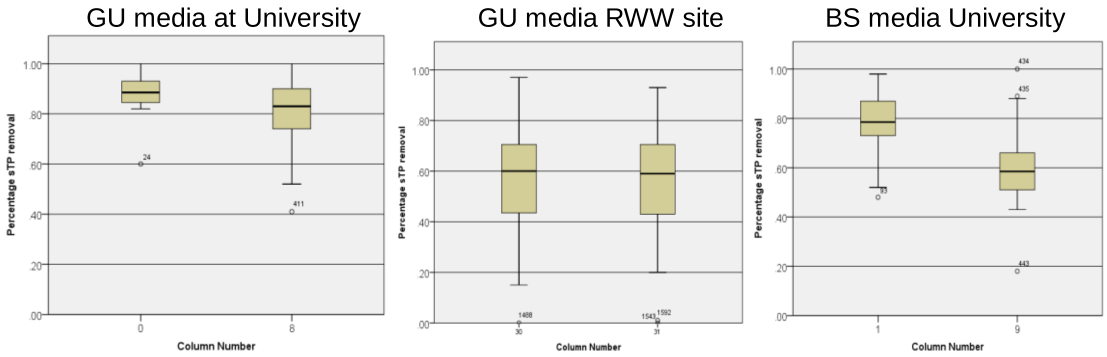


Figure 5.3 Box plots of % STP removal for three sets of repeated columns

The lack of repeatability of the columns can either be explained by experimental error, or by heterogeneity within the media. Although there is an experimental error associated with all the results, the majority of the equipment used for both operation and analysis had associated errors of no greater than 5% and it is most likely that the unrepeatable nature of the results is due to heterogeneity within the media samples.

The implication of these replicated experiments are that significant trends associated with the BS media required an effect size of >21%; whereas significance could be inferred for the GU results if the effect size was >7%.

5.4 Overview of phosphorus inlet and outlet results

5.4.1 Phosphorus results from University site

The P results from the 30 columns operated at the University have been split into 4 groups shown in Figure 5.4:

- Figure 5.4A shows results from 9 column experiments comparing the effect of media type. Eight different DWTR were used and one gravel control. All the columns had a contact and rest time of 6 hours and were fed with inlet concentration of 5mgL^{-1} STP.

- Figure 5.4 B and C show results from the 14 experimental columns used to compare the effect of contact and rest time 7 columns each used GU media (alum used as coagulant) and BS media (ferric used as a coagulant) with contact times from 0.5 to 24 hours and rest times from 1 hour to 24 hours. All the columns were supplied with inlet concentration of 5mgL^{-1} STP.

- Figure 5.5 shows results from the 5 columns fed with 1.23mgL^{-1} STP Two operated with GU media and two with BS media, and contact times of 6 and 12 hours and rest time of 6 hours. A gravel control was also included which operated with 6 hours contact and rest time.

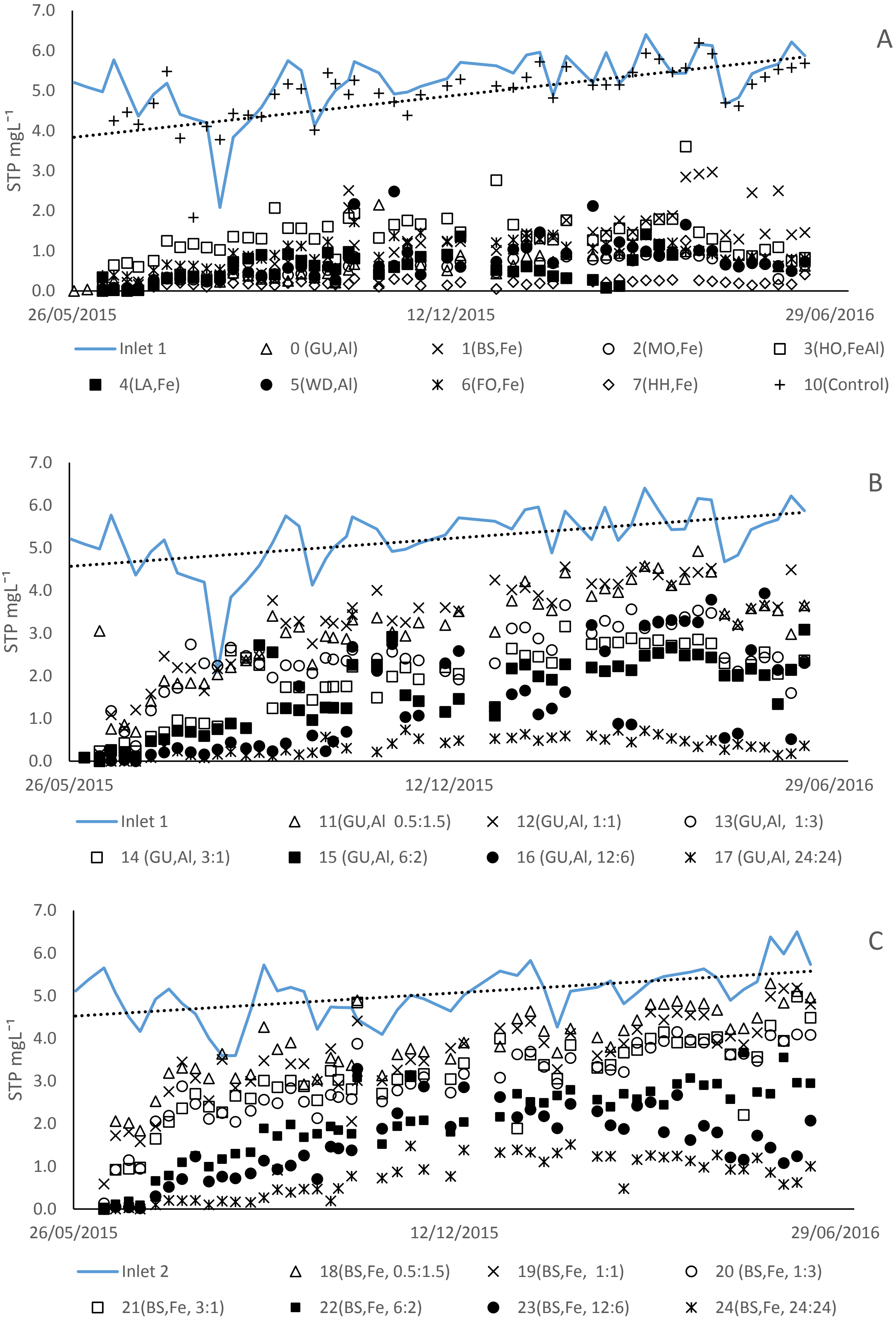


Figure 5.4 STP results from University experiments inlet 5mgL^{-1} A) different media B) GU media HRT 0.5 to 24 hrs C) BS media HRT from 0.5 to 24hrs

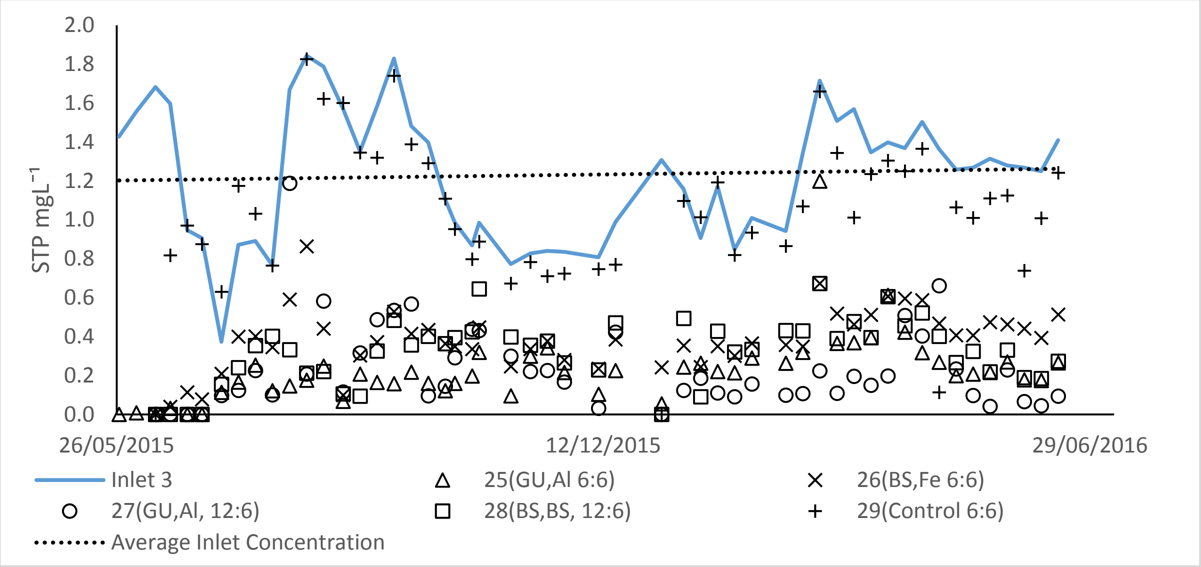


Figure 5.5 STP results from University experiments at inlet 1mgL^{-1} with BS and GU media with HRT 6 and 12 hrs.

Note on graph legends. The legend for the markers on the majority of graphs in this chapter include the column number of the experiment followed in brackets by the code for the media type, the type of coagulant used, the contact time and the rest time. For example 27(GU,Al,12:6) refers to column 27 which contained GU media, which used alum as a coagulant, had a contact time of 12 hours and was rested for 6 hours. If the numbers are not included the contact and rest time were 6 hours each.

All the columns containing DWTR removed P throughout the year long experiment. All the columns with a contact time of greater than three hours removed 100% of the STP entering the systems for the first two weeks of operation. At the end of the year long experiment the best performing columns fed with 5mgL^{-1}STP had an outlet concentration of 0.47mgL^{-1}STP whereas the worst performing columns were close to saturation with an outlet of 4.96mgL^{-1} STP.

The columns operating at a lower inlet P concentration of 1.23mgL^{-1} removed an average of between 67 and 80% of the STP. The two columns containing Al based media performed better than those with Fe (77-80% for GU and 67-71 for BS). By the end of the year the outlet from the best performing column filled with

GU media with a 12 hour contact time was approximately 0.1mgL^{-1} and the worst was 0.5mgL^{-1} (from the BS column with 6 hours contact time).

The average removal for all columns varied between 26 and 96%. The worst performing column contained BS media with a contact time of 30 minutes and a rest time of 1.5 hours. The best using HH media had 6 hours contact and rest time. The two gravel controls on average removed 5 and 14% of the STP entering the columns for concentrations of 5 and 1mgL^{-1} STP, respectively although there were many times when the gravel controls leached P.

5.4.2 Phosphorus inlet and outlet results from real waste water site.

5.4.2.1 Phosphorus measurements at RWW site

At the real waste water site measurements of STP and PO_4-P were made weekly and TP was measured monthly.

5.4.2.2 RWW site phosphorus inlet and outlet results

The raw TP results for the 5 columns and the two meso scale beds are shown in Figure 5.6.

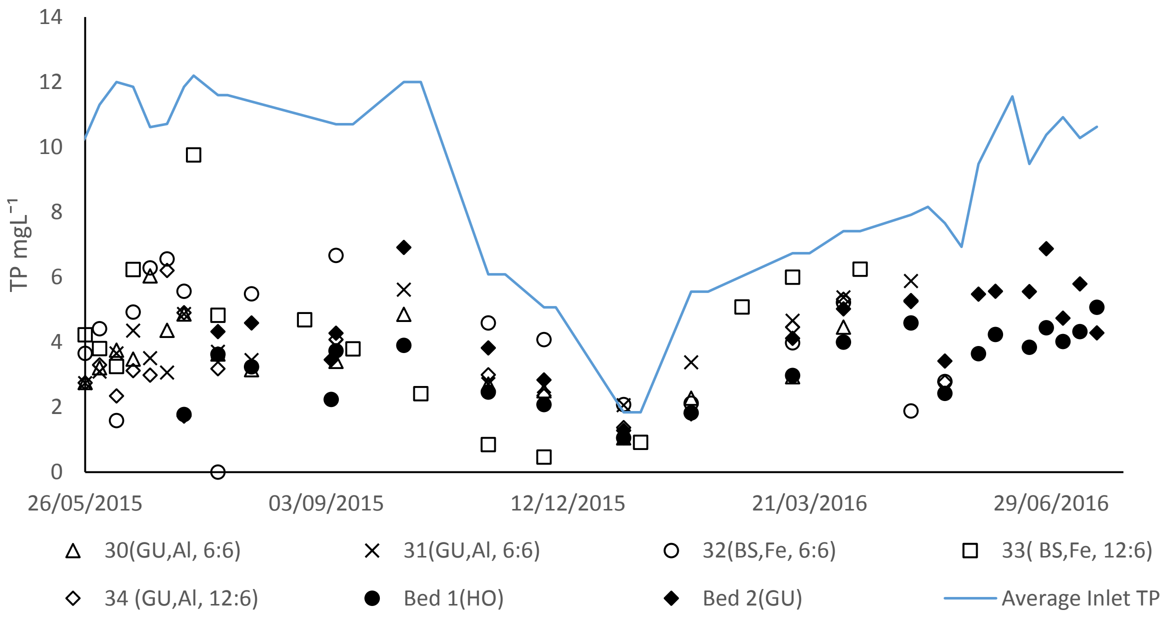


Figure 5.6 TP results for real waste water systems

The inlet P to the system showed a seasonal variation with heavy rainfall ingress into the treatment plant causing a substantial dilution to the P concentration of the waste water during the winter months. The inlet TP varied between 1.84-12.4 mgL^{-1} with an average and standard deviation of 9.37±2.59 mgL^{-1} .The average and standard deviation for the STP and PO_4-P were 8.35±2.89 and 8.20±2.74 mgL^{-1}, respectively (graph not shown).

Apart from one set of results, when the inlet concentration was at its lowest all the columns removed P from the inlet steam. The minimum level of TP in the outlets for all systems was 0.47mgL^{-1}TP with the majority of the columns having a minimum of approximately 1mgL^{-1}. The average TP outlet concentrations of the columns and beds was ≈3.5mgL^{-1}TP. The outlet concentration of the columns approximately followed the inlet concentration with column 32 and bed 2 having a significant correlation $r=0.635$, $p<0.01$ and $r=0.44$, $p<0.01$ between inlet and outlet TP, respectively.

The %TP removal for the columns varied between 50-62% with two of the columns leaching a small amount of P when the inlet concentration fell to 1.84mgL^{-1}TP. The two meso scale beds removed 60 and 47% for bed 1 and bed 2, respectively of the TP on average over the year. The percentage removal showed a great variation over the year and was highly dependent on the inlet concentration and is discussed in Section 5.7.

5.5 The effect of media type on phosphorus removal.

Ten of the columns operated at the University were fed with an identical inlet concentration of 5mgL^{-1} STP and had a contact and rest time of 6 hours, but all contained a different media (with 2 repeated columns containing GU and BS media) and a control containing gravel. By comparing the P results from these columns it is possible to assess which of the media is better at removing P.

Graphs displaying the results from the 10 columns and one control are shown in Figure 5.7 A and B. Figure 5.7A displays the data in terms of mass balance and B the percentage removal plotted against cycles (bed volumes) passed. The average percentage removal of each media over the year was calculated from the linear regression of the mass balance plots and is is summarised in Figure 5.8.

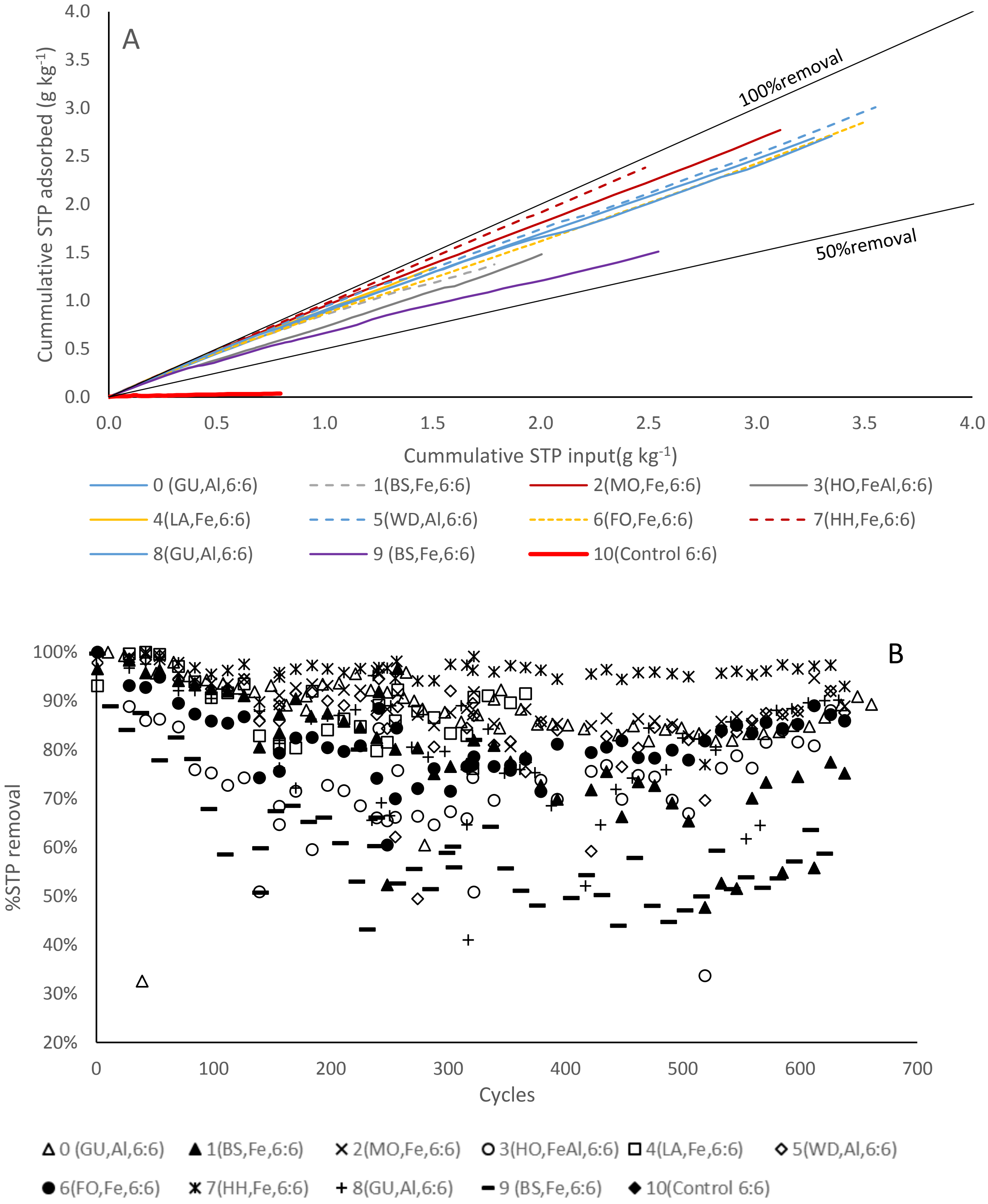


Figure 5.7 Phosphorus removal of columns with different media; contact time 6 hours, rest time 6 hours and input STP 5mgL^{-1} A)Mass balance, B)% removal.

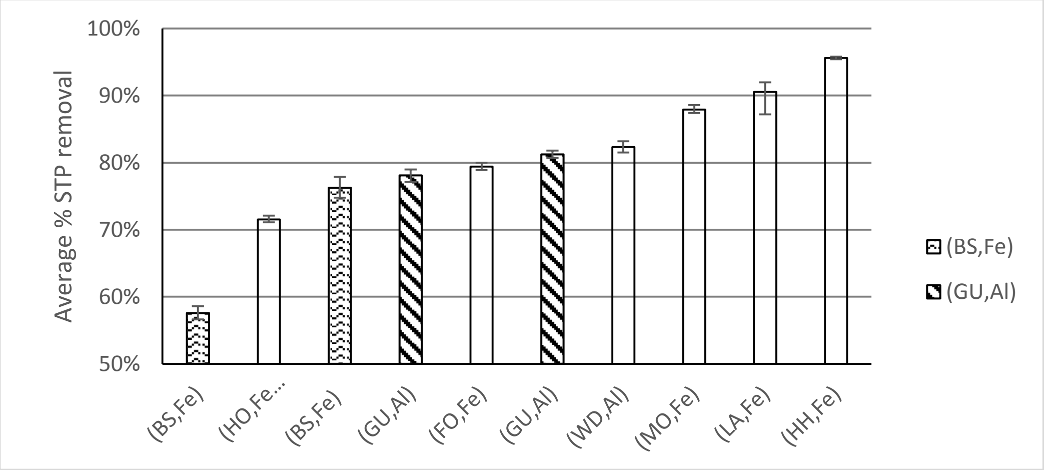


***Figure 5.8 Average percentage of phosphorus removal for different media over the year long experiments** (error bars represent 95% confidence intervals, the patterned bars represent repeated columns)*

It is clear from Figure 5.7 and 5.8 that the type of media used has a substantial effect on the amount of P removed. The HH media removed over 96% of the P on average and was still removing over 95% at the end of the year. The worst performing media was BS which removed only 57% of P input to the system, however as noted in section 5.4 the repeated BS columns showed a great variation in performance with the copied column removing 76% of STP input into the system. The gravel control removed 4% of the P entering the column on average but often leached P.

The best performing media HH removed over 38% more P than the worst media BS. Therefore the choice of media will make a very large difference to the effectiveness of any treatment system using DWTR. To assess what properties of the media, were responsible for this large difference, the P removal performance is correlated with all the physical and chemical parameters that were shown in Chapter 4. The correlations analysis is discussed in Chapter 9.

One finding of great interest from the results of media type was the relative performance of the ferric and alum media. A few papers have reported that alum based media is generally better at removing P than ferric based media (Makris et al., 2005a), but the results of these experiments would imply that this is not the case. This is discussed further in Chapter 9.

Unfortunately it was only possible to repeat two sets of columns. As discussed in Section 5.3 the repeats showed significant variation. It is likely that if some of the other column experiments had been repeated they too would have shown such a variation. Therefore, it is likely that both the spread of results and the order of the removal ability of the media may have been significantly different had more repeats been available. Further work is required to assess the relative amount of heterogeneity that is present within the media.

5.6 The effect of contact and rest time on phosphorus removal

The time that the waste water is in contact with the DWTR is of critical importance when designing an operational system. The lower the contact time the smaller the physical footprint of the system can be, and the lower the capital cost. However, from the literature review it was clear that as the contact time was reduced the P removal performance would inevitably decline and the purpose of this set of experiments was to assess if there was a contact time that would provide ‘relatively’ good performance while still allowing a minimal footprint.

The experiment to assess the effect of contact and rest time was split into two groups one using an alum based media (GU) and one a ferric based media (BS). The 16 columns assessed were operated with retention and rest times varying between 30 mins and 24 hours and rest times between 1 and 24 hours and all columns were fed with 5mgL^{-1} STP at the University. The column variables are detailed in Table 3.4. The experiments using lower inlet P concentration and RWW also used two contact times of 6 and 12 hours with a rest time of 6 hours and the effect of retention time on these columns is discussed in section 5.7 and 5.8.

The results from the 16 columns are displayed as a mass balance in Figure 5.9 A and B. The graphs clearly demonstrate that the columns running with very short contact times (30mins and 1 hour) never remove as much P as those with longer retention times. To compare the performance of the systems the average percentage STP removal that each column achieved over the year was calculated and the results are shown in Figure 5.10 A and B.

It is apparent from the graphs that all the columns with Al based media (Figure 5.9A) removed substantially more P than the Fe based media (Figure 5.9B), although it must be noted that this is unsurprising as the BS media was by far the worst performing in the comparative media tests.

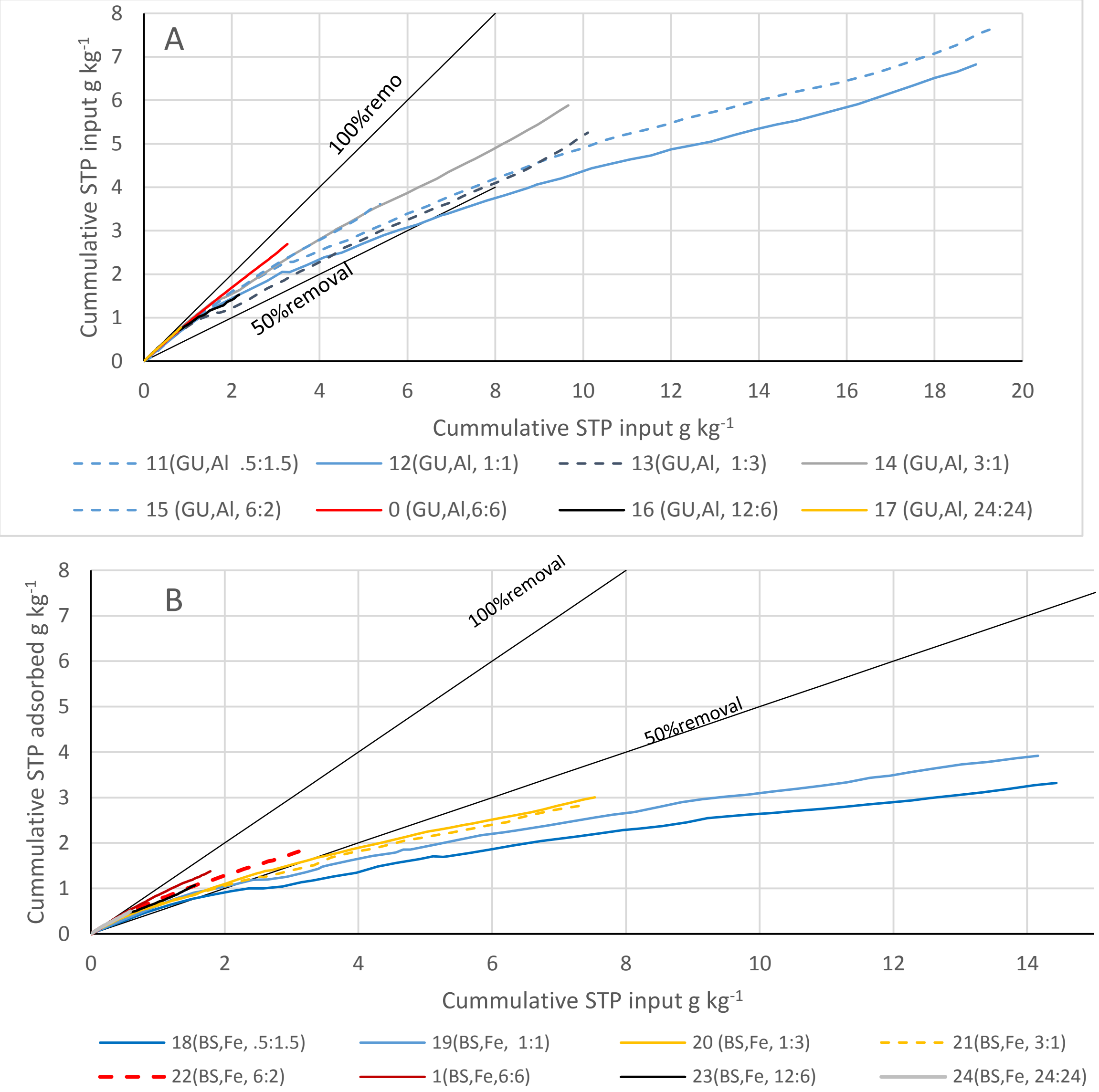


Figure 5.9 Models run with different contact and rest times from 0.5 to 24 hours. A)-Al and B) Fe based media.

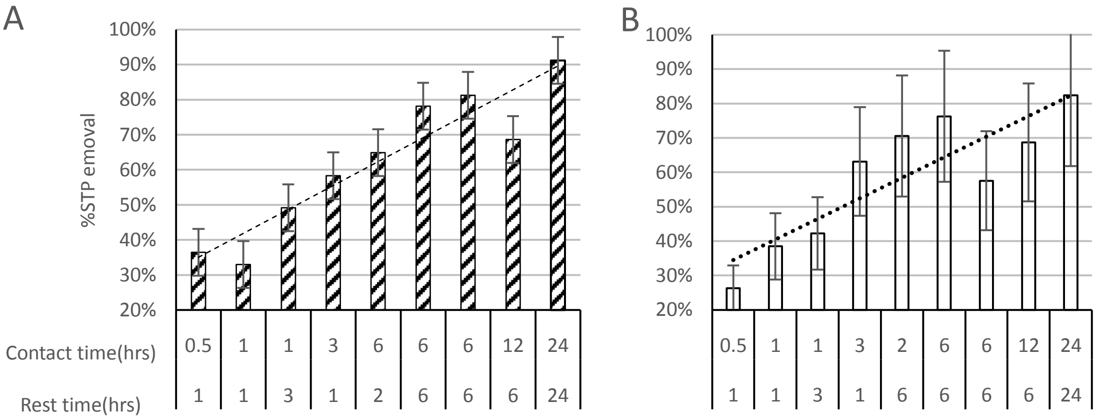


Figure 5.10 Percentage STP removal according to contact and rest time A) Al and B) Fe based media. Error bars represent error associated with the repeated columns.

The average yearly removal figures shown in Figure 5.10 would imply that as contact time is increased percentage P removal is increased even when taking into account the error associated with the repeated columns.

Although comparing the models over the year provides useful insights into the effect of contact and rest time, the models operating with 24 hours retention time only treated 150 bed volumes compared with over 3600 for the columns with 30 minute contact time. The columns operating with short contact time therefore treated approximately 24 times more water than those operating with a high contact time. To make direct comparisons between the systems the average %STP removal was compared across the first 150 bed volumes for all systems and the results are shown in Figure 5.11 A and B.

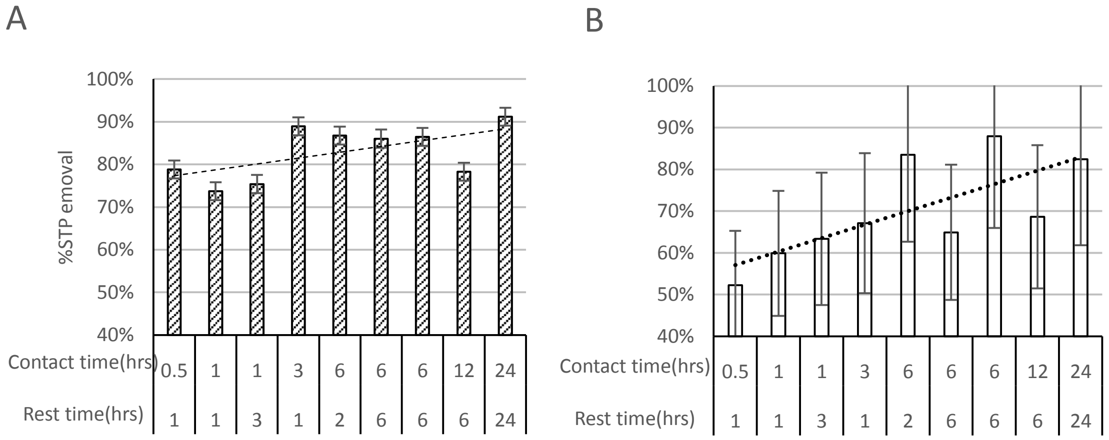


Figure 5.11 Percentage STP removal according to contact and rest time for the first 150 cycles. A) Al and B) Fe based media. Error bars represent error associated with the repeated columns.

When the data is assessed over the first 150 cycles or bed volumes passed by the system, the increase in percentage P removal as contact time is increased is not so apparent. The Al based media shown in Figure 5.11A shows a distinctive improvement when contact time is increased above 3 hours, and not much improvement above this time. Whereas the BS media shows a steady improvement from the 0.5 to 6 hours but no improvement after this point. Both data sets show a drop in performance when the contact time is increased to 12 hours but the rest time remains at 6 hour, but an improvement when the contact and rest time are increased to 24 hours. This implies there may be a disadvantage in increasing contact time without increasing rest time, which is discussed further in the next section. However the data from these experiments is surprising in its lack of consistency particularly in the ferric based columns. The most probable explanation for these apparently divergent results is the heterogeneity of the media within the columns. However, it is clear from the data that there is a disadvantage in reducing the contact time below three hours. To further assess the effect of retention times on the columns a detailed assessment was made of the P removal kinetics within two of the columns which is reported in Chapter 7 and the effect of contact and rest time in relation to system kinetics is discussed in Chapter 9.

5.6.1 The effect of rest time

To assess if the time the media was rested between loading periods had an effect on P removal, 8 of the models were compared (4 Al based and 4 Fe based). The comparative columns had identical contact times of 1 and 6 hours but different resting times of 6 and 2 hours. The results of the average percentage STP removal calculated from the linear regression of the mass balance data are shown in Table 5.2.

Table 5.2 Comparison between %STP removal of columns with different rest times but identical contact times over the first 300 cycles

Coagulant, Model	Contact time	Rest time	Average %STP removed first 300 bed volumes	Average %STP removed over the year
Alum 12 vs 13	1	1	74	33
	1	3	75	58
	Difference		1	25
Ferric 19 vs 20	1	1	60	26
	1	3	63	38
	Difference		3	12
Alum 0 vs15	6	2	87	65
	6	6	87	81
	Difference		0	16
Ferric 22 vs 1	6	2	83	63
	6	6	87	72
	Difference		4	9

The data clearly shows that increasing rest time has a positive effect on P removal performance however the effect is small over the first 300 bed volumes passed but substantially increases in significance as the amount of cycle's rises. This is demonstrated graphically in the mass balance graphs of the columns in Figure 5.12.

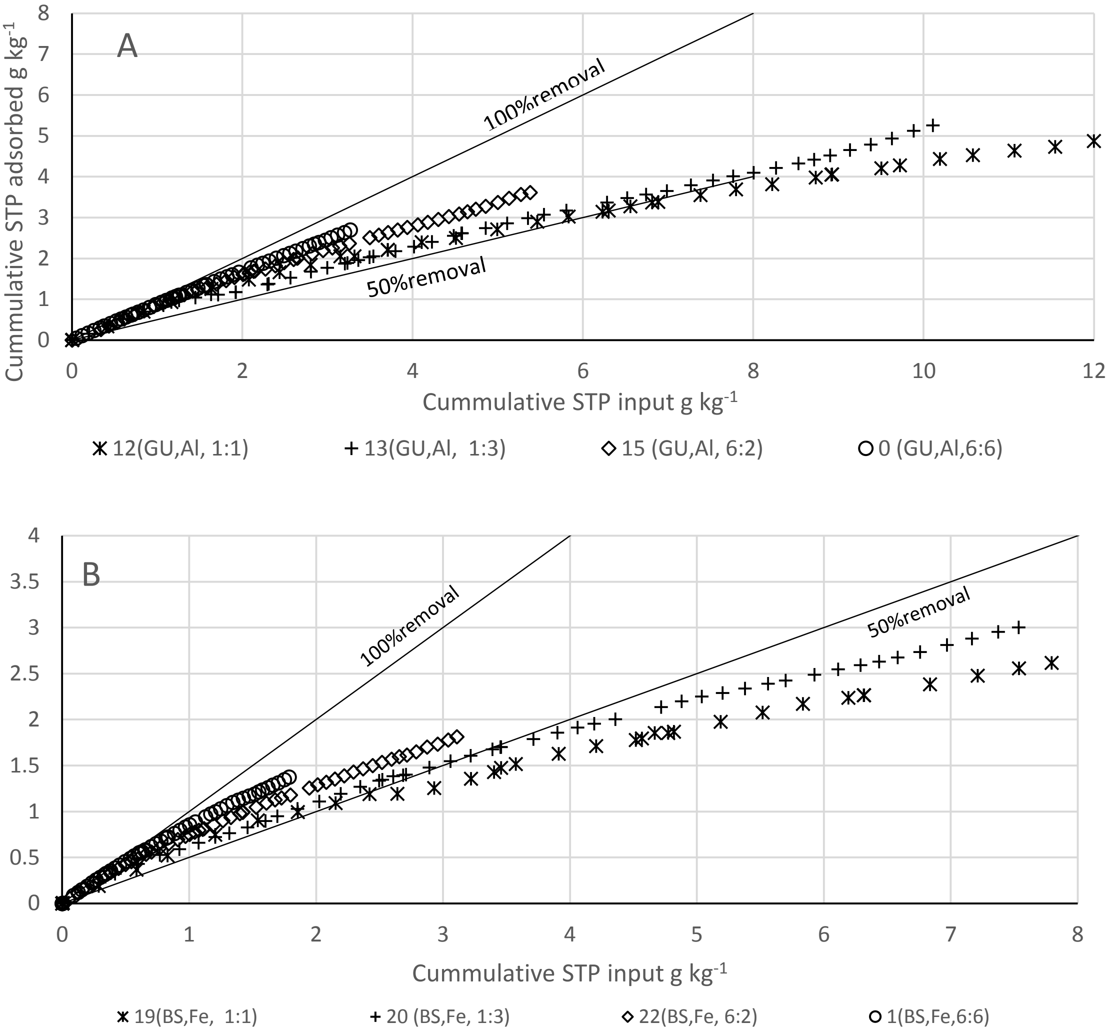


Figure 5.12 Mass balance comparing columns with identical contact times but different resting times A)Al based media B)Fe based media.

However it must be noted that the systems with larger rest times had treated significantly smaller volumes water than those with shorter rest times by the end of the year. The positive effect that increasing the rest time between load cycles also possibly explains why the columns with 24 hour load and rest time performed better that both the Fe and Al based columns with a 12 and 6 hour load and rest time. The 24 hour resting period allowed the media to recover between loading cycles. The effect of increasing rest time has not been assessed in the literature for such small time scales. But both Drizo et al (2008) and Penn (2011) found that steel slag adsorbed much more P after it had been rested for 5 weeks. They both conclude that the most likely explanation for the improvement in performance is a rearrangement in the surface charge and intraparticle diffusion during the resting periods which would free some of the previously bound surface sites to adsorb more phosphate. Further analysis would be required to prove this.

There is a positive advantage in increasing rest time between loading periods, however as rest time is increased the system footprint also has to increase. The data would imply that keeping the rest time between 3 and 6 hours would be advantage to the P removal capacity of the system.

5.7 Effect of inlet P concentration

Assessing the effect of inlet P concentration on the P removal capacity of the media helps define where in the treatment process a DWTR system should be placed. The P concentration of waste water falls at each stage as it passes through primary, secondary and tertiary treatment processes. Therefore if more P is removed at higher inlet concentrations the processes would operate more efficiently closer to the head of the works.

5.7.1 Effect of inlet P concentration on University experiments

Four of the columns at the University operated with a low inlet P concentration of approximately 1.2mgL^{-1}STP (as compared to 5mgL^{-1}STP for the majority of the columns) as detailed in Section 3.2.1.2. The columns contained both BS (Fe) and GU (Al) media and operated with 12 and 6 hours contact time, and a rest time of 6 hours. Graphs showing comparisons between equivalent columns with identical media and contact time but with low and high inlet concentrations are shown in Figure 5.13 A,B,C and D.

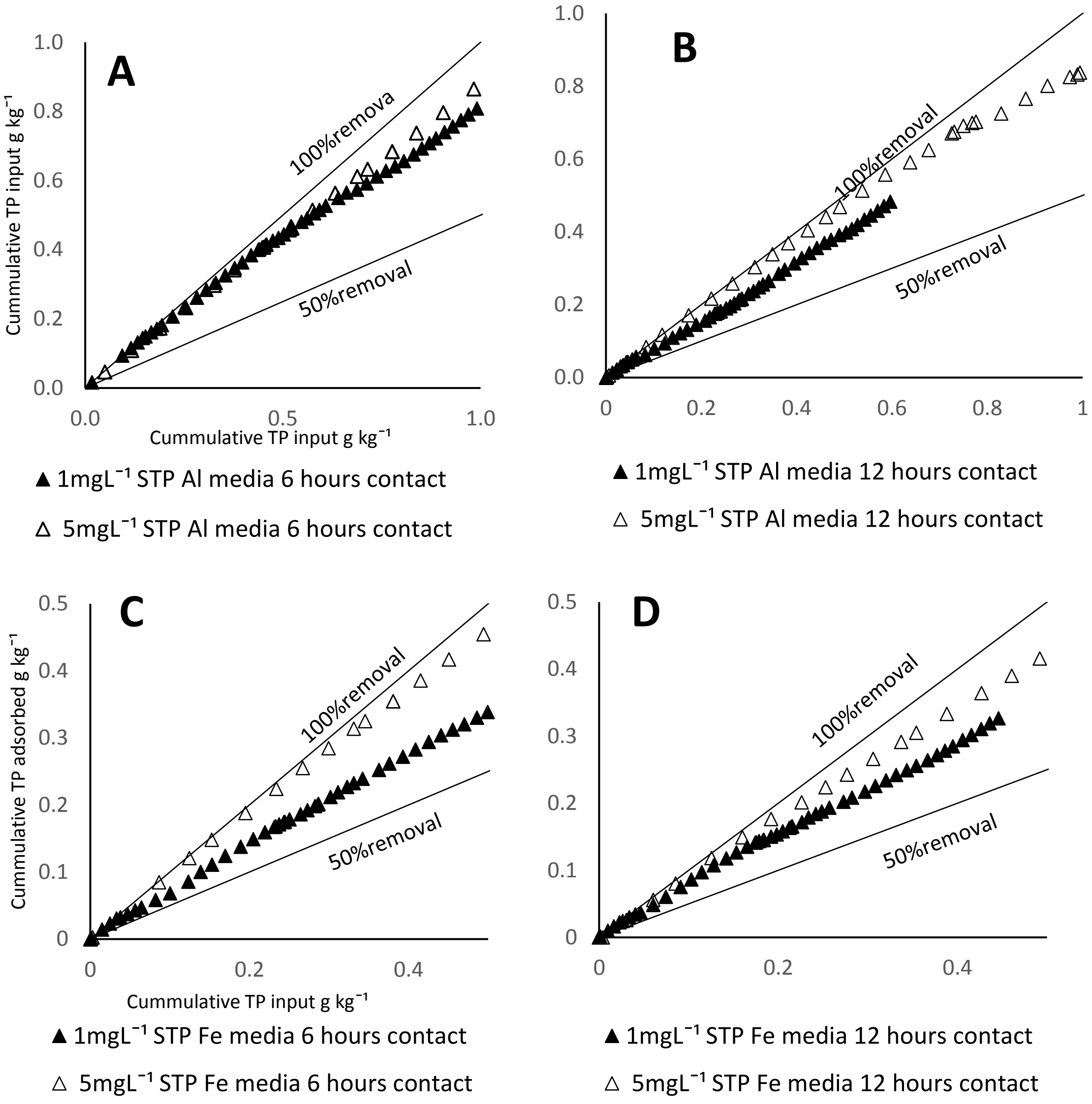


Figure 5.13 The effect of 5 and $1mgL^{-1}$ STP input to the columns with A) Al(GU) media 6 hours contact, B) Al(GU) media 12 hour contact, C) Fe(BS) media 6 hour contact and D) Fe(BS) media 12 hour contact.

The data shows that the models operating with an inlet concentration of $1mgL^{-1}$ do not remove as much P by mass as those operating with an inlet of $5mgL^{-1.}$ and the effect is greater for the Fe based media. However, the column with Al media and 6 hours retention performed almost identically at both concentrations for the first half of the year. The results from the linear regression analysis of % STP removal of the systems is shown in Table 5.3.

Table 5.3 Comparison between columns operating at low and high inlet concentration

Media type	Contact time (Hrs)	STP Influent concentration (mgL^{-1})	Average STP removal(%)	Difference (%)
Al (GU)	6	5	79	
		1	78	1
	12	5	72	
		1	63	9
Fe (BS)	6	5	68	
		1	57	11
	12	5	67	
		1	61	6

Although all the columns show a reduction in performance at lower inlet concentrations the reduction is relatively small and due to the heterogeneity of the media it is not possible to predict the strength of this effect.

5.7.2 Effect of inlet phosphorus concentration on RWW experiments

The columns at the RWW site operated with a continually changing inlet STP concertation which varied between 2 and 12.66mgL^{-1} STP. The percentage removal of STP from the columns also showed very variable results. Percentage STP removal data from one of the columns and meso scales is plotted in conjunction with influent concentration at the RWW site in Figure 5.14. It is apparent from the graph that the percentage STP removal tracks the inlet concentration closely. Analysis of all of the RWW systems reveals a correlation between %STP removal and inlet concentration $r=.495$ to $.633$ $p<.01$. This infers that DWTR remove more P at higher inlet P concentrations and would be better situated closer to the head of the works.

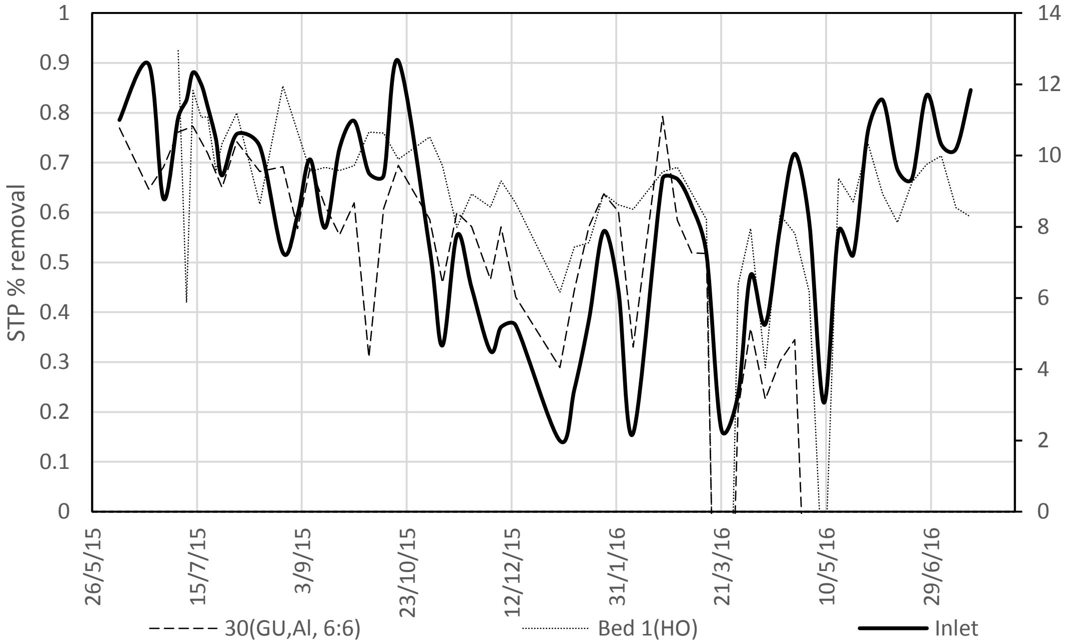


Figure 5.14 Relationship between inlet concertation and percentage phosphorus removal

The reason why the media removes more P at higher inlet concentrations is readily explained if adsorption is the main driving force for P removal in the media. Most commonly the driving force for adsorption is the concentration gradient between the surface of the sorbent and the bulk solution causing the sorbate to move into the pores of the sorbent (Gray et al., 2015). Thus as the concentration of the inlet P solution is decreased the concentration gradient is decreased and less P is adsorbed.

5.8 Effect of real waste water

The majority of the experiments undertaken for this thesis have used synthetic P dosed tap water. In an operational system the beds will inevitably be immersed in RWW. There are many advantages in using synthetic P dosed water as it allows control of inlet P concentration and removes the hazardous nature of RWW from the experimental work. Therefore this section seeks to compare the performance of columns that were operated under relatively identical conditions but were loaded with synthetic or RWW. The results elucidate not only the effect the RWW has on the P removal potential of the DWTR but could assist in the future prediction of the results from systems that purely use synthetic waste water.

Comparisons between four of the columns operated at the RWW site can be made with those at the University which contained identical media and had similar contact times of 6 and 12 hours (and rest times of 6 hours). However, as stated in section 5.7 the inlet STP concentration was highly variable at the RWW site which will have had an effect on the P removal performance of the media. The average and standard deviation of the inlet to the RWW systems was 8.35±2.89mgL^{-1} STP. Therefore on average a better performance would be expected from the RWW columns than those at the University loaded with 5mgL^{-1} STP in light of the findings that P removal increase with inlet concentration as discussed in section 5.7. The results of the comparative columns are shown in Figure 5.15 A, B, C and D.

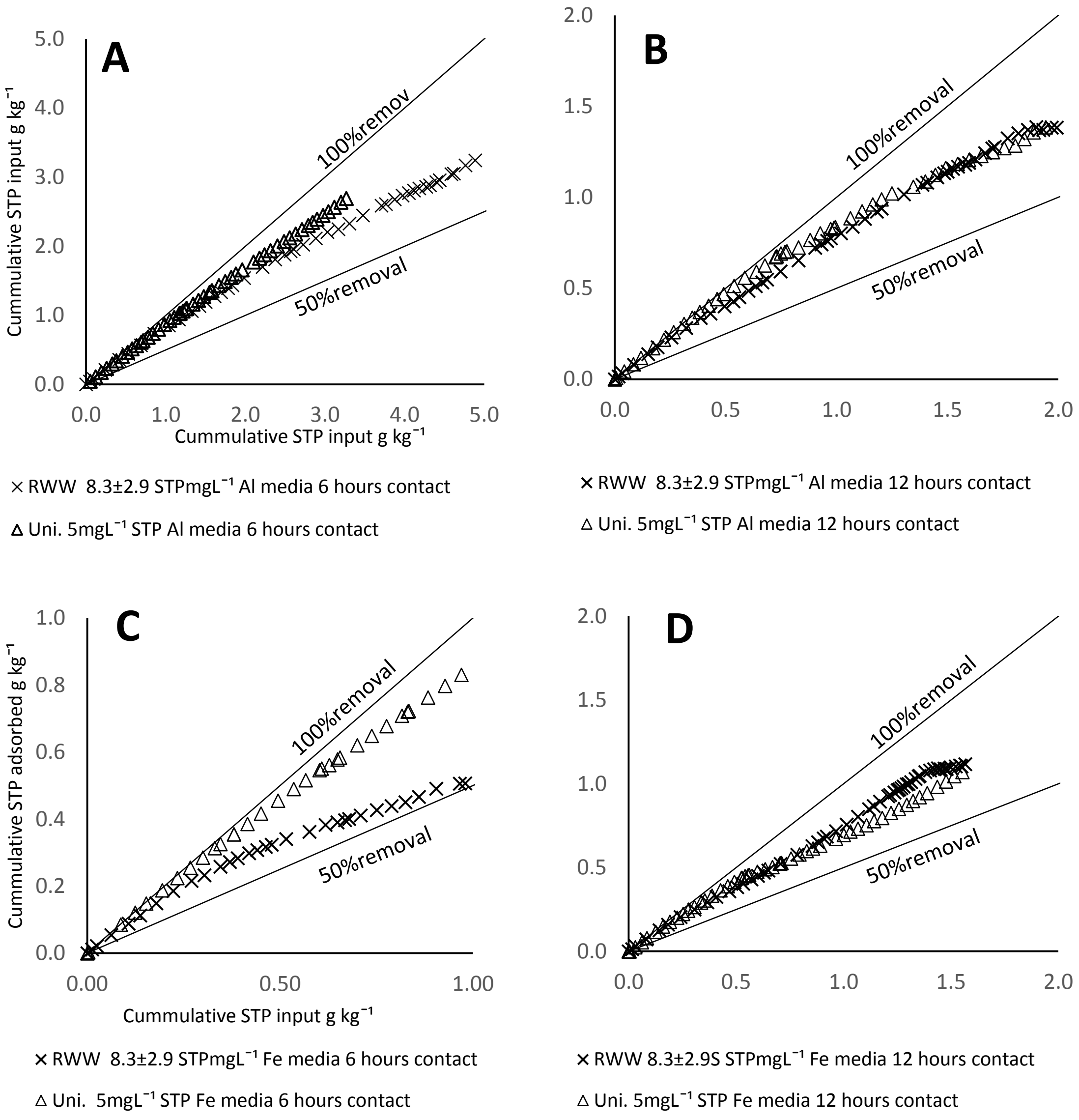


Figure 5.15. Comparing columns fed with RWW and synthetic P dosed water A) Al media 6 hours contact, B) Al media 12 hour contact, C) Fe media 6 hour contact and D) Fe media 12 hour contact.

For both the Fe and Al media operating with a contact time of 6 hours the RWW columns performed worse than the University columns and the effect increased as the experiments progressed through the year. A summary of the linear regression analysis of the data is shown in Table 5.4.

Table 5.4: Comparison of columns operating with real waste water and synthetic phosphorus dosed tap water.

Media type	Contact time(Hrs)	STP Influent concentration(mgL^{-1})	Average STP removal (%)	Difference (%)
Al (GU)	6	5 (Synthetic)	79	
		RWW	66	13
	12	5(Synthetic)	69	
		RWW	67	2
Fe (BS)	6	5(Synthetic)	66	
		RWW	44	22
	12	5(Synthetic)	66	
		RWW	72	-8

The columns operating with 6 hours retention showed an average reduction in performance of between 13 and 22% (for Al and Fe based media, respectively) when loaded with RWW rather than synthetic. However the models operating with 12 hours contact time showed a reduction of only 2% for the Al based media and an increase of 8% for the Fe based column. Although the column operated at the RWW site with 12 hours retention and Fe media was under loaded during the first few months of operation and thus the performance of this column has probably been slightly over predicted (as discussed in 3.5.2).

The data shows that increasing retention time from 6 to 12 hours removes the gap in performance between the beds operating with real and synthetic waste water. However, on further analysis of the results from the RWW columns it can also be seen that the Al based systems removed almost identical amounts of P with both retention times, 66 and 67% for 6 and 12 hours, respectively. This result adds further evidence that increasing contact time above 6 hours does not improve P removal performance. Therefore, the reason there is no difference in the results between the columns loaded with RWW and synthetic with a 12 hour contact time is the very poor performance of the columns at the University operating with 12 hours contact time. Why the results for the 12 hour columns at the University are so poor is not clear.

It can be concluded from this data set that with a 6 hour retention time using RWW has a negative effect on P removal as compared to synthetic water and this effect varied from 13 to 22% for the Al and Fe media, respectively. Although a conceivable explanation for this reduction in performance is competition for adsorption sites from other ions in the waste water, this is unlikely because research by Al-Tahmazi and Babatunde (2016) showed that DWTR favours phosphate over other common ions that are generally present in waste water. Therefore it is most likely that the media does not perform so well when RWW is used because of biofilm formation on the media surface blocking adsorption sites or occlusion of SS on the surface reducing hydraulic flow between the surface of the media and the water. (The formation of biofilm is assessed in Section 6.9)

5.9 The effect of scale

It is always desirable to be able to model a system at a small scale enabling assessment of many variables without the excessive costs of operating systems at meso or pilot scale. Therefore the objective of constructing and operating two meso scale beds was to observe if increasing scale had a positive or negative effect on the ability of the DWTR to remove P.

The design and details of the meso scale beds was described in section 3.4.3. The meso scale beds used approximately 30 times more media by mass, and had a surface area that was over 120 times greater than the column experiments.

The beds were filled with GU and HO media as it was originally thought that these two DWTR would represent the best potential for optimising P removal as they had the highest metal content of all the media. It was only possible to compare the bed filled with HO media with a column running with similar retention time at the University. Whereas the bed filled with GU media was compared with both a column loaded with identical RWW and a column at the University all running with similar rest and load times of 6 hours. The results of the comparisons are shown if Figure 5.16, and comparisons of the average percentage removal are shown in Table 5.5.

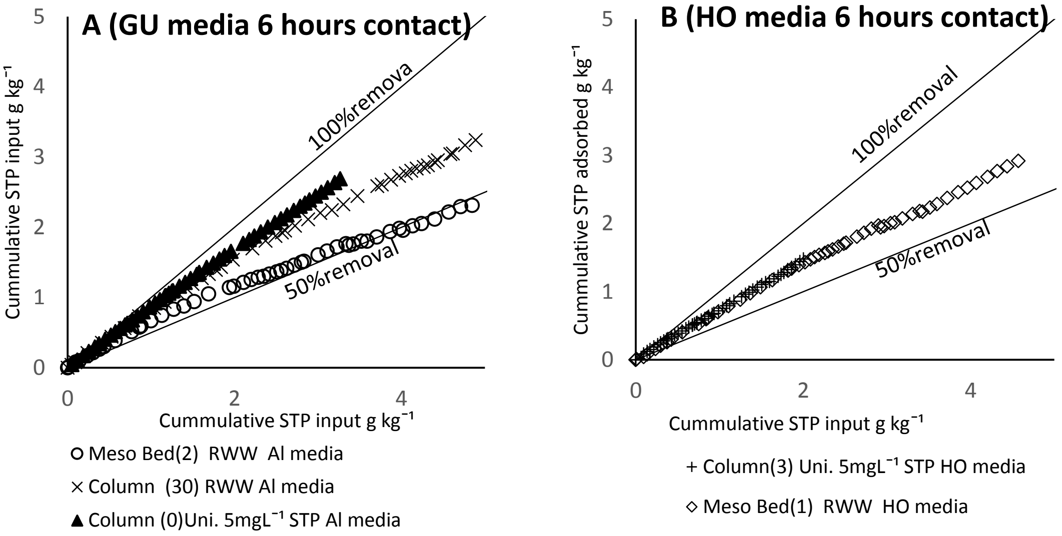


Figure 5.16 Comparing column systems with Meso scale bed performance A)Al(GU) media B) Al+Fe (HO) media

Table 5.5 Coefficients from linearized regression of graphs comparing columns and meso scale beds

Media type	Scale	STP Influent concentration(mgL^{-1})	Average STP removal (%)	Difference (%)
Al (GU)	Column	5(Synthetic)	79	
	Column	RWW	66	
	Meso*	RWW	50*	16
Fe+Al (HO)	Column	5(Synthetic)	72	
	Meso	RWW	70	2

*GU Meso bed was highly overloaded causing under performance

Unfortunately, the meso scale bed filled with GU media was highly overloaded with waste water (as discussed in 5.2.2.3) and therefore the beds performance was probably substantially reduced. However, the results from the other bed revealed that the performance of the column system at the University was almost identical to that of the scaled up bed. This is a promising result and would imply that the results from the experiments could be scaled up without too much concern.

Although a search of the literature reveals no work has been undertaken on the scaling up of DWTR based system other P removal systems have been assessed at different scale Adam et al (2006) found increasing scale reduced performance of a manufactured P removal media, whereas Martin (2010) found increasing scale on ion exchange resin to had a very positive effect on P removal. Therefore it was unclear what the effect of scaling up a system would be.

It would appear that increasing the scale of the system probably has little effect on the removal ability of the media. However it is noted that the data set is small, hence some caution is needed.

5.10 The change in phosphorus removal over the experimental period

Evaluating the life expectancy of a system that uses DWTR requires that the operational removal capacity of the media is known throughout the expected lifetime of the system and also that the final adsorption capacity of the media is known. None of the systems operated in the experiments for this thesis reached saturation and thus neither the total adsorption capacity nor the operational capacity of the system beyond the year long time frame of the experiments can be obtained directly from the experimental results. Therefore the objective of this section was to assess how the results from the experiments could be modelled to predict both the final adsorption capacity of the media and how the removal capacity might change in time frames longer than a year.

Although models are presented in this section, they are used to predict the life expectancy of a system in conjunction with a programme that was written in Matlab and is discussed in Chapter 9.

5.10.1 Predicting the final adsorption capacity of the media using isotherms

Ideally the final adsorption capacity and the life expectancy of the media could be predicted from analysis of both the Freundlich and Langmuir isotherm models. The theory of the use of isotherm models for predicting the amount of water treated at different inlet and outlet P concentrations is discussed in Appendix 1. The adsorption capacity of the DWTR used in this thesis was modelled using both the Freundlich and Langmuir isotherms by others in my research group and the modelling constants for the media are reported in Al-Tahmazi and Babatunde

(2016). The final adsorption capacities achieved by the columns and the beds in these experiments are reported in Appendix 1. The calculated amount of P adsorbed at the end of the year long experiments for the columns which compared the 8 different media types is plotted in relation to the calculated adsorption capacity as predicted by the Freundlich isotherm and the Langmuir q_m value in Figure 5.17.

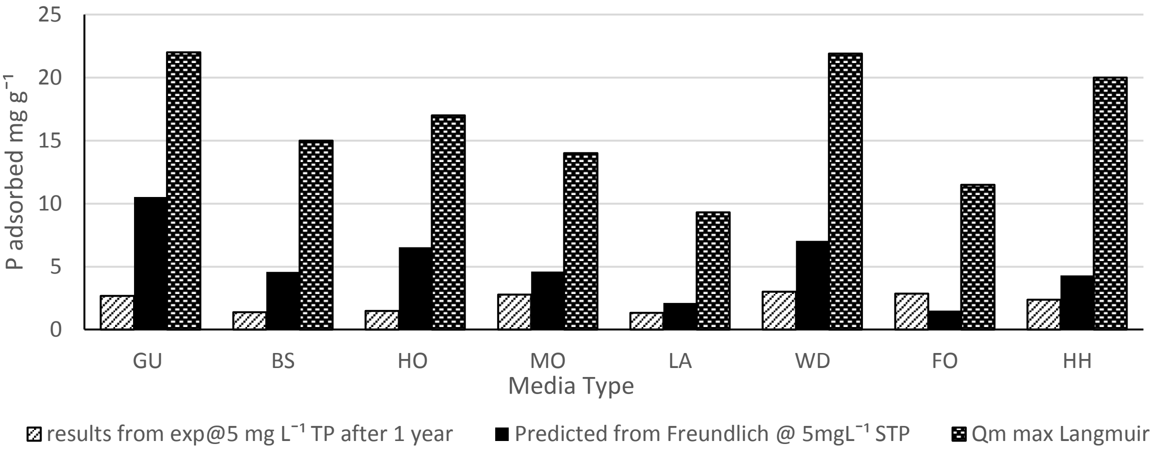


Figure 5.7 Graphs showing final amount of STP adsorbed by media after year long experiments compared with values predicted by Freundlich isotherm at calculated input 5mgL^{-1} STP, and for Langmuir Qm value for 8 columns with different media.

These graphs clearly demonstrate that none of the media was approaching the maximum monolayer adsorption capacity q_m, and apart from the FO media they had reached between ¼ and 2/3 (for the GU and MO media) of the Freundlich predicted adsorption capacity. However notably the FO media had already adsorbed more than double the amount of P as predicted by the Freundlich isotherm.

By the end of the year two of the columns operating with the shortest retention time were only removing 16 and 37% of the P entering the systems for the BS and GU media, respectively and were therefore closer to saturation than any of the other systems. The data for these columns is plotted aside similar columns with shorter retention times and the Langmuir and Freundlich calculated values in Figure 5.18.

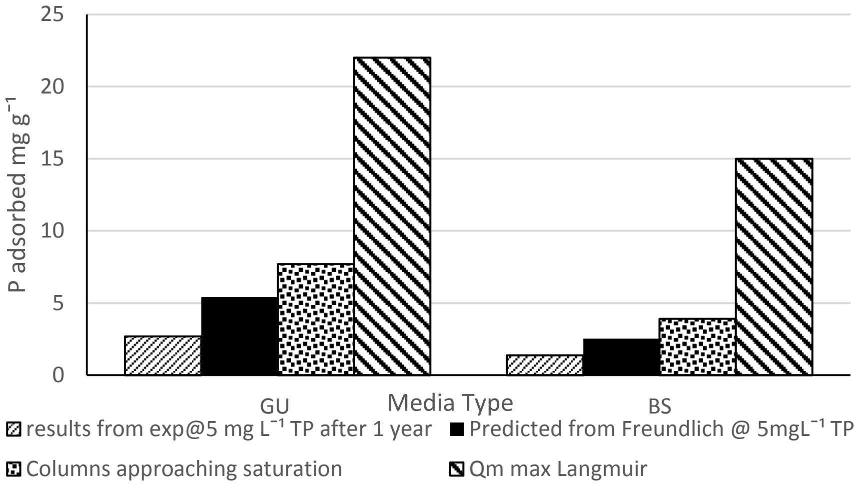


Figure 5.18 Comparing Langmuir Qm, Freundlich and nearly saturated experimental columns and unsaturated columns with BS and GU media.

The columns approaching saturation adsorbed substantially more P than those operated with longer contact times. The Freundlich model under predicts the adsorption values of these columns by approximately 30% and the Langmuir q_m value is clearly never going to be reached. The two columns with a small retention time have also been shown to be removing less P than the other systems as discussed in Section 5.6. Therefore the Freundlich prediction is likely to be a minimum of 30% below the actual capacity of the media.

Neither the Langmuir nor Freundlich isotherms are useful predictive models for the life expectancy of the media, as the Freundlich isotherm tends to under predict final P adsorption capacities and the Langmuir q_m value tends to over predict final values. Similar results have been found by other authors (Drizo et al., 2002) and the reason for this poor correlation between the isotherms and the data was discussed in Section 2.4.2.4.

Therefore, although the isotherm models can be a useful tool in screening whether a media has potential to adsorb P, they cannot be used to predict the final adsorption capacity of the media in a flow through type setting with relatively low inlet concentrations of P. There is no simple way to overcome the problem without running much longer experiments which would be operated until the media is saturated.

5.10.2 Basic linear model of the University systems.

The University systems all showed a relatively linear reduction in the amount of P that was adsorbed as the number of bed volumes passed increased. By plotting the weekly percentage P removal against bed volumes passed and linearising the data, a very basic linear model can be constructed which can be used to predict the likely P output level of the system as the amount of water passing through the system increases. An example of such a model is shown in Figure 5.19.

Although it is inevitable that the media will become saturated with P at some point, it was clear from assessment of the Freundlich isotherm data that the majority of the columns were a long way from saturation so the model for the majority of the systems at the University would probably hold true for at least another year.

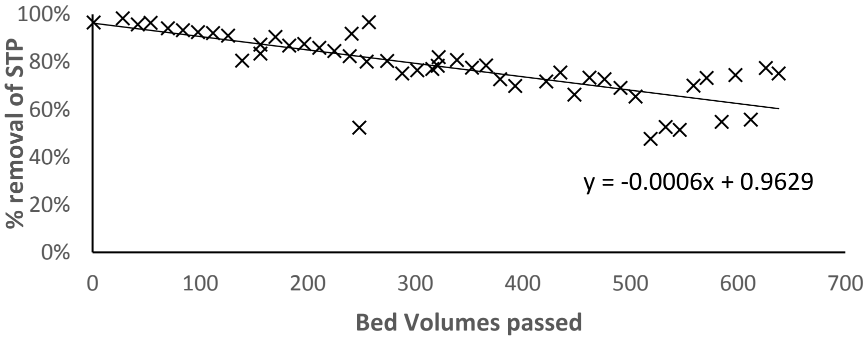


Figure 5.19 Basic linear model to predict future performance of system

5.10.3 Second order model

The majority of the data assessed in this chapter was analysed using a mass balance approach, in which the cumulative P adsorbed on the media was plotted against the cumulative amount of P input into the system and the data was normalised to the mass of media present. The cumulative P adsorbed per gram of media (q_{ad}) was fitted to the cumulative P input into each column per kg of media (q_{in}) for all 35 column models and 2 meso scale beds using the LINEST function in Excel (set to second order regression). The LINEST function calculates the first and second order regression constants as detailed in Equation 5.5 and also calculates the adjusted r^2 and standard error.

$$q_{ad} = n\left(q_{in}^{2}\right) + m(q_{in}) \qquad \textbf{\textit{Equation 5.5}}$$

Where
n = second order regression constant
m = first order regression constant

The fitted curves all had $r^2>0.99$. An example of two of the columns operating at the RWW site with their second order polynomial regression curves are shown in Figure 5.20

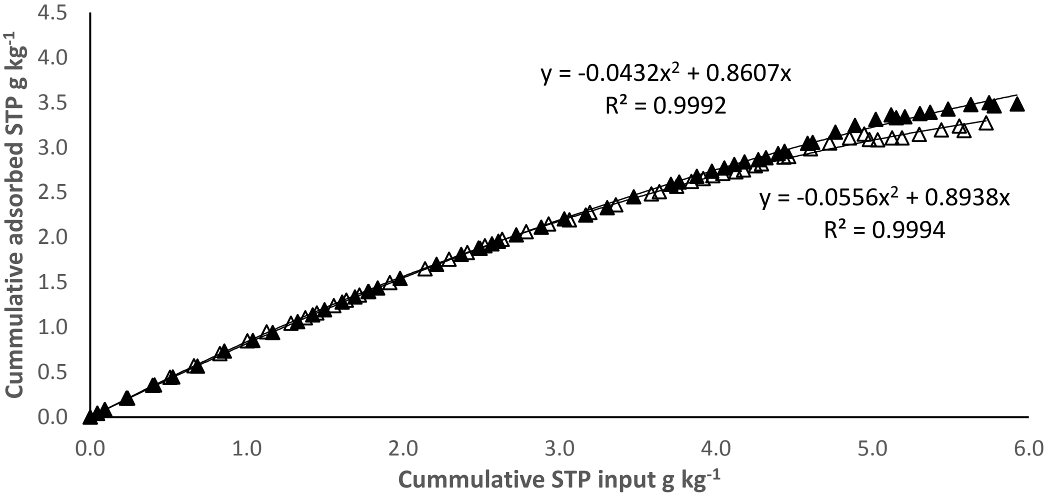


Figure 5.20 Second order polynomial regression showing good fit to data

The second order polynomial model can be used to predict the quantity of P that a known mass of media can remove, if the inlet P concentration and volume of water is known. The second order model is likely to be a much better predictor of the future life expectancy of the media than the basic linear model as the second order constant allows for a steady degrading of the media over time. However this model is also limited, as in a second order regression at some point the curve will reach a maximum and after this point the model will become inaccurate.

The first and second order model constants associated with all the experiments are shown in Figure 5.21

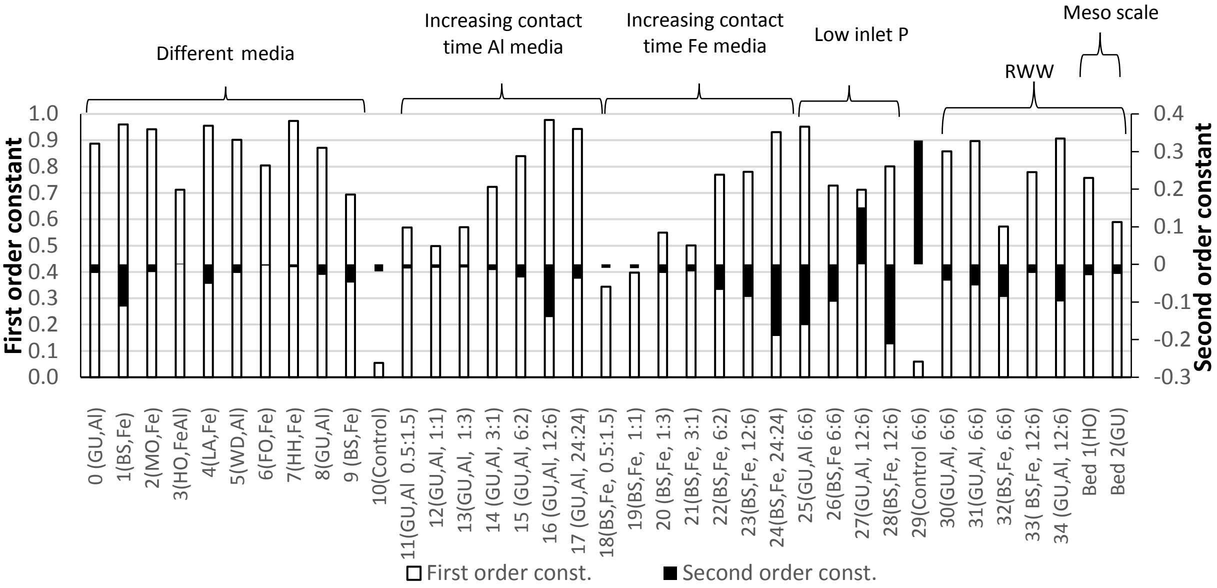


Figure 5.21 Second and first order constants associated with second order polynomial models of the adsorption data from all the experiments

The size of the second order rate constant dictates the rate at which the curve digresses from the linear model and it is interesting to note that both with higher contact times and lower inlet concentrations the media tended away from linearity possibly implying that saturation would occur sooner.

5.10.4 Breakthrough models

A traditional way of reporting the performance of adsorption system is by the use of breakthrough curves (Crittenden and Thomas, 1998). In a breakthrough curve the output concentration divided by the input concentration is plotted against bed volumes treated. It is possible to model the breakthrough curves produced from the experimental data by using an adapted form of the Freundlich isotherm as developed by Callery et al (2016) and discussed in section 2.6.7 Both the experimental data and modelled breakthrough curves for a variety of the column and mesoscale beds are shown in Figure 5.22.

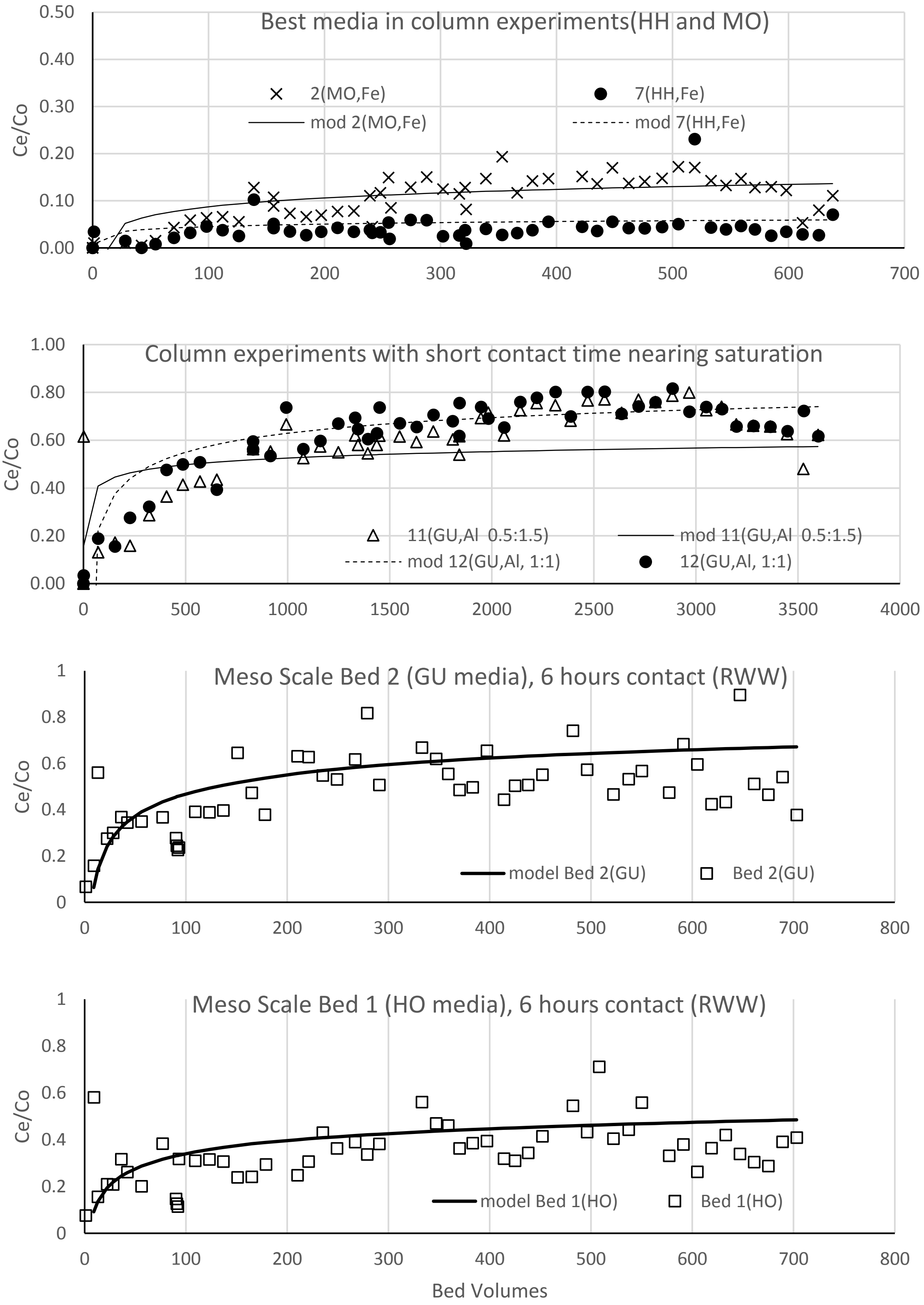


Figure 5.22 Raw and modelled data for the best media. Media approaching saturation and meso scale beds.

Co = Inlet STP mgL^{-1}, Ce = Equilibrium outlet concentration mgL^{-1}

When the data is plotted in the form of a breakthrough curve the nature of the change in removal rate over time is elucidated. It is very clear from the data that all of the media remove substantial amounts of P during the first few cycles and the rate of removal quickly falls during the first 10-200 bed volumes passed followed by a much longer period where the removal percentage falls at a very slow and fairly constant level. It is notable that the data from the two meso scale beds is far more spread out than the data from the University columns this is due to the changing performance of the beds in relation to the variation in inlet concentration.

The upper plot shows the performance of the best two media from the University both of which keep the Ce/Co ratio well below 0.2. The meso scale beds show a poorer performance with the removal rates oscillating between 0.4 and 0.6.

If a discharge consent of 1mgL^{-1} is required with an input flow of 8mgL^{-1}. The bed must operate with a Ce/Co ratio of 0.125 as can be seen from the plots only the HH media operating at the University site approaches anywhere near this level of treatment. Thus to make a viable system which would meet a required discharge consent the beds would have to be operated in series. With the outlet of the first bed leading into the inlet of the second etc. this is discussed in detail in Chapter 9.

The model proposed by Callery et al (2016) fits the data reasonably well but as with the linear regression the curves produced from the model do not provide a useful tool for predicting the time to saturation. When the model is extended beyond the data set provided by the experiments it predicts a very long and unrealistic time before the media would be saturated.

5.10.5 Model Summary

The four models proposed to assess how the performance of the media change over time all have their flaws. The Freundlich isotherm is a useful tool for initial media assessment and provides an indication of when the media might become saturated but tends to under predict the final adsorption capacity of the media by an unknown amount. Using a simple linear regression of the percentage removal results should provide a good indication of how the media will perform over an extended period as long as the media is not approaching the adsorption capacity. The second order polynomial fit of the mass balance data provides the best fit to the data and enabled a potential estimate of when the media might reach saturation, but once saturation is reached the model will fail. Using breakthrough data provides a useful insight into how the media performs especially over the first 200 cycles passed but the Callery model also fails to predict when the media will be saturated.

Therefore ideally to provide detailed predictions of how the media will perform over the long term more long term experiments are required.

A comparison of all the models is made in the Matlab programme discussed in Chapter 9.

5.11 Summary

One of the objectives of this thesis was to assess the key variables that affect the performance of DWTR. This chapter sought to do that by answering the questions listed in the introduction. The results are summarised below.

- The effect of media type on P removal is substantial with there being over 40 % difference between the best and worst media with the HH and MO media removing substantially more P than the BS.
- The effect of contact time is also substantial but not as great as media type. With contact times below three hours causing 10% less P to be removed from the alum based media and 20% less from the BS media. Above 3 hours contact time the experimental data is fairly disordered but this implies that there is no great advantage in increasing contact time beyond 3 hours, and could possibly cause a reduction in performance if increased above 12 hours without extending the rest period.

- Resting time between loading periods had a substantial effect on performance during the latter half of the year, by increasing the resting time from 2 to 6 hours the alum based media removed 16% more P and the ferric based media 9% more.
- The P removal was highly correlated to the inlet P concentration with an increasing inlet causing more P to be removed.
- Using RWW instead of synthetic P dosed tap water caused the columns with 6 hours retention to remove between 13 and 22% less P for the alum and ferric based media, respectively but this effect was not seen when retention time was increased to 12 hours.
- The effect of using larger scale beds was not clear from the experimental work but is most likely negligible.
- All the systems removed a high percentage of P during the first few cycles but then showed a decline up to approximately 200 bed volumes from which point the rate of percentage removal declined at a much slower and steadier rate.

Chapter 6. Further chemical results from the column and meso scale experiments.

6.1 Introduction

This chapter seeks to determine 1) if any of the key chemical and biological parameters that were monitored in the waste water mediated or assisted the P removal process and 2) to confirm that DWTR did not leach Fe or Al in quantities that would be toxic to the environment.

Thus the more specific research questions addressed in this chapter are:
- Does the DWTR leach Al or Fe and in what quantities?
- How is system pH affected by the DWTR and how might this change effect P removal?
- What quantities of calcium and sulphate are present in the water and how does the DWTR and presence of the P effect this?
- How does the level of dissolved oxygen change during the process cycle and could this have an effect on P removal?
- What percentage of COD was removed by the RWW systems and is this associated with P?
- Is there evidence of biofilm growth on the media and could this mediate P removal?

6.2 Aluminium and Iron Leaching

Both Al and Fe can be toxic to all forms of life if ingested in large quantities. Al is a neurotoxicant which has been shown to play a role in dialysis-associated disorders of the brain and bone. Al is also acutely toxic to fish in acid waters, and is also known to cause toxicity to aquatic habitats (Babatunde et al., 2011a). For drinking waters, the World Health Organization suggests a maximum limit of 0.2 mg L^{-1} (WHO, 2004). Iron is not as toxic as Al but can cause problems if ingested in large amounts, but represents more of a problem to taste and the aesthetics of drinking water. The U.S.EPA Drinking water Guidelines limit iron to

0.3mgL^{-1}(Crittenden et al., 2012) However generally the limits of iron in waste water are set at 2mgL$^{-1.}$(Metcalf et al., 2014).

6.2.1 Aluminium analysis from column and meso scale experiments

Aluminium was measured in the outlet for all systems for the first 4 weeks of operation. Only 2 of the columns containing HO and the HH media showed any detectable Al, the systems had maximum levels 0.0223 and 0.333mgL^{-1} Al for the HO and HH media, respectively. The maximum was reached on the second week of sampling and after this point the Al was beyond the detection limits of the ICP-OES.

Therefore in agreement with the majority of the literature Al leaching should not represent a problem for the use of DWTR (Babatunde et al., 2011a).

6.2.2 Iron analysis from column and meso scale experiments

6.2.2.1 Fe at the University site

All the system inlet and outlets were monitored for Fe throughout the course of the experiments. Although Fe was below measurable limits in all tap water samples, the inlet tanks showed low levels (< 0.04mgL^{-1}) of Fe on 5 separate occasions during the year. When Fe was measured in the inlet it was also measured at very similar levels in the outlet of the majority of the columns. This may therefore have been a measurement error with incorrect calibration of the ICP-OES feedstock, or it implies that the majority of the media have very little effect on free soluble Fe available in the water.

However, two of the columns containing HO and LA media leached Fe throughout the course of the experiments. The HO media used both ferric and alum as coagulant whereas the LA just used ferric. The average and standard deviation for both media were 0.93±0.56 and 0.25±0.55 mgL^{-1}Fe for HO and LA media, respectively.

It is very interesting to note that the highest values of Fe leaching occurred during the coldest period of operation. The winter was very mild, only on one day did temperatures approach freezing. The Fe outlet data for the two columns that leached iron in conjunction with average temperature is shown in Figure 6.1. On the coldest day of the year both the systems leached levels of Fe in excess of 2mgL^{-1}, but this quickly returned to lower levels as the weather improved.

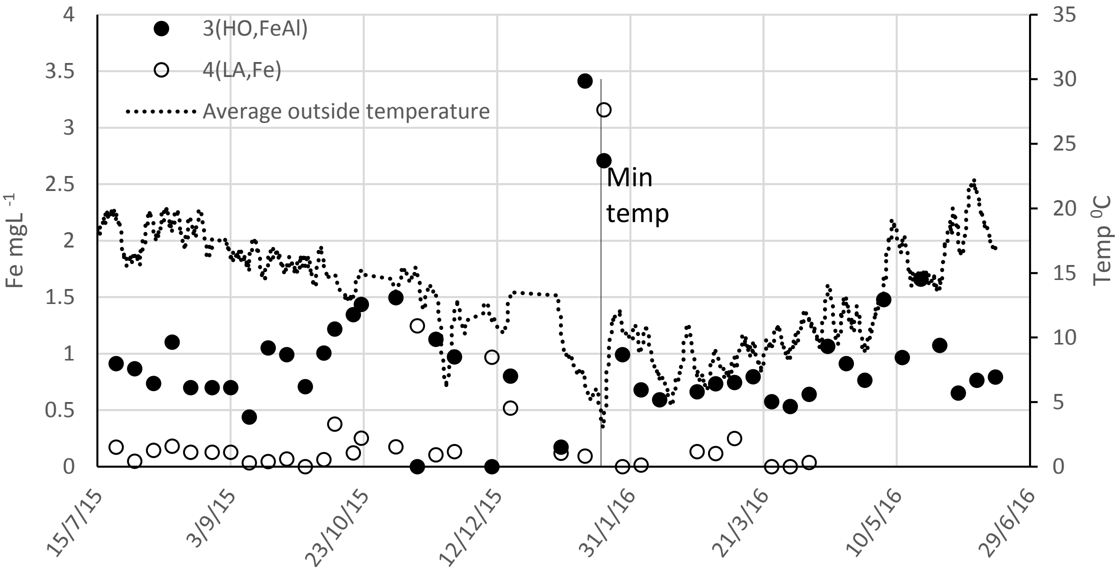


Figure 6.1 Fe leaching from University columns with HO and LA media plotted with average temperature data

The reason why the Fe should leach on the coldest days is most likely because the media was broken apart due to the action of ice, and this fracturing of the media caused the release of Fe. Collins et al., (1998) showed that DWTR could be dewatered to a solids content of >30% by using a freeze/thaw process. This implies that the structure of the DWTR is altered during the freezing of the media allowing previously entrapped water and metals to be removed.

6.2.2.2 Fe at the RWW site

The inlet to the real waste water columns contained an average of 0.09±0.14mgL^{-1} Fe. The outlet from the systems showed similarly low levels of iron with no single result of greater than 1mgL^{-1} see Table 6.1. Similarly to the column experiments at the University the meso bed containing HO media leached the most Fe.

Table 6.1 Average and standard deviation for Fe concentration in RWW systems

Col No. Media	Inlet	30 (GU)	31 (GU)	32 (BS)	33 (BS)	34 (GU)	Bed 1 (HO)	Bed 2 (GU)
Average Fe (mgL^{-1})	0.09	0.03	0.03	0.07	0.09	0.04	0.10	0.05
Standard deviation	0.14	0.04	0.06	0.07	0.10	0.05	0.17	0.05

6.3 pH

The pH of the water in contact with the DWTR has been reported in many papers to have a very large effect on the amount of P the media will adsorb (Yang et al., 2006b, Bai et al., 2014, Gao et al., 2013, Kim et al., 2003), with all studies agreeing that P removal is optimised in acidic conditions with pH between 4 and 5. In these experiments the system pH was not adjusted. It would be important that any treatment process using DWTR should not have to use additional chemicals. Furthermore, little research has assessed the effect of the media on system pH and whether the discharge from a DWTR based system would require pH correction. Therefore the inlet and outlet pH was measured for all the column and mesoscale experiments throughout the year.

6.3.1 University site

6.3.1.1 University Site Inlet

The three inlet tanks were monitored for pH as was the tap water feeding the tanks. The tap water had a mean pH of 7.79±0.16, although during the first summer of the experiments it was closer to 8 and showed a small drop throughout the course of the year.

For the first few months of the experiments the pH of the inlet tanks was generally 1 or 2 units above the tap water. During these months a lot of algae growth was observed in the tanks. [Algae increase the pH by absorbing CO_2 and reducing the levels of carbonate and bicarbonate in the water.] In the middle of August the tanks were thoroughly cleaned and were painted black to hinder the growth of algae. After this point the pH steadily fell and averaged 7.91±0.44, 7.83±0.32 and

8.36±0.72 for tanks 1,2 and 3 respectivly. The measured pH of the 3 inlet tanks and tap water are shown in Figure 6.2.

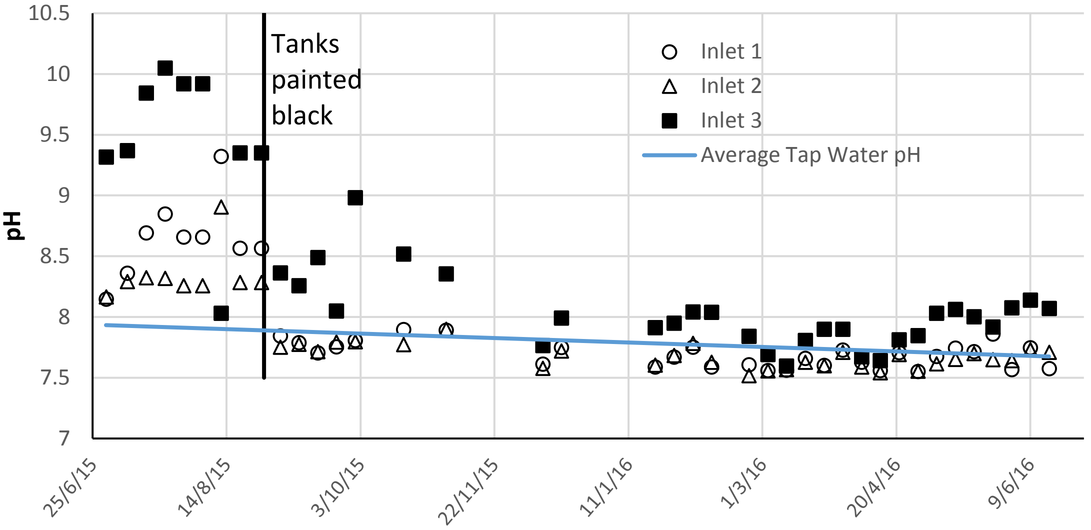


Figure 6.2 pH of inlet tanks and tap water feeding the tanks

6.3.1.2 *Column outlet pH at University site.*

During the first six months of the experiments the pH of the water was reduced as it passed through all the columns see Figure 6.2. However, this acidifying effect of the media generally became smaller as the experiments progressed and during the last six months of operation the WD and MO media showed a reverse of this trend with the water becoming slightly more alkaline as it passed through the columns. Once the tank pH had been reduced after the first two months the majority of the columns lowered the pH by approximately 1 unit, with the notable exception of the HH media which continued to acidify the outlet water by up to 1.5 units even after a year of operation, see Figure 6.3. There was a significant negative correlation between the average pH of the outlet water of the columns and the percentage P removal (r=-.707, p<.01). Therefore, in agreement with all the literature more P is removed at lower system pH. The lowering in pH across the systems is probably explained by the release of cations and anions such as Ca, Mg, Cl^-, SO_4^{2-} and TOC which increases or decrease the pH from its initial value (Al-Tahmazi and Babatunde, 2016), as the release of these ions decreases over time so does the change in pH.

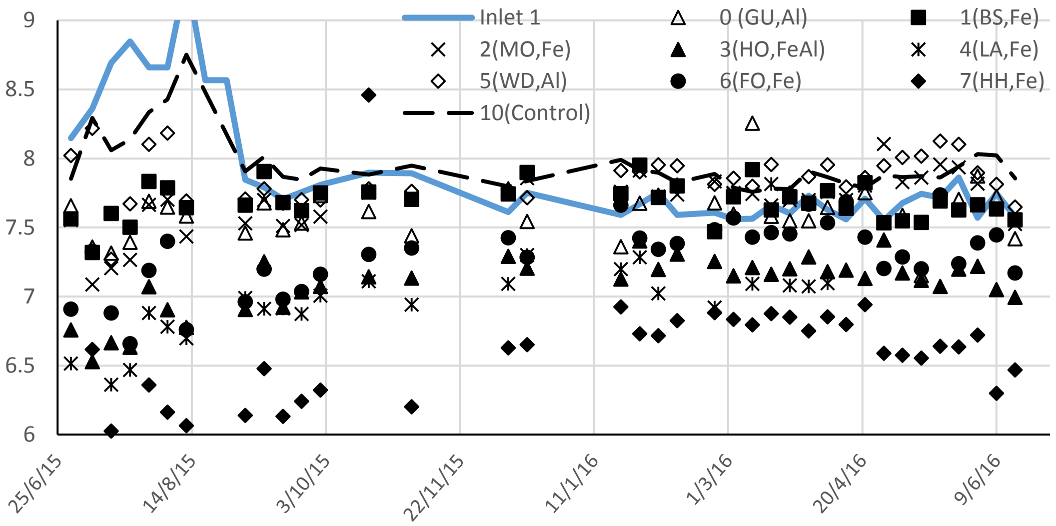


Figure 6.3 Inlet and Outlet pH of 8 columns with different media at the University

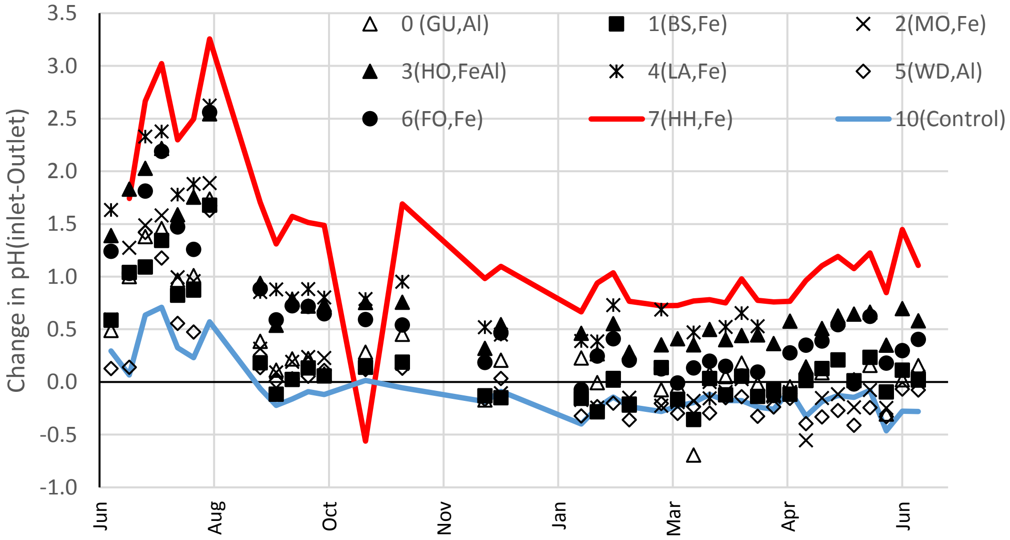


Figure 6.4 Change in pH across the columns for 8 different media.

The systems operating at variable contact time and lower inlet concentration all showed very similar trends to the experiments on media type. With a large drop in pH for the first 3 to 4 months followed by a reduction or increase in pH of less than 0.5. Figure 6.5 A and B shows pH change in columns with variable contact time.

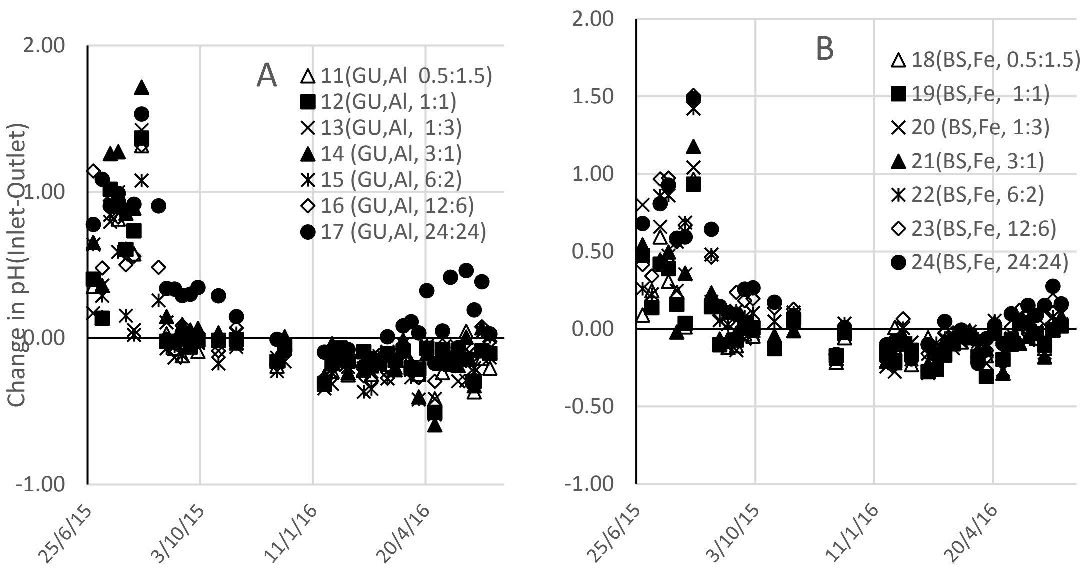


Figure 6.5 Change in pH for columns with different contact times, A) Alum media (GU) and B) Ferric based media BS.

6.3.1.3 Real Waste Water Site

The inlet pH of the real waste water was circumneutral and varied between 6.69 and 7.75 with a mean of 7.4±0.16. Excluding the very last result of 6.69 the minimum pH measured was 7.19.

As with the experiments with synthetic P dosed water at the University all the systems generally caused a decrease in pH. However the effect was not so marked in the RWW columns with an average reduction across all systems of 0.3 (see Figure 6.6). For most of the systems the change in pH did reduce over time but again this was not such a strong trend as at the University. The alum based media in the columns caused the highest reduction in pH followed by the ferric media and finally by the meso scale beds, with the meso scale beds generally never reducing pH by greater than 0.4 (see Figure 6.7).

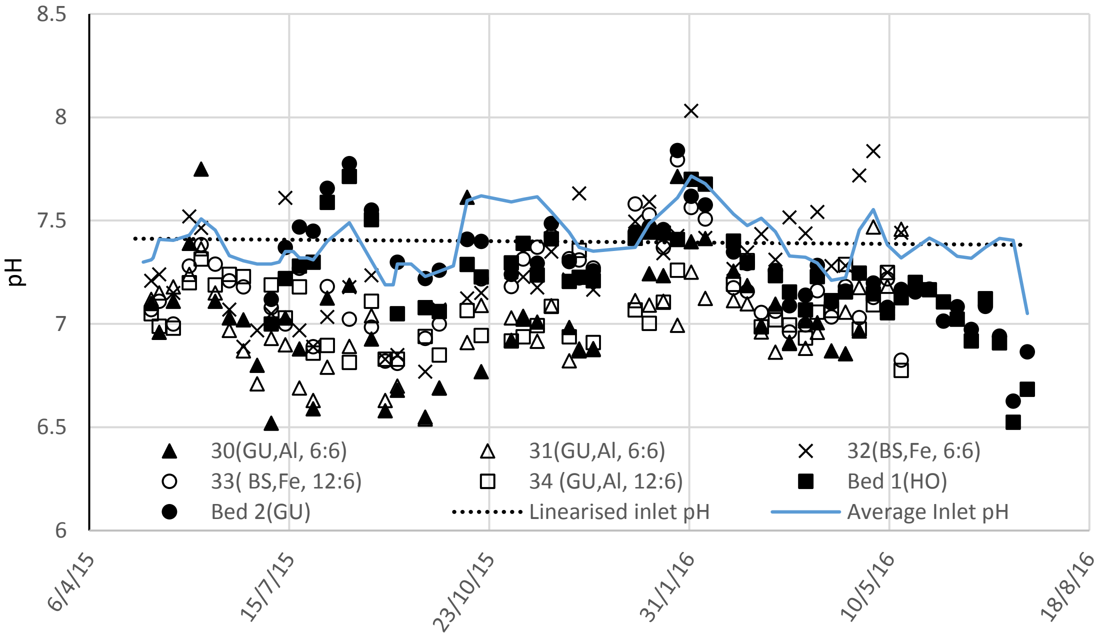


Figure 6.6 pH in and out for systems at real waste water site

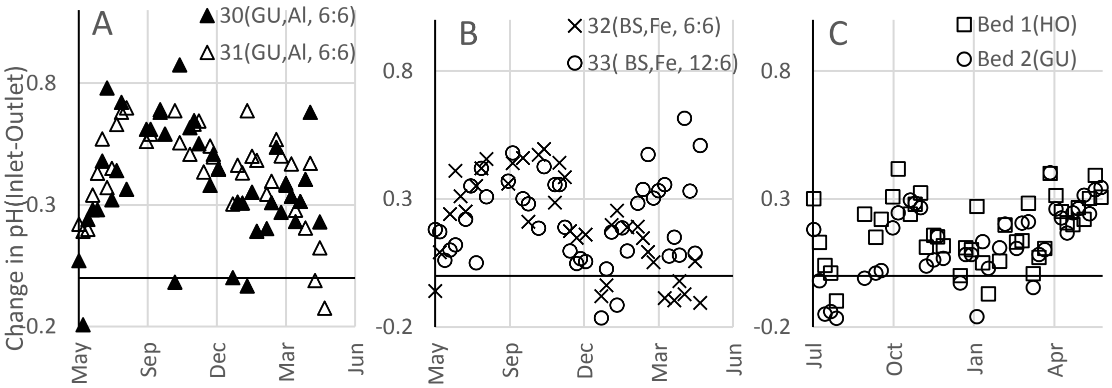


Figure 6.7 Change in pH (inlet-outlet) for real waste water systems for alum and ferric media A and B and for the meso scale beds C

6.4 Calcium

There has been much research undertaken on the ability of materials that have a high water soluble Ca content to remove P (e.g. blast furnace slag), as at elevated pH, phosphate can be removed from solution through precipitation of calcium phosphate (Klimeski et al., 2012, Bowden et al., 2009, Drizo et al., 2006). Although the 8 DWTR all had low levels of Ca in their chemical makeup (See Table 4.4) it has also been reported that Ca may preicipitate on the surface of the

DWTR and this may provide a pathway for P removal (Al-Tahmazi, 2016). Therefore, the inlet and outlet concnetrations of Ca were measured for all of the columns and meso scale beds.

6.4.1 Ca results from the University site

The average Ca content of the feed tanks at the University was 36.3±2.8mgL^{-1}. For the majority of the time all of the University systems removed Ca from the inlet stream (Figure 6.8 and 6.9). Average removal rates for the 8 columns with different media varied between 12 and 52% for BS and HH media, respectively. There is a significant correlation between average percentage P and Ca removal r=.858, p<.01 for the 30 columns at the University. The Ca removal reduced for all of the columns over the year showing a very similar trend to P removal.

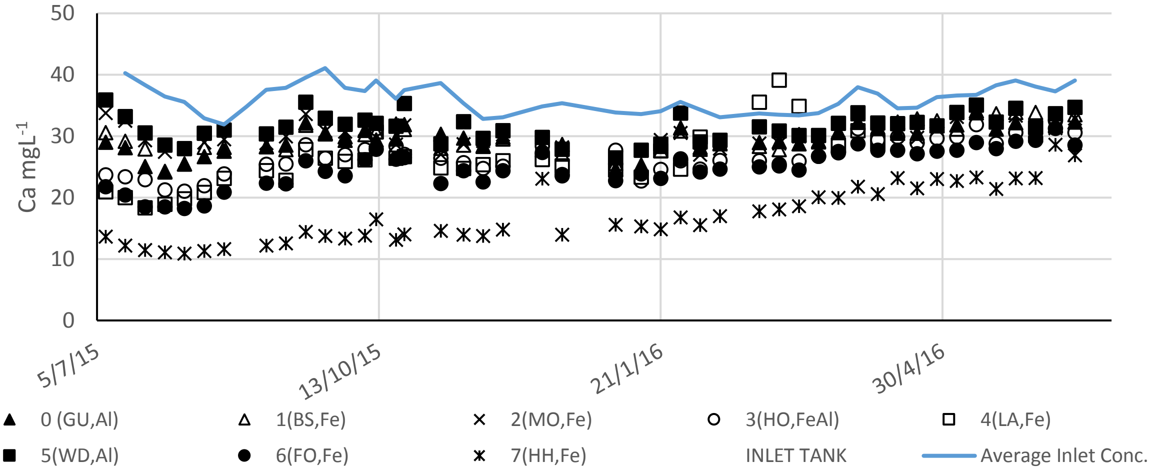


Figure 6.8 Ca in the outlet of the columns with 8 different media at the University site

Contact time had a large effect on Ca removal. The Ca results for the Fe and Al based media operating with 30mins,6 hours and 12 hours contact time are shown in Figure 6.9 A and B. It is clear from the graphs that systems operating with a small contact time removed far less Ca, although the Ca removal reduced much faster over time with longer contact times. The higher removal rate for Ca at 12 hours contact time is most probably due to the slow kinetics of any Ca based reactions.

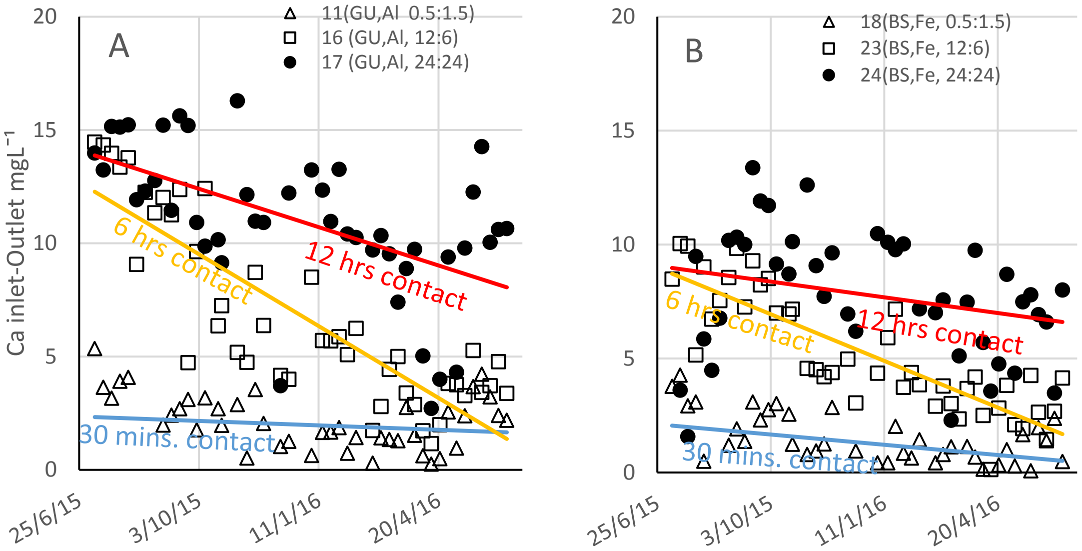


Figure 6.9 Calcium removal at 3 different contact times (0.5, 12 and 24 hours) with A) Al (GU) and B) Fe(BS) based media

To further quantify the relationship between Ca and P removal Figure 6.10 shows the Ca outlet concentration for equivalent columns running with 12 hours contact time but at 2 different P concentrations of 1 and 5 mg L^{-1} STP. It is notable from the graphs that less Ca is removed with lower inlet P concentration, implying a further link between Ca and P.

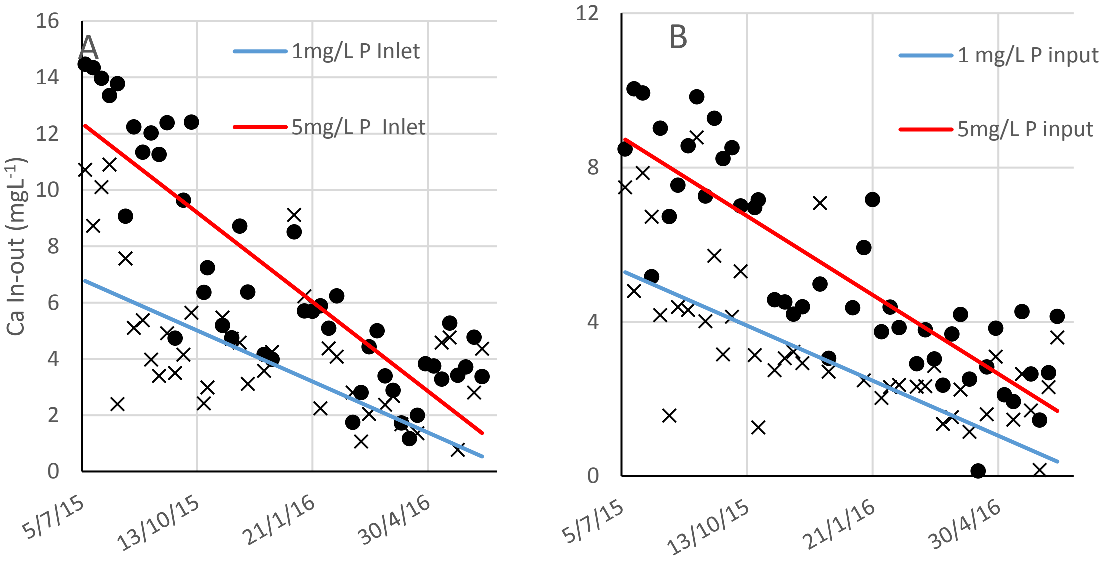


Figure 6.10 Calcium removal from A)Al and B)Fe media with 12 hours contact time with 1 and 5mgL^{-1} STP inlet concentration.

6.4.2 Ca at the RWW site

The average concentration of Ca in the RWW was 33±10mgL^{-1} which was similar to the value at the University. However in stark contrast to the columns at the University, the columns and beds at the RWW site removed almost no Ca. The Ca concentration in the inlet and outlet of the systems is shown in Figure 6.11 and the average difference between the inlet and outlet are shown in Table 6.2.

.

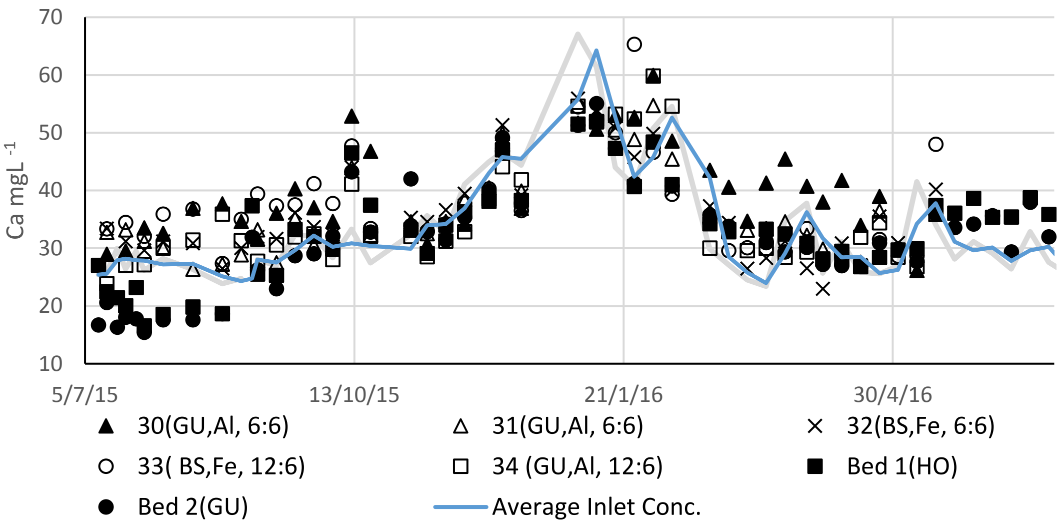


Figure 6.11 Ca inlet and outlet and real waste water site

Table 6.2 Average different between inlet and outlet of Ca at RWW site

Col/Bed No.	Inlet	30	31	32	33	34	Bed 1	Bed 2
Mean inlet/outlet Ca mgL^{-1}	33±10	40±8	36±8	36±8	37±8	35±9	33±8	32±9
Mean Ca In-out mgL^{-1}		3±12	-2±6	-1±6	-3±8	-1±6	-1±9	1±8

6.4.3 Discussion of the Ca results

The results of the Ca measurements clearly demonstrate that there is a link between Ca and P removal. The association that Ca has with P would be most readily explained by the precipitation of calcium phosphate on the surface of the media, which is commonly described as the removal mechanism for calcium rich materials. However all of these media tend to operate at very alkaline pH ranges generally >9, as calcium phosphate precipitation is favoured in alkaline conditions Al-Tahmazi et al.(2016), proposes that calcium phosphate should not precipitate below a pH of 7.7 and although the majority of the column systems operated on average very close to this pH value. The column that removed the most calcium and phosphate (HH) operated at an average pH of 6.6 well below the pH at which calcium phosphate should precipitate. This results is hard to explain and requires further investigation.

Although these experiments did not allow time to confirm the presence of calcium phosphate on the surface of the media EDXRF analysis of the saturated media revealed that the majority of the media had shown an increase in the presence of Ca in the makeup of the media over the course of the experiments see Figure 6.16.

6.5 Sulphur and Sulphate

A few papers have suggested that one removal pathway for P is associated with the ligand exchange of sulphate (Bai et al., 2014, Al-Tahmazi, 2016).

It was only possible to measure the quantities of sulphate present in the inlet and outlet streams of the RWW site due to time constraints. However, after October 2015 once the effect of sulphate became apparent, all inputs and outputs at all the sites were measured for sulphur(S) using the ICP-OES. Although there are many different sulphur compounds analysis of selected samples for both sulphur and sulphate revealed that the majority of the S measured was associated with sulphate. This is unsurprising as the coagulants used at the treatment works were either ferric or alum sulphate.

6.5.1 Sulphur inlet and outlet measurement at the University site

The average S at the inlet to the systems at the University site was 11.5±0.8 mgL^{-1}. The results for the 8 columns with different media are shown in Figure 6.12. For the majority of the time, there was an increase in S across the systems meaning that the media generally lost S to the outlet water, but this decreased over time and a few of the columns removed S towards the end of the experiment. There was a strong correlation between percentage S increase and percentage P removal, r=.637, p<.01 for all 30 columns at the University. It is likely that at least some of the S loss was therefore due to ligand exchange with phosphate molecules.

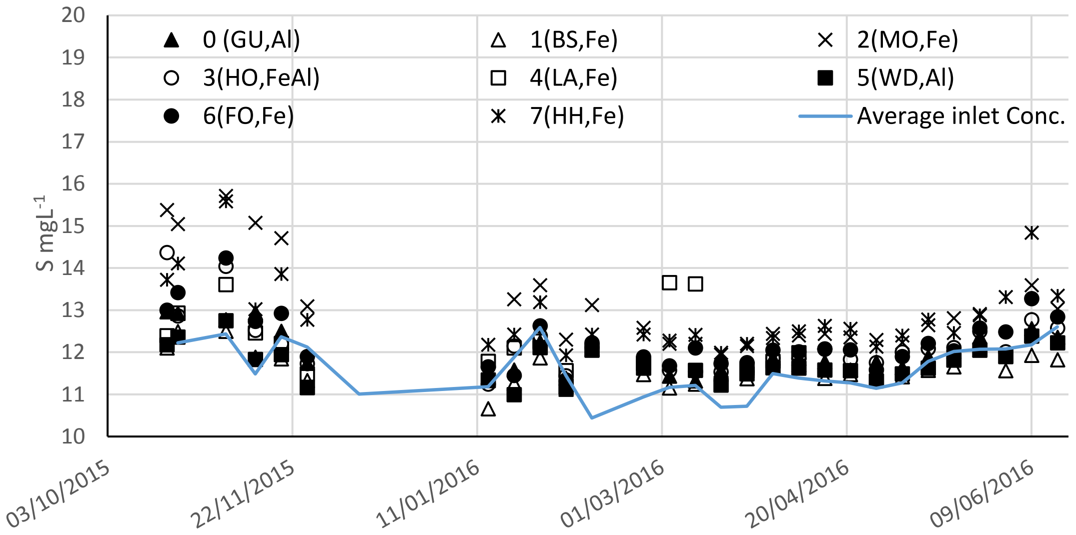


Figure 6.12 Sulphur in and out for 8 columns with different media at the University site

The effect of retention time on S removal was very pronounced for the Al (GU) media with much more S being removed from the media with a 24 hour contact time when compared to 30 minutes. However, the BS media did not show this effect (see Figure 6.13).

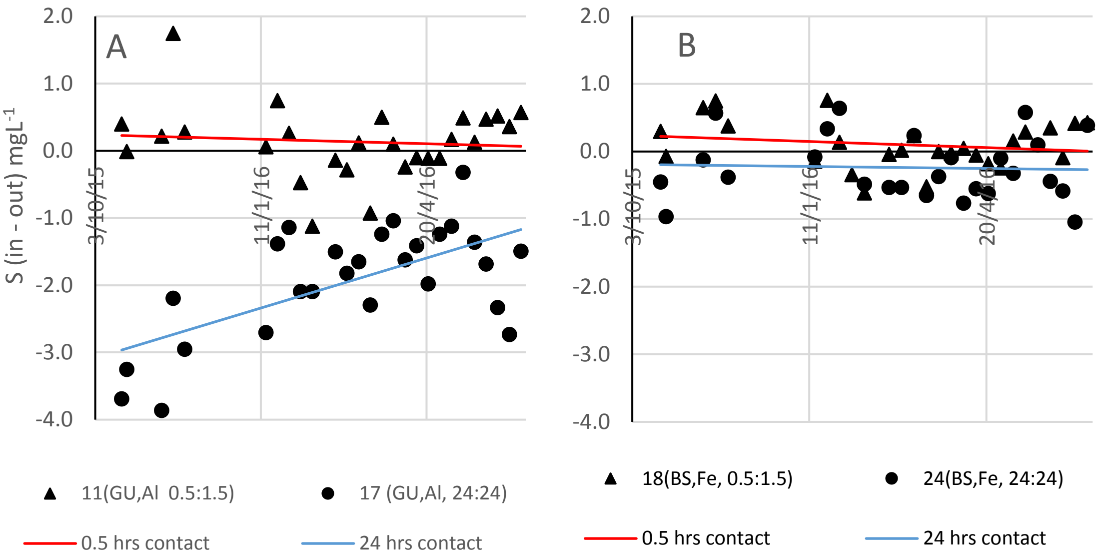


Figure 6.13 Effect of retention time on S removal A) Al (GU) media and B) Fe (BS) based media. Showing 0.5 and 24 hours retention time

6.5.2 Sulphate at the RWW site

The average sulphur and sulphate concentration in the real waste water were 15±4 and 30±22 mgL^{-1}respectivly. [Sulphate is 66.6% oxygen by mass and therefore it can be assumed that the vast majority of the Sulphur measured was in the form of Sulphate.]

The inlet and outlet sulphate and the difference between the inlet and outlet for all columns and beds at the real waste water site are shown in Figure 6.14 and 6.15.

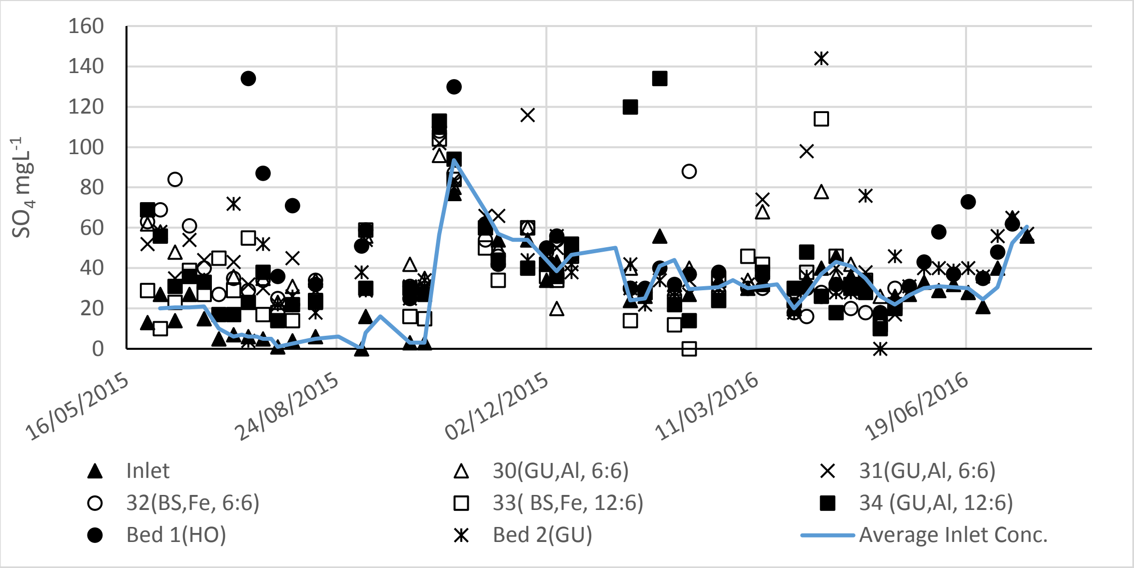


Figure 6.14 Sulphate results from RWW systems

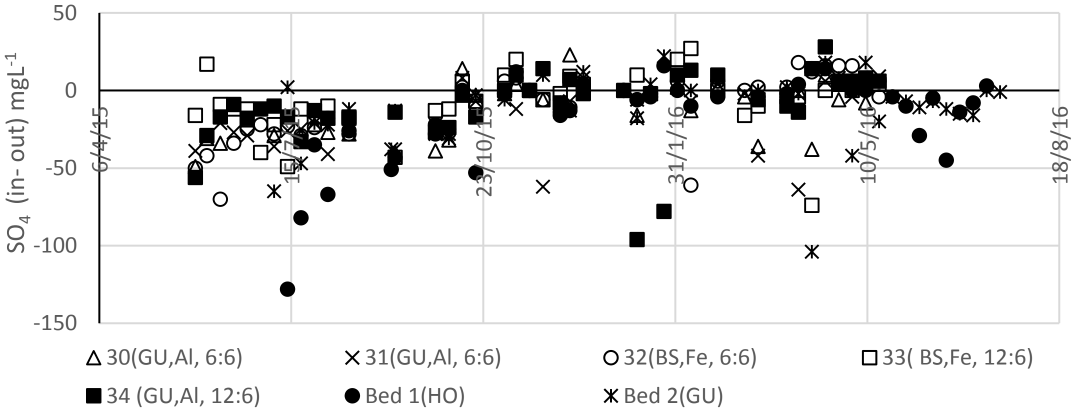


Figure 6.15 Sulphate inlet-outlet results for RWW systems

The sulphate entering the systems did not follow the trend of reduction during the wet weather. For the first 4 months of operation all the systems tended to leach large amounts of sulphate, towards the end of the experiments the systems tended to have a much smaller effect on sulphate sometimes leaching and sometimes removing sulphate. However, overall there was an average increase in sulphate across the systems and this can be seen in Table 6.3.

Table 6.3 Avergae inlet and outlet concnetnrations and avergae differnce of sulphate at RWW site

Col/Bed No.	Inlet	30	31	32	33	34	Bed 1	Bed 2
Mean inlet/outlet SO_4 (mgL^{-1})	30±22	44±24	46±24	41±23	36±24	41±29	48±27	43±26
Mean SO_4 in-out (mgL^{-1})		-13±18	-16±19	-11±21	-7±20	-11±24	-15±28	-10±23

Unlike the columns at the University site, no correlations were found between average percentage P removal and average increase in sulphate so although in the University systems the sulphate is probably exchanging with sulphate ions, in the RWW systems the sulphate may be exchanging with other ions present in the RWW.

6.6 Assessment of the effect of Ca, S and Fe using X-ray fluorescence (EDXRF) analysis on saturated media

There was not enough time or resources available to assess the saturated media using SEM or Fourier transform infrared spectroscopy (FTIR) but the quicker and less accurate technique of EDXRF was used to compare the Ca, Fe and S content of the raw media and DWTR that was extracted from the operational systems after nine months of operation. The results from the comparison are shown in Figure 6.16.

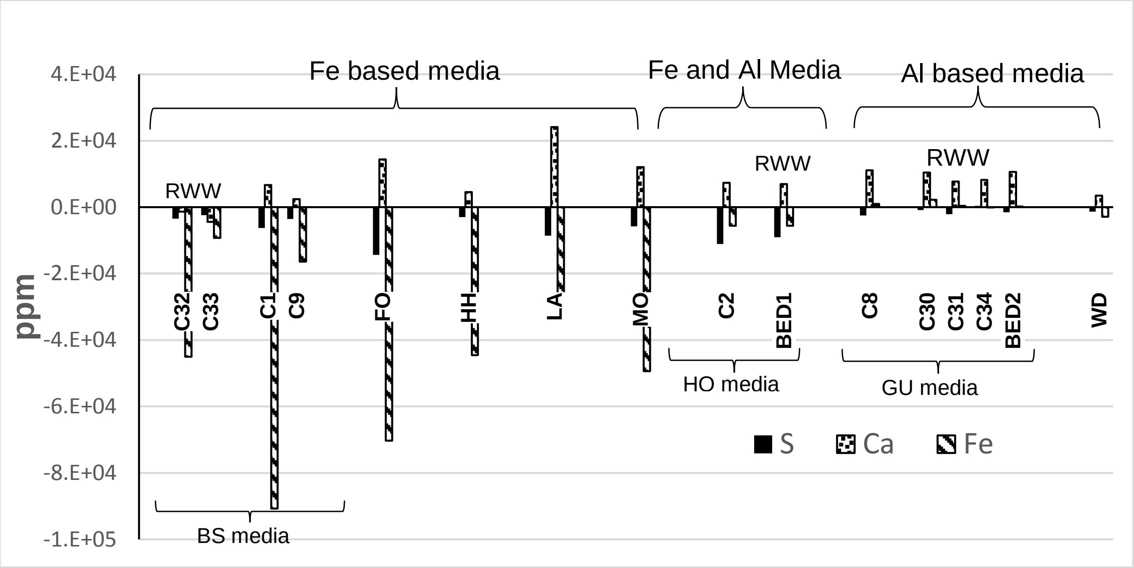


Figure 6.16 EDXRF Difference between raw media and media from columns after 9 months operation

The results show general agreements with the Ca, S and Fe results discussed in previous sections, with the ferric based media tending to loose Fe and S, and apart from the BS media columns, all systems show an increase in Ca. This may suggest calcium phosphate is precipitating on the surface of the media. The media from the RWW site tended to show generally smaller effects than those at the University, and the Al based media showed very small losses of S.

6.7 Dissolved Oxygen (DO), Oxidation and Reduction Potential (ORP), Conductivity

Several papers have discussed the possibility that P may be desorbed from DWTR when a system becomes anoxic or anaerobic (Oliver et al., 2011, Leader et al., 2008). It is also been suggested that the advantage of tidal flow systems is that they effectively pump oxygen in and out of the system as the water is moved in and out (Babatunde et al., 2010). Therefore to access the levels of DO in the two meso scale beds, a multi-parameter probe (as detailed in Section 3.6.5.2) was placed in the sampling points in the middle of meso scale Bed 1 and 2 at heights varying from 2 to 40cm The probe was left in the bed for 24 hours and the measurements were taken bi-monthly. The probe logged DO, ORP, pH and conductivity every 10 minutes.

There was no discernible differences between the DO, ORP and conductivity results during the year. Typical results from the probe for Bed 1 and Bed 2 are shown in Figure 6.17 and 6.18.

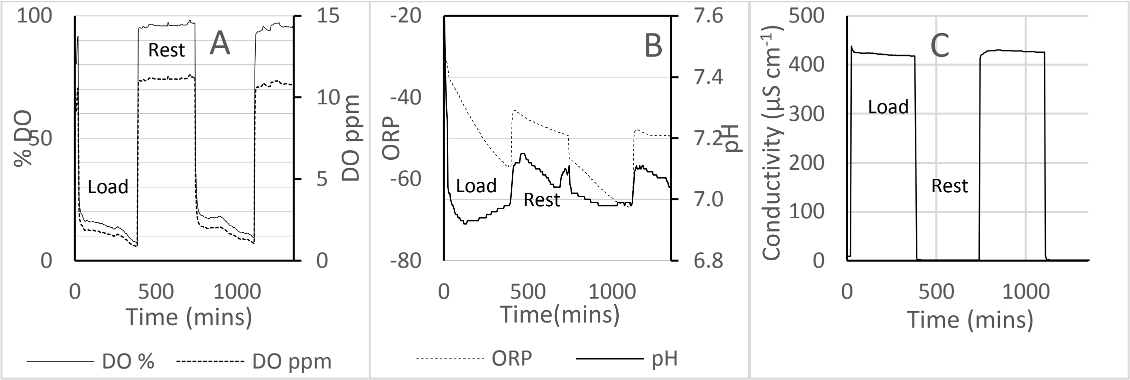


Figure 6.17 Results from 2 rest and load cycles from multi parameter probe placed at the bottom of Bed 1 A) DO% and ppm, B)pH and ORP, C) conductivity.

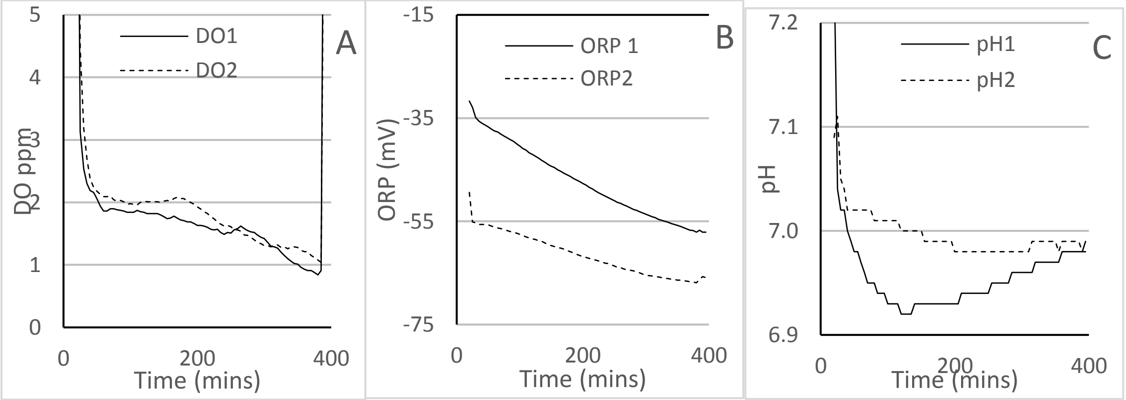


Figure 6.18 Results from multi parameter probe for A)DO, B)ORP and C)pH *For two fill cycles of Bed 2 during March 2016. The probe was set 2cm from the base of the bed.*

The DO of the inlet storage tank was also measured for the first few months of operation and averaged 1.42±0.96 ppm. When the water is pumped into the beds the DO increases from 1.42 to around 10ppm as air is captured in the water through surface entrapment and mixing. However, the DO falls very rapidly to around 2ppm in a matter of minutes. During the load cycle the DO showed a relatively steady decline from 2 to 1ppmm as the trapped free air in the system is used up, most probably due to microbial activity.

The ORP showed a similar trend to the DO falling from around -20 to -40 to -60mV during the 6 hour loading period. ORP measurement is known to be very unreliable but a measurement below 0 often implies that the system is anoxic or anaerobic.

The pH tended to drop very rapidly from 7.5 to 6.9 on entering the bed, and then increased back to 7 by the end of the loading period.

The conductivity of the water in the beds showed a very slight drop during the cycles from 440 to 420µScm^{-1}

The results from the muliti parameter probe imply that the systems are becoming anoxic during the load cycle. The loading period of the meso scale beds was 6 hours and the DO continued to fall throughout the loading period. Therefore when retention time is increased to 12 and 24 hours it is likely that the DO will fall further and the systems may become anaerobic. This may be another reason why increasing retention time above 6 hours could be a disadvantage,

6.8 Chemical Oxygen Demand (COD)

Although the removal pathways for COD and P are generally reported as independent of each other (Babatunde et al., 2011b), the measurement of COD provides an index to assess the effect discharged waste water will have on the receiving environment. Therefore the measurement of COD was undertaken for the majority of the RWW samples to both confirm there was no correlation between P removal and COD but also to provide an insight into how much COD the DWTR might usefully be expected to remove.

The average inlet COD to the waste water system was 243mgL^{-1} but this was very variable with a min. and max. of 16 and 507mgL^{-1}respectivly and a standard deviation of 143mgL^{-1}. As with the P, the COD was greatly affected by heavy rainfall events and the results show a similar trend to those of P (Figure 6.19 A and B) with reduced COD level during the wet winter months.

For the majority of the time all of the systems removed COD with average removal rates for the columns varying between 22 and 33% and for the meso scale beds between 45 and 38% see Table 6.4. No correlation was found between COD and P removal in implying that they have different removal pathways in agreement with the literature.

Several attempts were made to measure the biological oxygen demand (BOD) of the RWW using the Hach LCK 555 cuvettes in conjunction with the Hach DR3900 spectrophotometer. The tests was attempted with 5 different dilution ratios on 3 separate occasions but unfortunately none of the cuvettes produced a result that was readable by the DR3900. It was therefore not possible to measure how much of the COD was biological in nature or to assess the COD removal pathways.

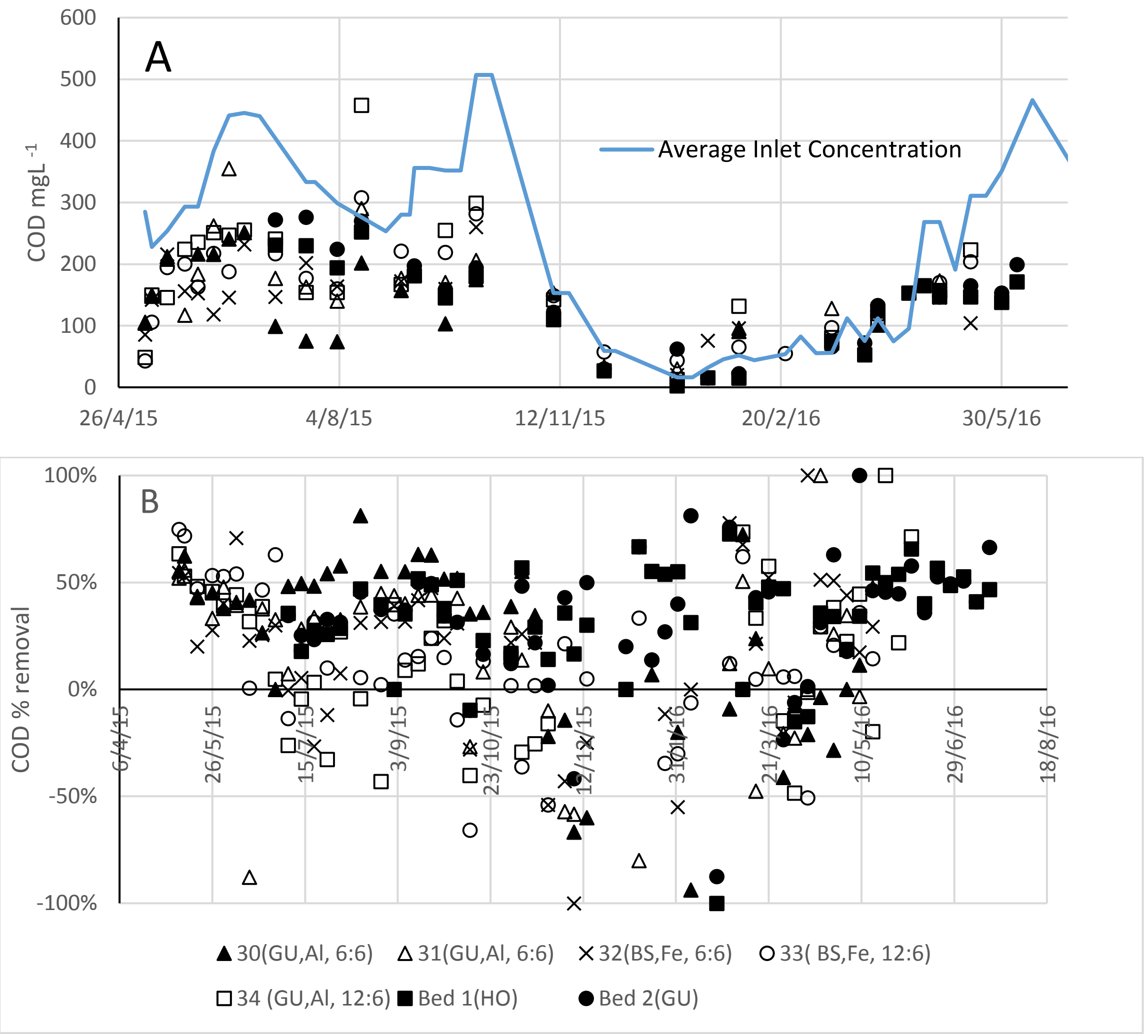


Figure 6.19 A) COD inlet and outlet B) COD % removal for columns and beds at real waste water site

Table 6.4 Measured COD results and % removal

Col No. Media	Inlet	30 (GU)	31 (GU)	32 (BS)	33 (BS)	34 (GU)	Bed 1 (HO)	Bed 2 (GU)
Average COD (mgL^{-1}) and Standard Deviation	247 ±143	143 ±65	168 ±71	148 ±61	159 ±75	188 ±95	134 ±74	148 ±83
Average COD% removal		33 ±43%	22 ±48%	24 ±55%	30 ±28%	23 ±55%	45 ±19%	38 ±18%
Average COD loading g $m^{-2}cycle^{-1}$		94.2	91.1	44.0	66.0	91.1	22.8	17.9

6.9 The effect of biofilm formation on the adsorption of phosphorus by DWTR

The RWW water sites removed less P than the University systems as discussed in Section 5.8 and it was hypothesized that this may be due to biofilm formation on the media blocking the surface sites or access to the intestinal pores of the DWTR.

Several attempts were made to assess the effect of biofilm formation on the ability DWTR to adsorb P. The experimental procedure used was detailed in Section 3.11. However the results from the experiments were all inconclusive and could not be validated statistically.

Many attempts were also made to observe the biofilm that would be expected to have formed on the media in the RWW columns. The media was taken out of the operating columns and was stained with a live dead stain and taken for analysis to the confocal microscope laboratory in the biosciences department at Cardiff University within three hours. A typical confocal image of the stained media is shown in Figure 6.20

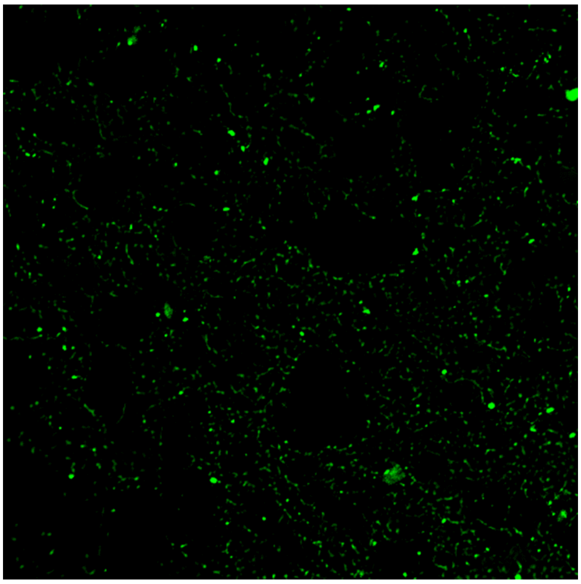


Figure 6.20 Typical confocal image taken of media from RWW after staining with live/dead stain

Although the levels of microorganisms present were not quantified, the highly experienced technician operating the microscope commented that “of the many observations of biofilm he had made over the previous 10 years he had rarely seen such a small quantity of microorganisms present”. Over ten samples of the DWTR were observed in this manner all with similar results. Considering all the media had been immersed in real waste water for over 6 months Figure 6.20 should be a bright glowing mass of fluorescing DNA.

The results from these observations could imply that there is some kind of anti-bacterial property of the media, however this is only conjecture and would need to be confirmed by more detailed research. It has been included in this thesis as an interesting observation.

6.10 Summary and conclusion

The results from both the Fe and Al analysis imply that neither chemical leaches from the majority of the media in quantities that should represent a problem to aquatic systems. The two media that did leach Fe (HO and LA) were not the best at removing P and therefore should not be used as media in a full scale treatment system.

The systems operated in the circumneutral pH range and although all the systems reduced the pH, for the majority of the media the effect was small and reduced over the year. However the HH media reduced the pH by an average of 1.5 units and continued to reduce the pH after the year of operation. There was a strong negative correlation between pH and P removal, therefore the lower the pH, the higher the P removal, which is in agreement with the literature. The DWTR caused only a very slight reduction in pH when RWW was used. No pH correction would be required at the outlet of a DWTR treatment system unless the HH media was used.

Ca removal from the water is highly correlated to the removal of P and it is therefore possible that some of the P is being removed by precipitation of calcium phosphate although this cannot be proved. For most of the year the media lost sulphate to the outlet water and it is likely that some of this sulphate is exchanging with phosphate on the media surface. The effect of reduction in pH, removal of Ca and increase in sulphate were almost non-existent in the RWW.

The media removed approximately 40% of the COD that entered the RWW systems and attempts to measure the effect of biofilm formation were a failure, although the results might imply that the media does not favour the formation of biofilms.

Chapter 7 Suspended solids and hydraulic conductivity

7.1 Introduction

One of the objectives of this thesis was to provide design advice for the use of DWTR in a full scale reed bed treatment system. For reasons discussed in 3.2.6, it was decided not to use reeds in the experimental models but this does not preclude their use in a full scale system. Whether reeds are used or not, the operation and construction of the system is likely to involve a solution that is very similar in nature to a reed bed. A very common problem with reed beds is that the hydraulic conductivity reduces over time and they become blocked. In sub surface flow horizontal wetlands as the hydraulic conductivity decreases the flow tends to short circuit over the surface (Cooper et al., 2008). As DWTR relies on adsorption processes to remove P it is vital that all the water remains in contact with the media and overland flow is not a viable option for treatment. Therefore, this section assess the measurements of hydraulic conductivity that were made in the operational columns and the results show how long a system using DWTR may last before blockage may become a problem.

Bed clogging is thought to be caused by (Kadlec and Wallace, 2008, Nivala et al., 2012, Knowles et al., 2011):

- Deposition of inert suspended solids.
- Accumulation of refractory organic material (resistant to microbial degradation)
- Deposition of chemical precipitates in the wetland bed
- Loading of organic matter (both suspended and dissolved) that stimulates the growth of microbial biofilms on the bed media.
- Development of plant root networks that occupy pore volume within the wetland bed.

In the case of the DWTR, it appears from the very basic biological analysis that was undertaken (Section 6.9) and through observations on site, that biofilm formation within the media is likely to be slow. Chemical precipitation is likely to be small, and the system will potentially operate without the use of plants. This leaves the main route to the blocking of the beds through deposition of suspended solids or breakdown of the media. Many authors report a positive correlation between systems clogging and SS loading rates (Knowles et al., 2011, Sani et al., 2013). Therefore, this section also includes an assessment of the SS removal that was achieved in the RWW and meso scale beds and discusses how this may relate to the reduction in hydraulic conductivity.

7.2 Suspended Solids (SS)

7.2.1 SS at the University systems and washout of DWTR

The university system was fed with tap water with no measurable SS. However, during the first two weeks of operation the outlet of many of the columns had high levels of SS >100mgL^{-1}. The release of SS from the columns must have been caused by washout of small DWTR particles.

It was hypothesized that the washout was being caused by high flow rates as the systems were being drained down at the end of the contact cycle; when the 22mm drain valve was fully open the flow rate exceeded 3l/min giving a velocity of water within the columns of >3m/min. At this high velocity the flow of water seemed to breakdown the media. To alleviate this problem valves were placed on the sample outlets (see Figure 7.1) and the maximum flow rate was restricted to 1L min^{-1}, giving an internal water velocity of 1m/min. After the installation of the valves the SS was reduced to <3mgL^{-1} and was not measured further at the University site.

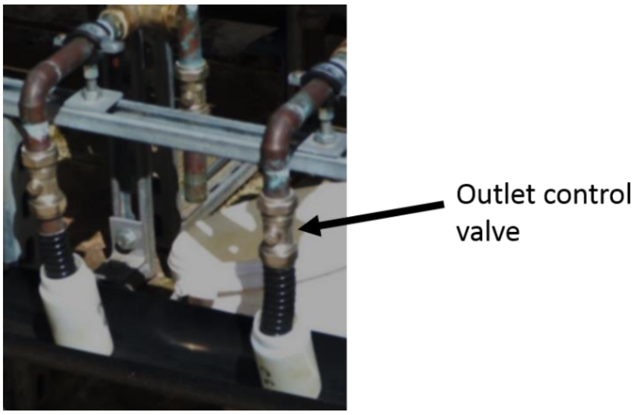


Figure 7.1 Outlet control valve on column outlets

7.2.2 SS at real waste water site

The SS inlet to the RWW system averaged 125±73 mgL^{-1} with a max. and min. of 5 and 251 mgL^{-1}, respectively. During the winter months, the heavy rainfall caused a dilution of the flow and the SS reduced to an average of 31 mgL^{-1} for this period. The SS of the inlet and outlets for all RWW systems are shown in Figure 7.2.

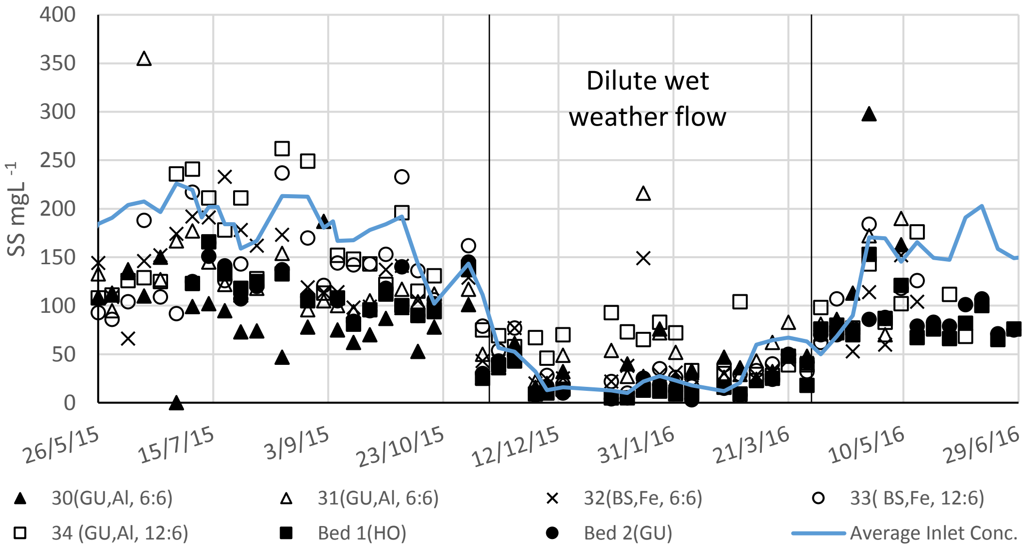


Figure 7.2 Suspended solids entering and leaving each system at real waste water site

It was not possible to control the outlet speed in the RWW columns, although the speed of rotation of the outlet valves was much slower which limited water column speed to 1.5m min^{-1}.

During the first few months of operation the columns removed between 30 and 50% of the SS entering the systems. However when flow became diluted and inlet SS dropped below 50ppm many of the columns acted as a source for SS, and the outlet flow occasionally had over double the SS of the inlet (Figure 7.3A). Even when the SS input increased again in the spring, the columns ability to remove SS was greatly reduced. This resulted in the majority of the columns releasing more SS than they removed over the course of the year and in some cases by as much as 30% (see Table 7.1). However the meso scale beds leached SS on only three occasions and for the majority of the year removed approximately 30% of the SS on average (see Figure 7.3B and Table 7.1).

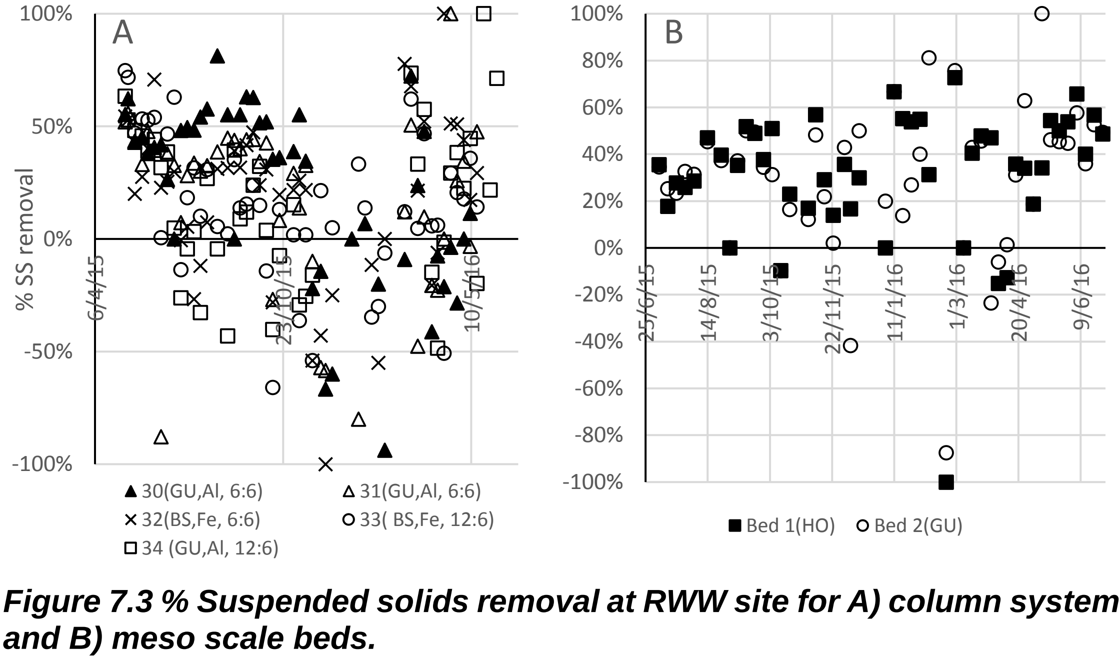


Figure 7.3 % Suspended solids removal at RWW site for A) column systems and B) meso scale beds.

The more consistent SS removal shown by the meso scale beds might be explained by the lower loading rate of SS per surface area of media and the much slower flow rates within the beds on drain down (outlet flow rate <0.5m min^{-1}.). The loading rate of the columns varied between 96 and 45 compared <23g m^{-2} day^{-1} for the beds (see Table 7.1). However, it may also have been caused by SS entrapment in the much larger gravel inlet and outlet areas

Table 7.1 SS loading rates and average percentage removal over the year for real waste water columns and beds

	Col No.	30	31	32	33	34	Bed 1	Bed 2
	Media	(GU)	(GU)	(BS)	(BS)	(GU)	(HO)	(GU)
Average SS % removal		3	-30	-7	-3	-34	33	31
Average SS Loading rate	$gm^{-2}day^{-1}$	95.8	92.6	44.8	50.35	69.45	23.2	18.2
	$gm^{-2}day^{-1}$	0.26	0.26	0.06	0.1	0.1	0.22	0.24

Another notable characteristic of the SS was its change in nature as it passed through the columns. It was apparent that the particle size of the SS leaving the columns was generally larger than that of the inlet SS. Although this effect was not quantified, the change can be clearly seen on the filter papers used to sieve the water before analysis (see Figure 7.4). The larger particle sizes could either have been small particles of media, or coagulated solids or both. Therefore, it is likely that the columns were removing substantial amounts of SS in the top layers of the column while simultaneously small particles of DWTR were being washed out from the media, however more analysis would be required to confirm this.

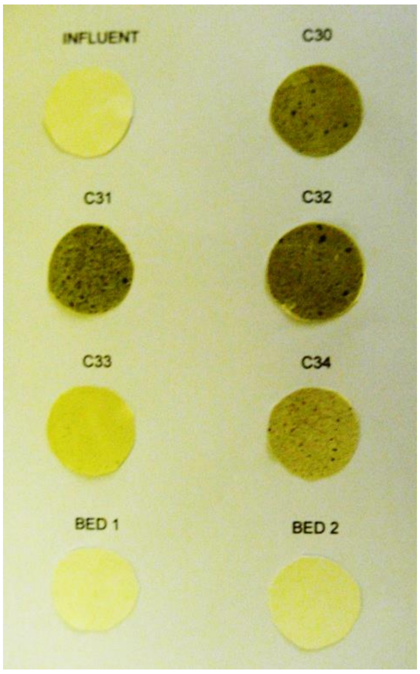


Figure 7.4 Filter papers from RWW systems and inlet showing particle washout in the columns but not the meso scale beds

7.3 Hydraulic conductivity

The hydraulic conductivity of the 8 DWTR were all measured in the laboratory before they were used in the columns (as detailed in 3.7.2.1), and the results of this analysis were displayed in Table 4.6. Hydraulic conductivity measurements were also made on the operational columns using the equipment and procedure discussed in 3.7.2.2. The next section reports the results of these experiments.

7.3.1 Hydraulic Conductivity measurements made on the operational test columns.

Hydraulic conductivity was measured in twenty of the operational columns at the University and all 5 columns at the RWW site.

7.3.1.1 Measurements on the University site

Initially it was hoped that multiple measurements of hydraulic conductivity could be made at the University during the year long experiments. However, it quickly became apparent that the high flow rates produced during the tests were washing much of the media away (see Figure 7.5). The red colour observed in figure 7.5 must have been caused by particles of the media washing out of the system. The inlet water had almost no suspended solids present and as the systems were newly installed there had not been time for any biofilm growth or precipitation products to form on the DWTR. This problem was similar to that discussed in 7.2.1, with high flow rates causing wash out of the media. Therefore the majority of columns were tested before and after the completion of the experiments.

Figure 7.5 Red colour showing washout of media during hydraulic conductivity test at University

The results of the hydraulic conductivity measurements for the 20 columns measured at the University are shown in Figure 7.6.

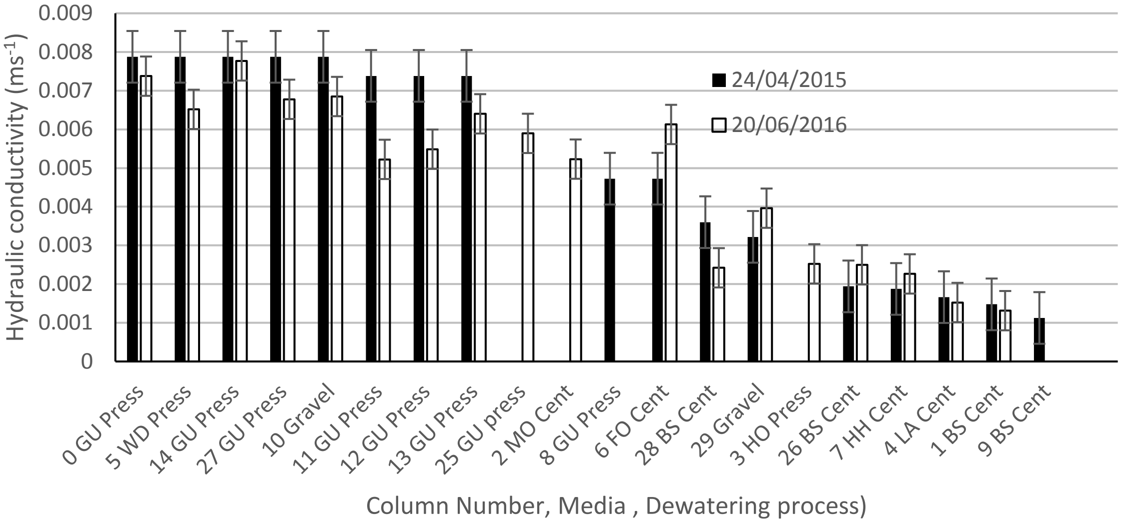


Figure 7.6 Hydraulic conductivity of 20 columns at University rig measured at start and end of the experiments.
In order of hydraulic conductivity as measured at start of experiments (error bars show standard error).

The results clearly demonstrate that the columns containing pressed media had a higher starting hydraulic conductivity than those containing centrifuged media. The majority of the columns showed a fall in hydraulic conductivity over the course of the experiments with a maximum fall of 26%, and the highest falls occurred in the two columns operating at the lowest contact times (i.e. they had the largest amount of water passing through them) As there was effectively no SS entering the systems this implies that the hydraulic conductivity was either being reduced by chemical precipitants blocking the columns or the water flow causing movement of the smaller media particles into the available void space. As there was no evidence of precipitates on the surface of the media when the DWTR was removed from the columns at the end of the experiments, it is most likely that the hydraulic conductivity was being reduced by the breakdown of the media.

A few of the columns containing centrifuged media showed an increase in hydraulic conductivity which was unexpected and may have been caused by channelling within the media. The average hydraulic conductivity of the pressed and centrifuged media at the start and end of the experiments are shown in Table 7.2.

Table 7.2 Average hydraulic conductivities of pressed and centrifuged media measured on University site before and after experiments.

Hydraulic Conductivity ms^{-1} of media in situ on University site						
	April 2015			June 2016		
Dewatering process/Gravel	**Press**	**Centrifuge**	**Gravel**	**Press**	**Centrifuge**	**Gravel**
Average Std. Dev.	0.0073 ±0.0011	0.0023 ±0.0013	0.0055 ±0.0033	0.0055 ±0.0015	0.0030 ±0.0015	0.0049 ±0.0013
Min	0.0047	0.0011	0.0032	0.0032	0.0015	0.0040
Max	0.0079	0.0047	0.0079	0.0078	0.0061	0.0058

The centrifuged sludge started with a conductivity which was on average 68% of the pressed sludge but this difference reduced to 46% by the end of the experiments. This implies that although the centrifuged sludge had a lower porosity at the beginning of the experiments the rate at which the conductivity decreased was slower than that for the pressed sludges. Therefore it is likely that the larger pore space available in the pressed media allowed for more movement of the smaller loose particles present in the DWTR. It is notable that the average hydraulic conductivity of the pressed media was still greater than the gravel at the end of the experiments.

7.3.1.2 Hydraulic conductivity measurements at the real waste water site

The hydraulic conductivity of the five columns at the real waste site were measured at the start, after 84 days and at the end of operation. The measured values are shown in Figure 7.7.

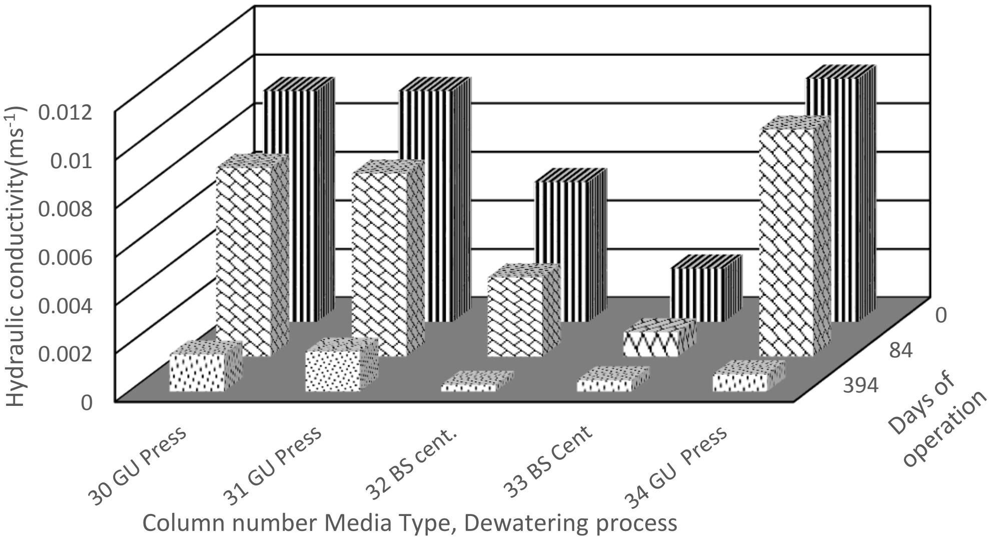


Figure 7.7 Change in hydraulic conductivity in the real waste water columns

All of the columns showed a substantial fall in hydraulic conductivity over the course of the year with levels dropping by between 83 and 92%. As with the University columns the centrifuged media started with a lower hydraulic conductivity than the pressed media, however the fall in HC was reasonably constant between all media. The drop in hydraulic conductivity was 4 to 5 times greater in the RWW columns than at the University and this would imply that the SS in the RWW was blocking the columns.

7.3.1.3 Hydraulic conductivity of meso scale beds

No measurements of hydraulic conductivity could be made on the meso scale beds, but observations of the flow rate out of the beds would indicate the hydraulic conductivity had not decreased as much as in the column systems.

7.3.1.4 Predicting the fall in hydraulic conductivity

When plotting the change in hydraulic conductivity against time for the RWW columns (Figure 7.8), the drop in hydraulic conductivity showed surprising linearity with R^2 values of >0.98 for the GU media (see Table 7.3).

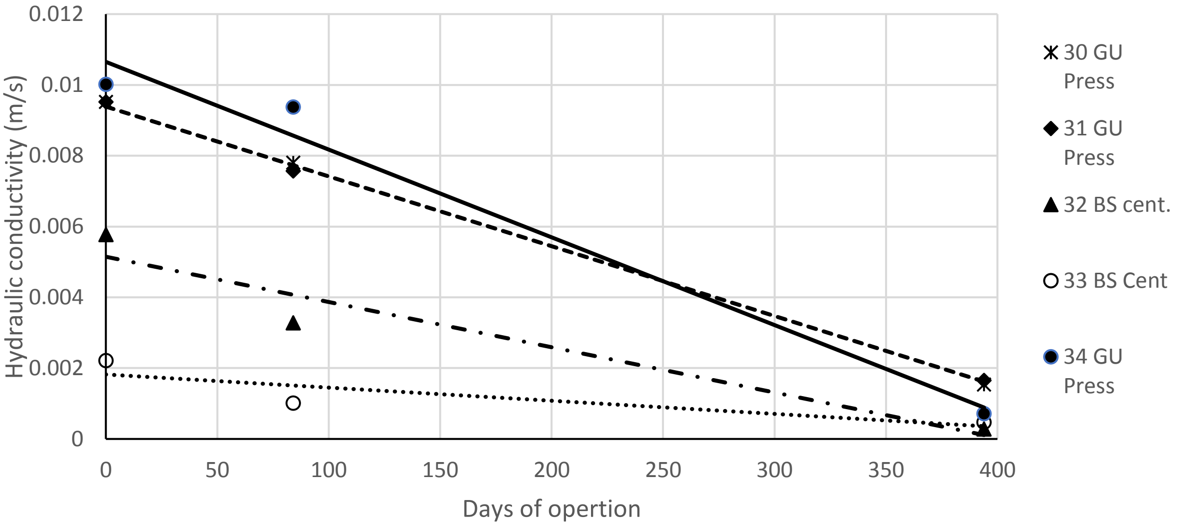


Figure 7.8 Linearized Hydraulic conductivity for real waste water column models

The gradient of the linear regression lines in Figure 7.8 represents the fall in hydraulic conductivity over time in $ms^{-1}d^{-1}$. Although drawing conclusions from a 3 point data set is limited, the values provide a useful estimate of the predicted drop in hydraulic conductivity. By using the gradient it is possible to predict when the hydraulic conductivity will not be high enough to allow time for the system to drain between loading periods which would be somewhere in the order of $1*10^{-4}$ m/s. The average rate of decrease in hydraulic conductivity was calculated as $2.11x10^{-5}$ $ms^{-1}d^{-1}$. Assuming the loss of hydraulic conductivity remained linear, the columns would have been effectively blocked after 500 days of operation.

Table 7.3 Linearized coefficients from RWW Hydraulic conductivity test

Linerised regression factors and fit for RWW model columns		
Column Number	R^2	Gradient ($ms^{-1}d^{-1}$) ± Standard Error
30	0.999	-2.02E-05 ± 4.70E-08
31	0.998	-1.97E-05 ± 7.29E-07
32	0.931	-1.97E-05 ± 3.48E-06
33	0.741	-3.71E-06 ± 2.19E-06
34	0.98	-2.48E-05 ± 3.53E-06
Average (Excluding 33)		-2.11E-05 ± 1.95E-06

Although the columns may have been blocked after 500 days of operation this does not imply that an operational system would become blocked so quickly as all of the SS loaded into the columns had to pass through the relatively narrow entrance meaning there was a very high load of SSm^{-2} as shown in Table 7.1 The SS inevitably collected on the gravel surface on top of the columns and as time progressed more and more of the void space within the top gravel would have been filled with SS. As the measurement of hydraulic conductivity involves sealing the columns and pushing water through from the top to the bottom; a thin layer blocking the surface of the columns would reduce the hydraulic conductivity of the whole system even if the remainder of the columns remained very porous. Thus by carefully designing inlet structures to spread the inlet load of SS, hydraulic life expectancy could be greatly increased.

7.4 Summary and Conclusion

The RWW columns did not prove to be good at removing SS with four of the columns leaching rather than removing SS. However, it may be that the columns are removing the SS in the top layers of the column while releasing small particles of DWTR into the outlet, and this was evident from the large particles that were present in the outlet from the columns. However the meso scale beds removed around 40% of the SS entering the system, most probably because of the much lower unit area loading rate and the much lower internal flow rate when draining down the beds.

The University site showed a much smaller reduction in hydraulic conductivity than the RWW systems and this is most likely due to the high SS levels in the RWW. However, the RWW column systems had very high loading rates of SSm^{-2} due to their small diameter, which probably reduced the hydraulic conductivity of the columns much faster than in the meso scale beds.

Therefore, to lengthen the hydraulic life of a full scale bed system they would ideally be used as a tertiary treatment process where inlet SS would be at a minimum. However, if the beds must have a high input SS then the inlet area to the system should be maximised.

The University and RWW columns showed substantial media washout if the internal flow speed was above 1m/min. Therefore the outlet of the system should be flow controlled to keep the internal flow rate <1m/min.

Chapter 8. Results of kinetic and particle size experiments.

8.1 Introduction

This chapter details the results from two distinct experiments.

1. The effect of particle size on; P adsorption and P adsorption kinetics
2. The change in kinetics of P adsorption within two columns over the course of a year.

The results of the two experiments have been included in the same section as the same theoretical analysis was used in both investigations.

The literature revealed that the bulk particle size could have a large effect on the ability of DWTR to remove P (Yang et al., 2006a, Lee et al., 2015). The experiments and results discussed in Section 4.4.2 showed that the 8 DWTR used in these experiments had a broad spread of particle sizes, and this led to the hypothesis that the particle size may have a greater effect on P removal than the chemical properties of the DWTR. To quantify the nature and strength of this effect a series of experiments was undertaken to assess how much P would be removed when particle size was controlled. The experiments were designed not only to elucidate how much P different sized DWTR could adsorb but also to assess how particle size effected the kinetics of adsorption.

The literature search revealed that although many studies have assessed the kinetics of P removal by DWTR (Babatunde et al., 2009, Yang et al., 2006b). No studies have observed how the kinetics changes over time. A change in the length of time it takes for the P to be removed from the waste water can elucidate not only how long the retention time needs to be to maximise P removal, but can also help in the understanding of how the P removal pathways may change over time. Therefore an experiment was designed to assess how the kinetics of P removal changed over the course of the year long experiments.

8.2 Experiments on the effect of DWTR particle size

The experimental procedure used to assess the effect of particle size were detailed in Section 3.10. In brief a ferric(BS) and alum(WD) media were air dried and graded into 4 particle sizes 20-6, 6-2, 2-0.6, <0.6mm. 10g of the media were shaken for up to 96 hours in water dosed with 6 concentrations of STP 1000, 500, 100, 50, 10 and 5 mgL^{-1}. Small samples were taken out at regular intervals to assess how percentage P removal changed over time.

8.2.1 Percentage phosphorus removal

Results for the 4 different particle sizes at the 6 different initial concentrations of STP are shown in Figure 8.1. For operational reasons the experiments that used a concentration of 1000mgL^{-1}STP were only equilibrated for 6 hours, all others were shaken for a minimum of 24 hours.

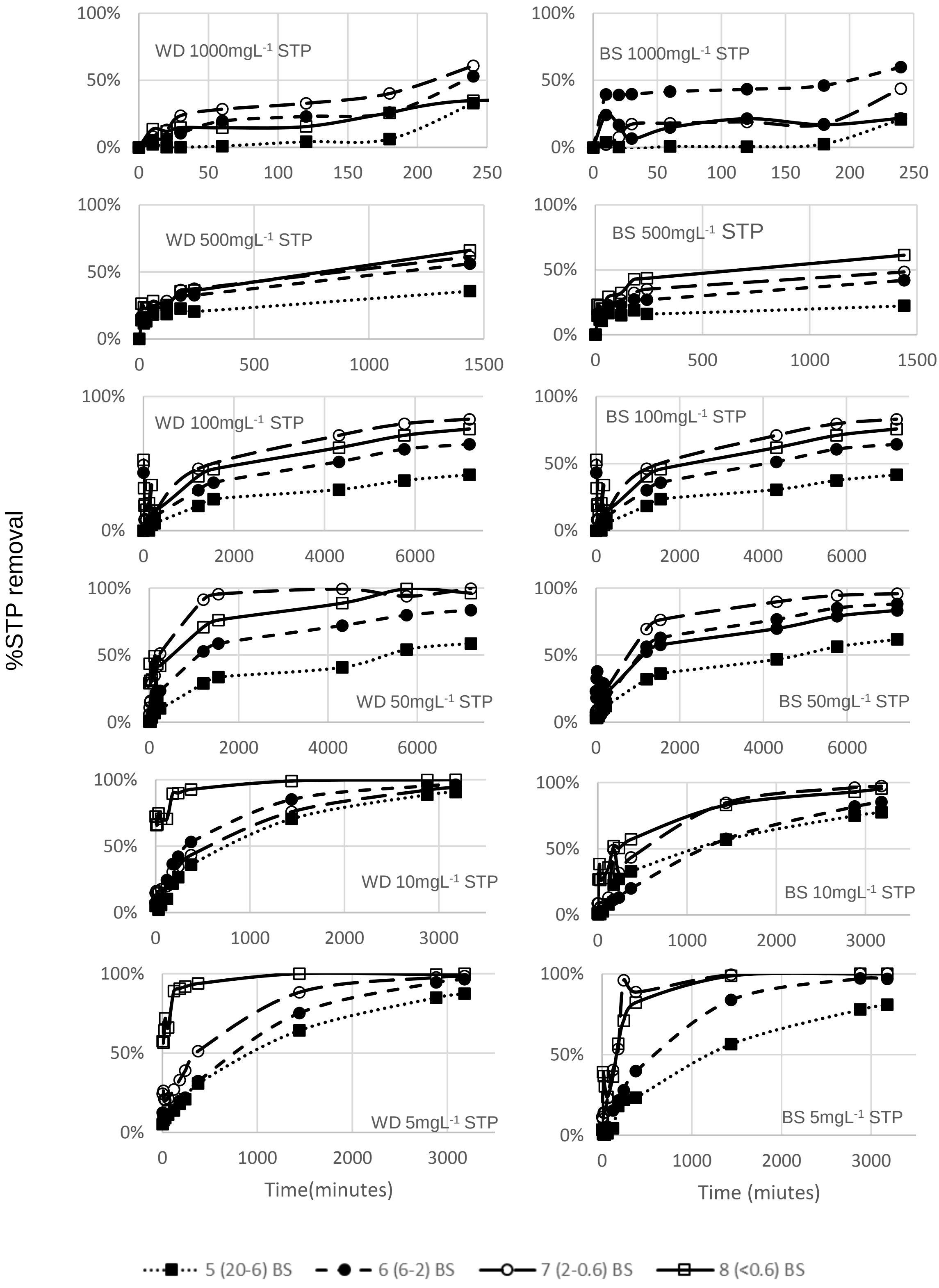


Figure 8.1 Percentage removal of STP against time in minutes for 4 different media sizes (20-6, 6-2, 2-0.6, <0.6mm), 2 media (WD and BS) at 6 inlet concentrations (1000, 500, 100, 50, 10 and 5mgL^{-1} STP)

All the results show a clear trend, with the larger particle sizes removing substantially less P from solution, especially over the first 4 or 5 hours. At concentrations of <10mgL^{-1} STP all the particle sizes smaller than 2 mm removed very close to 100% of P in solution after 2 days of operation, and these were the only experiments in which equilibrium was reached.

At concentrations of P of <10mgL^{-1} STP the WD media with size range<0.6mm removed over 90% of the P in the first three hours, whereas the BS media took nearly 24 hours to reach similar levels. Also at the lower concentrations all media with particle size of <6mm tended to remove close to 100% of the P present after two days, but the media of size 20-6mm only removed approximately 80% of the P after 2.5 days.

From these experiments it is clear that media size has a substantial effect (>50%) on the ability of DWTR to remove P from solution, but that effect changes greatly over time. To assess the nature of that change kinetic analysis of the data was undertaken.

8.2.2 Kinetic modelling of the particle size experiments

In order to examine the mechanism of the adsorption process the adsorption rate data was analysed using three models. The pseudo first order (PFO) (Lagergren, 1898, Yuh-Shan, 2004), the pseudo second order (PSO) (Ho and McKay, 1999), and the intra particle diffusion (Weber and Morris, 1963). It is generally proposed that the PFO kinetic model indicates physisorption; whereas data fitting a PSO model implies chemisorption (Das et al., 2014). If the data fits the intra particle diffusion model then intraparticle diffusion will be the rate limiting step of the adsorption process. To calculate the constants required for the various models, the kinetic equations needed to be rearranged into a linear form. By manipulating the experimental data to fit the linear forms of the equations, constants for the models can then be found from the slope and intercept of the graphs produced. The linearized forms of the three equations and required plots are shown in Table 8.1.

Table 8.1 Kinetic models used for analysis with their linearized forms

Kinetic model	Formula	Linear Form	Plot
PFO	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	$\log(q_e - q_t)\ vs\ t$
PSO	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	$\frac{t}{q_t}\ vs\ t$
Intra-particle	$q_t = f(t^{0.5})$	$q_t = k_p t^{0.5}$	$q_t\ vs\ t^{\frac{1}{2}}$

[The variables have been previously defined in Section 2.4.3.1]

Once the constants have been calculated, a model of the system can be constructed using non-linear forms of the equations. The non-linear forms of the PFO and PSO used for the analysis are shown in equation 8.1 and 8.2, respectively (Lin and Wang, 2009).

$$\boldsymbol{q_t = q_e\left(1 - e^{-k_1 t}\right)}$$ ***Equation 8.1***

$$\boldsymbol{q_t = \frac{k_2\, q_e^2\, t}{1 + k_2 q_e t}}$$ ***Equation 8.2***

8.2.2.1 Model fits

Due to the inherent bias resulting from linearization, three different error functions were used to help ascertain the best fitting model, the correlation coefficient R^2 (Equation 8.3) was used to assess the fit of the linearized data, whereas the sum of the square of the errors SSE (Equation 8.4) and normalised standard deviation NSD (Equation 6.5) were used to assess the fit of the kinetic models produced by the PFO and PSO.

$$\boldsymbol{R^2 = \frac{\sum\left(q_{t,calc} - \bar{q}_{t,exp}\right)^2}{\sum\left(q_{t,calc} - \bar{q}_{t,exp}\right)^2 + \sum\left(q_{t,calc} - q_{t,exp}\right)^2}}$$ ***Equation 8.3***

Where $q_{t,calc}$ = Concentration at time t calculated from model
q_{exp} = Measured concentration at time t

$$SSE = \sum_{i=1}^{n} \left(q_{e,calc} - q_{e,exp}\right)_i^2 \qquad \textbf{Equation 8.4}$$

$$NSD = \sqrt{\frac{\sum\left[\left(q_{t,exp} - q_{t,cal}\right)/q_{t,exp}\right]^2}{(n-1)}} \qquad \textbf{Equation 8.5}$$

Where n = number of data points.

8.2.2.2 Linearized kinetic models

An example of the linearized results for the pseudo first, second order and intraparticle model for 4 particle sizes with an inlet concentration of 50mgL^{-1} STP are shown in Figure 8.2. The data shown in Figure 8.2 are representative of the many results produced.

The PFO and PSO show reasonably good fits to the majority of the data and the R^2 values for all the fitted graphs are shown in Table 8.2 to 8.4. For the intraparticle diffusion model to represent a good fit to the data it should show a strong linear relationship with the a straight line passing through the origin (Babatunde and Zhao, 2010). For concentrations below 500mgL^{-1}STP the data from the largest particle size fitted this pattern well (Table 8.4), implying that intraparticle diffusion is the rate limiting step for the larger particle sizes.

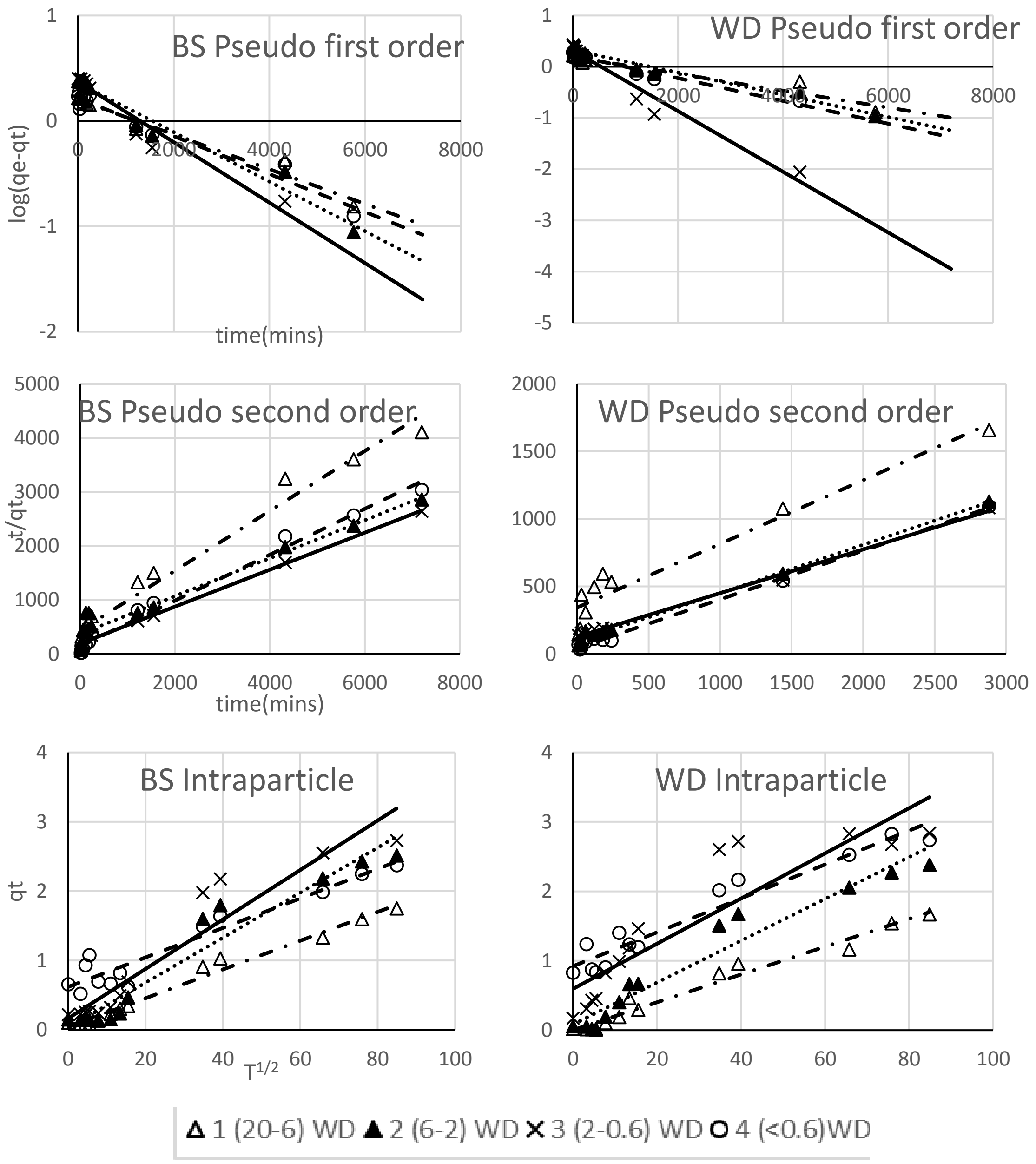


Figure 8.2 Linearized plots for WD and BS media, with 4 particle sizes at inlet concentration of 50mgL^{-1}

8.2.2.3 Non-linearized models

The PFO and PSO models constructed using the constants calculated from the Figure 8.2 using the non-linear forms of the PFO and PSO are shown in Figure 8.3. Models were produced for all concentrations, Figure 8.3 is typical of the majority of the results produced.

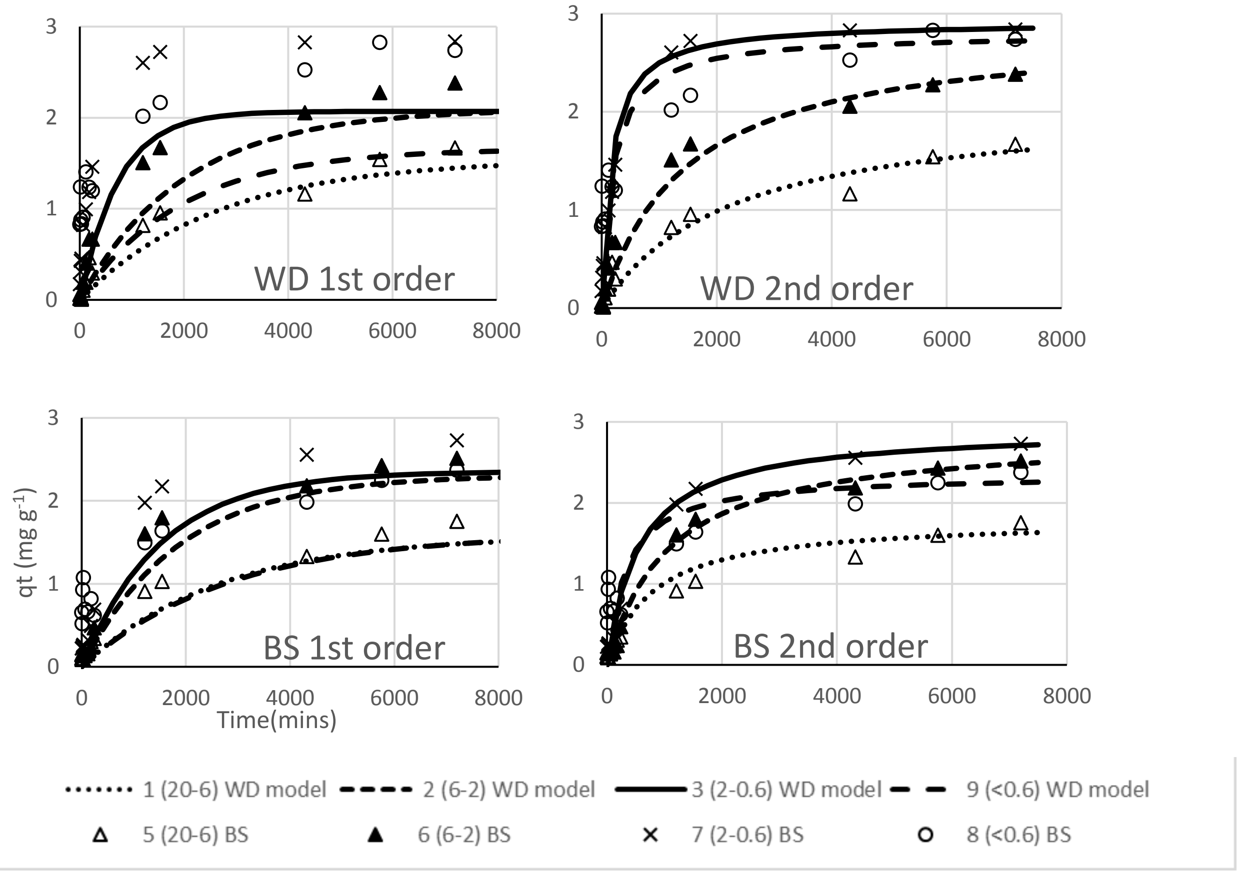


Figure 8.3 PFO and PSO non linearized models and experimental data for 4 different particle sizes at 50mgL^{-1} concentration.

Generally the PSO shows a much better fit to the data than the PFO model. However, it is notable that the PFO tends to fit the larger particle sizes better than the smaller sizes. The constants and errors produced from all the models are shown in Table 8.2 to 8.4.

The maximum equilibrium adsorption capacity obtained for the 20-6mm and <0.6mm was 0.57-0.649 and 0.267-0.315mg g^{-1} for the WD media at 5 and 10mgL^{-1}, respectively. This represents a 17% drop in maximum achievable adsorption capacity with the larger media, and this effect is confounded when contact time is taken into account with the second order model predicting that after 6 hours the media <0.6mm will have adsorbed over 3 times as much P as the larger particle sizes although, this reduces to nearer 2 after 12 hours and 1.4 after 24 hours. ..

WD Media(alum)													
Inlet P conc. (mgL^{-1})		**Pseudo First Order**						**Pseudo Second Order**					
	Particle Size (mm)	**qe_{CALC} (mg g^{-1})**	**qe_{EXP} (mg g^{-1})**	**k_1 X 10^{-2} (min^{-1})**	**R^2**	**SSE**	**NSD**	**qe_{CALC} (mg g^{-1})**	**qe_{EXP} (mg g^{-1})**	**K_2 X 10^{-2} (g mg^{-1} min^{-1})**	**R^2**	**SSE**	**NSD**
1000	20-6	18.643	18.320	0.123	0.967	23.152	2.870	-1.221	18.320	0.344	0.526	42.123	0.592
	6-2	26.854	29.395	0.366	0.896	12.202	0.309	36.175	29.395	0.017	0.605	11.457	0.236
	2-0.6	28.854	33.690	0.544	0.902	110.593	0.745	38.286	33.690	0.031	0.857	8.885	0.172
	<0.6	27.602	31.390	0.298	0.854	14.914	0.561	34.497	31.390	0.017	0.526	12.038	0.484
500	20-6	7.285	10.285	0.289	0.666	9.832	0.745	10.717	10.285	0.111	0.986	2.180	0.391
	6-2	13.127	16.195	0.316	0.879	10.499	0.640	17.182	16.195	0.053	0.987	2.807	0.356
	2-0.6	14.563	17.700	0.350	0.898	11.027	0.609	18.779	17.700	0.050	0.990	2.772	0.331
	<0.6	13.896	19.090	0.217	0.611	29.899	0.763	20.165	19.090	0.044	0.974	10.142	0.480
100	20-6	2.062	2.188	0.034	0.918	0.046	0.652	2.208	2.188	0.059	0.962	0.029	0.390
	6-2	3.333	3.523	0.044	0.915	0.126	0.592	3.700	3.523	0.038	0.991	0.021	0.189
	2-0.6	4.682	5.086	0.063	0.981	0.203	0.555	5.447	5.086	0.031	0.998	1.039	0.148
	<0.6	3.006	5.300	-0.006	0.014	5.126	1.080	4.700	5.300	0.204	0.921	1.457	0.464
50	20-6	1.548	1.669	0.038	0.924	0.031	0.543	2.106	1.669	0.021	0.695	0.014	0.709
	6-2	2.097	2.382	0.050	0.967	0.105	0.534	2.868	2.382	0.024	0.844	0.026	0.722
	2-0.6	2.069	2.838	0.136	0.963	0.749	0.697	2.916	2.838	0.206	0.999	0.025	0.226
	<0.6	1.660	2.739	0.051	0.946	1.178	0.819	2.796	2.739	0.180	0.995	0.239	0.416
10	20-6	0.567	0.570	0.127	0.989	0.000	0.391	0.718	0.570	0.163	0.841	0.000	0.431
	6-2	0.569	0.626	0.156	0.995	0.004	0.453	0.694	0.626	0.402	0.973	0.001	0.368
	2-0.6	0.537	0.613	0.124	0.991	0.007	0.582	0.640	0.613	0.518	0.970	0.003	0.391
	<0.6	0.142	0.649	0.066	0.090	0.252	1.005	0.653	0.649	6.743	1.000	0.028	0.227
5	20-6	0.260	0.267	0.117	0.982	0.000	0.461	0.291	0.267	0.657	0.919	0.000	0.411
	6-2	0.296	0.304	0.126	0.985	0.000	0.458	0.340	0.304	0.535	0.900	0.001	0.451
	2-0.6	0.257	0.306	0.157	0.996	0.003	0.583	0.324	0.306	1.259	0.979	0.001	0.405
	<0.6	0.072	0.315	0.135	0.799	0.055	0.961	0.316	0.315	18.798	1.000	0.003	0.143

Table 8.2 ***Pseudo first and second order constants and fits for WD media***

BS Media(ferric)													
Inlet P conc. (mgL^{-1})		**Pseudo First Order**						**Pseudo Second Order**					
	Particle Size (mm)	**qe$_{CALC}$ (mg g^{-1})**	**qe$_{EXP}$ (mg g^{-1})**	**k$_1$ X 10^{-2} (min^{-1})**	**R^2**	**SSE**	**NSD**	**qe$_{CALC}$ (mg g^{-1})**	**qe$_{EXP}$ (mg g^{-1})**	**K$_2$ X 10^{-2} (g mg^{-1} min^{-1})**	**R^2**	**SSE**	**NSD**
1000	20-6	11.810	11.585	0.068	0.621	12.221	1.063	13.793	11.585	0.004	0.002	16.951	1.096
	6-2	15.753	33.100	0.476	0.440	365.218	0.920	31.372	33.100	0.198	0.958	19.590	0.224
	2-0.6	20.297	24.235	0.263	0.501	90.332	0.919	25.641	24.235	0.029	0.445	14.816	0.415
	<0.6	7.592	15.745	0.259	0.131	33.757	0.612	16.304	15.745	0.099	0.002	20.713	0.473
500	20-6	3.339	6.385	0.440	0.472	9.427	0.856	6.508	6.385	0.401	0.996	1.400	0.333
	6-2	8.662	12.075	0.346	0.774	12.694	0.763	12.554	12.075	0.106	0.992	2.410	0.352
	2-0.6	11.057	13.940	0.466	0.892	9.236	0.641	14.568	13.940	0.091	0.996	1.687	0.293
	<0.6	13.365	17.675	0.439	0.879	20.513	0.689	18.405	17.675	0.076	0.995	4.191	0.331
100	20-6	2.169	2.200	0.037	0.967	0.017	2.723	4.090	2.200	0.004	0.032	0.025	2.270
	6-2	2.941	3.411	0.042	0.851	0.506	0.715	3.499	3.411	0.042	0.883	0.493	1.238
	2-0.6	3.802	4.405	0.049	0.922	1.042	0.642	4.802	4.405	0.024	0.944	1.323	0.722
	<0.6	2.899	2.430	0.035	0.491	4.169	0.894	2.477	2.430	0.322	0.934	3.193	0.574
50	20-6	1.585	1.754	0.038	0.966	0.037	0.631	1.804	1.754	0.071	0.975	0.011	0.312
	6-2	2.310	2.515	0.054	0.968	0.055	0.492	2.847	2.515	0.033	0.954	0.010	0.487
	2-0.6	2.355	2.729	0.066	0.950	0.530	0.624	2.920	2.729	0.061	0.987	0.020	0.448
	<0.6	1.604	2.373	0.036	0.908	0.620	0.808	2.355	2.373	0.129	0.986	0.197	0.508
10	20-6	0.478	0.487	0.114	0.983	0.001	1.294	1.167	0.487	0.024	0.107	0.003	0.697
	6-2	0.605	0.554	0.109	0.981	0.003	4.039	0.251	0.554	-0.417	0.394	0.028	1.421
	2-0.6	0.597	0.632	0.151	0.989	0.003	0.395	0.760	0.632	0.219	0.897	0.002	0.445
	<0.6	0.438	0.604	0.118	0.977	0.035	0.782	0.621	0.604	1.155	0.992	0.006	0.384
5	20-6	0.254	0.570	0.110	0.981	0.101	0.879	0.258	0.247	0.111	0.006	0.002	0.692
	6-2	0.303	0.640	0.139	0.999	0.114	0.852	0.400	0.305	0.294	0.932	0.000	0.266
	2-0.6	0.217	0.650	0.360	0.820	0.167	0.862	0.329	0.311	2.200	0.995	0.001	0.232
	<0.6	0.233	0.650	0.291	0.973	0.170	0.884	0.328	0.315	2.714	0.995	0.002	0.415

Table 8.3 Pseudo first and second order constants and fits for BS media

Table 8.4 Intraparticle constants and fits for BS and WD media

Inlet P conc. (mgL^{-1})		**WD Media**			**BS Media**	
		Intraparticle				
	Particle Size (mm)	K_p	R^2		K_p	R^2
1000	20-6	0.837	0.517		0.056	0.027
	6-2	1.624	0.862		-0.288	0.082
	2-0.6	1.955	0.942		0.013	0.000
	<0.6	0.782	0.934		0.286	0.432
500	20-6	0.225	0.841		0.118	0.544
	6-2	0.389	0.926		0.268	0.833
	2-0.6	0.431	0.915		0.332	0.837
	<0.6	0.414	0.873		0.404	0.822
100	20-6	0.025	0.995		0.028	0.979
	6-2	0.044	0.974		0.037	0.739
	2-0.6	0.065	0.965		0.049	0.790
	<0.6	0.067	0.782		0.025	0.279
50	20-6	0.020	0.971		0.021	0.984
	6-2	0.030	0.946		0.032	0.944
	2-0.6	0.033	0.813		0.023	0.444
	<0.6	0.024	0.934		0.021	0.923
10	20-6	0.011	0.979		0.008	0.713
	6-2	0.011	0.945		0.009	0.766
	2-0.6	0.010	0.983		0.010	0.644
	<0.6	0.004	0.713		0.007	0.480
5	20-6	0.005	0.991		0.005	0.980
	6-2	0.005	0.972		0.006	0.973
	2-0.6	0.005	0.957		0.005	0.697
	<0.6	0.002	0.631		0.005	0.782

Error analysis of the non-linear form of the PSO and PFO models shows that for the majority of the experiments the PSO fits the data better than the PFO. The calculated NSD of the error for both media types for the PFO and PSO models is shown graphically in Figure 8.4 A and B. As discussed in section 2.4.3 data fitting the PSO is generally thought to imply that chemisorption is the dominating adsorption process.

The PFO kinetic constant K_1 varied between (0.466 - 0.035) and (0.544 – 0.034) for the BS and WD media, respectively. The constant showed no clear trend in variation, although the values tended to be slightly higher for the WD than BS media. The values for the PSO constant K_2 are shown graphically in Figure 8.5.

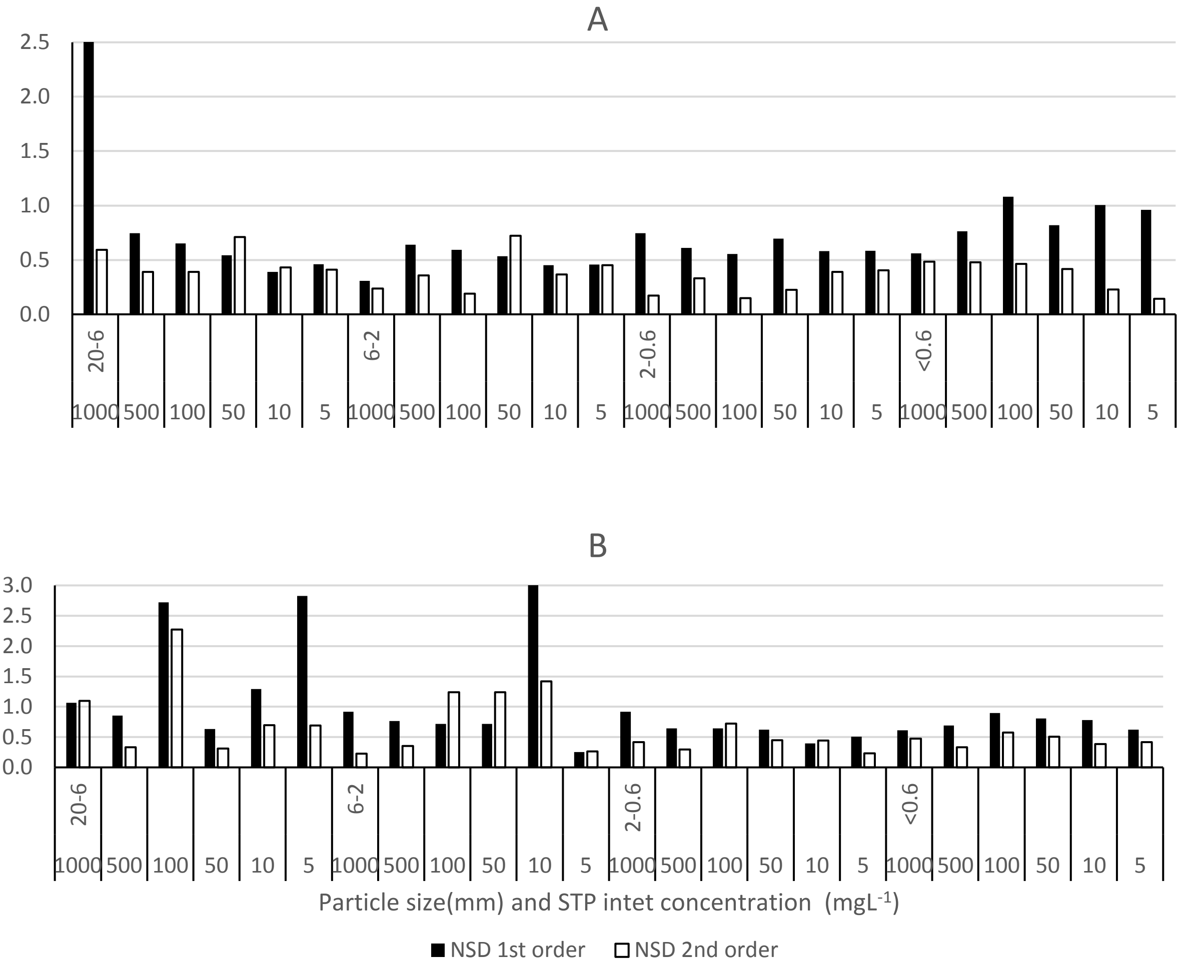
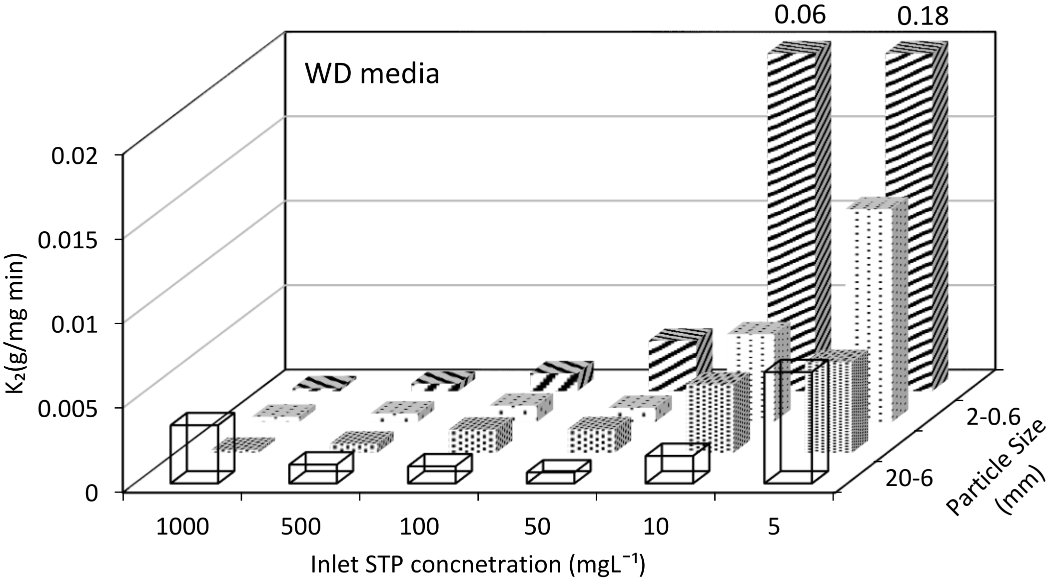


Figure 8.4 NSD error data for PFO and PSO kinetic models for A) WD and B) BS media.



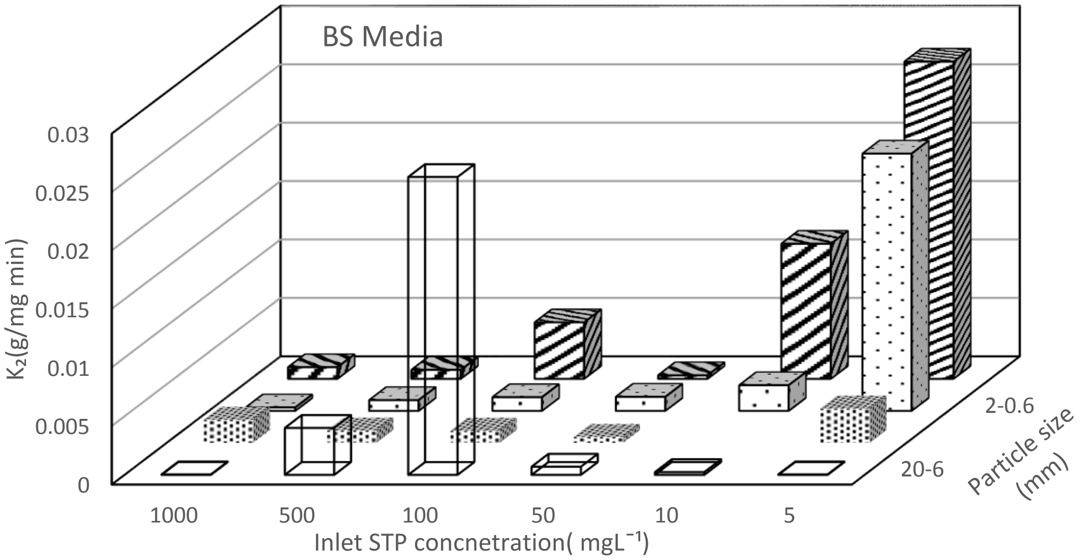


Figure 8.5 K_2 constants for Pseudo Second order kinetic model for WD and BS media with 4 different particle sizes at 6 initial inlet concentrations

The PSO constant K_2 shows a very clear trend of increasing as both the inlet concentration and the particle size are reduced. The trend is clearer in the WD media and there is a big increase in the constant for the particle size<0.6mm at concentrations of both 5 and 10mgL^{-1} STP. Note this could not be accommodated on the graph because it was so much bigger. The increase in the constant as the particle size is decreased is not surprising as the available surface area for adsorption is greatly increased. However, the increase of the constant as the inlet concentration is reduced is an interesting result. Babatunde and Zhao (2010) investigated the effect of inlet concentration on the second order rate constant and also found that the rate constant increased as the inlet concentration was reduced.

The K_2 constant dictates the shape of the curve when plotting the amount of P adsorbed per gram of media over time (as shown in Figure 8.3), with the higher the value of K_2 the steeper the initial part of the curve and the faster the majority of the P is removed. However, the calculation of K_2 is related to the concentration of P and the relative mass of media present. Therefore although at lower inlet concentrations the removal rate is much faster the relative amount of P adsorbed is greatly reduced. The equilibrium concentration (q_e) at an inlet of 1000mgL^{-1} was approximately 16 and 31mg g^{-1} for the BS and WD media, respectively compared with 0.3 mgg^{-1} for both media with an inlet of 5mgL^{-1} STP. These results therefore imply that the mass of media present compared to the concentration of P has a greater effect on the kinetic removal rate than the P concentration gradient across the media.

8.2.3 Modelling the effect of particle size at low inlet concentration

The models of the columns at the University all operated with an inlet concentration of 5mgL^{-1} TP and with a 6 hour retention time. By plotting the percentage of P removal achieved after 6 hours, and fitting the data to a curve using Excel an expression can be produced which provides a basic model for the effect of particles size in the columns operating at the University. The results are shown in Figure 8.6. This model is used in Chapter 9 to normalise the outlet data in relation to particle size.

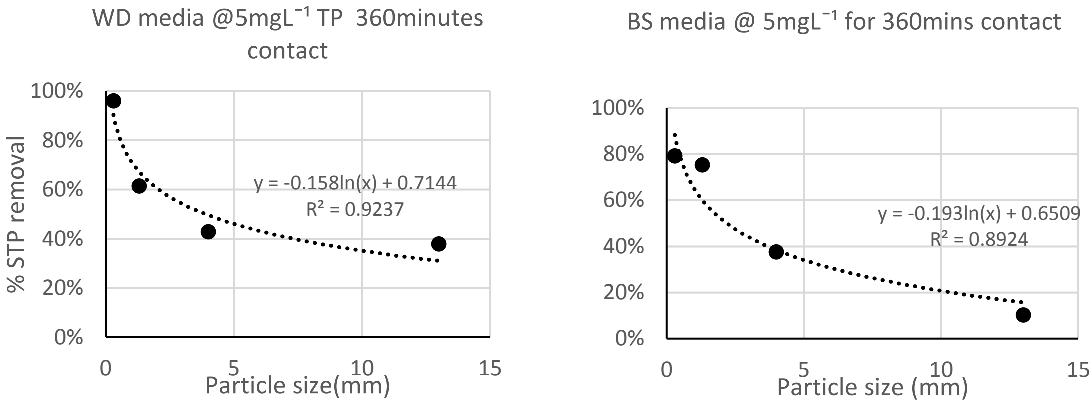


Figure 8.6 Effect of media particle size on adsorption of STP after 6 hours contact with inlet STP of 5mgL^{-1}

8.2.4 Isotherm adsorption models from particle size experiments

The data from the particle size experiments was also analysed using both the Langmuir and Freundlich isotherm models which were discussed in Section 2.4.2. The isotherms can be linearized and constants calculated by plotting the experimental data as for the kinetic models. The linearized forms and required plots are shown in Table 8.5.

Table 8.5 Linearized forms of the Freundlich and Langmuir equations and required plots. [The constants have been previously defined]

Isotherm	Formula	Linear Form	Plot
Langmuir	$q_e = \dfrac{q_m K_l L}{1 + bC_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m} C_e + \dfrac{1}{q_t b}$	$\dfrac{C_e}{q_e}\ Vs\ C_e$
Freundlich	$q_e \ = K_F C_e^{1/n}$	$Log\ q_e = \log K_F + \dfrac{1}{n} \log C_e$	$\log q_e\ vs \log C_e$

The non-linearized Langmuir and Freundlich models plotted against the experimental data are shown in Figure 8.7.

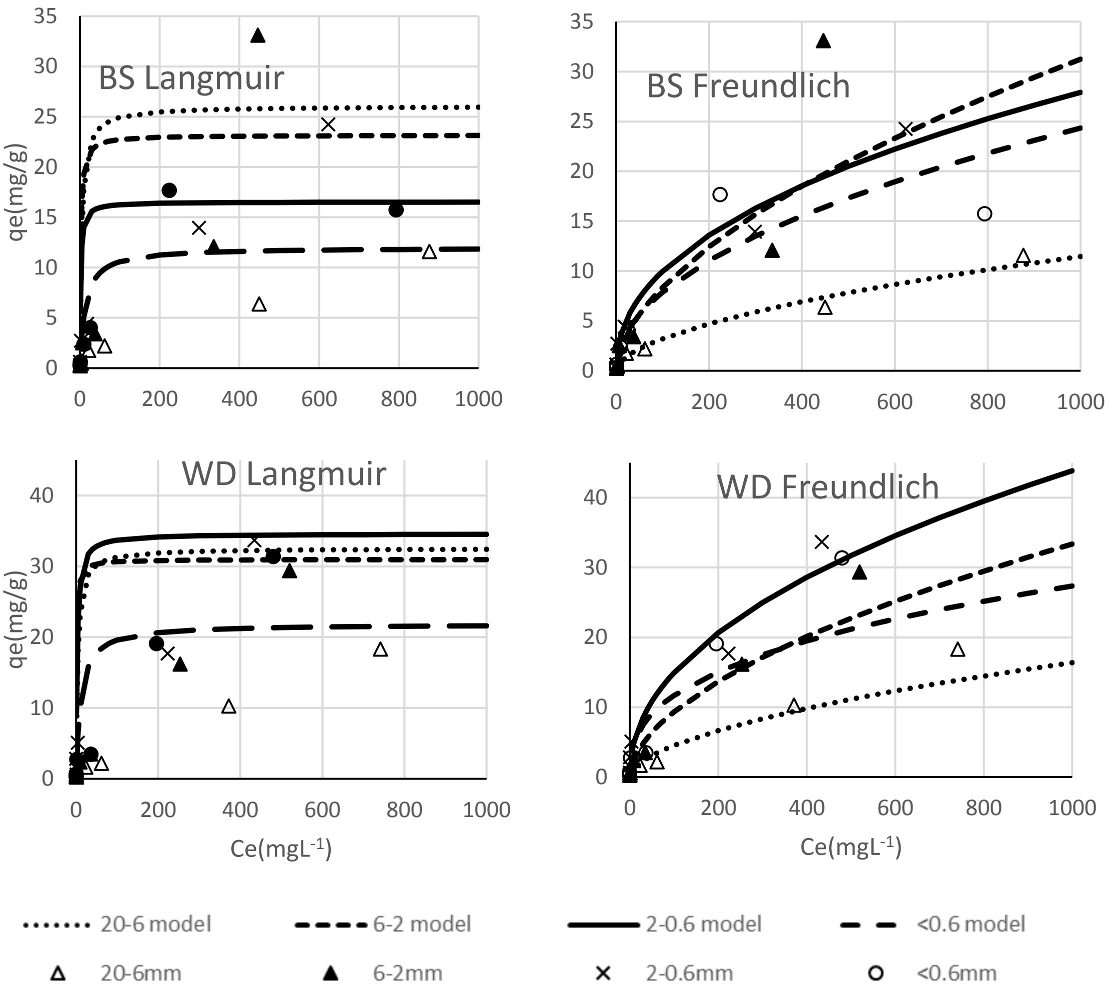


Figure 8.7 Model vs real data for Langmuir and Freundlich isotherms

Constructing isotherms from the particle size data has limitations because only very few of the experiments reached full equilibrium and only 6 data points were available for each model. However, it was clear from the models that as for the kinetic analysis, the largest particle size 20-6mm has a very negative effect on the maximum amount of P that could be adsorbed at all inlet concentrations. The data from the models is summarised in Table 8.6.

The Freundlich model fits the linearized data much better than the Langmuir models with the majority of the R^2 values below 0.9 for the Langmuir model and above 0.9 for the Freundlich model. This is in agreement with most other researchers and is not surprising as the Langmuir model does not take account of the heterogeneous nature of the adsorption sites available on the DWTR.

Table 8.6 Langmuir and Freundlich constants and R^2 values for BS and WD media with 4 different particle sizes

Langmuir and Freundlich Parameters for WD and BS media at 4 different particle sizes					
	Particle size(mm)	20-6	6-2	2-0.6	<0.6
BS Langmuir	K_L (L mg^{-1})	0.075	0.219	0.501	0.558
	q_m (mg g^{-1})	11.999	26.067	23.182	16.541
	R^2	0.859	0.569	0.908	0.987
WD Langmuir	K_L (L mg^{-1})	0.087	0.253	0.916	0.371
	q_m (mg g^{-1})	21.846	32.536	30.986	34.613
	R^2	0.681	0.761	0.871	0.692
BS Freundlich	n	1.811	1.747	2.239	2.041
	K_f (mg g^{-1})(L mg^{-1})$^{1/n}$	0.253	0.599	1.276	0.824
	R^2	0.989	0.944	0.972	0.964
	% K_f compared to <0.6mm	31%	73%	155%	100%
WD Freundlich	n	1.788	1.809	2.141	2.704
	K_f (mg g^{-1})(L mg^{-1})$^{1/n}$	0.344	0.733	1.741	2.125
	R^2	0.962	0.982	0.823	0.901
	% K_f compared to <0.6mm	16%	34%	82%	100%

The Freundlich K_f constant is related to the bonding energy of the media and 1/n is a heterogeneity factor ranging between 0 and 1, becoming more heterogeneous as its value becomes closer to zero (Al-Tahmazi, 2016). The value of n is greater than 1 in all cases which indicates that P adsorption on DWTR is heterogeneous. The Freundlich K_f constant falls with increasing particle size (apart for the 2-0.6mm in the BS media) thus the media exhibit higher affinity for P binding with smaller particle sizes. The WD media shows a marked fall in K_f value when particle size is <2mm with the K_f value for particle sizes of 20-6 and 6-2mm being only 16 and 34% of the value of the particle size<0.6mm. This further demonstrates the large effect particle size has on P adsorption.

8.2.4.4 Concluding remarks on Particle size experiments

Particle size has a large effect on both removal kinetics and maximum adsorption capacity of the media. The final equilibrium capacity of the media was found to be approximately 17% smaller for both alum and ferric media with a 10mgL^{-1} STP inlet concentration when particle size is increased from <0.6 to 20-6mm after 4 days of shaking. This effect was greatly enhanced when kinetics were taken into consideration. The kinetic models show that the smaller particle size range (<0.6mm) remove over 3 times more P after 6 hours, 2 times after 12 hours and 1.5 times more after 24hours when compared to particles of 6-20mm.

8.3 The change in phosphorus adsorption kinetics over the experimental period

The kinetics of the P removal from two of the columns at the University were assessed approximately bi-monthly as detailed in Section 3.9. The results from the two column plotted as percentage STP removal against time are shown in Figure 8.8.

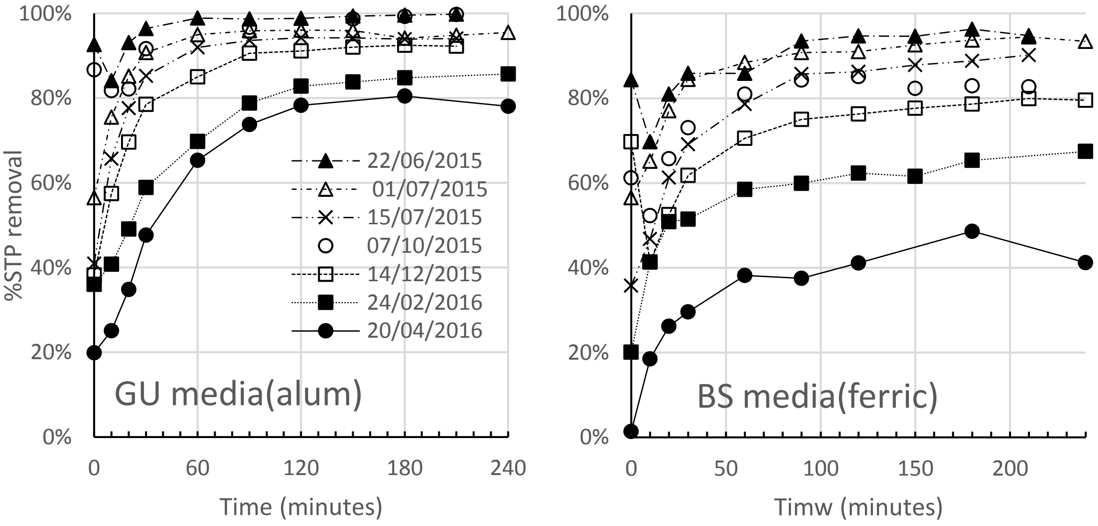


Figure 8.8 Variation in percentage removal of STP over 6 hour loading period measured in two of the columns at the University over a period of 10 months.

Both the columns showed a similar reduction in performance over the 10 months of monitoring. The GU and BS columns removed 100 and 96% of the P load at the start of the measuring period and this reduced to 80 and 52% towards the end of the year. Equilibrium was reached after approximately 30 and 90 minutes (for the GU and BS) columns, respectively at the start of the year and that increased to 3 and 4 hours by the end of the year.

It is interesting to note that for the first few measuring periods over 90% of the P was removed by both media almost instantaneously. After 10 minutes both columns then showed a fall in removal performance by between 10 and 14%. This is effect is most likely explained by the sampling procedure. The sampling outlets were one third of the way up the columns and were left open during the column loading cycle, the first sample was taken as soon as water came out of the sample tap. Initially the P loaded water would have filtered through to the bottom of the column before rising up to the sample point giving it access to a relatively large volume of media that had just been through a 6 hour resting period. This effect was not seen after the first four months as the media became more saturated with P and the easily accessible surface sites became less available.

8.3.1 Pseudo First and second order kinetic models

Although both media showed the expected two stage kinetic curves at the start of the experiments. (A fast initial removal caused by surface interactions followed by a slower longer removal period as the P moves into the interstitial spaces of the media.) After the first six months the rate of initial removal was greatly decreased and the curves were tending towards a more linear removal rate. To further analyse this effect, the curves were modelled using pseudo first and second order models as discussed in Section 8.2.2 the constants and R^2 values from this analysis are summarised in Table 8.7.

Pseudo first and second order constants and error values for BS and GU media

	Date	22/06/15	01/07/15	15/07/15	07/10/15	14/12/15	24/02/16	20/04/16
	Operational days	11	20	34	118	186	258	314
	Bed volumes passed	22	40	68	236	372	516	628
PFO	K_1(min^{-1})	0.023	0.015	0.033	0.018	0.034	0.017	0.012
GU	Qe mod.(mg g^{-1})*10^{-2}	0.48	0.67	1.60	1.81	3.07	2.70	2.33
	Qe exp.(mg g^{-1})*10^{-2}	5.56	5.37	5.50	5.33	5.93	5.07	5.05
	R^2	0.8466	0.5726	0.8924	0.4636	0.9853	0.9729	0.7428
	NSD	0.994	0.975	0.807	0.837	0.593	0.632	0.706
PFO	K_1(min^{-1})	0.041	0.019	0.020	0.030	0.016	0.014	0.008
BS	Qe mod.(mg g^{-1})*10^{-2}	1.59	1.51	2.56	1.32	1.65	1.65	1.30
	Qe exp.(mg g^{-1})*10^{-2}	5.34	5.26	5.27	4.41	5.14	3.92	2.73
	R^2	0.7969	0.9494	0.9742	0.9243	0.8682	0.8977	0.3320
	NSD	0.786	0.844	0.668	0.805	0.818	0.745	0.694
PSO	K_2(g mg^{-1} min^{-1})	203	158	64	70	33	17	12
GU	Qe mod.(mg g^{-1})* 10^{-2}	5.62	5.39	5.59	5.37	6.08	5.32	5.26
	Qe exp.(mg g^{-1})* 10^{-2}	5.56	5.37	5.50	5.33	5.93	5.07	5.05
	R^2	0.9999	0.9998	0.9996	0.9998	0.9992	0.9912	0.9955
	NSD	0.033	0.054	0.058	0.036	0.051	0.106	0.163
PSO	K_2(g mg^{-1} min^{-1})	53.3	51.1	23.1	68.6	23.2	30.5	24.7
BS	Qe mod.(mg g^{-1})* 10^{-2}	5.46	5.35	5.42	4.52	5.28	3.99	3.00
	Qe exp.(mg g^{-1})* 10^{-2}	5.34	5.26	5.27	4.41	5.14	3.92	2.73
	R^2	0.9992	0.9996	0.9982	0.9989	0.9987	0.9979	0.9802
	NSD	0.028	0.030	0.053	0.091	0.055	0.047	0.072

Table 8.7 Pseudo first and second order constants and error values for BS and GU media

The data shows a poor fit for first order kinetics with R^2 ranging from 0.46-0.98 and 0.32-0.97 for GU and BS media, respectively whereas both media show an excellent fit to second order kinetics with all R^2 values being greater than 0.98 for both media. The second order rate constant K_2 varied between 203 -12 and 53 - 24 mg g^{-1} min^{-1} for the GU and BS media, respectively. The rate constants are between 100 and 1000 times bigger than those found in the laboratory experiments on particle size. The K_2 levels found in the particle size experiments agree with most other studies found in the literature. However all studies use small quantities of sludge shaken in containers as per my experiments. A few studies have used small scale columns and found results as high as 2.5 mg $g^{-1}min^{-1}$ (Song et al., 2011, Martins et al., 2017). However, a search of the literature reveals no other studies assessing PSO kinetics in larger scale systems. The high value for the K_2 results can be ascribed to the very large amount of media present in comparison to the volume of water treated which represented a proportional increase of approximately 30 times in my study. i.e. the ratio of media to water treated was around 30 times bigger in the columns than in the particle size experiments.

The models constructed using the non-linear PSO equation in comparison to the initial and final experimental results are shown in Figure 8.9.

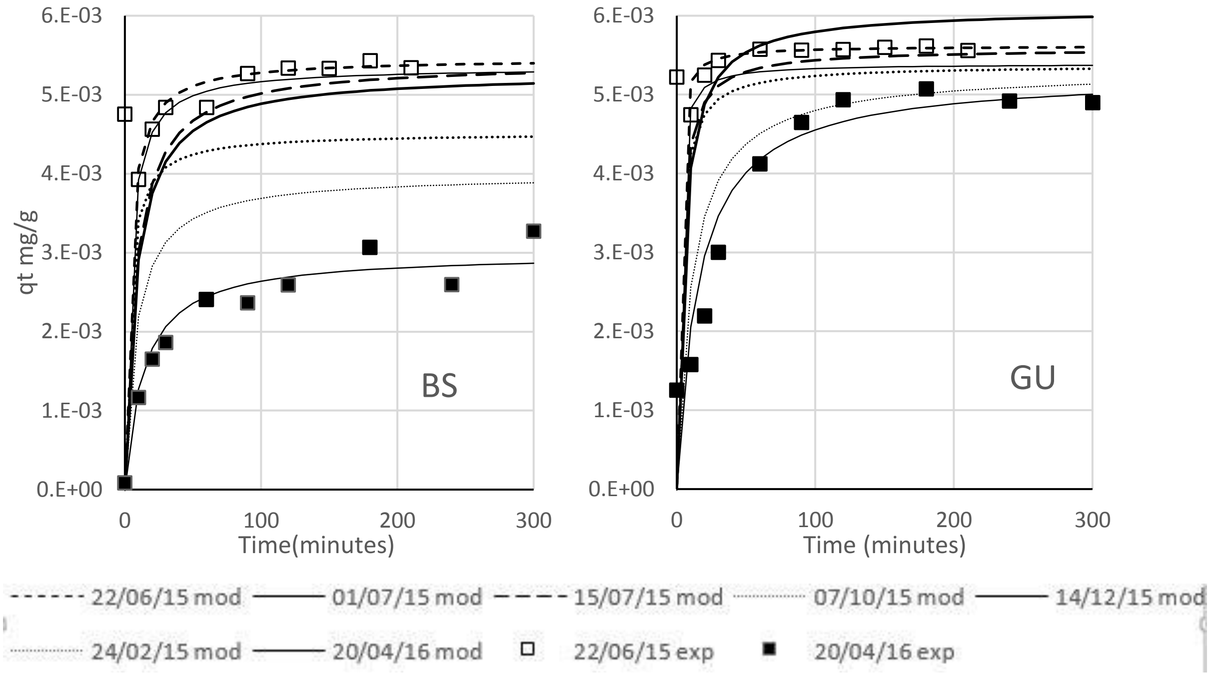


Figure 8.9 Comparison between model and experimental kinetic data for 2 columns measured over 10 months.

The models show a very good fit to the data with NSD error ranging between 0.163-0.033 and 0.028-0.072 for the GU and BS media, respectively. The models therefore fitted the BS media better and the fits tended to worsen for the results produced in the latter half of the year. Interestingly the model does not show an orderly progression of reducing kinetic rate during the first half of the year with the curves crossing at varies points, however during the second half of the year the decline in rate seems to stabilise. To elucidate this further plots of the PSO rate constant K_2 against operational time in days are shown in Figure 8.10.

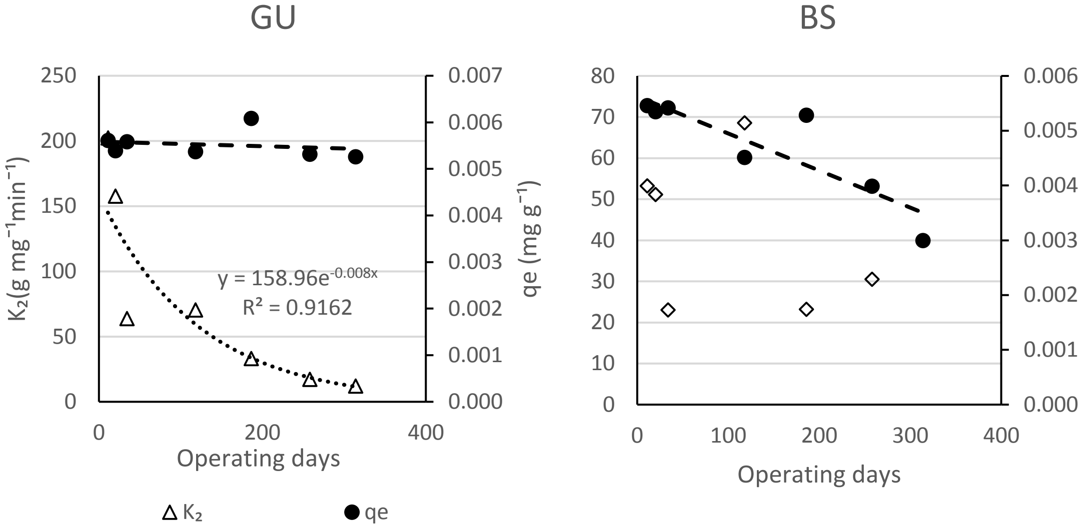


Figure 8.10 Change in second order kinetic rate k_2 and q_e over 10 months operating 2 columns.

The change in K_2 shows a clear exponential decrease over time for the GU media with R^2 of 0.9162, although no such trend was apparent with the BS media.

At the end of the year the GU and BS media were reaching equilibrium in similar timescales of 2 to 3 hours, however the equilibrium P concentration of the BS media was approximately 30% lower than the GU media (Figure 8.10). Therefore, although the K_2 factor did not show a large drop in the BS media the available adsorption sites had greatly reduced so equilibrium could be reached faster. In the GU media there were still a lot of adsorption sites available but these were harder to access thus the K_2 constant had to reduce (this is discussed in Section 9.3). To ascertain how the change in adsorption occurred the data was also analysed using the intraparticle model as discussed below.

8.3.2 Intraparticle diffusion model

To show how the mechanisms of P removal changed over time the kinetic data from the two columns was analysed using the intraparticle model as shown in Table 8.1. As previously discussed for the intraparticle diffusion model to represent a good fit to the data it should show a strong linear relationship with a straight line passing through the origin. If the data shows a good fit to this model intraparticle diffusion is most likely to be the rate limiting step. The data was analysed using the intraparticle model and the results of the R^2 error and value of the intersection with the y axis are plotted against the time of the experiments in Figure 8.11 A and B. The results clearly demonstrate that for both systems the intercept approached closer to 0 as the systems aged and for the GU media the model also became a more linear fit. This implies that as the systems age and the easily accessible surface sites are used up, intraparticle diffusion becomes the rate limiting step.

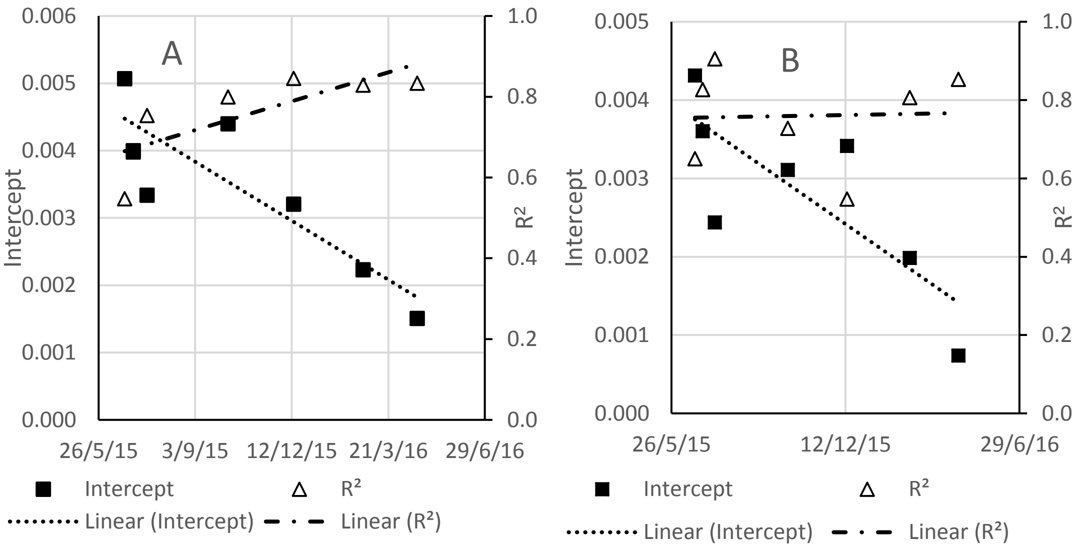


Figure 8.11 Change in R^2 error and intersect when using intraparticle model on kinetic data from A) alum (GU) media B) ferric (BS) media

8.4 Kinetics of Real Waste Water Systems

Five attempts were made to measure the P removal kinetics at the RWW site. However due to experimental complications (most probably because of cross contamination between samples) only one useable data set was obtained. One data set from two columns containing BS and GU media after 302 days of operation and one set from the two meso scale beds after 282 days of operation. The data was modelled using the PSO and PFO and the results from the analysis are shown in Table 8.8. As for all the other systems, the data showed a much better fit to the PSO rate equation.

Table 8.8 Constants from 1st and 2nd order kinetic analysis of real waste water systems.

Pseudo first and second order constants and error values for BS and GU media					
		Columns		Meso Scale Beds	
Column/Bed No. Media Type.		C32, BS	C30, GU	Bed1, HO	Bed2,GU
Operational days		302	302	282	282
Pseudo 1st order GU	K_1(min^{-1})	0.0116	0.0124	0.0048	0.0063
	Qe calc.(mg g^{-1})*10^{-2}	0.0260	0.2575	0.0772	0.0771
	Qe exp.(mg g^{-1})*10^{-2}	0.0697	0.5306	0.3250	0.2972
	R^2	0.4710	0.9534	0.1191	0.1883
Pseudo 2ndorder	K_2(g mg^{-1} min^{-1})	103	17	41	84
	Qe calc.(mg g^{-1})* 10^{-2}	0.071	0.536	0.319	0.294
	Qe exp.(mg g^{-1})* 10^{-2}	0.070	0.531	0.325	0.297
	R^2	0.980	0.991	0.995	0.998

The models produced from the PSO equation and the experimental data are shown in Figure 8.12.

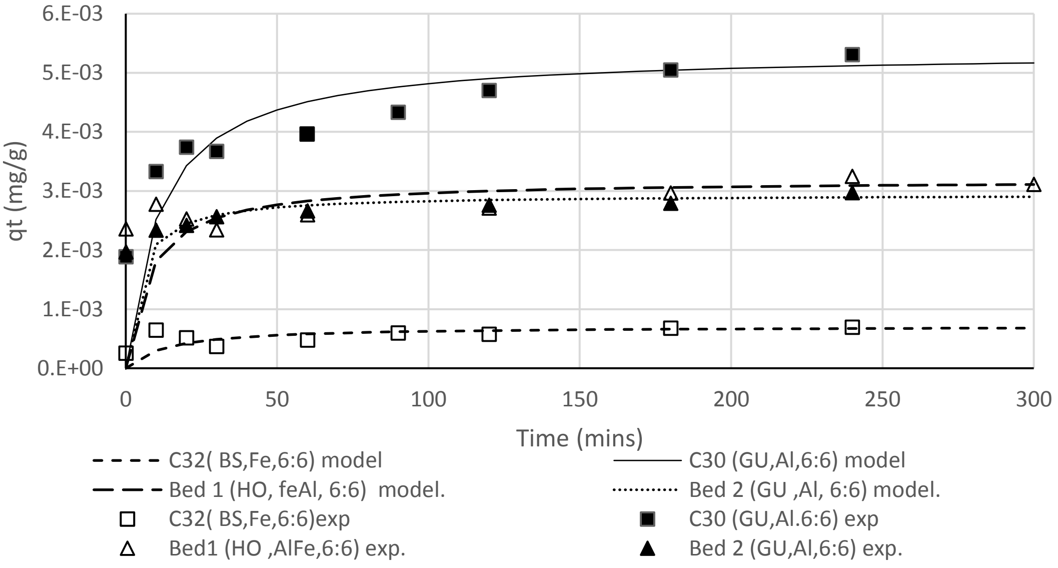


Figure 8.12 PSO model and experimental results for two columns and two beds at the RWW site after approximately 300 days of operation.

All the RWW systems monitored reached equilibrium between approximately one and three hours with the majority of the P being removed after the first 30 minutes. Modelling of the two meso scale beds revealed faster kinetics for bed 2 containing the GU media with K_2 values of 84 compared to 41g mg^{-1} min^{-1} for bed1. This is an interesting result with a doubling of the kinetic constant implying that the GU media removes the P much faster than the HO media, although on analysis of the graph this equates to just a few minutes of difference before equilibrium. An equivalent result was found when comparing the GU and BS columns with the GU media having a much larger K_2 103 versus 17. However, it must be noted that column 32 containing GU media had many operational problems as discussed in section 5.2.2.3.

8.4.1 Comparing the kinetics of the columns and particle size experiments.

It is interesting to compare the results from the particle size experiments, the column kinetic experiments at the University and those undertaken at the RWW site. The comparisons are shown graphically in Figure 8.13 A and B.

In Figure 8.13A the PSO models produced for columns loaded with RWW are compared with similar columns at the University that were loaded with synthetic P dosed water after approximately 300 days of operation. It is fascinating to note that the kinetic removal of the two columns containing GU media was almost identical with the two models almost perfectly overlaying each other. The BS models did not show similar performance with the RWW having a much greater negative effect on the BS media, although as previously noted C32 never operated correctly.

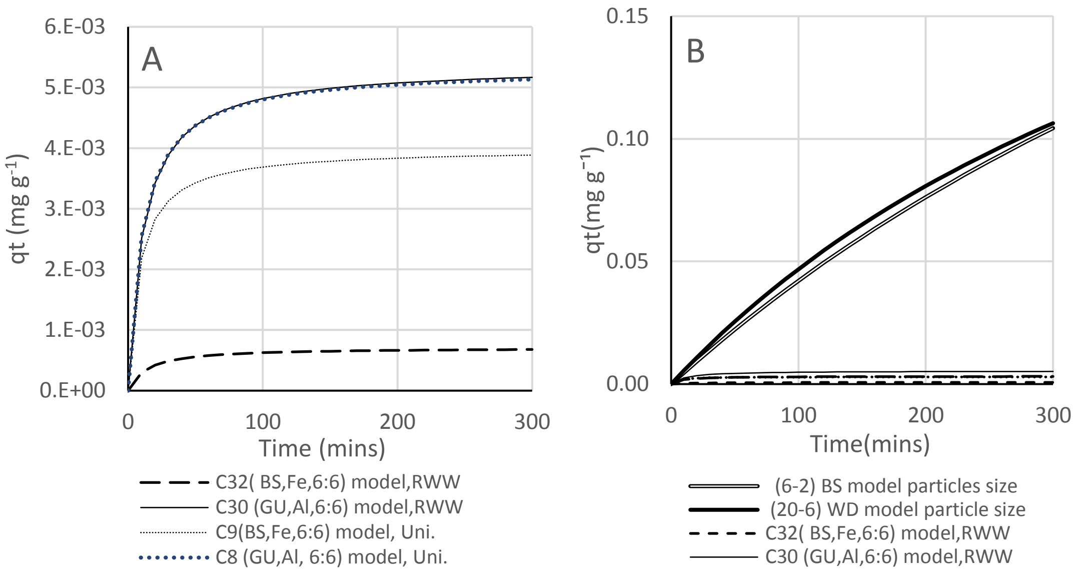


Figure 8.13 Comparison of PSO models A) between similar columns at the University and RWW site after 300 days of operation B) between Particle size experiments and RWW columns.

A final comparison can be made between the columns and the experimental results obtained from the particle size experiments which is shown in Figure 8.13B. The solid lines on the graph show two representative results from the particle size experiments. The particle size experiments operate at a range of q_t almost 100 fold greater than the column experiments. This clearly shows how laboratory experiments using new media that is shaken in a P containing solution produce very different results than those from operational systems. It is therefore important that data from any such experiments is carefully validated before it is used in any designed system.

8.5 Conclusion of ancillary experimental results

Increasing the particles size of the DWTR from 0.6 to 20mm was shown to reduce P adsorption of the media by up to 17% when left to equilibrate for up to 4 days, but at low concentrations(<10mgL^{-1}TP) and short retention times <3 hours the reducing effect could increase to over 50%.

The rate at which P was removed from all the systems showed a typical biphasic curve with very fast removal during the first 30 minutes followed by a long period in which it is suggested that the P moves into the intraparticle pores of the media.

During the year of operation the biphasic shape of the curve tended to linearize with the first fast stage taking up to 90 minutes by the end of the year. The kinetic data fitted the intraparticle model more closely as the systems aged suggesting that intraparticle diffusion becomes the rate limiting step as the DWTR become more saturated.

The second order kinetic constants for the operating columns were found to be over 100 times bigger than those often reported in the literature, and to those calculated for the particles size experiments. This discrepancy is likely because the ratio of media to water was much larger in the column experiments, but also because the relative amount of P adsorbed per gram of media per minute is over 100 times smaller in the operating columns when compared to the average batch scale laboratory experiment.

Chapter 9 Discussion

9.1 Introduction

This chapter brings together all the findings from the previous chapters in an attempt to synthesise it to inform our knowledge and understanding of the use of DWTR for P removal. This is then used to provide engineering design recommendations for the practical application of DWTR in a full scale P removal system.

9.2 What makes a DWTR good at removing phosphorus?

The experimental work showed that the DWTR from the 8 treatment works each removed very different quantities of P. These findings are discussed in light of previous research. In addition, to calculate if any of the physio-chemical properties of the media, or the inlet water quality parameters, or chemicals dosed in the production process, could be correlated with the ability of the 8 DWTR to remove P; a statistical analysis of the data was undertaken using SPSS. The data produced from both the column experiments (Chapter 5) and physio-chemical analysis of the media and raw water (Chapter 4) were compared with the average percentage P removal achieved by the columns at the University, using correlation analysis, multiple linear regression and rotated principle component analysis.

9.2.1 Physical and chemical properties of the media and phosphorus removal

This section discusses the correlation between the physical and chemical properties of the media.

9.2.1.1 Fe and Al content of the media and phosphorus removal

All previous studies agree that the major P retention mechanism in DWTR is phosphate sorption involving ligand exchange with Fe and Al hydroxides which are present in large quantities in DWTR (Dayton et al., 2003, Ippolito et al., 2011, Makris et al., 2005b, Yang et al., 2006b, Klimeski et al., 2012). It is therefore logical to conclude that the quantities of Al and Fe present in the media may be related to its ability to remove P. Although such relationships have been found in the past, most noticeably by Dayton et al (2003), in this research no correlation was found between the content of Al, Fe, Fe_{ox} and Al_{ox} and the average percentage removal of P from the media at the 90% confidence level. Many other studies have also found no relationship between metal content and P removal in agreement with this research (Al-Tahmazi and Babatunde, 2016, Makris et al., 2005a, Leader et al., 2008). The reason for this conflict in the findings between different research groups is most likely because in Dayton et al's (2003) research, comparisons were made between the Al and Fe content of the media and the maximum mono layer adsorption capacity (q_m) as calculated from the Langmuir equation. However, as has been shown in chapter 5 the q_m value is likely to represent a large over prediction of the adsorption capacity that can be achieved in a tidal flow system with low inlet P concentrations (See Figure 5.19). Similar results have been found by many other research groups (Drizo et al., 2002, Makris and Harris, 2006) .

The reason for the discrepancy may be explained further by assessing basic stoichiometry of P adsorption. The highest adsorption capacity of the media found in this research was 7.7 mgP g^{-1}_{media}, and the average quantity of Fe and Al in the media was 231 and 109 mg g^{-1}_{media} for the ferric and alum based media, respectively. The atomic masses of P, Al and Fe are 31, 27 and 55, respectively. Assuming that one phosphate ion can be adsorbed by one Fe or Al ion, about 1g of Al could adsorb 1g of P, whereas, 2g of Fe would be required to adsorb 1g of P. Thus at low inlet concentrations, less than one tenth of the Al or Fe contained within the media needs to be available for surface adsorption to remove P. As the P inlet concentration is increased the ratio of available metal surface sites to P will be greatly reduced. Hence the amount of Fe or Al in the media is more likely to be correlated to the amount of P that can be adsorbed, and the Langmuir q_m value.

9.2.1.2 TC in the media and phosphorus removal

Many authors have reported a possible link between the amount of carbon that is present in the DWTR and its ability to remove P (Oliver et al., 2011, Makris et al., 2005a, Wang et al., 2011, Al-Tahmazi and Babatunde, 2016). Wang et al (2011) proposed that the presence of organic carbon (OC) may inhibit the crystallization of amorphous Fe and Al and thus provide more adsorption sites for P. Al-Tahmazi et al (2016) suggested that the total carbon (TC) may provide additional ligand exchange sites for the phosphate ions.

In this research the amount of TC in the media was not correlated to its ability to remove P (at the 90% confidence level). Nonetheless, as can be seen from Figure 9.1, the media that consistently removed the most P (HH) contained considerably more TC than any other media, and the two worst performing media in this trial (BS and HO) contained the lowest quantities of TC. Although no statistically significant correlation was found, the sample size was small and there is building evidence within our research group that the presence of carbon in the media has strong influence on P removal. Al-Tahmazi has undertaken a substantial study (unpublished) of 4 of the DWTR used in this research in a flow through setting using an experimental technique discussed by Stoner et al (2012) and Lyngsie et al (2015). The study measured both the outlet concentration of P and TC from flow through cells and found a correlation between P removal and TC.

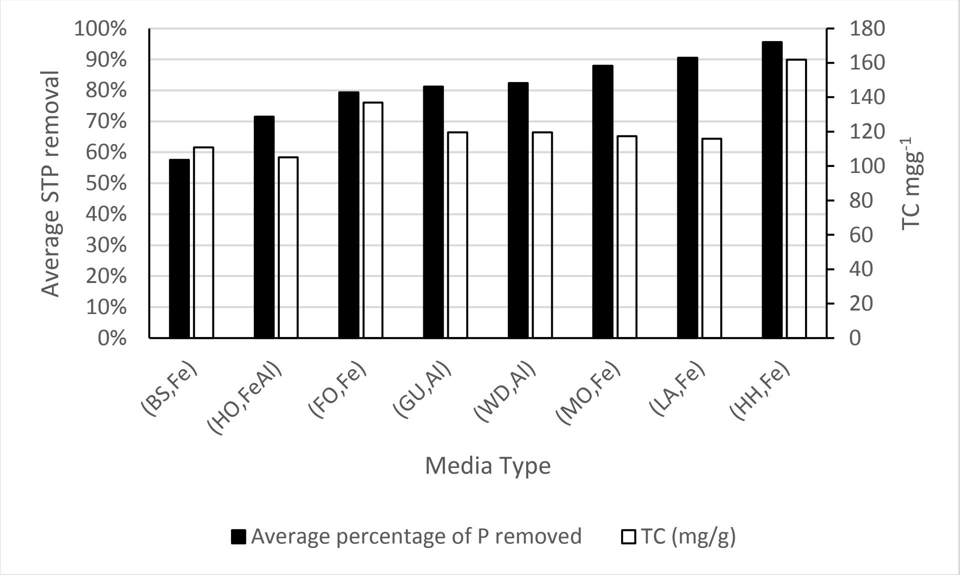


Figure 9.1: Comparison of TC content of the media and average % phosphorus removal

9.2.1.3 Media particle size and phosphorus removal

No direct correlations were found between the average particle size of the media and average percentage P removal in this research. This is a surprising result as both this study and studies by Wang et al (2011) and Yang et al (2006a) show that bulk particle size has a huge effect on P adsorption often with removal rates decreasing by over 50% as particle size is increased from <1mm to >4mm.

Bulk particle size of the media is affected by both the process used to make the media and the handling procedures associated with the movement of the media post processing. This means that there is inevitably heterogeneity in the bulk particle size of the media.

The measurement of the bulk particle size proved to be very complex and open to a high degree of error as discussed in Section 3.7.4. Thus the lack of correlation between particle size and P removal could be due to a lack of accurate measurement and/or the heterogeneity in the relatively small amounts of media used in the column experiments.

9.2.2 Correlations between phosphorus removal, raw water quality and coagulant dosed

Although no correlations were found in this work between the chemical makeup of the DWTR and its ability to remove P, there are interesting correlations between the measured parameters of the water entering the 8 treatment works, the amount of coagulant dosed and the P removal performance of the media. (Note the data used for the water quality parameters and coagulant dosed are averages of the previous year to the date of the experiments and the data was provided by Northumbrian Water and is shown in Tables 4.1 and 4.2). There was a very strong negative correlation between the average amount of coagulant added to the water, and the average amount of P removed from the media ($r=-.857$, $p>0.01$), and there was also a weaker negative correlation between the average turbidity of the water entering the treatment works and amount of P removed ($r=-.69, p<0.1$). Unsurprisingly, there was an identical but positive correlation between turbidity and coagulant dose $r=.69$, $p<0.1$, as the coagulant is often dosed in proportion to measured turbidity. These results imply that as more coagulant is dosed in the processing of the DWTR, its ability to remove P decreases, and further this would seem to imply that as the Al and Fe content of the media increases the P removal decreases. However, no correlation was found between the Fe and Al content of the media and the coagulant dosed. Reasons for this are outlined in section 9.2.2.1.

The implication of this result are either 1) there is a negative correlation between the amount of Fe or Al in the media and its ability to remove P, or 2) the addition of more coagulant is altering the properties of the media in a way that is unconducive to P removal. It seems very unlikely that there is a negative correlation between the amount of Al and Fe in the media and its ability to remove P as no other research has reported this. This research has clearly demonstrated that as bulk particle size increases P removal decreases. Although the particle size analysis had a high degree of error associated with it, there is a small but positive correlation at the 90% confidence level ($r=0.647$ $p<0.1$) between bulk particle size and coagulant dose. Thus, it is possible that as coagulant dose is increased the average bulk particle size increases and P removal decreases.

9.2.2.1 Coagulant dose and metals content

A surprising result from this study is that there was no correlation between the Al and Fe content and the amount of coagulant dosed as the Al and Fe content of the media must derive from the coagulant. The coagulants were dosed at an average rate of approximately 100mgL^{-1} across all the works and as both river and reservoir water feeding the 8 treatment works contain very low levels of Fe and Al (average of 295µg/l and 655µg/l for Al and Fe, respectively; data supplied by Northumbrian Water) the coagulant must supply the majority of the Al and Fe present in the DWTR. Although the data for the inlet feeds to the works was taken from the previous year's records, they remain relatively constant from year to year (personal communication Northumbrian Water operations management). This leaves three possibilities for the lack of correlation between metals content and coagulant dose:

1. On the day that the DWTR samples were taken for this experimental work cleaning operations had altered the average properties of the DWTR (no records for maintenance work were available)
2. The chemical analysis of the media requires very small quantities of DWTR and it was evident from the repeated experimental columns that even on the scale of kilograms the media is very heterogeneous in nature. Thus very careful sampling regimes would be required over days or weeks to provide a representative sample of the media.
3. The chemical process involved in the production of DWTR are highly complex and are not fully understood. It is therefore possible that an important process has been missed.

However, the most likely explanation for the lack of correlation between metal content and coagulant dose is the generically heterogeneous nature of the media. In reality the results of the average chemical analysis of the raw water feed to the works and chemicals dosed at the works are probably more representative of the average parameters associated with the properties of the DWTR and may provide a better guide to the ability of the DWTR to remove P.

9.2.3 Linear regression and principle component analysis (PCA)

9.2.3.1 Linear regression analysis

The previous section discussed simple correlations between P removal and various parameters of the media and raw water. To ascertain how the key physio chemical variables associated with the media may interact with each other, stepped linear regression analysis was undertaken. Thus average percentage P removal as the dependent variable was used in this study and the 28 measured physical and chemical parameters of the media and raw water were used as independent variables. The analysis revealed three significant factors; coagulant dose, TOC in the raw water and measured degree of saturation. Together the three parameters could explain over 99% of the variability in percentage P removal. The variables in the model could explain 70.4%, 22.2% and 6.5% of the percentage variation of P removal for coagulant dose, TOC (in raw water) and degree of saturation, respectively. The model reveals that the P removal of the media in the experiments carried out in this study was most effected by the coagulant dosed, the amount of organic carbon in the infeed water and how much water is available for movement between voids within the particles; with the coagulant dose being the most important parameter.

The result from the multiple linear regression is in agreement with the previous discussion regarding the major effect of carbon and coagulant dose, but adds an important factor associated with the physical makeup of the media. The degree of saturation of the media is associated with the processes used to make the media, as the pressed sludges tended to have a lower degree of saturation when compared to the centrifuged media. Therefore, using the linear regression model the centrifuged media would tend to perform slightly better at removing P than the pressed media, all other factors being equal.

9.2.3.1 Principal component analysis

Rotated principal component analysis is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. Thus it is possible to reduce the 28 variables associated with the physio-chemical properties of the media to four principle components or less. This method was used by Bai et al (2014) and Al-Tahmazi et al (2016). Both studies found that the most important component in regard to P removal is associated with the Fe and Al content of the media and the specific surface area (SSA). In this research, although the Al and Fe content of the media were collected in one component, the SSA was not. Different measuring techniques reveal very different results for the SSA of the media (See Table 4.5). Therefore, although it can be concluded that the media generally have high SSA compared to other natural waste products, the results are not reliable enough to be used in PCA analysis.

The PCA produces factor scores which were used in linear regression analysis with percentage P removal as the dependent variable. No significant models were found. The factor scores for the principal component model are shown in Appendix C. It is recommended that a minimum of 20 data sets should be used when using the technique of PCA. Hence the lack of statistically significant models from this research may have resulted from the use of only 8 data points (Field, 2013).

9.2.4 Normalising the phosphorus removal data to particle size

The previous discussion has mentioned the importance of particle size and drawn some links between the P removal and particle size. The P removal results produced from the 8 columns operating with different media can be normalised to the effect of particle size by using equation 6-6 and creating a normalisation factor dependent on the average particle size measured for the media as detailed in 4.5.2. The resulting normalised data is shown in Figure 9.2.

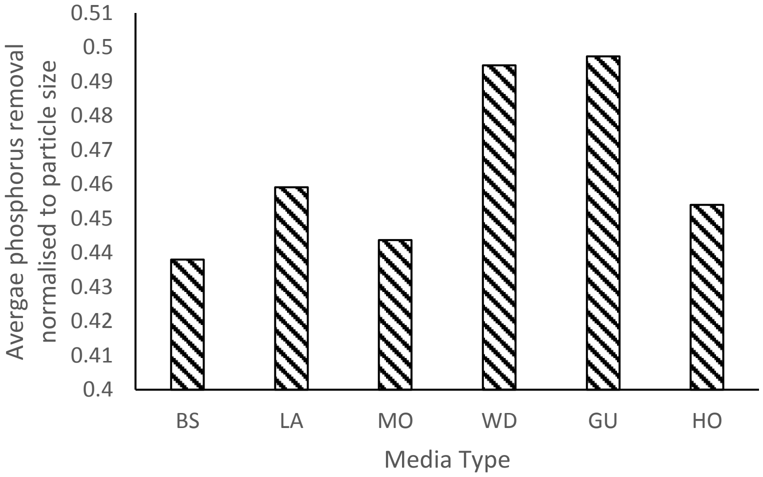


Figure 9.2 Phosphorus removal data normalised to media particle size

The two media that had to be air dried namely HH and FO have been excluded from this graph as the dried media size was not representative of the raw media size. Figure 9.2 reveals two very interesting points.

1. The two media that use Al as a coagulant (WD and GU) remove relatively more P than all the Fe based media, when particle size is accounted for.
2. The spread of performance of the remaining Fe based media is much less. Of the group shown in Figure 9.2 the MO media removed consistently more P than the BS media but the variation in performance can largely be accounted for by the difference in particle size.

Makris et al (2005b) analysed 8 different DWTR and also found that the Al media tended to remove more P than Fe media. The reason why Al media removes more P is unclear but can perhaps be explained by the changing redox states associated with Fe. It is possible that as the systems become more anoxic over time (as shown in Figure 6.17) some of the P associated with the Fe is desorbed (Roy-Poirier et al., 2010). However, further analysis would be required to prove this.

9.2.5 The effect of polymer type

Although limited information was available for the amount of polymer that was dosed at each site, it is very interesting to note that the two media that performed best in this trial also used starch as a coagulant, rather than polyelectrolytes. Although the dose was small (<2mgL^{-1}) it would add considerably to the organic carbon present in the media and it is possible that the OC present in the starch is more readily exchangeable than other OC present in the media. More research would be required to confirm this. There are no reports of this in the research literature.

9.2.6 Optimised phosphorus removal in relation to DWTR type

There is a complex relationship between the physio-chemical characteristics of the media and how they removed P. The experiments in section 8 clearly revealed that the bulk particles size of the media played a key role in the ability of the media to remove P. The negative correlation between coagulant dose and P removal would be most readily explained by an increase in particle size. The linear regression analysis also revealed that the saturated moisture content of the media had a significant effect on P removal and it is possible that water movement is inhibited in the interstitial spaces of the pressed media, suggesting that centrifuged media may be more beneficial for P removal. There was also a correlation between the TOC content of the raw water and the P removal and there is gathering evidence that a high carbon content within the media is likely to lead to higher P adsorption (Al-Tahmazi, 2016).

Unfortunately, the pressed media in these experiments all used Al as a coagulant. When normalising the P removal data to particle size it was evident that the Al media is generally slightly better at removing P than the Fe media. However, this effect was masked in the experiments due to both the larger particle sizes of the pressed media and the inhibition of water movement as discussed above.

Therefore an optimal DWTR would require a site which had:

- as high an inlet TOC as possible
- an organic based polymer
- as little coagulant as possible
- a sludge with as small a particle size as possible while maintaining structural properties
- a centrifuge rather than a press, and
- alum rather than ferric as a coagulant.

9.3 Correlation between chemical parameters in the inlet and outlet water and phosphorus removal

9.3.1 Calcium, Sulphate and pH

As detailed in chapter 6 the outlet concentrations of calcium, sulphur as well as the pH were measured for all the columns and beds for the majority of the year. The DWTR tended to remove calcium, add sulphur and reduce the pH of the inlet water. The data was averaged over the year and correlated with average percentage P removal for each column. All three factors were significantly correlated with average percentage P removal at the 99% confidence level (r=.858, -.867 and,-.81 for % change in Ca, S and change in pH). Thus as the media became more saturated with P its ability to remove calcium was also depleted, the loss of sulphur reduced and the outlet pH tended toward the inlet pH.

To assess the strengths of these effects, linear regression analysis was undertaken on the outlet data from the 30 columns operating at the University. The regression analysis revealed that the modelling of all three parameters could only predict 13.8% of the associated percentage removal of P with the loss of calcium explaining 6.1%, increase in sulphur 3.3% and change in pH 4.4% of the total percentage variance in outlet P concentration. Thus, although the correlation between the P removal and calcium, sulphur and change in pH were very strong the effect they had on the ability of the media to remove P was relatively small.

9.3.2 The effect of real waste water

The previous discussion on the analysis of calcium, sulphate and pH has not included the performance of the RWW systems, as the effect of all three parameters was markedly different when RWW was used. On average the columns and meso scale beds at the RWW site removed no calcium and added no sulphate to the outlet water and only decreased the pH by 0.3 compared with 0.5 at the University site. The reason why these effects are not shown in the RWW are most probably explained by the much more complex chemistry and biological activity associated with RWW when compared to the infeed water to the University site which was primarily chlorinated tap water with the addition of small amounts of di-potassium phosphate. The complex system chemistry associated with the interactions of the RWW and the DWTR inhibited both the formation of calcium phosphate and the exchange of sulphate on the surface of the media. It is also possible that biofilms on the surface of the media inhibited these reactions. Further work would be required to ascertain whether chemical or microbial inhibition were the predominating factors. However, the lack of calcium removal and sulphate exchange may explain why the RWW systems did not generally remove as much P as the systems at the University site.

9.4 Optimising system contact and rest time

9.4.1 Contact time

The results from the contact time experiments revealed that increasing contact time from 30 minutes to 6 hours increased the amount of P that could be removed by the DWTR over the year. Increasing contact time inevitably increases the system footprint and capital cost. However, if the media removes more P with longer contact times there may be a reduction in maintenance cost as the media would not need to be replaced or regenerated so often. Therefore, there is a need to ascertain if there is an optimal level of contact time above which the improvement in overall P removal is small.

To deduce how contact time may affect P removal in DWTR, detailed kinetic analysis was undertaken in relation to particle size, age of the system and effect of RWW. The results from this analysis have been shown in chapter 8 and will be discussed here in relation to the contact time results achieved in the column experiments (Chapter 5).

9.4.2 Physical implications of the pseudo second order rate equation

All of the kinetic data evaluated fitted the pseudo second order (PSO) kinetic model well, in fact the columns and RWW systems generally fitted the model exceptionally well with r^2>.99

The derivation of the PSO was based on the classical Langmuir model of adsorption kinetics in which adsorption is seen as a chemical reaction occurring on the energetically homogeneous solid surface (Plazinski et al., 2013) and the assumptions associated with this theory have been discussed in 2.4.2.2.

The PSO is generally formulated as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

The equation and variables have previously been defined in section 2.1.1.3. The equation states that the amount of adsorbate adsorbed at time t is dependent on the equilibrium capacity of the media q_e and the rate constant k_2.

9.4.2.1 The equilibrium constant q_e

The value of the q_e depends upon the physio-chemical properties of the media, the inlet concentration and the nature of the solute sorbent interactions (Ho and McKay, 2000). The equilibrium constant of the media can be hard to calculate accurately, especially at the low concentrations, and in the flow through conditions that were used in these experiments as discussed in section 5.10.1. However, there is no doubt that the q_e value for the 8 DWTR measured showed a broad range.

9.4.2.2 The rate constant k_2

The rate constant k_2 has been defined by Liu (2008) as the inverse of the relaxation time of a chemical reaction, and therefore represents the relaxation time of an adsorption process. Physically this means that an adsorption process with a very high relaxation time (low value of k_2) adapts slowly to its equilibrium state, while a process with a very small relaxation time (high value of k_2), adapts in a very short time. This means that as the k_2 value decreases the kinetic adsorption curve tends to flatten (Liu, 2008).

9.4.2.3 Relationship between PSO and the long term kinetic experiments

Both the columns which were monitored for kinetics throughout the year showed substantial increases in the time it took for the media to reach equilibrium as the year progressed; from less than 10 minutes at the start to close to 3 hours at the end of the year (Section 8.3). However, both columns showed quite different characteristics in relation to the change in the value of q_e and k_2 (see Figure 8.10). While the column with the GU media showed an exponential decline in the value of k_2 from 200 to 12, it only showed a small drop in the final value of q_e from 0.0056 to 0.005 mgg^{-1}. The column containing the BS media, which was ferric based, showed no logical pattern in the value of k_2, (although it did generally have a reducing trend), but a substantial reduction in the value of q_e from 0.053 to 0.0039mgg^{-1}.

Therefore, in terms of the PSO equation the column containing BS media showed a reduction in the rate of adsorption as the available adsorption sites were reducing in number, whereas the GU media showed a reduction because the adsorption processes was taking longer. This is further qualified by assessment of the intraparticle diffusion model as shown in Figure 8.11 which showed that intraparticle diffusion was becoming more prominent as the rate limiting step as time progressed (particularly in the GU media). Intraparticle diffusion is thought to take longer due to the internal adsorption sites being physically much harder to access.

The results from this analysis is most likely explained, in a similar fashion to that proposed in many studies for the biphasic nature of media adsorption kinetics (Makris et al., 2005a, Song et al., 2011, Babatunde and Zhao, 2010, Gao et al., 2013). In the first fast phase of P adsorption, sorption on easily accessible surface sites is followed by a slower phase where intraparticle diffusion dominates. As the water flows into a column or bed the easily accessible surface sites at the top of the bed are used up first. As the system ages, the remaining easily accessible sites move down through the bed as the top layers become saturated; until at a certain time only interstitial sites remain. Once all the easily accessible surface sites are used up, the kinetics will purely involve intra particle diffusion. Although this will take longer it is possible the interstitial pores are more evenly spread throughout the media and therefore require a similar amount of time to access and this would explain the kinetics seen in the GU media.

Predicting how the kinetics of the media would change over periods extended beyond the measurement period is complex, but could be undertaken by further analysis of the models as discussed in Liu (2008), [the analysis was beyond the scope of this thesis]. However, it seems likely that the q_e of the BS media would continue to fall and thus the time to reach equilibrium would increase at a steady rate. In the GU, media the time it takes for the media to reach equilibrium would increase. However, the increase would occur at a slower rate until the media approached it’s adsorption capacity.

9.4.2.4 Comparison of PSO and results achieved in the contact time experiments

The results from the previous kinetic analysis agree with those seen from the contact time experiments. The BS media showed a more pronounced improvement at P removal with increased contact time, whereas the GU media did not improve much when retention time was increased above 3 hours (Figure 5.12).

9.4.2.5 Implications for contact time in full scale system

The physical implications of this analysis is that there is probably a very limited advantage in increasing retention times above 4 - 6 hours for the GU media or any media with a high adsorption capacity until many thousands of bed volumes have been passed. However, there is a positive advantage in keeping retention time to a minimum of 3 hours. In the case of the BS media increasing retention time to 12 or 24 hours would be beneficial, but the BS media would be a poor choice as the adsorption capacity is so low.

9.4.2.6 Modelling the effect of retention time

Although there was not time to use the PSO model to construct a predictive model related to retention time, it was possible to model the results produced from the experimental columns operating at different retention times using the second order regression analysis shown in 5.10.3. The results from this analysis were used in the Matlab programme discussed in Section 9.6 which calculated how retention time may affect output P over the lifetime of a system. Examples of the expected output from a system using GU and BS media with an input of 10mgL^{-1} TP over the first 100 bed volumes passed are shown in Figure 9.3.

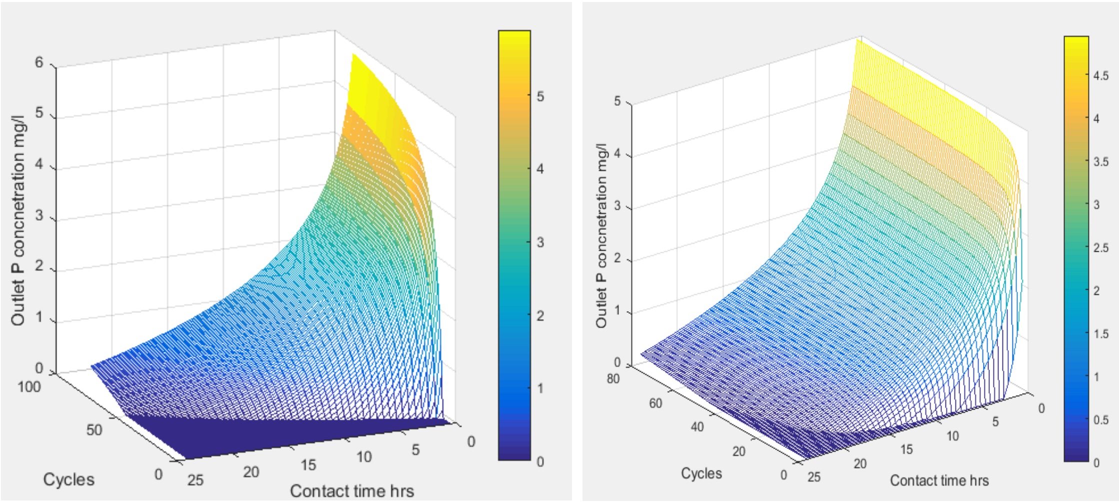


Figure 9.3 BS and right GU media with 10mgL^{-1} TP input over first 100 cycles *(Note: the coloured bar represents the predicted outlet phosphorus concentration)*

The data shows graphically how as retention time is increased the removal performance gets substantially better, with a rapid fall if retention time is less than 3 hours. However, the effect is not quite so pronounced as the number of bed volumes passed is increased to 1000 and the media becomes more saturated with P as can be seen in Figure 9.4 which shows the same systems operated over 1000 bed volumes passed.

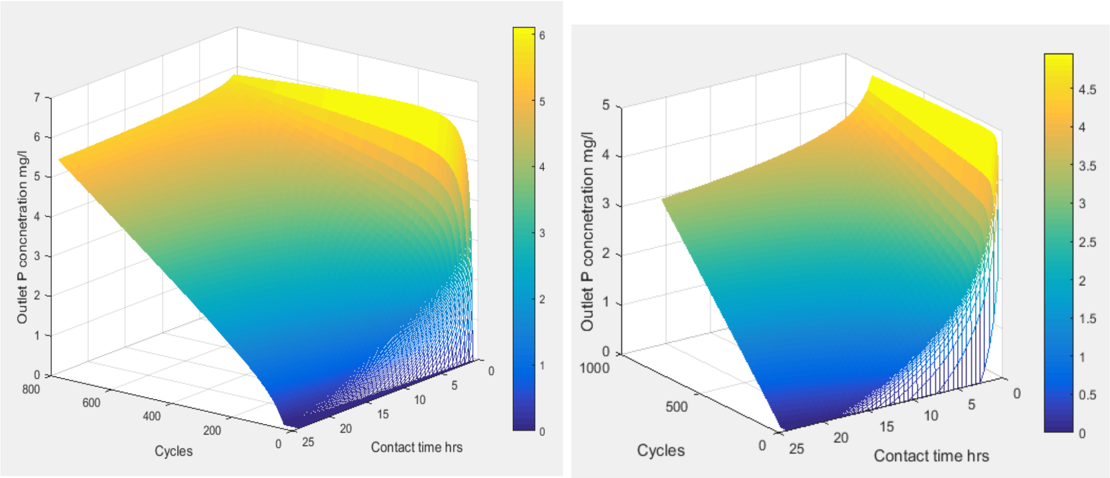


Figure 9.4 TP output for BS (left) GU (right) media with contact time from 0 to 24 hours plotted over 1000 cycles.

9.4.3 The effect of rest time

This research has shown that, increasing the time that the system is rested between loading periods from 1 to 6 hours had a positive effect on P removal. But the effect was very small over the first 300 bed volumes passed, and then steadily increased. This is probably because, during the early stages of treatment, there are still many easily accessible surface sites available as discussed 9.4.2.3, and resting the media has little effect on these adsorption sites. Although a few studies have observed a positive effect in resting media over long periods of time, both Drizo et al (2008) and Penn (2011) found that steel slag adsorbed much more P after it had been rested for 5 weeks. Few papers have investigated the effect on P removal systems by changing the length of resting period in the scale of hours. However, Sibrell et al (2009) used acid mine drainage (AMD) sludge in column experiments to remove P with oscillating load and rest times of 12 hours, they propose the basis for the improvement in media capacity upon resting may be due to intra-particle diffusion of P within the extensive pore structure of the AMD sludges. Therefore, it is likely that during the resting time the P on the surface of the DWTR is moving into the intraparticle pores of the media thus producing new easily accessible surface sites. However, careful assessment of the media would be required to ascertain if this hypothesis it true.

Two of the columns were rested for 24 hours between loading cycles, but the loading period was also increased to 24 hours, therefore it was not possible to ascertain if increasing rest time above 6 hours had a significant effect on P removal.

The effect of increasing the resting time of the media is not as pronounced as changing the contact time. Therefore, in a full scale system, it would be prudent to have a minimum rest time of 2 hours between load cycles. However, if space allows increasing the rest time would probably increase P removal performance of the system especially as it ages.

9.5 The effect of inlet phosphorus concentration.

Although traditional water treatment systems are not very good at removing P, at each treatment step some P is generally removed especially when it is associated with the suspended solids (Metcalf et al., 2014). Dueñas et al (2003) found about 30% of TP was removed in primary clarifiers, and the Environment Agency (2012) suggest that around 50% of TP is removed after secondary treatment. Therefore, should a DWTR system be optimally placed after primary or secondary treatment?

The results in Section 5.7 and 5.8 clearly show that as the P inlet concentration falls the percentage of P removal also falls and this is readily explained by a reduction in the concentration gradient between the sorbate and the sorbent. The effect was not strong in the University systems as the difference in inlet concentrations was small (<4mgL^{-1} TP) but the RWW systems showed a very strong correlation between the weekly percentage removal and the inlet P concertation (r= .495 to .633 p<.01) for all the columns and beds. So as the inlet concentration fell, so did the percentage removal of P. These results are in agreement with Babatunde et al (2009) who found that percentage P removal increased steadily with increase in adsorbent dosage up to 10mgP L^{-1}. However, it is interesting to note that this relationship does not hold true as inlet concentrations increase above 10mgPL^{-1} (Babatunde et al., 2009, Babatunde et al., 2011b). Above this point, the media is more saturated and percentage removal does not increase as much with rising inlet concentration. Therefore as long as the outlet of the primary treatment systems is not above 10mgL^{-1} TP, [which is very unlikely as average concentrations entering works is usually between 3.7 and 11mgL^{-1} TP (Metcalf et al., 2014)] the beds should be placed as close to the inlet as is possible as not only will the performance of the beds be more efficient, the mass of P entering the system will be greater and therefore the more P per unit mass of media will be adsorbed.

The nearer the system is placed to the entrance of the treatment works the higher both the organic and SS load to the beds would be. This would have a negative effect on the percentage P removal as was clearly shown by the identical systems operating at the University and the RWW sites. The columns at the RWW site removed approximately 15% less P on average and the disparity between the systems grew as the year progressed. The most likely explanation for this disparity has been previously discussed in Section 5.8 and is probably because of the entrapment of SS and the growth of biofilm blocking adsorption sites. Although it may also be caused by the lack of sulphate exchange and calcium precipitation as discussed in section 8.3.1.1. Therefore, although it is would be desirable for the system to be placed after primary treatment to maximise P removal, the beds may well become blocked quickly. The blocking of the adsorption sites by increased biological activity may negate the advantage of increased P removal at higher inlet concentrations.

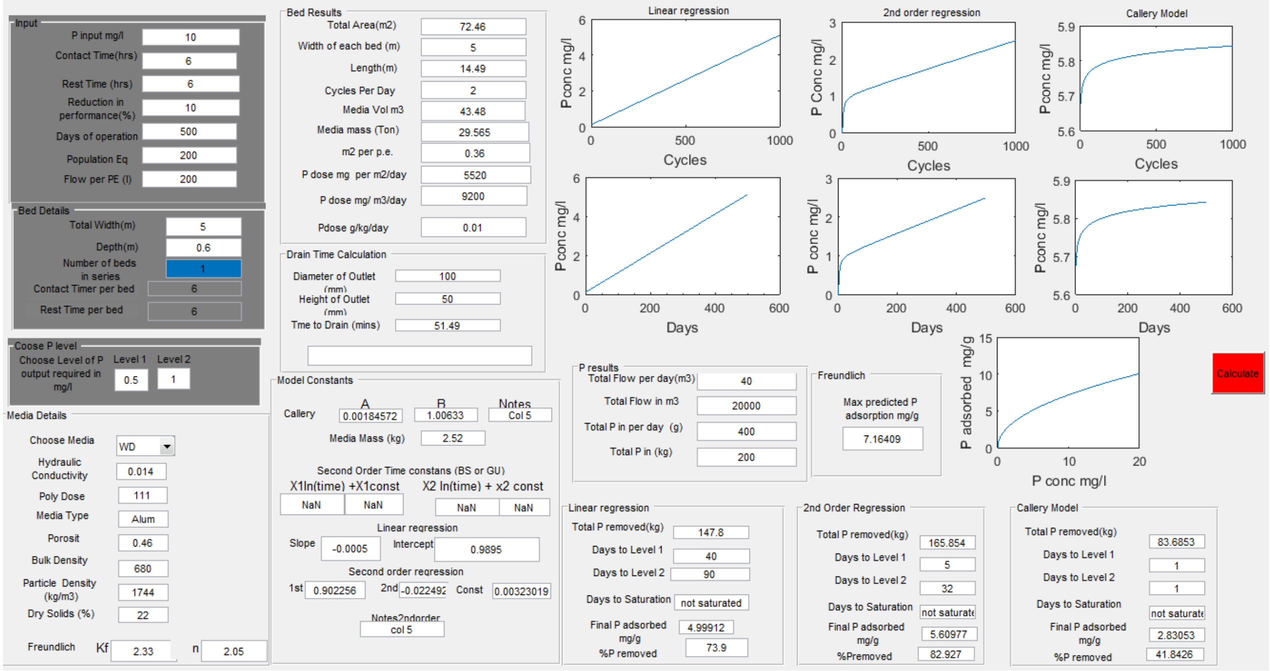
The final positioning of the system will therefore be site specific depending on the requirements of the P removal system and the amounts of SS and BOD at the various stage of the treatment process. If the site has a good SS removal system the beds can be used near the inlet of the works. If DWTR beds are required to polish small amounts of P they could be placed after secondary settlement.

9.6 Life expectancy and size of system

9.6.1 Matlab modelling programme

The experimental data from this thesis was used to analyse the physical properties of the media and its ability to remove P under various conditions. Four different models were proposed in Section 5.10 to predict how much P the media may remove in time scales extended beyond the experimental time period. To bring all this data together and enable predictions of how large a full scale system would have to be and how long it should be run for, a programme was constructed in Matlab. Data from both the physical and chemical experiments were input into the programme, in conjunction with other user input variables. The programme used the four mathematical models of the P removal data to estimate how long a full scale system might usefully last, depending on inlet and outlet requirements and media type. The programme also calculated the size of the bed in relation to contact time, flow rate requirements and media type. Although the programme produced very useful outputs it must be noted that the predictive models used were all very primitive and it is intended as the starting point for a more complex analysis system that could more reliably predict system performance once more experimental and field data becomes available.

Note: All the data input and output from the programme was undertaken through a graphical user interface (GUI), an example screen shot of the GUI is shown in Figure 8.5 and the full programme is attached in Appendix D.



Input
P input mg/l 10
Contact Time(hrs) 6
Rest Time (hrs) 6
Reduction in performance(%) 10
Days of operation 500
Population Eq 200
Flow per PE (l) 200

Bed Details
Total Width(m) 5
Depth(m) 0.6
Number of beds in series 1
Contact Timer per bed 6
Rest Time per bed 6

Coose P level
Choose Level of P output required in mg/l
Level 1 0.5
Level 2 1

Media Details
Choose Media WD
Hydraulic Conductivity 0.014
Poly Dose 111
Media Type Alum
Porosit 0.46
Bulk Density 680
Particle Density (kg/m3) 1744
Dry Solids (%) 22
Freundlich Kf 2.33 n 2.05

Bed Results
Total Area(m2) 72.46
Width of each bed (m) 5
Length(m) 14.49
Cycles Per Day 2
Media Vol m3 43.48
Media mass (Ton) 29.565
m2 per p.e. 0.36
P dose mg per m2/day 5520
P dose mg/ m3/day 9200
Pdose g/kg/day 0.01

Drain Time Calculation
Diameter of Outlet (mm) 100
Height of Outlet (mm) 50
Tme to Drain (mins) 51.49

Model Constants
Callery A 0.00184572 B 1.00633 Notes Col 5
Media Mass (kg) 2.52
Second Order Time constans (BS or GU)
X1ln(time) +X1const NaN NaN
X2 ln(time) + x2 const NaN NaN
Linear regression
Slope -0.0005 Intercept 0.9895
Second order regression
1st 0.902256 2nd -0.022492 Const 0.00323019
Notes2ndorder col 5

P results
Total Flow per day(m3) 40
Total Flow in m3 20000
Total P in per day (g) 400
Total P in (kg) 200

Freundlich
Max predicted P adsorption mg/g 7.16409

Linear regression
Total P removed(kg) 147.8
Days to Level 1 40
Days to Level 2 90
Days to Saturation not saturated
Final P adsorbed mg/g 4.99912
%P removed 73.9

2nd Order Regression
Total P removed(kg) 165.854
Days to Level 1 5
Days to Level 2 32
Days to Saturation not saturate
Final P adsorbed mg/g 5.60977
%Premoved 82.927

Callery Model
Total P removed(kg) 83.6853
Days to Level 1 1
Days to Level 2 1
Days to Saturation not saturate
Final P adsorbed mg/g 2.83053
%P removed 41.8426

Figure 9.5 Example screen shot of GUI for the Matlab programme

9.6.2 Model inputs

The model allows the user to input:

- the inlet P concentration in (mgL^{-1})
- population equivalent (p.e) and flow rate per p.e.(L)
- width and depth of the bed (m)
- number of beds operating in series
- the contact and rest time required
- the number of days of system operation
- the required level of P that the system should discharge (mgL^{-1}), and
- type of media, from the 8 Northumbrian water DWTR sampled (The input data associated with each media is discussed below).

9.6.2.1 Experimental variable inputs

For each media type the physical properties and modelling results from the experiments were stored in a spread sheet that was imported into Matlab. The data included:

Physical properties:

- bulk density, and
- porosity (and many other factors that were not used in the model).

Experimental results:

- Freundlich constants K_f and n, from (Al-Tahmazi, 2016)
- results from the basic linear regression analysis of the percentage P removal performance plotted against bed volumes passed (Section 5.10.2)
- results from the polynomial second order regression analysis of the mass balance plots associated with P removal (Section 5.10.3), and
- constants associated with the Callery model of P breakthrough curves (Section 5.10.4).

Note: Although for the majority of the media results were only available from the University columns, experimental data from the meso scale beds and RWW columns was also available for the HO,GU and BS media and they could also be input to the system.

9.6.3 Model outputs

The model outputs a variety of graphs and tables to the GUI
(The output for the effect on contact time was shown in Figure 9.3 and 9 .4)

9.6.3.1 Physical model outputs

The key physical outputs from the model were:

- the length and area of the bed (m and m^2)
- the number of full cycles run per day
- media volume (m^3)
- mass of media (tonnes)
- the size of beds in terms of (m^2/p.e), and
- input P dose to the system in mg of P per m^2 of bed area, m^3 of bed volume and kg of media.

Note: If multiple beds were used the total area, contact and rest time were divided equally between the input number of beds, and the result was displayed for each smaller bed.

9.6.3.2 Life expectancy outputs for a single bed system

The programme produces 4 predictions of how long it will take for the output of the system to reach the pre-set level of P concentration using the four previously discussed models:

The programme displays the results for the first three models in the form of graphs, an example output is shown in Figure 9.6. The programme also produces a plot of the Freundlich isotherm for each media, the curve for the BS media is shown in Figure 9.7.

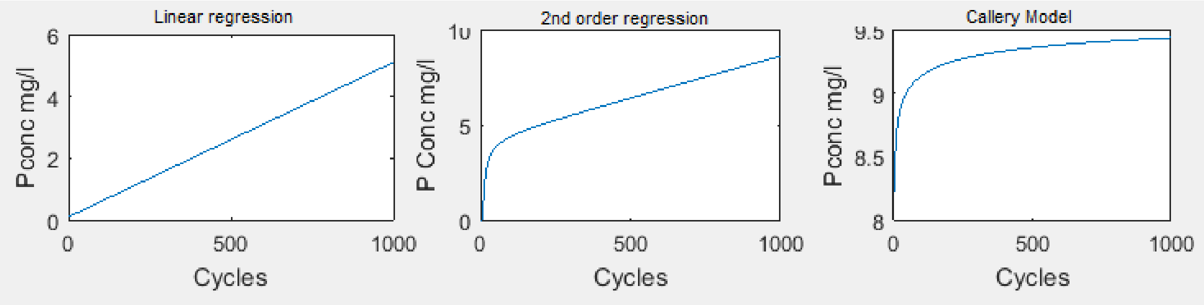


Figure 9.6 Three comparative graphs produced by the Matlab programme using linear model, second order model and Callery model for BS media with input of 10mgL^{-1}TP and 6 hours contact time

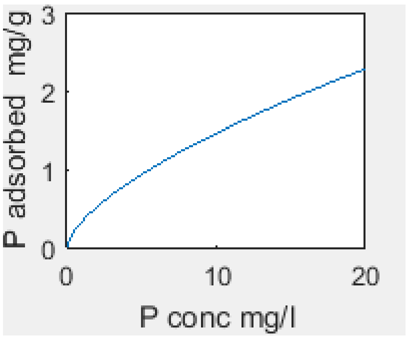


Figure 9.7 Freundlich isotherm curve for BS media, data from this curve is used to model treatable outlet volumes.

It quickly became evident from modelling single bed systems that the P output levels would not remain low for very long, thus the programme included a feature to enable the analysis of multiple beds running in series.

9.6.3.3 Life expectancy outputs for multiple bed systems

Multiple beds in series are modelled by a process of iteration where the value produced for the outlet of the first bed is used as the input for the second. In the second bed the removal of P is modelled in a similar method as the first. However, a user input factor is included to reduce the removal performance of the media with the inclusion of each new bed. As discussed in Section 9.5, the experiments showed that reducing the inlet concentration in the University columns reduced the P removal performance. For the majority of models run the reduction factor was set at 10% which was probably higher than the media would experience in practice. [Changing the value of the reduction factor did not have a strong effect on the output variables of importance.] Only the linear and second order models could be used for the multiple bed system analysis as the Callery model produced unstable results when more than one bed was added to the system.

The programme output both 2 and 3 dimensional graphs to help visualise the operational system. Example results produced for a 5 bed system using BS media and an inlet concertation of $10mgL^{-1}$TP operating for 1000 days are shown in Figure 9.8. Figure 9.9 shows the same data in 3d on the left and an equivalent system using GU media on the right.

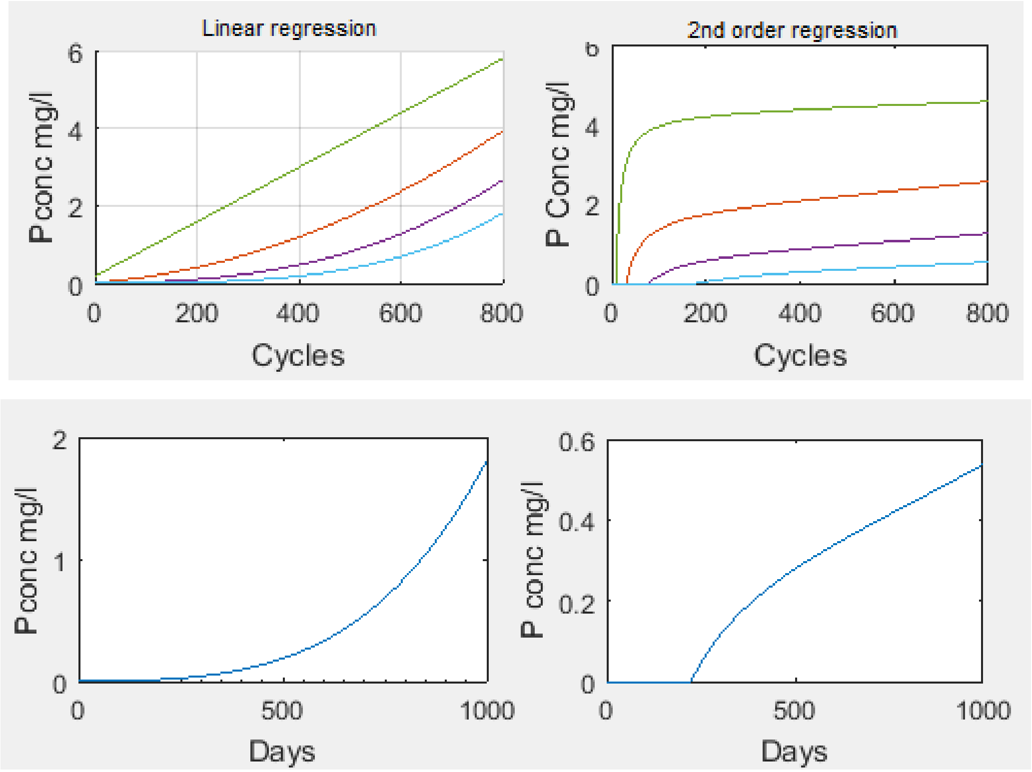


Figure 9.8 Results from Matlab for BS media with 24 hour retention 6 hours rest and 10mgL^{-1}TP for 4 beds operating in series, top graphs showing predicted TP outlet concentration for each bed against cycles passed, bottom graphs showing predicted output of TP from the system over 1000 days.

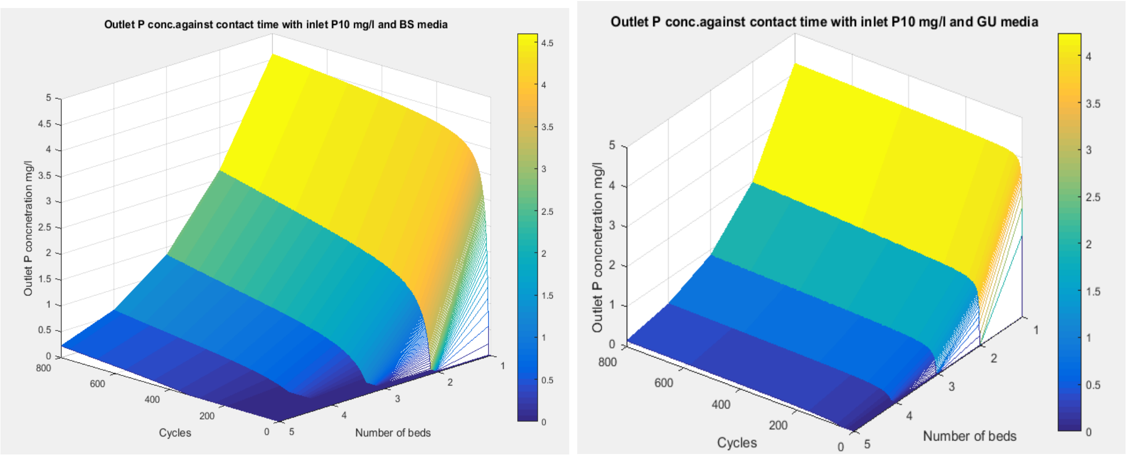


Figure 9.9 Graphs showing predicted phosphorus removal from BS and GU media with TP input of 10mgL^{-1} and 5 beds operating in series for 1000 days with total contact time for system 24 hours and rest time 6 hours (4.8 hrs contact per bed) *Note: The coloured bar represents the predicted outlet P concentration.*

9.6.4 Limitations of the programme

- **Partial saturation**: As none of the media were fully saturated the modelling curves only represent partially saturated media. Although the second order curves may provide a reasonable representation of the future performance of the system, this cannot be confirmed without running experiments for longer.

  The Callery model used to predict the break through curves suffered from lack of data. As although the curves modelled the experimental data reasonably well they tended to predict that the percentage of P removal would fall very quickly and then carry on removing P at lower level almost indefinitely, an example of this failure in prediction is shown in Figure 9.10.

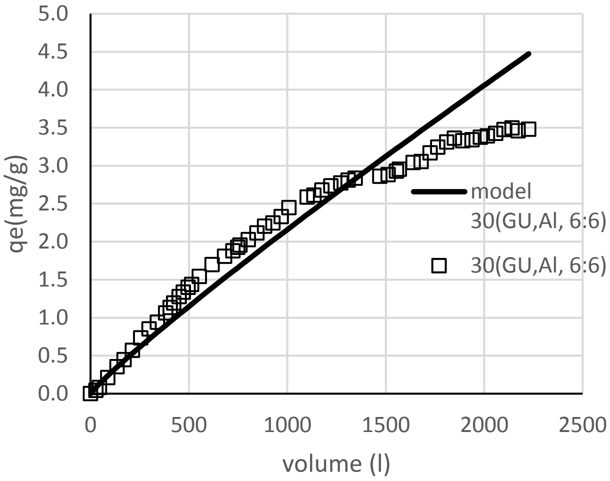


Figure 9.10 Callery model versus real data showing how the models do not tend to converge with the data leading to almost unlimited life expectancy in the models.

- **Hydraulic conductivity** No inclusions were made for hydraulic conductivity in the model. The beds will inevitably become blocked over time and this is discussed in Chapter 7 and section 9.7.
- **Retention or rest time:** Although retention time models were constructed in the programme for the GU and BS media, this was for a single pass system as shown in Figure 9.8 and 9.9. This model was constructed

effectively as a standalone part of the programme and all other calculations did not account for the effect of retention or rest time. The model assumes the same performance at all retention times. The data used by the model was mostly produced at retention times of 6 hours with 6 hours rest time. This means that the beds may perform slightly better than predicted with retention times >6 hours and will perform substantially worse with retention times of <3 hours and this effect would likely get worse as the number of bed volumes is increased.

- **Inlet concentration:** the data for the model was obtained from experiments that were mostly run with a 5mgL^{-1} TP input. It is possible to put any input P into the model, and apart from the Freundlich model, the linear regression and second order models assume that the same rate of removal will be achieved whatever the inlet concentration of P. This assumption is probably reasonable within the ranges of 10 to 1mgL^{-1} TP as discussed in section 9.5. However with inputs above 10 mgL^{-1}the model will inevitably become more inaccurate.
- **Very low concentrations:** Using multiple bed systems the programme predicts very low exit concentrations well below 0.1mgL^{-1}. Little research has been undertaken on using DWTR with such low inlet concentrations and it is possible that the media may become a source rather than a sink for P at such low concentrations. Further work would be required to ascertain this.

9.6.5 Using the programme to predict life expectancy of the media

The model has been run many times observing the effect of the different media and the modelling equations. As more beds are added the three different mathematical models show very divergent results. Two sets of data from the model are shown in Table 9.1 and 9.2

The models shown in the tables were run with the following inputs:

- 3 media types BS,MO, GU (data from column experiments) and GU(data from mesoscale bed experiments)
- input flow of 40m^3 per day (equivalent to 200 p.e. site).

- 24 hours total contact time and 6 hours total rest time
- system operation for 1000 days
- number of beds in series from 1 to 4, and
- total retention time for system 24 hours and rest time 6 hours.

Table 9.1 and 9.2 use an input of 10mgL^{-1} and 5mgL^{-1}TP, respectively.

Media (Data Source)	BS(University column)				MO(University column)				GU(University column)				GU (data from meso bed)			
Ref. [Inlet conc.]	A[10]				B[10]				C[10]				D[10]			
Length(m)	9.01				10.42				8.13				8.13			
Total Area(m$^{2)}$	135				156				122				122			
m^{2}/p.e.	0.68				0.78				0.61				0.61			
Media volume(m^{3})	135				156				122				122			
Media Mass(ton)	111				150				75				75			
P dose(mg/m^{3}/day)	2960				2560				3280				3280			
No of beds	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Retention time/bed	24	12	8	6	24	12	8	6	24	12	8	6	24	12	8	6
	Linear model															
Days to 0.1mgL^{-1}	1	78	243	404	1	153	443	724	1	173	nr	nr	1	1	1	1
Days to 0.5 mgL^{-1}	57	287	512	682	116	520	913	nr	124	nr	nr	nr	1	1	1	60
	2nd order model															
Days to 0.1mgL^{-1}	12	41	112	290	13	395	nr	nr	3	32	nr	nr	2	4	11	37
Days to 0.5mgL^{-1}	14	53	217	927	55	nr	nr	nr	4	nr	nr	nr	2	5	33	nr
Total P removed%(2nd order regression)	45	80	87	88	92	94	98	99	74	93	96	98	52	81	92	94
P removed after 1000 days (mg/g)	1.61	2.86	3.17	31.	2.44	2.62	-	-	3.94	5.15	5.19	-	2.77	4.39	4.87	5.08
	Freundlich model															
Days to 0.1mgL^{-1}	21	286	544	800	132	1028	1899	2761	159	1200	2214	3216	159	1200	2214	3216
Days to 0.5 mgL^{-1}	62	345	622	898	302	1253	2182	3104	359	1465	2545	3616	359	1465	2545	3616

Table 9.1 Outputs from model with an input flow of 40m^{3}/day (200p.e.) and input TP of 10mgL^{-1} and fixed bed width of 15m and depth of 1 m operated for 2000 days (nr concentration not reached in calculated operational time)

Media (Data Source)	BS(University column)				MO(University column)				GU(University column)				GU (meso scale bed)			
Ref.[Inlet conc.]	A[5]				B[5]				C[5]				D[5]			
Length(m)	9.01				10.42				8.13				8.13			
Total Area(m$^{2)}$	135				156				122				122			
m^{2}/p.e.	0.68				0.78				0.61				0.61			
Media volume(m^{3})	135				156				122				122			
Media Mass(ton)	111				150				75				75			
P dose(mg/m^{3}/day)	1480				1280				3280				3280			
No of beds	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Retention time/bed	24	12	8	6	24	12	8	6	24	12	8	6	24	12	8	6
	Linear model															
Days to 0.1mgL^{-1}	3	146	341	510	23	273	614	910	1	333	788	nr	1	1	1	1
Days to 0.5 mgL^{-1}	146	450	683	841	273	804	1210	1489	333	nr	nr	nr	1	1	60	391
	2nd order model															
Days to 0.1mgL^{-1}	25	87	256	779	31	nr	nr	nr	5	398	nr	nr	3	8	27	151
Days to 0.5mgL^{-1}	31	162	1358	nr	1571	nr	nr	nr	14	nr	nr	nr	3	17	nr	nr
Total P removed%(2nd order regression)	56	83	89	92	94	98	99	99	80	94	97	98	56	83	93	96
P removed after 1000 days(kg)	1.01	1.49	1.57	-	1.24	1.30	-	-	2.13	2.48	2.55		1.48	2.19	2.45	2.52
	Freundlich model															
Days to 0.1mgL^{-1}	43	387	723	1057	267	1564	2826	4076	322	1840	3317	4780	322	1840	3317	4780
Days to 0.5 mgL^{-1}	131	525	912	1297	637	2102	3540	4968	758	2471	4152	5822	758	2471	4152	5822

Table 9.2 Outputs from model with an input flow of 40m^{3}/day (200p.e.) and input TP of 5mgL^{-1} and fixed bed width of 15m and depth of 1 m and operated for 2000 days(nr concentration not reached in calculated operational time period)

The results from the Matlab model reveal many interesting observations on how the DWTR may operate in a full scale system. The physical parameters are discussed in Section 9.6.7, and the life expectancy results are given below.

9.6.5.1 Experiments which were modelled in Tables 9.1 and 9.2

The first three columns of data (A-C) shows results from column experiments undertaken at the University; the first column being one of the worst performing media (BS) and the second one of the best (MO) and the third (GU) performed averagely. The data for the last column (D) models the very poorly performing meso scale bed operating with GU media and RWW. This bed was overloaded as detailed in Section 5.2.2.3. The last 2 columns (C and D) enable the comparison of model performance between the University column and the meso scale bed supplied with RWW, both filled with GU media.

9.6.5.2 Comparing the three life expectancy models

The main parameters of interest are the three predictions that the programme makes for the time it would take for the output from the beds to reach a concentration of 0.1 and 0.5mgL^{-1} TP. The results clearly show that, apart from the BS media, the Freundlich isotherm model tends to predict much longer and unrealistic life expectancies than the other two models, which were based on the experimental data. Very small changes in the Freundlich model parameters lead to very large changes in life expectancy prediction, and thus unless the Freundlich parameters can be produced more accurately they are not a useful way of estimating long term system performance.

The linear and second order models produce much more comparable results with the second order model tending to predict a higher life expectancy, although this is media dependent. The second order model is fitted to the experimental data much more accurately than the other two models and the remainder of this discussion uses information produced by this model (highlighted in the tables).

9.6.5.3 Life expectancy predictions using second order model

When the systems are modelled with only one bed in operation, even the best media (A) would reduce the P concentration to below 0.1mgL^{-1} for no more than 30 days, for either an inlet concentration of 5 or 10mgL^{-1}. Although the MO media is predicated to keep the outlet level below 0.5mgL^{-1} for over three years if the inlet concentration was kept below 5mgL^{-1}. However, the outlet from the GU media shown column D is predicted to rise above 0.5mgL^{-1} after only a few days.

By adding beds in series the programme predicts that the length of time the systems will keep the concentration of P to below 0.5mgL^{-1} can be vastly extended. With the best media (B), using 2 beds in series should allow concentrations of P to be kept below 0.1mgL for a number of years. However, the results from the GU media in column D do not reveal quite such optimistic results, requiring the addition of four beds in series to keep the outlet level below 0.1mgL^{-1} for just 37 and 151 days with 5 and 10mgL^{-1} TP input, respectively. But using the same poorly performing model the level would not reach 0.5mgL^{-1} in the measured time frame of 1000 days and would still remove over 94% of the P input to the system.

By comparing the GU column at the University with the meso scale bed (Column C and D) operating with the same media, a very large discrepancy is apparent. The data from the column experiments predicts that output would be below 0.1mgL^{-1} for nearly a year when two beds are used in series, while the equivalent output would be reached in just a day for the meso scale bed model (D). It is probable that although the model of the overloaded meso scale bed is overly pessimistic, the results are more realistic than the modelled data from the University site, due to the reduction in performance of the systems associated with RWW.

As more beds in series are added to the systems, there comes a point when the addition of extra beds has very little effect on the outlet concentration. For all the systems modelled, adding more than 4 beds in series had little effect on the final outlet concentration, and it is unclear how the media would perform with very low inlet P concentrations.

A small increase in average percentage removal of the media very quickly leads to a large increase in lifetime expectancy and a decrease in the requirement for extra beds in series. Therefore, the number of beds required to reach a useful life expectancy is strongly effected by media type. However, none of the best performing media were used in the RWW experiments, and the fantastic performance offered by the MO media (B) is likely to be mediated in a RWW water situation. So even with the best media to produce TP levels below 0.1 mgL^{-1} for more than a year, it would probably require three beds in series.

9.6.5.4 Phosphorus removal by mass

The preceding discussion has assumed that the life expectancy of the DWTR based beds will be used to reach a discharge consent of 0.1 or 0.5mgL^{-1} TP, and once the output has been reached the system will need replacing (this is discussed further Section 9.8.3). However it is worth noting that even though some of the media would not be able to keep P levels below a set level of 0.1 or 0.5mgL^{-1} they still remove a substantial percentage of the P entering the systems. For example, even though the model predicts that the meso bed data (D) would only keep the TP level below 0.5mgL^{-1} for 17 days (in a 2 bed system, with 5mgL^{-1} TP input), the model predicts that over the 1000 day operational period, over 83% of the TP input into the system would be removed. Therefore the beds would be well suited to a catchment permitting scenario where the total mass of P removed over time was more important than the outlet concentration.

9.6.6 Physical parameters produced by the model

9.6.6.1 Bed sizing dependent on media type

Throughout this thesis it has been proposed that an optimal system using DWTR would use a tidal flow hydraulic regime. When designing a tidal flow scheme the sizing of the structures is related simply to the porosity of the media and the contact and rest time of the system. Once the contact and rest time have been fixed and the media type chosen the system can be sized; and the mass of the media required can be calculated from the bulk density. Further, if the average TP input to the system is known the P loading rate to the system in terms of mass and volume can also be calculated. The output from the Matlab programme comparing the system sizes that would be required by the 8 different media, assuming an input flow of 40m^3 a day, a contact time of 24 hours and rest time of 6 hours, and an input P of 10mgL^{-1} are shown in Table 9.3.

Table 9.3 Outputs from Matlab model with Input 10mgL^{-1} TP, bed sized for 200p.e with 200l flow 40m^3 /day, 1m deep bed of media and 24 hrs contact time and 6 hours drain time

Media	Media Volume/Area m^3 and m$^{2\,\#}$	Mass of media (Tonnes)	Dose (gPm^3/day)and (gPm^2 day^{-1})$^\#$	Dose gP/kg/day (*10^{-3})	m^2/p.e
BS	135	112	2.96	3.57	0.68
FO	102	67	3.92	5.98	0.51
GU	122	76	3.28	5.28	0.61
HH	114	94	3.52	4.25	0.57
HO	114	72	3.52	5.5	0.57
LA	128	122	3.12	3.27	0.64
MO	156	150	2.56	2.66	0.78
WD	109	74	3.68	5.41	0.54

$^\#$ loading by volume and area are the same if depth = 1m

Table 9.3 shows that using different media results in different sized beds (from 100 to 150m^2) if the contact time is be kept constant. The differences arise because the media have a wide range of bulk porosity. The difference in bulk density of the media also leads to a doubling in the amount of P that is dosed into the system per kg of media. Varying between 0.00266 and 0.00598 gP/kg$_{media}$.day for the MO and FO media, respectively. However, the experimental results have shown no correlation between bulk density and P removal.

9.6.6.2 *Bed sizing dependent on contact time, rest time and input flow.*

By increasing the contact time, the daily volumetric flow rate the system can treat is decreased and the dose of P per kg and m^3 of media also decreases. The effect of increasing contact time on a system using MO media with 10mgL^{-1} TP input and a flow rate of 40m^{3}day^{-1} is shown in Table 9.4.

Table 9.4 Effect on system volume and phosphorus dose as contact time is increased for MO media with 10mgL TP input and 40m^3/day input flow and bed depth 1m.

Contact time (hrs)	Rest time (hrs)	Media Volume or Area (m^3 or m^2)	Dose (gP/m^3/day)	Dose (gP/kg/day) (*10^{-3})	m^2/p.e
1	1	10	38.4	39.87	0.05
4	2	31	12.8	13.29	0.16
6	3	47	8.5	8.86	0.23
12	6	94	4.3	4.43	0.47
24	6	156	2.6	2.66	0.78
36	6	219	1.8	1.9	1.09
48	6	281	1.4	1.48	1.41
72	6	406	0.98	1	2.03

It is likely that P adsorption beds would be used in a similar way to reed beds at treatment works. Seven Trent have installed many tertiary/secondary flow reed beds at their smaller treatment works. The beds are predominantly horizontal flow gravel based beds, 0.7m deep, and are used to polish the BOD and SS (Cooper et al., 2008). Many of the reed beds have been working very successfully for over 20 years. The data from Seven Trent provides a useful starting to point as to the footprint that is economically available at small treatment works. Fort (2013) provided details of 17 reed beds used by Seven Trent. They vary in size from 187m^2 to 1800m^2 and the smallest works has a p.e. of 222 and the largest 4,864. The beds were designed with 1m^2/p.e., if they were treating secondary waste and 0.5m^2/p.e. if they were treating tertiary waste. The Empty Bed Contact Time (EBCT) varied between 15 and 59 hours (Fort, 2013). Thus it can be seen that a comparative size adsorption bed using DWTR could be operated with total contact varying between 12 and 36 hours with a drain time of 6 hours. A four stage system with each stage having a loading period of 6 hours and a rest period of 1.5 hours, would have a footprint of less than 0.5m^2/p.e., comparable to the tertiary stage reed beds currently in operation at Severn Trent.

9.6.6.3 Scale of the system

As stated above, Seven Trent have used reed beds on sites ranging in scale from 222 to 4864 p.e. A DWTR based system, using 24 hours contact time and 6 hours rest time with MO media and a bed sized for 1000 p.e., would require approximately 800m^3 or around 1000 tonnes of media. This represents more than the yearly output of DWTR from some of the treatment plants assed but less than one month's output of sludge for the larger sites (See Table 4.3). Therefore, it would be technically possible to supply a DWTR treatment system on the scale of 1-2000 p.e. with media, but much above this scale the practicalities of supplying the DWTR may become complex.

9.6.6.4 Conclusion of modelled data

The data produced by the model for predicting the life expectancy of the media cannot be confirmed with any degree of accuracy due to the limitations of the model described in section 9.7.4. However, the programme outputs reveal that even when modelling the worst performing experimental system which was highly overloaded, a viable treatment system could be constructed.

The model also shows that to make a system with a viable life expectancy, beds will need to operate in series, with the number of beds depending on the removal capacity of the media. There are several advantages in using beds in series, by splitting the load between two adsorption beds it can be shown theoretically that the adsorption potential of the media is much greater. (The theory behind this is shown in Appendix B). It also means that small volumes of media can be replaced at regular intervals while keeping the system operational, and inevitably the first bed in the series will have the highest SS load, thus the hydraulic conductivity of the system as a whole can be kept high by replacing the first bed in the series relatively often (See Section 9.8.1). However, using multiple small beds in series adds to the operational and capital costs of the system.

9.6.7 Comparison of model results with previous studies

The only large scale multi bed system using DWTR reported in the literture Zhao et al (2010) has prevoiusly been discuseed in detail in Section 2.7.6. The system operated for over a year using 4 stages, each with a contact time of 4 hours, and rest time of 4 hours, with the outlet from one stage leading to the inlet of the next. The Soluble reactive P (SRP) and reactive P (RP) output from each stage of the system were measured and the results from each stage of the treatment process are shown in the Table 9.5.

Table 9.5 Performance of 4 stage pilot plant using Al-DWTR adapted from (Zhao et al., 2010)

Parameter	Influent mgL^{-1}	Stage 1	Stage 2	Stage 3	Stage 4
		mgP or SS/l (cumulative percentage removal)			
SRP	21	2.3(89)	1.2(94)	0.86(96)	0.47(98)
RP	45.3	8.9(80)	5.7(87)	3.7(91)	3.0(93)
SS	218	72.9(67)	39.8(82)	29.2(87)	19.3(92)

Although the input P level in the experimental system was over double the input of the systems modelled in Table 9.1 and 9.2, the results from this study show general agreement with the Matlab model. The majority of the P was removed in the first bed, 80% and 89% of the SRP and RP, respectively. The following stage removed between 5% and 7%. The final two stages only contributed 2% each to the final removal of the P. From these results Zhao et al (2010) predict a service life of the system for P removal of 4-17 years. However, they had already experienced some pooling on the surface of the system by the end of the year long experiment. With such high SS loading rates it is likely that the system would become blocked long before the media was saturated with P. They also comment that the size of the system was equivalent to a design loading of $0.5m^2$/p.e., which is also in agreement with the model outputs for a bed operating with 16 hours total contact time and 8 hours rest time. Therefore, this would suggest that the model is a good prediction of what will happen in a real system, and hence be a useful design tool.

9.7 Minimising the loss of hydraulic conductivity

Although the Matlab model predicts that a DWTR based system could potentially remove P to very low levels for many years, no inclusion was made in the model for the loss of hydraulic conductivity (HC) that will inevitably occur over time. In an operational system the life expectancy will be dictated not only by the amount of P that is removed, but also how long it takes before the hydraulic conductivity of the media reduces below an unacceptable level.

A factor could be included into the Matlab model which would enable the prediction of the rate of fall in HC depending on the SS loading and initial value of HC. However before such an algorithm could be included in the programme, more detailed experimental work would be required to assess the nature of the fall in HC in relation to SS loading.

9.7.1 Experimental results

The columns at the University showed an average reduction of 14% in HC over the yearlong experiment. However, the HC in the columns operating with RWW reduced by 86% on average (Figure 4.4). Assuming the reduction in HC had carried on in a linear fashion the columns would have operated satisfactorily for approximately 500 days before becoming blocked. However, this huge loss in HC can be ascribed to the very small area of the columns. An equivalent SS loading rate of between 100 and 50gm^{-2}day^{-1} for the systems operating with 6 and 12 hours contact time, respectively, would be between 10 and 20 times the SS loading rate recommended by Kadlec and Wallace (2008) as discussed below.

9.7.2 Recommended loading rates

Many authors report a positive correlation between system clogging TSS and COD loading rates (Knowles et al., 2011, Sani et al., 2013). Kadlec and Wallace (2008) and Knowles et al (2011) suggest for continued operation of vertical flow constructed wetlands that the solids loading should not exceed 5g/m^{2}day and the COD loading should be less than 20gm^{-2}day^{-1}. However this figure will obviously be dependent on the nature of the solids and the original hydraulic conductivity of the media as discussed below.

9.7.3 The importance of particles size

Hydraulic conductivity is defined by the Darcy's Law. As hydraulic conductivity decreases volumetric flow rate must decrease, unless either the flow path is shortened, the available area for fluid transfer is increased or the hydraulic head through the system is increased. Very commonly in sub-surface flow horizontal wetlands, as the HC decreases the flow short circuits over the surface (Cooper et al., 2008). As DWTR relies on adsorption processes to remove P, it is vital that all the water remains in contact with the media and overland flow is not a viable option for treatment. In a tidal flow system, as used in the experiments for this thesis, all the water must pass through the bed; thus the wetted area and flow path remained fixed. Therefore, to keep the system operational the media should ideally have the highest available hydraulic conductivity when placed in the bed and the system should be designed to allow a reduction in volumetric flow rate as the system ages. The hydraulic conductivities of the media in all but two of the columns at the start of the experiments was relatively high; values in the range of 2-7 x 10^{-3} ms^{-1}. The pressed media had a higher HC than the columns filled with 6mm gravel. Thus, the majority of the DWTR should allow flow for a substantial period of time.

The hydraulic conductivity of a porous media is very sensitive to media size, as emphasized by the squared relationships in the Kozeny-Carmen equation for flow through porous media (Kadlec and Knight, 1996). Despite this, smaller media, such as soil and sands, were originally used in early reed bed designs as they were believed to offer superior treatment performance when compared to larger media. Indeed, this research has shown that the smaller the particle size, the greater the ability of the media to remove P. However, there is a much greater likelihood of suspended solids interception due to narrower pore diameters. This makes fine media prone to rapid clogging by pore occlusion from filtration and the bridging of surface accumulations. More recent work has shown that using larger media, with median diameters between 6 and 11 mm, allow for much greater longevity of systems without blocking (Knowles et al., 2011). However, the jury is still out on the ideal media size and obviously it depends on the application. Various recommendations from international guidelines on reed bed design are shown in Table 9.6.

Table 9.6 Example of media size distributions recommended by various design guidelines adapted from (Knowles et al., 2011)

Country	Size Distribution	Source
Austria	0-4mm(grey water) 1-4mm(tertiary treatment) 4-8mm(primary treatment)	(ÖNORM, 2005)
International Water Association	8-16mm	(IWA, 2001)
European design Guidelines	3-6mm 6-12mm	(Cooper, 1990)

The DWTR in these experiments had median sizes of 3 to 13mm. Thus the majority of the media should be suitable for treatment of tertiary water but only around half would be suitable for secondary treatment beds.

9.7.4 Predicted suspended solids loading rates on DWTR systems

The outlet from the Matlab programme in Table 9.4, shows the required size of a treatment system in relation to contact time. Therefore, it is possible to construct a similar table showing the expected SS loading rates that would occur with differing input concentrations of SS and systems with variable contact times, were used.

Table 9.7 Predicted SS loading rates dependent on contact time and SS input

Contact time (hrs)	1	4	6	12	24
Rest time (hrs)	1	2	3	6	6
SS input mgL^{-1}	Approximate SS loading in gm^{-2}.day				
5	20	6	4	2	1
10	40	12	8	4	2
25	100	31	21	10	6
50	200	62	43	21	12
100	400	125	87	42	25

It can be seen that to keep the SS loading below 5gm^{-2} either long retention times or very low SS inputs to the system are required. Typical domestic waste water has SS values 130-389mgL^{-1} (Metcalf et al., 2014) and it is generally reported that primary treatment removes 50-70% of this load (EPA, 1997). Therefore, beds treating primary treated sewage could be expected to have SS loadings of between 40 and 195 mgL^{-1}. This loading rate would inevitably cause the systems to block at some point. However, the system used by Zhao et al (2010) received an average inlet concentration of 218mgL^{-1} and successfully operated for over a year (Table 9.5).

The SS concentrations expected after secondary treatment are much harder to predict as it is dependent on the processes involved. The Severn Trent reed bed systems that Fort (2013) assessed had SS inputs ranging from 3 to 17mgL^{-1}. So it is likely that DWTR systems operating as tertiary treatment beds would become saturated with P long before they were blocked.

9.7.5 Cleaning blocked systems

Many attempts have been made to remove SS from blocked reed bed systems Nivala et al (2012) suggest six ways in which hydraulic conductivity can be rejuvenated:

- Moving the inlet flow distribution, most beds tend to clog around the inlet area, so moving the inlet may increase longevity of the beds.
- Resting the system which is thought to mineralise the organic component of the SS. However, for this method to be effective the resting period would probably need to be days or weeks (which is much greater than the resting period used in the proposed systems).
- Backwashing with water and air (recommended rates of backwash 9-15L/m^{2}s).
- Washing with chemicals. Hydrogen peroxide has proved very effective at cleaning the media in situ.
- Introduction of earthworms, earthworms and their burrowing activities contribute to the aeration and drainage of soil. There have been successful trials introducing 0.5kgm^{-2} of earthworms to vertical flow reed beds which have increased hydraulic conductivity within ten days (Li et al., 2011).
- Finally, the media can be dug out and replaced.

Thus even if the systems do become blocked it may be possible to clean them without excessive cost.

9.8 Engineering design and operation of the system

This section discusses how a system using DWTR could be constructed and operated in light of the experimental data, and the output from the Matlab models.

9.8.1 System operation and control

9.8.1.1 Sequential operation

Many commercial adsorption systems are operated with beds in series (Crittenden and Thomas, 1998). Using beds in series maximises adsorption capacity as has been previously discussed (theory shown in Appendix B). However, to further increase the system performance the inlet to the beds should be transferred from one bed to the next in the series as the first bed approaches saturation (Figure 9.11). Using this method of system operation optimises final adsorption capacity of the media, but adds greatly to the cost of control and pipework. Sung et al (1979) assessed the operation of beds operating in series and parallel and concluded beds operating in series offer higher removal performance as the leading bed in a series system can achieve higher solute saturation. Activated carbon adsorption systems are also commonly operated in series as this allows continuous operation of the systems as once the first bed reaches breakthrough it can be taken off line and flow is directed into the second bed Cooney (1998).

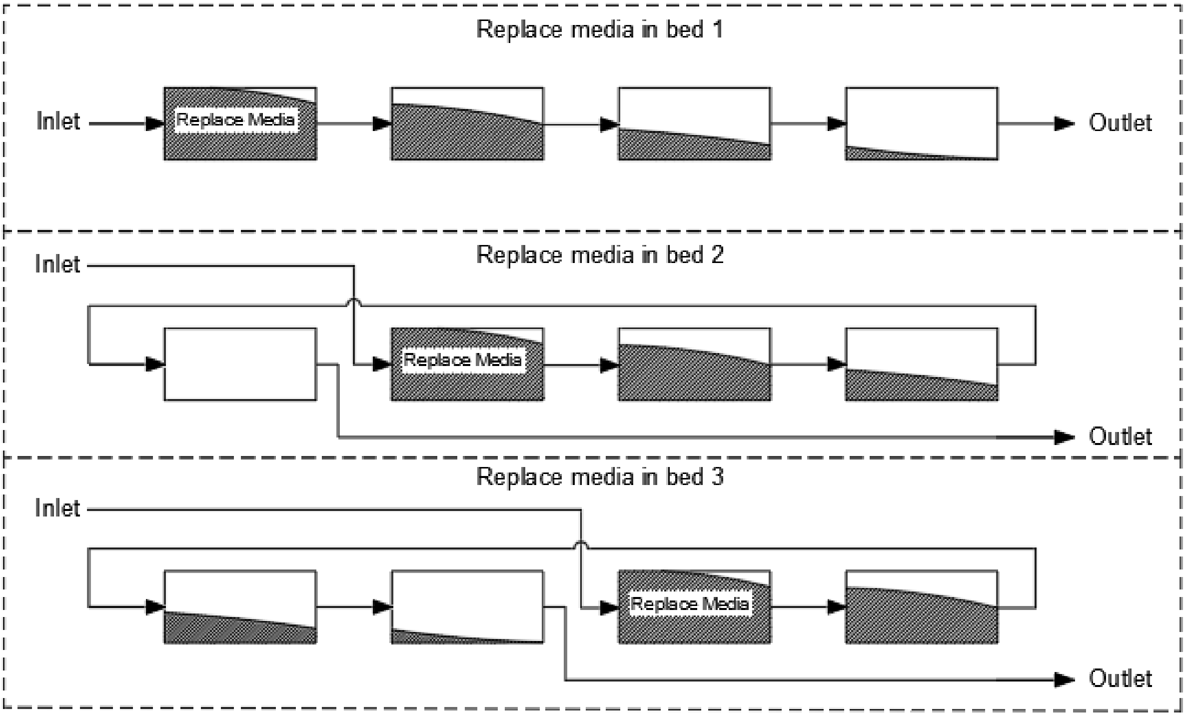


Figure 9.11 Operating beds sequentially to maximise system performance

9.8.1.2 The problem of continuous input flow

Operating the systems in tidal flow has the disadvantage that the flow cannot be continually input into the systems. The majority of treatment works receive flows 24 hours a day albeit in a diurnally variable pattern with less flow at night (Metcalf et al., 2014). To allow for continual input flow, the system would either require an input balancing tank or two parallel process lines, (Figure 9.12). Again, both option adds to system cost and whichever method is chosen would depend on the specifics of the flow to each site and the availability of suitable tanks and control systems.

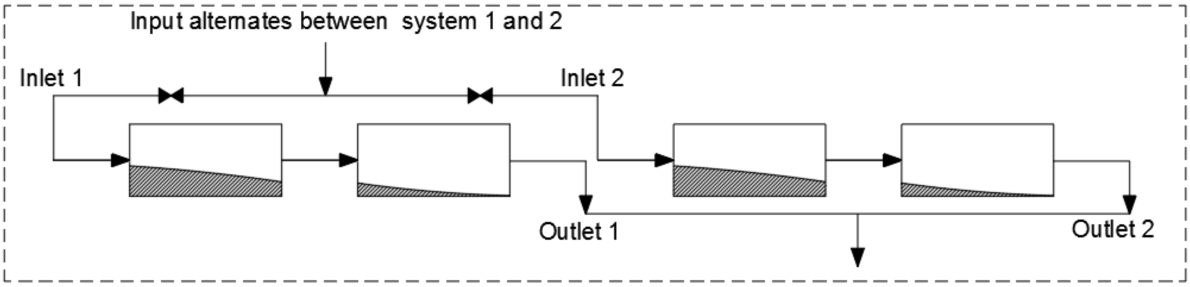


Figure 9.12: Operating two process streams in parallel to allow for continual input flow.

9.8.2 Replacement of bed media

The Matlab programme and the results from the hydraulic conductivity experiments suggest that a system would last anywhere from 1 to 5 years, depending on media type and inlet conditions and outlet requirements. After this point the media would have to be changed. Therefore, the system must be designed to make removal and replacement of the media simple and fast.

Traditionally, reed bed systems have been rectangular boxes which are usually buried in the ground or surrounded by earth bunds and sealed with a water proof membrane (Kadlec and Wallace, 2008). Such designs make it very hard to replace the media. To make removal of the media easier and cheaper the beds would have to be constructed with a concrete or steel base and an inlet slope into the system which would allow easy access to a digger. See Figure 9.13

Figure 9.13 Front slope in system and concrete base to allow replacement of media

9.8.3 Use of gravel for inlet and outlet distribution

9.8.3.1 Inlet and outlet designs

Traditionally all tidal flow and vertical flow reed beds have used large gravel (>20mm) inlet and outlet areas to distribute the flow and protect the media (Cooper, 1990). The gravel can represent anywhere from 5 to 30% of the total media volume (Knowles et al., 2011). In many reed bed designs gravel is the only media used, and the inlet and outlet areas can be thought of as an extension to the treatment area. The two gravel controls used in the experiments for this thesis were filled with 6mm gravel and removed between 5 and 14% of the inlet P compared with 50 to 90% for the DTWR. Therefore, to maximize P removal in a given volume of treatment media, the gravel distribution areas should be minimized.

The media has similar porosities to gravel, and has proven to be hydraulically stable over the course of the experiments. Therefore, there is probably no need to use a gravel inlet area, just protective concrete pads to stop erosion from inlet flow (Figure 9.14). However, there would be a need to protect the outlet drainage pipe from ingress of small particulate matter and this would require a gravel surround. Three options for the inlet and outlet designs are shown in Figure 9.14 A, B and C.

Minimizing the amount of gravel in the system also makes it easier to replace and recycle the media, as the DWTR removed would not be mixed with gravel. However, to reduce the loss of hydraulic conductivity the interface between the gravel and the DWTR should be maximized so option C in Figure 9.14 may block quicker than option A and B. Ideally, option B would be used as this would allow for easy removal of the media, as the gravel and inlet pipe could be protected from the actions of the digger. In option B the solids in the gravel could also easily be washed out with a pressure washer once the media had been removed. However, the gravel would have to be held within a gabion structure which would add greatly to the cost of the system.

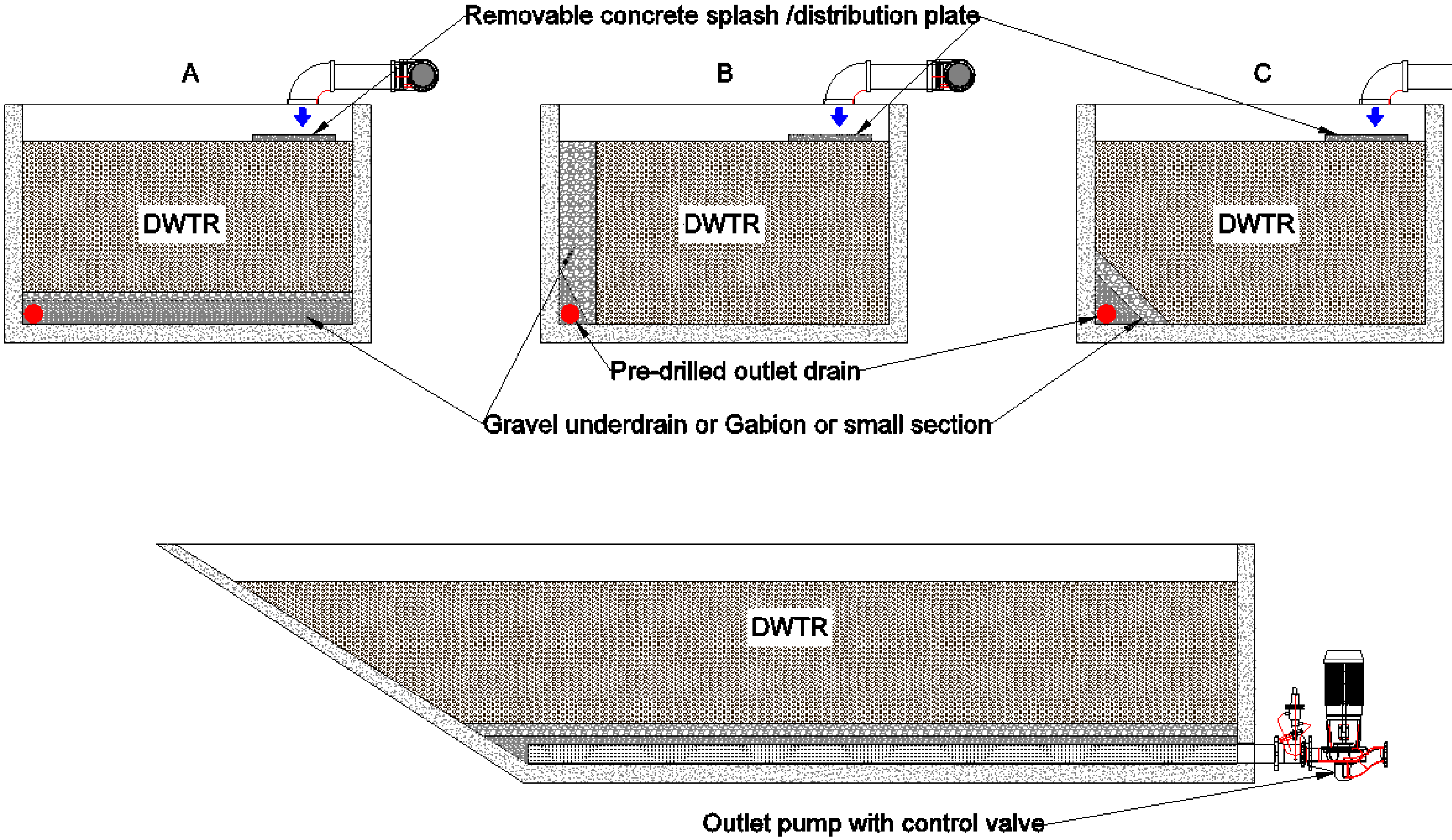


Figure 9.14 Sections through proposed bed design showing different options for gravel outlet design and concrete splash plates at the inlet.

9.8.4 Optimising system operating and construction costs

To reduce construction costs a 4 bed series system could be constructed as one unit. Such a system is visualised in Figure 9.15

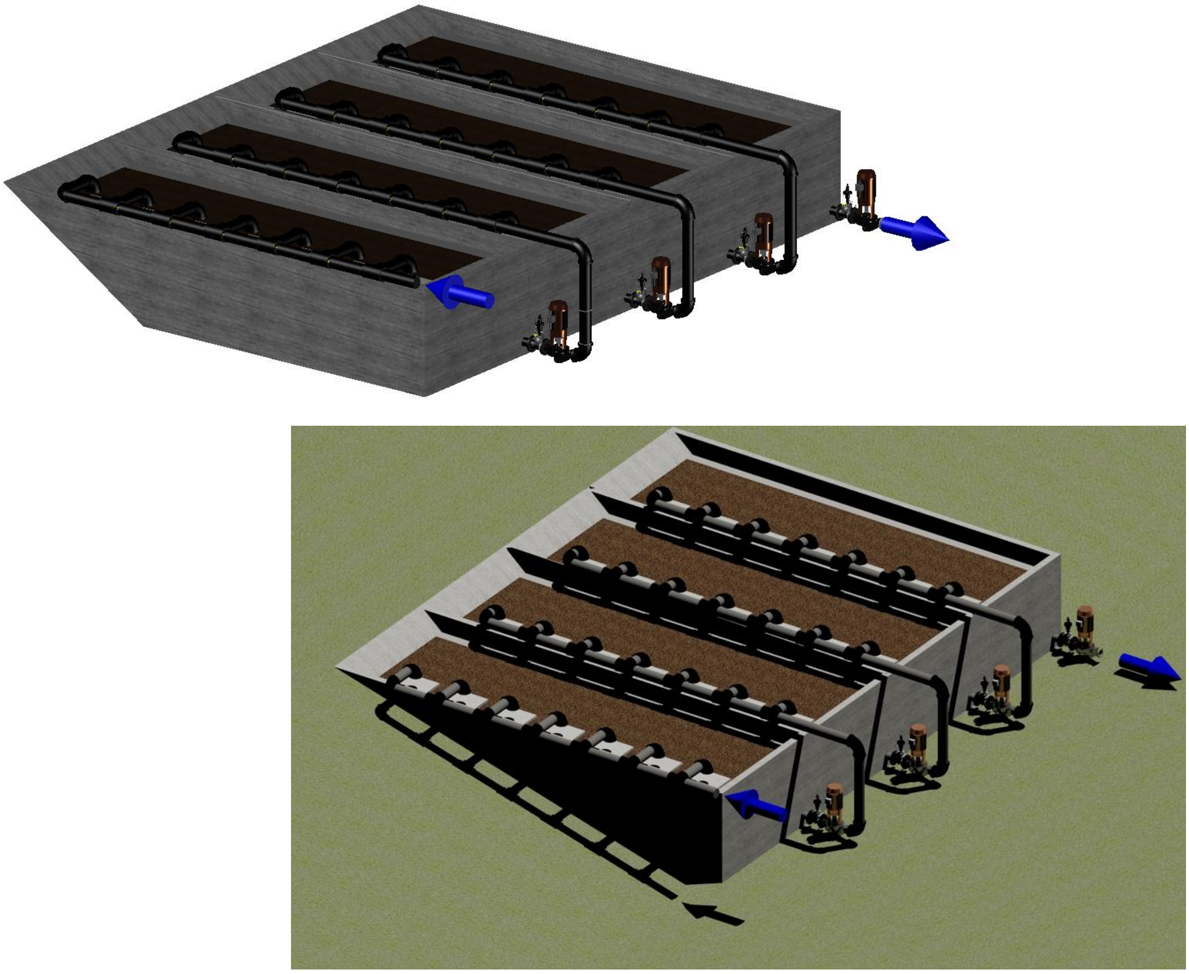


Figure 9.15 A series of four systems in series constructed as one unit, with the outlet of one system feeding the inlet of the next.

The front end of the system would have to be buried in the ground to allow digger access and the back end would have to be above ground level or within access wells to allow for pump and valve maintenance. The configuration of the pipework would have to be much more complex than shown if the series of bed operation were configured as for Figure 9.13 or 9.14.

Using beds in series adds considerably to the pumping costs of the treatment system as all the water has to be pumped from one bed to the next. A final option to alleviate the pumping costs would be to place the beds on a slope with one bed feeding the next under gravity. The pumps would be replaced by control valves. This option would only be possible if there was a suitable slope on the site, and using this type of system would not allow for changing the sequential operation of the beds, but would provide a more environmentally friendly option. The system is visualised in Figure 9.16.

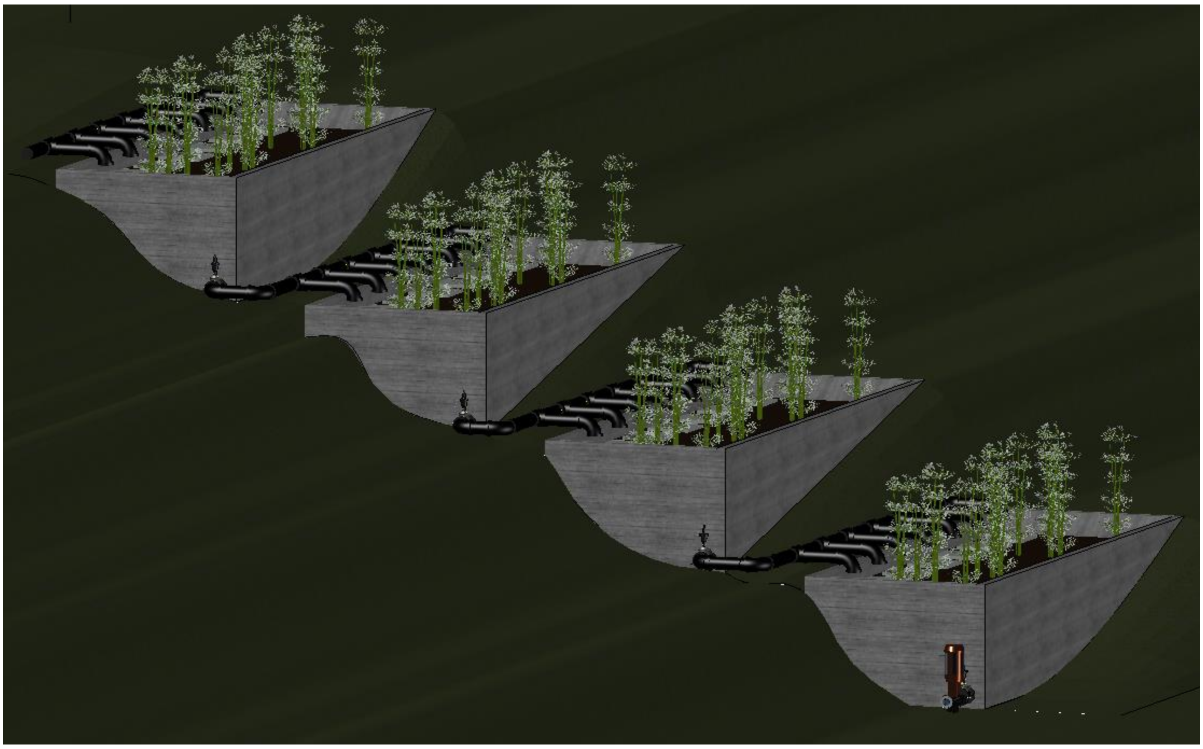


Figure 9.16 Using a series system on a slope to remove pumping costs.

9.8.5 Should plants be used?

Using reeds in a DWTR adsorption system may increase the total P removal capacity of the system and Babatunde et al (2010) have shown that reeds will happily survive in a purely DWTR based wetland. The plants uptake P to grow and the rhizomes would increase the microbiological population of the system (Mitsch and Gosselink, 2000). However, the effect of the plants on P removal is a debated question and has been discussed in Section 2.7.4.2. The plants would increase the aesthetic appeal of the system and provide a habitat for larger invertebrates and birds. But there is also continuing debate as to whether reeds increase or decrease hydraulic conductivity of the beds and using reeds would greatly complicate the removal of the media. More research still needs to be undertaken as to whether reeds would be a positive or negative addition to a DWTR based system.

9.8.6 Recycling the media

Generally commercial adsorbents are regenerated once they are fully saturated, as they are very expensive to produce. As DWTR is a waste product it is likely that regeneration would not be a financially viable option and the media would simply be replaced. A full life cycle assessment of the system would be required to ascertain how often it would be viable to replace the media. It may be possible to recapture the P contained within the media and there has been a substantial amount of research undertaken in this field (Kunaschk et al., 2015, Morse et al., 1998, Wang et al., 2013). Whether this would ever be economically viable is open to question and beyond the scope of this research.

Chapter 10 Conclusion and further work

10.1 Conclusion of experimental results and analysis

This thesis has assessed how the nature and production processes of DWTR effect their ability to remove P from waste water and provided a compressive appraisal of the key parameters that would affect the engineering design of a full scale system.

This research has clearly shown that the bulk particle size of the media and the nature of the production processes including the amount and type of coagulant dosed and drying process have a significant effect on how much P the DWTR can remove. With increasing particle size and coagulant dose having a negative effect on P removal. Whereas, increasing the carbon content of the media has a positive effect. Alum based media tend to remove more P than ferric based media when particle size is taken into account and assessment of the saturated moisture content would imply that centrifuged media would tend to remove more P than pressed media. However, the very heterogonous nature of the media and small sample size (8 media) makes the significance of these effects unprecise.

The beds operate more efficiently and remove more P by mass with higher inlet P concentration. Increasing the inlet concentration to the systems up to 10mgL^{-1} TP improves percentage P removal performance and increases P mass removal rates. This is above the levels that would be expected at a domestic sewage treatment works and higher than the levels used in these experiments. Standard water treatment works are reported to remove up to 50% of the P load that enters the works. Therefore, the closer to the head of the works the system could be placed the higher the P removal. However, there is likely to be a higher load of suspended solids nearer the head of the works and this could cause the systems to block before they are saturated with P.

The results from both the Fe and Al analysis imply that neither chemical leaches from the majority of the media in quantities that should represent a problem to aquatic systems. The two media that did leach Fe (HO and LA) were not the best at removing P and therefore should not be used as media in a full scale treatment system.

There were strong associations between calcium, sulphate and phosphorus removal, and these correlations are most probably explained by the precipitation of calcium phosphate and the ligand exchange of sulphate. A decrease in system pH encourages the exchange of hydroxide ions with phosphate and also improves removal performance. These associations were not seen in the RWW site probably due to the inhibiting effect of the ions in the waste water and formation of biofilm.

No correlations were found between the chemical properties of the 8 DWTR used in the experimental columns and their ability to remove P.

The beds would be best operated in a tidal flow hydraulic regime with a loading period followed by a resting period. The ability of the beds to remove P would be curtailed if the retention time was reduced below 3 hours, but not much improvement in performance would be seen if the retention time was increased above 6 hours (for media with a high adsorption capacity), at least not for the first 1000 bed volumes passed. After this time increasing retention time may have a positive effect.

The results of the experiments showed that increasing the amount of time the beds are left to rest between loading periods has a positive effect on P removal. However, the effect is relatively small especially during the first 300 bed volumes passed. It is unclear if increasing the rest time above 6 hours has a positive effect on the system but it would be prudent to keep the resting time above 2 hours.

Modelling the systems revealed that a single bed is unlikely to remove P to useful levels for more than a few weeks. To use DWTR in a treatment process, multiple beds would be required to operate in series if the output P level was required to meet a discharge consent of less than 0.5mgL^{-1} for more than a few months. The amount of beds operating in series would be dependent on the type of media used and the nature of the P inlet concentration. However, operating beds in series would require substantial pumping energy unless the beds could be placed on a slope.

To maximise the P removal potential of multiple bed systems the first bed in the series should be dug out periodically and the inlet feed should be fed to the next bed in the series. This would not only maximise the use of the media but should keep the hydraulic conductivity high, as the bulk of the solids will be removed in the first bed of the series. However, complex pipework and valve arrangements would be required to run the systems in this way, and the beds could not be used on a slope.

To balance the requirements of P removal and loss of hydraulic conductivity, it would be advisable to keep the media bulk particle size above 4mm. This would increase the initial hydraulic conductivity and in turn allows for a greater void space for the suspended particles to collect in. It would probably also be advisable to keep the bed depth or flow path to less than 1m, as the longer the flow path the greater will be the loss of hydraulic conductivity. However, this is partly dependent of the arrangement of inlet and outlet flow.

Standard reed bed systems use extensive gravel inlet and outlet areas, however the gravel in a DWTR based system would add almost no P removal potential (<5%) to the system. The majority of the raw media tested had hydraulic conductivities equivalent to 20-30mm gravel and therefore there is no requirement for an inlet distribution system. However, an outlet gravel drainage area would be required to protect any outlet pipe from the ingress of small particulates. A vertically placed outlet drain would not only provide a large interface between the media and DWTR but would provide access of the inlet water to the base of the media should the surface become blocked. However, such an inlet are would have to be held in place by a supporting structure that must not corrode, this would add to the cost of the system.

It has always been envisaged that DWTR would be suitable for small scale applications. By comparing the foot print of the reed beds used by Severn Trent, it was reasoned that many water companies may have similar space available, and by comparing the removal performance that could be expected from the DTWR per system area it has been reasoned that such a system would be appropriate for water treatment works of scales from 100 to 2000 p.e. Further by assessing the amount of DWTR produced at the 8 treatment works studied for this investigation it was clear that the supply of DWTR would be plentiful although not from all of the works.

10.2 Summary of design recommendations for the use of DWTR in a phosphorus removal system

Design recommendations for the future use of DWTR in a full scale system are provided. Numerical values are included where they are backed up by the data.

Media

- The media should have as small a particle size as possible yet highest porosity; media size >4mm and < 6mm.
- The media should have a high carbon content.
- The dry solids content of the DWTR should not be below 19%.

Raw water feed and processing of the DWTR

- Preferably alum coagulant and as low a dose as possible.
- Preferably a polymer that is organic in nature.
- Media processed with a centrifuge rather than a press as long as the moisture content can be kept low enough.

Location of the processes

- Ideally placed after primary treatment to maximise P removal but would block much faster due to higher SS loading. However it must also be noted that P captured by primary and secondary treatment systems is generally recycled to land; and if this route is not available to the P saturated DWTR then the use of such a P adsorption system earlier in the process train may hinder rather than benefit the overall recycling of P.

- Using the processes as a tertiary treatment step will extend the life expectancy, but it is not clear how well the media will perform with very low inlet concentrations of P (<$0.1mgL^{-1}$).
- Ideally the SS loading rate would be kept below $5gm^{-2}day^{-1}$.

System operation

- Depending on media type, 2 to 4 beds should be operated in series.
- The beds should be operated in a tidal flow.
- The flow rate inside the beds when being drained down should not exceed 1m/min.
- Beds should have a contact time of 4-6 hours and a resting period of 2 - 6 hours.
- The front bed in the system should be dug out when nearing saturation and the next bed in line should replace it as the first bed in the system.
- To allow for continual flow, two systems would need to be operated in parallel or a balancing tank would be required.

Engineering and scale

- A DWTR based system could be used for works up to 2000 p.e.
- The bed depth should not be greater than 1m resulting in an area requirement for the system of 0.5-$0.75m^2$/p.e.
- An inlet slope into the system and concrete construction would allow for easy media removal.
- Gravel inlet and outlet structures should be minimised in volume
- Building multiple beds as one unit would keep construction costs down.
- Ideally beds would be placed on a hill to alleviate large pumping costs.

10.3 Further Work

An ideal outcome from this research would be that in the future P removal systems were constructed using DWTR as a media. However, there are still many questions that need answering before that will come into fruition. This list of further work has been to some extent ordered in the research that would be required before a full scale system could be constructed and operated.

10.3.1 Pilot plant

The results from the experiments in this thesis has demonstrated that using DWTR as a P removal system could be viable, efficient and environmentally friendly. However, the effects of scaling up the system are still unclear. The next logical step in the design procedure would be to build a pilot plant utilising four beds in series operating at a suitable waste water treatment plant.

10.3.2 Life Cycle Analysis and costings

At first sight the process for removing P using DWTR appears to be very environmentally friendly. In addition, the cost of a DWTR based system should be favourable when compared to other P treatment options, as DWTR is a waste product controlled by the water companies themselves.

However, using the DWTR would require the construction of expensive beds, and a relatively complex control system. Therefore, a detailed analysis of the costs (financial and environmental) would be required. This would probably be easiest undertaken in conjunction with a pilot plant.

10.3.3 Total Carbon (TC) and Total Organic Carbon (TOC)

This work and others have shown that there is a correlation between the amount of carbon in the media and the amount of P it can remove. Unfortunately, it was not possible to measure how TC or TOC changed in the inlet and outlet over the course of these experiments. Column experiments conducted in the future should measure the TC and / or TOC in the inlet and outlet of the system to show further how TC and P removal are related.

10.3.4 Media Heterogeneity

The results from the repeated experiments revealed substantial difference between models running with the same media and identical operating conditions. More research is required to assess the cause of this difference. I would recommend that if any of the experiments from this thesis were repeated a minimum of three copies of each column were used.

10.3.5 Life expectancy

None of the experimental systems operated in this research reached P saturation. Although the life expectancy of a system may not be finally dependent on the maximum adsorption capacity of the media, much more accurate predictive models could be constructed if the experiments could have been run until the media had been saturated. Columns similar to those used in these experiments could be used with 4 hours retention time and operated with similar inlet concentrations of 5mgL, but operated for up to three years or until the media was saturated.

10.3.6 Running systems in series

An ideal system would use beds operated in series. To assess how beds would perform in series it would be worthwhile operating smaller column models in series to see if there are any adverse effects of series operation. Also using 4 columns in series and observing their breakthrough characteristics would enable the calculation of adsorption media life expectancy using the empty bed contact time method. Which is a standard model used in the water industry.

10.3.7 Centrifuged, belt pressed and pressed media.

The results from the experiments implied a relationship between P removal and the dewatering process although the correlation is not strong. However, to prove if there is a correlation an experiment would have to be undertaken using similar inlet water and coagulant but different dewatering processes. The media produced could then be assessed using isotherms to see if there is a difference in the P retaining properties of the media. This experiment could be undertaken at laboratory scale.

10.3.8 The use of starch as a polymer

The two systems that contained DWTR which had come from works using starch as a polymer removed the most P. From the data set it was impossible to tell if it was the polymer that was the source of the improved performance. It would be relatively easy to assess if there was a difference in P removal capacity between starches or polyelectrolyte based polymers in a laboratory manufactured media.

10.3.9 The effect of rest time

Increasing the resting period had a positive effect on the P removal capacity of the system. However, it is unclear from the experiments how long an optimal rest period should be or how increasing the rest time improves performance. More research is required to assess both the mechanism associated with resting the media and how retention time should be optimised.

10.3.10 Using Reeds

Whether reeds would make a positive contribution to a DWTR based system has been discussed in detail in several places in this thesis. If a long term pilot scale system were constructed ideally two parallel systems could be operated one containing reeds and another without. Both the P removal performance and hydraulic conductivity of the system would need to be closely assessed.

10.3.11 Formation of biofilm

A simple experiment was undertaken in this thesis to assess if the formation of biofilm inhibited the ability of the DWTR to remove P but it did not produce any significant results. An experiment designed in conjunction with a micro biological expert to prove whether the effect of biofilm was significant or not would be helpful.

10.3.12 Quantifying the particles size

The results from these experiments have highlighted the significance of particles size in relation to P removal. Although the system used to assess particle size in this thesis proved to be effective it was very time consuming; which did not allow for many repeats. Ideally the experiment should be repeated many times with the same media to assess both the errors associated with the measuring system and provide further information regarding the heterogeneity of the DWTR in relation to particle size.

10.3.13 Producing media with smaller particle size

The media is easily broken up into smaller particle sizes by hand. It is therefore likely that the larger particles sizes would be broken up by machine as the DWTR was loaded into a large scale bed. It would be useful to research the type of machinery that is available that could make the media size smaller and more homogeneous as it is placed in the bed.

10.3.14 Recovering the phosphorus

It would be good to recover the P that is captured by the DWTR. However, at present, all methods to do this require a lot of chemicals or complex equipment and would not be economically viable. The P may be available to plants as a very slow release fertiliser if the saturated media was spread on the land. A detailed assessment of both the effect of spreading saturated media on the land and possible other recycling options is required to evaluate the most economical option for recovering the sorbed P from the DWTR.

10.3.15 Nitrogen and other chemicals

Although this research has concentrated on P removal, the DWTR has potential to remove many other chemicals. Optimising the beds for nitrogen removal may require a slightly different load and rest time regime as discussed. Therefore further work is required to assess how the beds would treat many of the contaminants of interest within a waste water treatment system. If the beds are shown to remove other chemicals of interest it would make their use much more attractive.

10.3.16 Removing phosphorus to very low levels

Modelling multiple bed systems implied that P could be removed to very low levels (<0.1mgL^{-1}). However, the DWTR may perform very differently with such low concentrations of P, as the concentration gradient between the media and the waste water would be almost non-existent. Further work is required to assess if the DWTR would remove P at such low concentrations.

References

ADAM, K., KROGSTAD, T., VRÅLE, L., SØVIK, A. K. & JENSSEN, P. D. 2007. Phosphorus retention in the filter materials shellsand and Filtralite P™—Batch and column experiment with synthetic P solution and secondary wastewater. *Ecological Engineering,* 29**,** 200-208.

ADAM, K., SOVIK, A. K. & KROGSTAD, T. 2006. Sorption of phosphorous to Filtralite-P TM - The effect of different scales. *Water Research,* 40**,** 1143-1154.

AHMAD, T., AHMAD, K., AHAD, A. & ALAM, M. 2016. Characterization of water treatment sludge and its reuse as coagulant. *Journal of environmental management,* 182**,** 606-611.

AL-TAHMAZI, T. & BABATUNDE, A. 2016. Mechanistic study of P retention by dewatered waterworks sludges. *Environmental Technology & Innovation,* 6**,** 38-48.

AL-TAHMAZI, T. M., A. BABATUNDE,A. 2016. An experimental and theoretical investigation of P adsorption by dewatered waterworks sludges. Unpublished.

ANDERSON, B. H. & MAGDOFF, F. R. 2005. Relative movement and soil fixation of soluble organic and inorganic phosphorus. *Journal of Environmental Quality,* 34**,** 2228-2233.

ARNEPALLI, D. N., SHANTHAKUMAR, S., HANUMANTHA RAO, B. & SINGH, D. N. 2008. Comparison of Methods for Determining Specific-surface Area of Fine-grained Soils. *Geotechnical and Geological Engineering,* 26**,** 121-132.

ASIMOV, I. 1975. *Asimov on chemistry*, Macdonald and Jane's.

BABATUNDE, A. & ZHAO, Y. 2007. Constructive approaches toward water treatment works sludge management: an international review of beneficial reuses. *Critical Reviews in Environmental Science and Technology,* 37**,** 129-164.

BABATUNDE, A. O., KUMAR, J. L. & ZHAO, Y. 2011a. Constructed wetlands using aluminium-based drinking water treatment sludge as P-removing substrate: should aluminium release be a concern? *J Environ Monit,* 13**,** 1775-83.

BABATUNDE, A. O. & ZHAO, Y. Q. 2010. Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge. *J Hazard Mater,* 184**,** 746-52.

BABATUNDE, A. O., ZHAO, Y. Q., BURKE, A. M., MORRIS, M. A. & HANRAHAN, J. P. 2009. Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environ Pollut,* 157**,** 2830-6.

BABATUNDE, A. O., ZHAO, Y. Q., DOYLE, R. J., RACKARD, S. M., KUMAR, J. L. G. & HU, Y. S. 2011b. Performance evaluation and prediction for a pilot two-stage on-site constructed wetland system employing dewatered alum sludge as main substrate. *Bioresource Technology,* 102**,** 5645-5652.

BABATUNDE, A. O., ZHAO, Y. Q., YANG, Y. & KEARNEY, P. 2008. Reuse of dewatered aluminium-coagulated water treatment residual to immobilize phosphorus: Batch and column trials using a condensed phosphate. *Chemical Engineering Journal,* 136**,** 108-115.

BABATUNDE, A. O., ZHAO, Y. Q. & ZHAO, X. H. 2010. Alum sludge-based constructed wetland system for enhanced removal of P and OM from wastewater: concept, design and performance analysis. *Bioresour Technol,* 101**,** 6576-9.

BAI, L., WANG, C., HE, L. & PEI, Y. 2014. Influence of the inherent properties of drinking water treatment residuals on their phosphorus adsorption capacities. *Journal of Environmental Sciences,* 26**,** 2397-2405.

BARCA, C., TROESCH, S., MEYER, D., DRISSEN, P., ANDRES, Y. & CHAZARENC, F. 2012. Steel slag filters to upgrade phosphorus removal in constructed wetlands: two years of field experiments. *Environmental science & technology,* 47**,** 549-556.

BARNARD, J., MURTHY, S. & DEBARBADILLO, C. 2011. Development of Sustainable Approaches to Achieving Low Phosphorus Effluents. *Proceedings of the Water Environment Federation,* 2011**,** 324-335.

BAUMANN, H. & TILLMAN, A. 2004. The hitchhiker's guide to LCA: an orientation in life cycle assessment methodology and application. 2004. *Lund: Student Literature*.

BENISCH, E. A. Can Tertiary Phosphorus Removal Reliably Produce 10ug/L? Pilot Results from Coer D'Alene ID. Nutrient Removal, 2007.

BENISCH, M., FISHER, C., KEIL, D., CLARK, D. & NEETHLING, J. 2011. Reliability of Low P Technologies in the Real World—First Results from a Two-Year Demonstration Program. *Proceedings of the Water Environment Federation,* 2011**,** 1013-1036.

BERNARD, J. M. 1999. Seasonal growth patterns in wetland plants growing in landfill leachate. *Constructed wetlands for the treatment of landfill leachates***,** 223-233.

BLANCHARD, G., MAUNAYE, M. & MARTIN, G. 1984. Removal of heavy metals from waters by means of natural zeolites. *Water research,* 18**,** 1501-1507.

BLANEY, L. M., CINAR, S. & SENGUPTA, A. K. 2007. Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Res,* 41**,** 1603-13.

BOYER, T. H., PERSAUD, A., BANERJEE, P. & PALOMINO, P. 2011. Comparison of low-cost and engineered materials for phosphorus removal from organic-rich surface water. *Water Research,* 45**,** 4803-4814.

BRENNAN, R. B., FENTON, O., RODGERS, M. & HEALY, M. G. 2011. Evaluation of chemical amendments to control phosphorus losses from dairy slurry. *Soil Use and Management,* 27**,** 238-246.

BRETT, S. 1997. *Phosphorus removal and recovery technologies*, Selper.

BRIX, H. 1999. How 'green' are aquaculture, constructed wetlands and conventional wastewater treatment systems? *Water Science and Technology,* 40**,** 45-50.

BRIX, H., ARIAS, C. A. & DEL BUBBA, M. 2001. Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands. *Water Science and Technology,* 44**,** 47-54.

BROWNING, K. & GREENWAY, M. 2003. Nutrient removal and plant biomass in a subsurface flow constructed wetland in Brisbane, Australia. *Water Science and Technology,* 48, 183-189.

CALLERY, O., HEALY, M., ROGNARD, F., BARTHELEMY, L. & BRENNAN, R. 2016. Evaluating the long-term performance of low-cost adsorbents using small-scale adsorption column experiments. *Water Research*, 101, 429-440.

CARTER, D., HEILMAN, M. & GONZALEZ, C. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Science,* 100**,** 356-360.

CERATO, A. B. & LUTENEGGER, A. J. 2002. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. *Geotechnical Testing Journal,* 25**,** 315-321.

CHEUNG, K., VENKITACHALAM, T. & SCOTT, W. 1994. Selecting soil amendment materials for removal of phosphorus. *Water Science and Technology,* 30**,** 247-256.

CHILDERS, D. L., CORMAN, J., EDWARDS, M. & ELSER, J. J. 2011. Sustainability Challenges of Phosphorus and Food: Solutions from Closing the Human Phosphorus Cycle. *BioScience,* 61**,** 117-124.

COLLINS, A. G., DEMPSEY, J.P., PARKER, P.J. 1998. Effects of Freezing Rate, Solids Content, and Curing Time on Freeze/Thaw Conditioning of Water Treatment Residuals. *Environmental Science and Technology,* 32**,** 383-387.

COOPER, D., GRIFFIN, P. & COOPER, P. 2008. Factors affecting the longevity of subsurface horizontal flow systems operating as tertiary treatment for sewage effluent. *Wastewater treatment, plant dynamics and management in constructed and natural wetlands.* Springer.

COOPER, J. & CARLIELL-MARQUET, C. 2013. A substance flow analysis of phosphorus in the UK food production and consumption system. *Resources, Conservation and Recycling,* 74**,** 82-100.

COOPER, J., LOMBARDI, R., BOARDMAN, D. & CARLIELL-MARQUET, C. 2011. The future distribution and production of global phosphate rock reserves. *Resources, Conservation and Recycling,* 57**,** 78-86.

COOPER, P. 2009. What can we learn from old wetlands? Lessons that have been learned and some that may have been forgotten over the past 20 years. *Desalination,* 246**,** 11-26.

COOPER, P. F. 1990. European design and operations guidelines for reed bed treatment systems.

COONEY, D. 1998. Adsorption design for wastewater treatment. *CRC press*

CORDELL, D. 2013. Peak phosphorus and the role of P recovery in achieving food security. *Source Separation and Decentralization for Wastewater Management, TA Larsen, KM Udert and J. Lienert (eds.), IWA Publishing, London, UK*, 29-44.

CORDELL, D., ROSEMARIN, A., SCHRÖDER, J. J. & SMIT, A. L. 2011. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. *Chemosphere,* 84**,** 747-758.

CORRELL, D. L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review. *Journal of Environmental Quality,* 27**,** 261-266.

CRITES, R. & TECHNOBANOGLOUS, G. 1998. *Small and decentralized wastewater management systems*, McGraw-Hill.

CRITTENDEN, B. & THOMAS, W. J. 1998. *Adsorption technology & design*, Butterworth-Heinemann.

CRITTENDEN, J. C., TRUSSELL, R. R., HAND, D. W., HOWE, K. J. & TCHOBANOGLOUS, G. 2012. *MWH's water treatment: principles and design*, John Wiley & Sons.

DAS, B., MONDAL, N., BHAUMIK, R. & ROY, P. 2014. Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil. *International Journal of Environmental Science and Technology,* 11**,** 1101-1114.

DAWSON, C. J. & HILTON, J. 2011. Fertiliser availability in a resource-limited world: Production and recycling of nitrogen and phosphorus. *Food Policy,* 36**,** S14-S22.

DAYTON, E. A. & BASTA, N. T. 2005. A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. *J Environ Qual,* 34**,** 1112-8.

DAYTON, E. A., BASTA, N. T., JAKOBER, C. A. & HATTEY, J. A. 2003. Using treatment residuals to reduce phosphorus in agricultural runoff. *Journal (American Water Works Association),* 95**,** 151-158.

DEBARBADILLO, C., SHELLSWELL, G., CYR, W., EDWARDS, B., WAITE, R., SABHERWAL, B., MULLAN, J. & MITCHELL, R. 2010. Development of full-scale sizing criteria from tertiary pilot testing results to achieve ultra-low phosphorus limits at innisfil, Ontario. *Proceedings of the Water Environment Federation,* 2010**,** 976-997.

DEFRA 2012. Waste water treatment in the United Kingdom-2012 Implemenatation of the European Union Urban Waste Water Treatment Directive-91/271/EEC. *In:* DEPARTMENT FOR ENVIROMENT, F. A. R. A.

DHARMAPPA, H. B., HASIA, A. & HAGARE, P. 1997. Water treatment plant residuals management. *Water Science and Technology,* 35**,** 45-56.

DIRECTORATE, E. E. 2002. Phosphates and alternative detergent builders-final report.

DIXON, A., SIMON, M. & BURKITT, T. 2003. Assessing the environmental impact of two options for small-scale wastewater treatment: comparing a reedbed and an aerated biological filter using a life cycle approach. *Ecological Engineering,* 20**,** 297-308.

DOBBIE, K., HEAL, K., AUMONIER, J., SMITH, K., JOHNSTON, A. & YOUNGER, P. 2009. Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater. *Chemosphere,* 75**,** 795-800.

DRIZO, A., COMEAU, Y., FORGET, C. & CHAPUIS, R. P. 2002. Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems. *Environmental science & technology,* 36**,** 4642-4648.

DRIZO, A., CUMMINGS, J., WEBER, D., TWOHIG, E., DRUSCHEL, G. & BOURKE, B. 2008. New evidence for rejuvenation of phosphorus retention capacity in EAF steel slag. *Environmental science & technology,* 42**,** 6191-6197.

DROSTE, R. L. 1997. *Theory and practice of water and wastewater treatment*, John Wiley & Sons Incorporated.

DUEÑAS, J. F., ALONSO, J. R., REY, À. F. & FERRER, A. S. 2003. Characterisation of phosphorous forms in wastewater treatment plants. *Journal of Hazardous Materials,* 97**,** 193-205.

DUNNE, E. & REDDY, K. 2005. Phosphorus biogeochemistry of wetlands in agricultural watersheds. *Nutrient management in agricultural watersheds: a wetland solution. Wageningen, The Netherlands: Wageningen Academic Publishers***,** 105-119.

ELKHATIB, E., MAHDY, A., SHERIF, F. & HAMADEEN, H. 2015. Evaluation of a Novel Water Treatment Residual Nanoparticles as a Sorbent for Arsenic Removal. *Journal of Nanomaterials,* 2015.

ELLIOTT, H., DEMPSEY, B., HAMILTON, D. & DEWOLFE, J. 1990a. Land application of water treatment sludges: Impact and management. *Am. Water Works Assoc. Res. Foundation, Denver, CO*.

ELLIOTT, H., DEMPSEY, B. & MAILLE, P. 1990b. Content and fractionation of heavy metals in water treatment sludges. *Journal of environmental quality,* 19**,** 330-334.

ELLIOTT, H., O'CONNOR, G., LU, P. & BRINTON, S. 2002. Influence of water treatment residuals on phosphorus solubility and leaching. *Journal of Environmental Quality,* 31**,** 1362-1369.

ELLIS, E. P. & CATHCART, A. H. 2008. Selection, Installation, Startup and Testing of the World's First Full-Scale CoMag Phosphorus Reduction Tertiary Treatment System. *Proceedings of the Water Environment Federation,* 2008**,** 3602-3621.

EMSLEY, J. 2001. *The Shocking History of Phosphorus: A Biography of the Devil's Element*, Pan Books.

ENVIRONMENT AGENCY 2012. Review of best practice in treatment and reuse/recyling of phosphorus at wastewater treatment works. Bristol.

ENVIRONMENT AGENCY. 2000. Aquatic eutrophication in England and Wales: a management stratergy. Bristol.

EPA 1997. Waste Water Treatment Manuals: Primary, Secondary and Tertiary Treatment. *Environmental Protection Agency, Wexford, Ireland*.

FALCONER, H. R., BENISCH, M., BILL, K., SID FREDRICKSON, H., FISHER, C., CARLETON, B., NEETHLING, J. & CLARK, D. 2011. Operation of a Dual Stage Continuous Upflow Media Filter under Dynamic Conditions to Achieve Ultra-Low Phosphorus Limits. *Proceedings of the Water Environment Federation,* 2011**,** 336-353.

FALK, M. W., REARDON, D. J. & NEETHLING, J. 2011. Striking a Balance Between Nutrient Removal and Sustainability. *Proceedings of the Water Environment Federation,* 2011**,** 520-539.

FAUST, S. D. & ALY, O. M. 2013. *Adsorption processes for water treatment*, Elsevier.

FIELD, A. 2013. *Discovering statistics using IBM SPSS statistics*, Sage.

FINDLAY, A. & LEVITT, B. P. 1972. *Findlay's practical physical chemistry.* Longman

FITZPATRICK, J., AOKI, H., KOH, S., DEBARBADILLO, C., MIDORIKAWA, I., MIYAZAKI, M., OMORI, A. & SHIMIZU, T. 2010. First US Pilot of a New Media for Phosphorus Removal and Recovery. *Proceedings of the Water Environment Federation,* 2010**,** 914-936.

FITZPATRICK, J., AOKI, H., KOH, S., DEBARBADILLO, C., MIDORIKAWA, I., MIYAZAKI, M., OMORI, A. & SHIMIZU, T. 2011. Phosphorus Recovery with New Ultra-Low Adsorption Process. *Proceedings of the Water Environment Federation,* 2011**,** 647-658.

FOLEY, J., DE HAAS, D., HARTLEY, K. & LANT, P. 2010. Comprehensive life cycle inventories of alternative wastewater treatment systems. *Water Research,* 44**,** 1654-1666.

FONSECA, N. 2016. BOF steel slag and apatite in full-scale constructed wetlands for sustainable phosphorus removal. *In paper presented to Innovations in Wastewater Treatment Conference, 2016 Leeds. Aqua Enviro.*

FONSECA, N. 2016. Sustainable phosphorus removal with BOF steel slag and apatite in full-scale constructed wetlands. *In paper presented to 12th Annual CWA Conference, 2016b Manchester.*

FORT, R. P. 2013. Assessment of Tertiary Reed Beds in Chemically-Dosed Wastewater Treatment Plants for Phosphorus Removal*. Masters, Cranfield University.*

FUHS, G. W. & CHEN, M. 1975. Microbiological Basis of Phosphate Removal in the Activated Sludge Process for the Treatment of Wastewater. *Microbial Ecology,* 2**,** 119-138.

GAO, S., WANG, C. & PEI, Y. 2013. Comparison of different phosphate species adsorption by ferric and alum water treatment residuals. *Journal of Environmental Sciences,* 25**,** 986-992.

GBUREK, W. J. & SHARPLEY, A. N. 1998. Hydrologic controls on phosphorus loss from upland agricultural watersheds. *Journal of Environmental Quality,* 27**,** 267-277.

GEORGANTAS, D. & GRIGOROPOULOU, H. 2005. Phosphorus removal from synthetic and municipal wastewater using spent alum sludge. *Water science and technology,* 52**,** 525-532.

GEORGANTAS, D. & GRIGOROPOULOU, H. 2007. Orthophosphate and metaphosphate ion removal from aqueous solution using alum and aluminum hydroxide. *Journal of Colloid and Interface Science,* 315**,** 70-79.

GILMORE, R. L., MURTHY, S., TAKACS, I. & SCOTT SMITH, D. 2011. Application of a Factorial Design to Study Chemically Mediated Phosphorus Removal. *Proceedings of the Water Environment Federation,* 2011**,** 949-965.

GRAY, H., PARKER, W. & SMITH, S. 2015. State of Knowledge of the Use of Sorption Technologies for Nutrient Recovery from Municipal Wastewaters. *Water Intelligence Online,* 14**,** 9781780407319.

GU, A., LIU, L., NEETHLING, J., STENSEL, H. & MURTHY, S. 2011. Treatability and fate of various phosphorus fractions in different wastewater treatment processes. *Water Science & Technology,* 63, 804-810

GU, A. Z., LIU, L., ONNIS-HAYDEN, A., SMITH, S., GRAY, H., HOUWELING, D. & TAKÁCS, I. 2014. Phosphorus Fractionation And Removal In Wastewater Treatment-Implications For Minimizing Effluent Phosphorus. *Water Intelligence Online,* 13**,** 9781780406893.

GUEST, J. S., SKERLOS, S. J., BARNARD, J. L., BECK, M. B., DAIGGER, G. T., HILGER, H., JACKSON, S. J., KARVAZY, K., KELLY, L., MACPHERSON, L., MIHELCIC, J. R., PRAMANIK, A., RASKIN, L., VAN LOOSDRECHT, M. C. M., YEH, D. & LOVE, N. G. 2009. A New Planning and Design Paradigm to Achieve Sustainable Resource Recovery from Wastewater. *Environmental Science & Technology,* 43**,** 6126-6130.

HARTIKAINEN, S. H. & HELINÄ HARTIKAINEN, H. 2008. Phosphorus retention by phlogopite-rich mine tailings. *Applied Geochemistry,* 23**,** 2716-2723.

HEAD, K. H. & EPPS, R. 1986. *Manual of soil laboratory testing*, Pentech Press London.

HEDSTRÖM, A. 2006. *Reactive filter materials for ammonium and phosphorus sorption in small scale wastewater treatment.* PhD, Lulea University of Technology, Sweden

HO, Y.-S. & MCKAY, G. 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water research,* 34**,** 735-742.

HO, Y. S. & MCKAY, G. 1999. Pseudo-second order model for sorption processes. *Process Biochemistry,* 34**,** 451-465.

HU, X., XIE, L., SHIM, H., ZHANG, S. & YANG, D. 2014. Biological Nutrient Removal in a Full Scale Anoxic/Anaerobic/Aerobic/Pre-anoxic-MBR Plant for Low C/N Ratio Municipal Wastewater Treatment. *Chinese Journal of Chemical Engineering,* 22**,** 447-454.

HU, Y., ZHAO, Y., ZHAO, X. & KUMAR, J. 2012. Comprehensive analysis of step-feeding strategy to enhance biological nitrogen removal in alum sludge-based tidal flow constructed wetlands. *Bioresource technology,* 111**,** 27-35.

HUANG, S. & CHISWELL, B. 2000. Phosphate removal from wastewater using spent alum sludge. *Water Science & Technology,* 42**,** 295-300.

IPPOLITO, J. 2015. Aluminum-Based Water Treatment Residual Use in a Constructed Wetland for Capturing Urban Runoff Phosphorus: Column Study. *Water, Air, & Soil Pollution,* 226**,** 1-8.

IPPOLITO, J. A., BARBARICK, K. A. & ELLIOTT, H. A. 2011. Drinking Water Treatment Residuals: A Review of Recent Uses. *Journal of Environment Quality,* 40**,** 1.

IWA 2001. *Constructed wetlands for pollution control: processes, performance, design and operation*, IWA Publ.

JARVIE, H. P., NEAL, C. & WITHERS, P. J. 2006. Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment,* 360**,** 246-253.

JARVIE, H. P., WITHERS, J. & NEAL, C. 1999. Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. *Hydrology and Earth System Sciences,* 6**,** 113-131.

JASINSKI, S. 2014. *Mineral Commodity Summaries* [Online]. http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/. [Accessed 2016].

JOHANSSON WESTHOLM, L. 2006. Substrates for phosphorus removal-potential benefits for on-site wastewater treatment? *Water research,* 40**,** 23-36.

JONG, E. D. 1999. Comparison of three methods of measuring surface area of soils. *Canadian journal of soil science,* 79**,** 345-351.

KADLEC, R. & KNIGHT, R. 1996. *Treatment wetlands.* CRC press.

KADLEC, R. H. & WALLACE, S. 2008. *Treatment wetlands*, CRC press.

KEELEY, J., JARVIS, P. & JUDD, S. 2012. An economic assessment of coagulant recovery from water treatment residuals. *Desalination,* 287**,** 132-137.

KIM, J. G., KIM, J. H., MOON, H.-S., CHON, C.-M. & AHN, J. S. 2003. Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. *Chemical Speciation & Bioavailability,* 14**,** 67-73.

KLIMESKI, A., CHARDON, W. J., TURTOLA, E. & UUSITALO, R. 2012. Potential and limitations of phosphate retention media in water protection: A process-based review of laboratory and field-scale tests. *Agricultural and food science,* 21**,** 206-223.

KNOWLES, P., DOTRO, G., NIVALA, J. & GARCÍA, J. 2011. Clogging in subsurface-flow treatment wetlands: occurrence and contributing factors. *Ecological Engineering,* 37**,** 99-112.

KOSTURA, B., KULVEITOVA, H. & LEŠKO, J. 2005. Blast furnace slags as sorbents of phosphate from water solutions. *Water Research,* 39**,** 1795-1802.

KUMARA, G., HAYANO, K. & OGIWARA, K. 2012. Image analysis techniques on evaluation of particle size distribution of gravel. *Int. J. Geomate,* 3**,** 290-297.

KUNASCHK, M., SCHMALZ, V., DIETRICH, N., DITTMAR, T. & WORCH, E. 2015. Novel regeneration method for phosphate loaded granular ferric (hydr) oxide. A contribution to phosphorus recycling. *Water research,* 71**,** 219-226.

LAGERGREN, S. 1898. Zur theorie der sogenannten adsorption gelöster stoffe, K*ungliga Svenska Vetenskapsakademiens*. Handlingar.

LANGMUIR, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society,* 40**,** 1361-1403.

LEADER, J., DUNNE, E. & REDDY, K. 2008. Phosphorus sorbing materials: sorption dynamics and physicochemical characteristics. *Journal of environmental quality,* 37**,** 174-181.

LEADER, J., REDDY, K. & WILKIE, A. 2005. Optimization of low-cost phosphorus removal from wastewater using co-treatments with constructed wetlands. *Water Science & Technology,* 51**,** 283-290.

LEE, L. Y., WANG, B., GUO, H., HU, J. Y. & ONG, S. L. 2015. Aluminum-Based Water Treatment Residue Reuse for Phosphorus Removal. *Water,* 7**,** 1480-1496.

LI, H. Z., WANG, S., JIANFENG, F. Y., XU, Z. X. & JIN, W. 2011. A practical method for the restoration of clogged rural vertical subsurface flow constructed wetlands for domestic wastewater treatment using earthworm. *Water Science and Technology,* 63**,** 283-290.

LI, L. & STANFORTH, R. 2000. Distinguishing adsorption and surface precipitation of phosphate on goethite (α-FeOOH). *Journal of colloid and interface science,* 230**,** 12-21.

LI, Y., LIU, C., LUAN, Z., PENG, X., ZHU, C., CHEN, Z., ZHANG, Z., FAN, J. & JIA, Z. 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *Journal of hazardous materials,* 137**,** 374-383.

LI, Z., JIANG, N., WU, F. & ZHOU, Z. 2013. Experimental investigation of phosphorus adsorption capacity of the waterworks sludges from five cities in China. *Ecological Engineering,* 53**,** 165-172.

LIANG, Q. 2007. Simultaneous phosphorus and nitrogen removal using aluminum based water treatment residual*. PhD, Colorado State University.*

LIN, J. & WANG, L. 2009. Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon. *Frontiers of Environmental Science & Engineering in China,* 3**,** 320-324.

LIN, Y.-F., JING, S.-R., LEE, D.-Y. & WANG, T.-W. 2002. Nutrient removal from aquaculture wastewater using a constructed wetlands system. *Aquaculture,* 209**,** 169-184.

LIU, R., ZHAO, Y., SIBILLE, C. & REN, B. 2016. Evaluation of natural organic matter release from alum sludge reuse in wastewater treatment and its role in P adsorption. *Chemical Engineering Journal,* 302**,** 120-127.

LIU, Y. 2008. New insights into pseudo-second-order kinetic equation for adsorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 320**,** 275-278.

LOGANATHAN, P., VIGNESWARAN, S., KANDASAMY, J. & BOLAN, N. S. 2014. Removal and recovery of phosphate from water using sorption. *Critical Reviews in Environmental Science and Technology,* 44**,** 847-907.

LOPSIK, K. 2013. Life cycle assessment of small-scale constructed wetland and extended aeration activated sludge wastewater treatment system. *International Journal of Environmental Science and Technology,* 10**,** 1295-1308.

LYNGSIE, G., PENN, C. J., PEDERSEN, H. L., BORGGAARD, O. K. & HANSEN, H. C. B. 2015. Modelling of phosphate retention by Ca- and Fe-rich filter materials under flow-through conditions. *Ecological Engineering,* 75**,** 93-102.

MACHADO, A. P., URBANO, L., BRITO, A., JANKNECHT, P., SALAS, J. & NOGUEIRA, R. 2007. Life cycle assessment of wastewater treatment options for small and decentralized communities. *Water Science & Technology,* 56, 15-22.

MAHER, C., NEETHLING, J., MURTHY, S. & PAGILLA, K. 2015. Kinetics and capacities of phosphorus sorption to tertiary stage wastewater alum solids, and process implications for achieving low-level phosphorus effluents. *Water research,* 85**,** 226-234.

MAINSTONE, C., PARR, W., DAY, M. 2000. *Phosphorus and river ecology: tackling sewage inputs*, English Nature.

MAINSTONE, C. P. & PARR, W. 2002. Phosphorus in rivers — ecology and management. *Science of The Total Environment,* 282–283**,** 25-47.

MAKRIS, K. C., EL-SHALL, H., HARRIS, W. G., O'CONNOR, G. A. & OBREZA, T. A. 2004a. Intraparticle phosphorus diffusion in a drinking water treatment residual at room temperature. *Journal of colloid and interface science,* 277**,** 417-423.

MAKRIS, K. C. & HARRIS, W. G. 2006. Time dependency and irreversibility of water desorption by drinking-water treatment residuals: Implications for sorption mechanisms. *Journal of colloid and interface science,* 294**,** 151-154.

MAKRIS, K. C., HARRIS, W. G., O'CONNO, G. A. & OBREZA, T. A. 2004b. Phosphorus immobilization in micropores of drinking-water treatment residuals: implications for long-term stability. *Environmental science & technology,* 38**,** 6590-6596.

MAKRIS, K. C., HARRIS, W. G., O'CONNOR, G. A. & EL-SHALL, H. 2005a. Long-term phosphorus effects on evolving physicochemical properties of iron and aluminum hydroxides. *Journal of colloid and interface science,* 287**,** 552-560.

MAKRIS, K. C., HARRIS, W. G., O'CONNOR, G. A., OBREZA, T. A. & ELLIOTT, H. A. 2005b. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. *Environmental science & technology,* 39**,** 4280-4289.

MARTIN, B. 2010. *Removal and Recovery of Phosphorus from Municipal Wastewaters using a Ferric Nanoparticle Adsorbent.* PhD, Cranfield University.

MARTIN, B. D., PARSONS, S. A. & JEFFERSON, B. 2009. Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Science and Technology,* 60**,** 2637-2645.

MARTINS, M. C., SANTOS, E. B. H. & MARQUES, C. R. 2017. First study on oyster-shell-based phosphorous removal in saltwater — A proxy to effluent bioremediation of marine aquaculture. *Science of The Total Environment,* 574**,** 605-615.

MARTÍN, M., GARGALLO, S., HERNÁNDEZ-CRESPO, C. & OLIVER, N. 2013. Phosphorus and nitrogen removal from tertiary treated urban wastewaters by a vertical flow constructed wetland. *Ecological Engineering,* 61**,** 34-42.

MCKELVIE, I. D., PEAT, D. M. & WORSFOLD, P. J. Analytical perspective. Techniques for the quantification and speciation of phosphorus in natural waters. Analytical Proceedings *Including Analytical Communications, 1995. Royal Society of Chemistry*, 437-445.

METCALF, EDDY & AECOM 2014. *Wastewater Engineering Treatment and Recovery*, McGraw-Hill Education.

MEULEMAN, A. F., VAN LOGTESTIJN, R., RIJS, G. B. & VERHOEVEN, J. T. 2003. Water and mass budgets of a vertical-flow constructed wetland used for wastewater treatment. *Ecological Engineering,* 20**,** 31-44.

MITSCH, W. J. & GOSSELINK, J. G. 2000. *Wetlands,5th Edition,* Wiley.

MOHAMMED, A., AL-TAHMAZI, T. & BABATUNDE, A. 2016. Attenuation of metal contamination in landfill leachate by dewatered waterworks sludges. *Ecological Engineering,* 94**,** 656-667.

MONCLÚS, H., SIPMA, J., FERRERO, G., RODRIGUEZ-RODA, I. & COMAS, J. 2010. Biological nutrient removal in an MBR treating municipal wastewater with special focus on biological phosphorus removal. *Bioresource technology,* 101**,** 3984-3991.

MORSE, G. K., BRETT, S. W., GUY, J. A. & LESTER, J. N. 1998. Review: Phosphorus removal and recovery technologies. *Science of the Total Environment,* 212**,** 69-81.

MORTULA, M. M. & GAGNON, G. A. 2007. Alum residuals as a low technology for phosphorus removal from aquaculture processing water. *Aquacultural Engineering,* 36**,** 233-238.

NEETHLING, J., B, FALK, M., W, REARDO, D., J, CLARK, D., L & AMIT, P. WERF Nutrient Challenge-Nutrient Regulations, Treatment Performance, and Sustainability Collide. *Proceedings of the Water Environment Federation,* 2011**,** 647-658

NESET, T. S. & CORDELL, D. 2012. Global phosphorus scarcity: identifying synergies for a sustainable future. *J Sci Food Agric,* 92**,** 2-6.

NGUYEN, T., NGO, H., GUO, W., PHAM, T., LI, F., NGUYEN, T. & BUI, X. 2015. Adsorption of phosphate from aqueous solutions and sewage using zirconium loaded okara (ZLO): fixed-bed column study. *Science of the Total Environment,* 523**,** 40-49.

NIVALA, J., KNOWLES, P., DOTRO, G., GARCÍA, J. & WALLACE, S. 2012. Clogging in subsurface-flow treatment wetlands: Measurement, modeling and management. *Water research,* 46**,** 1625-1640.

O'HARE, J., P & PERRY, T. Investigating treatment options to meet 70ug/L phosphorus discharge limit in Boise River in Idaho. WEFTEC, 2010. 908-913.

O'KELLY, B. C. 2008. Geotechnical properties of a municipal water treatment sludge incorporating a coagulant. *Canadian Geotechnical Journal,* 45**,** 715-725.

OLIVER, I. W., GRANT, C. D. & MURRAY, R. S. 2011. Assessing effects of aerobic and anaerobic conditions on phosphorus sorption and retention capacity of water treatment residuals. *J Environ Manage,* 92**,** 960-6.

OUVRARD, S., SIMONNOT, M.-O., DE DONATO, P. & SARDIN, M. 2002. Diffusion-controlled adsorption of arsenate on a natural manganese oxide. *Industrial & Engineering Chemistry Research,* 41**,** 6194-6199.

O'NEILL, S. W. & DAVIS, A. P. 2011. Water treatment residual as a bioretention amendment for phosphorus. II: Long-term column studies. *Journal of Environmental Engineering,* 138**,** 328-336.

PARK, W. 2009. Integrated constructed wetland systems employing alum sludge and oyster shells as filter media for P removal. *Ecological Engineering,* 35**,** 1275-1282.

PENN, C., MCGRATH, J., BOWEN, J. & WILSON, S. 2014. Phosphorus removal structures: A management option for legacy phosphorus. *Journal of Soil and Water Conservation,* 69**,** 51A-56A.

PENN, C. J. 2011. Predicting Phosphorus Sorption onto Steel Slag Using a Flow-through approach with Application to a Pilot Scale System. *Journal of Water Resource and Protection,* 03**,** 235-244.

PHOSPHORUSFUTURES.NET. 2016. *http://phosphorusfutures.net/the-phosphorus-challenge/* [Online]. http://phosphorusfutures.net/the-phosphorus-challenge/. [Accessed 2016].

PLAZINSKI, W., DZIUBA, J. & RUDZINSKI, W. 2013. Modeling of sorption kinetics: the pseudo-second order equation and the sorbate intraparticle diffusivity. *Adsorption,* 19**,** 1055-1064.

PRAKASH, P. & SENGUPTA, A. K. 2003. Selective coagulant recovery from water treatment plant residuals using Donnan membrane process. *Environmental science & technology,* 37**,** 4468-4474.

PRATT, C., SHILTON, A., PRATT, S., HAVERKAMP, R. G. & ELMETRI, I. 2007. Effects of redox potential and pH changes on phosphorus retention by melter slag filters treating wastewater. *Environmental science & technology,* 41**,** 6585-6590.

PREPAS, E. E., CHARETTE, T., HOLLAND, H. D. & TUREKIAN, K. K. 2003. 9.08 - Worldwide Eutrophication of Water Bodies: Causes, Concerns, Controls. *Treatise on Geochemistry.* Oxford: Pergamon.

RAZALI, M., ZHAO, Y. & BRUEN, M. 2007. Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution. *Separation and Purification Technology,* 55**,** 300-306.

ROY-POIRIER, A., CHAMPAGNE, P. & FILION, Y. 2010. Bioretention processes for phosphorus pollution control. *Environmental Reviews,* 18**,** 159-173.

RUSTIGE, H., TOMAC, I. & HONER, G. 2003. Investigations on phosphorus retention in subsurface flow constructed wetlands. *Water Science and Technology,* 48**,** 67-74.

RUTTENBERG, K. 2003. The global phosphorus cycle. *Treatise on geochemistry,* 8**,** 585-643.

SAKADEVAN, K. & BAVOR, H. 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. *Water Research,* 32**,** 393-399.

SANI, A., SCHOLZ, M., BABATUNDE, A. & WANG, Y. 2013. Impact of Water Quality Parameters on the Clogging of Vertical-Flow Constructed Wetlands Treating Urban Wastewater. *Water, Air, & Soil Pollution,* 224.

SCHOLZ, R. W. & WELLMER, F.-W. 2013. Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus? *Global Environmental Change,* 23**,** 11-27.

SEDLAK, R. I. 1991. *Phosphorus and nitrogen removal from municipal wastewater: principles and practice*, CRC Press.

SENGUPTA, S. & PANDIT, A. 2011. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. *Water Research,* 45**,** 3318-3330.

SHARPLEY, A., JARVIE, H. P., BUDA, A., MAY, L., SPEARS, B. & KLEINMAN, P. 2013. Phosphorus legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. *Journal of environmental quality,* 42**,** 1308-1326.

SHAW, A., DEBARBADILLO, C., TARALLO, S. & KADAVA, A. 2011. Life Cycle Assessment of the Relative Benefits of Meeting Ultra-Low Nutrient Limits at WWTPs. *Proceedings of the Water Environment Federation,* 2011**,** 540-551.

SHILTON, A. N., ELMETRI, I., DRIZO, A., PRATT, S., HAVERKAMP, R. G. & BILBY, S. C. 2006. Phosphorus removal by an 'active' slag filter-a decade of full scale experience. *Water Research,* 40**,** 113-118.

SIBRELL, P. L., MONTGOMERY, G. A., RITENOUR, K. L. & TUCKER, T. W. 2009. Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water research,* 43**,** 2240-2250.

SIM, C. H., QUEK, B. S., SHUTES, R. B. E. & GOH, K. H. 2013. Management and treatment of landfill leachate by a system of constructed wetlands and ponds in Singapore. *Water Science and Technology,* 68**,** 1114-1122.

SMIL, V. 2000. Phosphorus in the environment: natural flows and human interferences. *Annual review of energy and the environment,* 25**,** 53-88.

SMITH, S., SZABÓ, A., MURTHY, S., LICSKÓ, I. & DAIGGER, G. 2007. The Significance of Chemical Phosphorus Removal Theory for Engineering Practice. *Proceedings of the Water Environment Federation,* 2007**,** 1436-1459.

SMITH, V. H., TILMAN, G. D. & NEKOLA, J. C. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution,* 100**,** 179-196.

SOLEIMANIFAR, H., DENG, Y., WU, L. & SARKAR, D. 2016. Water treatment residual (WTR)-coated wood mulch for alleviation of toxic metals and phosphorus from polluted urban stormwater runoff. *Chemosphere,* 154**,** 289-292.

SONG, X., PAN, Y., WU, Q., CHENG, Z. & MA, W. 2011. Phosphate removal from aqueous solutions by adsorption using ferric sludge. *Desalination,* 280**,** 384-390.

STONER, D., PENN, C., MCGRATH, J. & WARREN, J. 2012. Phosphorus removal with by-products in a flow-through setting. *Journal of environmental quality,* 41**,** 654-663.

SULIMAN, F., FRENCH, H. K., HAUGEN, L. E. & SØVIK, A. K. 2006. Change in flow and transport patterns in horizontal subsurface flow constructed wetlands as a result of biological growth. *Ecological Engineering,* 27**,** 124-133.

SUN, G., GRAY, K., BIDDLESTONE, A. & COOPER, D. 1999. Treatment of agricultural wastewater in a combined tidal flow-downflow reed bed system. *Water Science and Technology,* 40**,** 139-146.

SUNG, E., HAN, C. & RHEE, H. (1979) Optimal design of multistage adsorption-bed systems. *American Institute of Chemical Engineers Journal*, 1, 87-100

TANNER, C. C. 2001. Growth and nutrient dynamics of soft-stem bulrush in constructed wetlands treating nutrient-rich wastewaters. *Wetlands Ecology and Management,* 9**,** 49-73.

TANNER, C. C., SUKIAS, J. P. S. & UPSDELL, M. P. 1999. Substratum phosphorus accumulation during maturation of gravel-bed constructed wetlands. *Water Science and Technology,* 40**,** 147-154.

THANALECHUMI, P., YUSOFF, A. R. M., PONRAJ, M. & AWAB, H. 2015. Leachability Study of Metals from Synthetic and Natural Alum Sludge using Different Eluting Medium. *Chiang Mai J.Sci.*42, 1-9

TOBIS,J. & VORTMEYER, D. 1988. The near wall channeling effect on isothermal constant pattern adsorption. *Chemical Engineering Science*, 6, 1363-1369.

TOZER, H., G, WOODARD & CURRAN 2007. Study of Five Phosphorus Removal Processes Select Comag to meet Concord, Massachusetts Stringent New Limits. *Proceedings of the Water Environment Federation,* 2007**,** 1492-1509*.*

UGURLU, A. & SALMAN, B. 1998. Phosphorus removal by fly ash. *Environment International,* 24**,** 911-918.

UKWIR 2008. Source Control of Phosphorus from Domestic Sources-Options and Impacts. UKWIR.

URIBARRI, J. & CALVO, M. S. 2003. Hidden sources of phosphorus in the typical American diet: Does it matter in nephrology? *Seminars in Dialysis,* 16**,** 186-188.

VALSAMI-JONES, E. 2004. *Phosphorus in environmental technologies: Principles and applications*, IWA Publishing.

VERRELLI, D. I., DIXON, D. R. & SCALES, P. J. 2009. Effect of coagulation conditions on the dewatering properties of sludges produced in drinking water treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 348**,** 14-23.

VOHLA, C., KÕIV, M., BAVOR, H. J., CHAZARENC, F. & MANDER, Ü. 2011. Filter materials for phosphorus removal from wastewater in treatment wetlands—A review. *Ecological Engineering,* 37**,** 70-89.

VYMAZAL, J. 2007. Removal of nutrients in various types of constructed wetlands. *Science of The Total Environment,* 380**,** 48-65.

WANG, C., GUO, W., TIAN, B., PEI, Y. & ZHANG, K. 2011. Characteristics and kinetics of phosphate adsorption on dewatered ferric-alum residuals. *J Environ Sci Health A Tox Hazard Subst Environ Eng,* 46**,** 1632-9.

WANG, C., YUAN, N., BAI, L., JIANG, H.-L., PEI, Y. & YAN, Z. 2016a. Key factors related to drinking water treatment residue selection for adsorptive properties tuning via oxygen-limited heat treatment. *Chemical Engineering Journal,* 306**,** 897-907.

WANG, C., YUAN, N. & PEI, Y. 2014. Effect of pH on metal lability in drinking water treatment residuals. *Journal of environmental quality,* 43**,** 389-397.

WANG, C., YUAN, N., PEI, Y. & JIANG, H.-L. 2015. Aging of aluminum/iron-based drinking water treatment residuals in lake water and their association with phosphorus immobilization capability. *Journal of environmental management,* 159**,** 178-185.

WANG, MC., HULL, JQ., JAO, M., DEMPSEY, BA. & CORNWELL DA. 1992. Engineering behaviour of water treatment sludge. *Journal of Environmental Engineering*, 118, 848-864.

WANG, W., MA, C., ZHANG, Y., YANG, S., SHAO, Y. & WANG, X. 2016b. Phosphate adsorption performance of a novel filter substrate made from drinking water treatment residuals. *Journal of Environmental Sciences*.

WANG, X., WANG, Y., ZHANG, X., FENG, H., LI, C. & XU, T. 2013. Phosphate recovery from excess sludge by conventional electrodialysis (CED) and electrodialysis with bipolar membranes (EDBM). *Industrial & Engineering Chemistry Research,* 52**,** 15896-15904.

WEBER, W. J. & MORRIS, J. C. 1963. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division,* 89**,** 31-60.

WEINBERG, E., HEERWANI, P., VISWANATHAN, T. & FINLAY, C. 2011. Innovative Chemically Enhanced Nutrient Removal and Recovery Technology. *Proceedings of the Water Environment Federation,* 2011**,** 668-696.

WHO, W. H. O. 2004. World Health Organization guidelines for drinking water quality. *Health Criteria and Other Supporting Information*.

WOODWARD, S. & ANDRYSZAK, R. Ballasted Biological Process Achieves Low Nitrogen and Phosphorus without Tertiary Filtration.

WU, R. S., LAM, K. H., LEE, J. & LAU, T. 2007. Removal of phosphate from water by a highly selective La (III)-chelex resin. *Chemosphere,* 69**,** 289-294.

WU, T. & SANSALONE, J. 2013a. Phosphorus Equilibrium. I: Impact of AlOx Media Substrates and Aqueous Matrices. *Journal of Environmental Engineering,* 139**,** 1315-1324.

WU, T. & SANSALONE, J. 2013b. Phosphorus Equilibrium. II: Comparing Filter Media, Models, and Leaching. *Journal of Environmental Engineering,* 139**,** 1325-1335.

XU, D., XU, J., WU, J. & MUHAMMAD, A. 2006. Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere,* 63**,** 344-352.

YANG, Y., TOMLINSON, D., KENNEDY, S. & ZHAO, Y. 2006a. Dewatered alum sludge: a potential adsorbent for phosphorus removal. *Water Science and Technology,* 54**,** 207-213.

YANG, Y., ZHAO, Y., BABATUNDE, A., WANG, L., REN, Y. & HAN, Y. 2006b. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Separation and Purification Technology,* 51**,** 193-200.

YANG, Y., ZHAO, Y. Q. & KEARNEY, P. 2008. Influence of ageing on the structure and phosphate adsorption capacity of dewatered alum sludge. *Chemical Engineering Journal,* 145**,** 276-284.

YUH-SHAN, H. 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics,* 59**,** 171-177.

ZENG, L., LI, X. & LIU, J. 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research,* 38**,** 1318-1326.

ZHAO, D. Y. & SENGUPTA, A. K. 1998. Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Research,* 32**,** 1613-1625.

ZHAO, X., ZHAO, Y. & KEARNEY, P. 2011a. Transformation of beneficially reused aluminium sludge to potential P and Al resource after employing as P-trapping material for wastewater treatment in constructed wetland. *Chemical engineering journal,* 174**,** 206-212.

ZHAO, Y., BABATUNDE, A., HU, Y., KUMAR, J. & ZHAO, X. 2011b. Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. *Process Biochemistry,* 46**,** 278-283.

ZHU, T., MAEHLUM, T., JENSSEN, P. D. & KROGSTAD, T. 2003. Phosphorus sorption characteristics of a light-weight aggregate. *Water Science and Technology,* 48**,** 93-100.

ÖNORM, B. 2005. 2505. *Bepflanzte Bodenfilter (Pflanzenkläranlagen)—Anwendung, Bemessung, Bau und Betrieb (Subsurface-flow constructed wetlands—Application, dimensioning, installation and operation). Vienna, Austria: Österreichisches Normungsinstitut*.

ÖZACAR, M. 2003. Equilibrium and kinetic modelling of adsorption of phosphorus on calcined alunite. *Adsorption,* 9**,** 125-132.

Appendix A: Phosphorous species and summary of results

A.1 Results from the analysis of different species of P in the waste water

Results of the concentration of TP, STP, PO_4-P and PP of the inlet, one of the columns and one of the meso scale beds are shown in Figure A.1. The results shown are typical of those obtained from the other columns and meso scale bed.

Note: the PP was calculated as the difference between TP and STP as discussed in section 3.6.2.4.

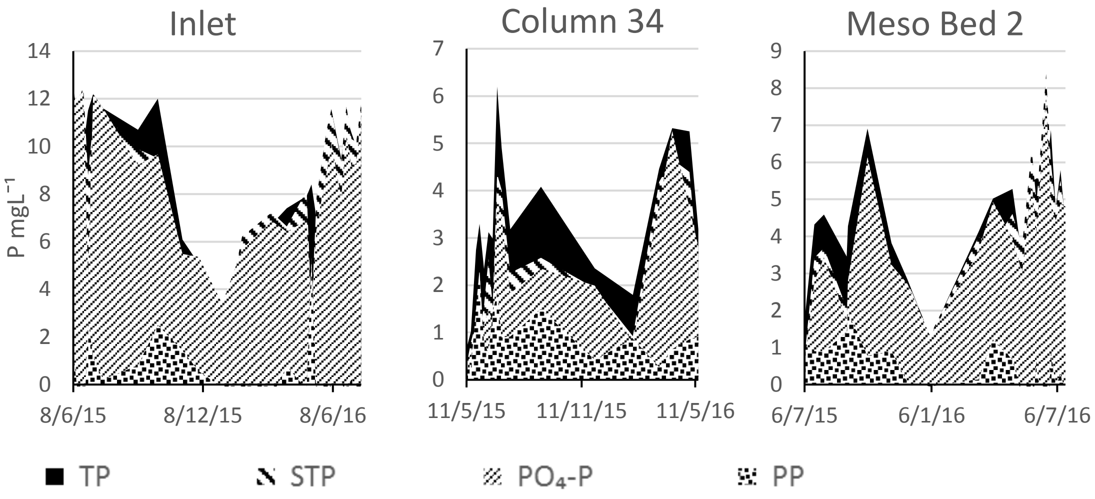


Figure A.1 Measured TP, STP, PO_4-P and calculated PP in the inlet and one column and meso scale bed.

The average makeup of the inlet water as a percentage of TP was 95% STP, 90%PO_4-P and 5% PP.

The columns removed on average 60% of the TP, and 70% of both the STP and PO_4-P, but there was an average increase in PP.

The meso scale beds removed on average 57% of the TP, and 69% of STP, 71% of PO_4-P, and bed 2 removed 12% of the PP but, bed 1 showed an increase in PP.

The average makeup of the inlet and outlet from the columns as a percentage of TP is shown in Figure A.2

.

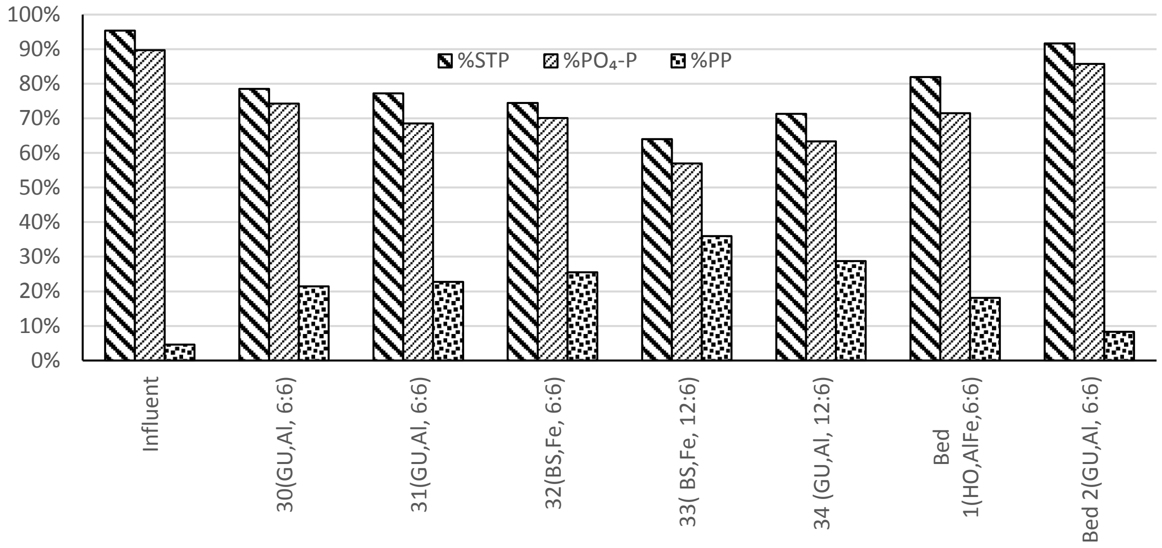


Figure A.2: Average quantity of STP, PO_4-P and PP in influent and effluent as a percentage of TP.

The ratio between STP and PO_4-P remained very consistent as the phosphorus was adsorbed by the columns however as can be clearly seen from Figure A.1 the PP made up a larger proportion of the TP. All the columns favourably removed STP and PO_4 when compared with TP and PP.

A.2 Summary of phosphorus removal results from all columns

A summary of the phosphorus removal results for all the columns and meso scale beds are shown in Table A.1 to A.5 . The tables include the amount of P input into each system and adsorbed by each system in g/kg, the average %STP removal, number of bed volumes and total volume treated, and the average amount of phosphorus removed in grams per m^2, m^3 and kg of media per day.

Table A.1 Final results from experiments on media type

Col Num.(Media)	0 (GU,Al)	1(BS,Fe)	2(MO,Fe)	3(HO,FeAl)	4(LA,Fe)	5(WD,Al)	6(FO,Fe)	7(HH,Fe)	8(GU,Al)	9 (BS,Fe)	10(Control)
Final g kg^{-1} of P on media	2.69	1.38	2.77	1.48	1.34	3.01	2.85	2.38	2.71	1.51	0.04
P input g/kg of media	3.27	1.79	3.11	2.00	1.50	3.55	3.50	2.48	3.35	2.55	0.79
Overall removal	82%	77%	89%	74%	89%	85%	82%	96%	81%	59%	5%
Bed volumes	661	638	638	638	379	638	638	638	633	621	624
Volume of water treated(l)	1606	957	1659	1212	842	1723	1850	1659	1772	1348	1423
Inlet P conc.(mgL^{-1})	5	5	5	5	5	5	5	5	5	5	5
	Average Amount of P(grams) removed per area, volume and mass of media per day										
gP m^{-2} day^{-1}	2.63	1.52	3.04	1.84	2.61	3.00	3.11	3.27	2.98	1.69	0.14
gP m^{-3} day^{-1}	4.41	2.55	5.10	3.09	4.37	5.04	5.21	5.49	4.99	2.83	0.23
gP kg^{-1} day^{-1}	7.58E-03	4.30E-03	8.66E-03	4.63E-03	7.46E-03	9.40E-03	8.91E-03	7.44E-03	8.54E-03	4.86E-03	1.16E-04

Table A.2 Final results from Al contact time experiments

Col No..(Media, Contact,Rest))	**11(GU,Al 0.5:1.5)**	**12(GU,Al, 1:1)**	**13(GU,Al, 1:3)**	**14 (GU,Al, 3:1)**	**15 (GU,Al, 6:2)**	**16 (GU,Al, 12:6)**	**17 (GU,Al, 24:24)**
Final g kg^{-1} of P on media	7.70	6.82	5.26	5.88	3.61	1.53	0.78
P input g/kg of media	19.46	18.94	10.11	9.66	5.38	2.16	0.84
Overall removal	40%	36%	52%	61%	67%	71%	92%
Bed Volumes	3598	3600	1866	1866	1008	419	156
Volume of water treated(l)	9895	9540	5225	4572	2722	1165	424
Inlet P conc.(mgL^{-1})	5	5	5	5	5	5	5
	Average Amount of P(grams) removed per area, volume and mass of media per day						
gP m^{-2} day^{-1}	8.58	7.53	5.74	5.88	3.47	1.67	0.80
gP m^{-3} day^{-1}	14.39	12.62	9.62	9.85	5.82	2.80	1.34
gP kg^{-1} day^{-1}	2.57E-02	2.28E-02	1.69E-02	1.89E-02	1.07E-02	4.86E-03	2.48E-03

Table A.3 Final results from Fe contact time experiments

Col No..(Media, Contact,Rest))	18(BS,Fe, 0.5:1.5)	19(BS,Fe, 1:1)	20 (BS,Fe, 1:3)	21(BS,Fe, 3:1)	22(BS,Fe, 6:2)	23(BS,Fe, 12:6)	24(BS,Fe, 24:24)
Final g kg^{-1} of P on media	3.32	3.92	3.00	2.81	1.81	1.07	0.49
P input g/kg of media	14.44	14.16	7.53	7.29	3.11	1.55	0.59
Overall removal	23%	28%	40%	39%	58%	69%	84%
Bed Volumes	3696	3541	1897	1896	948	416	151
Volume of water treated(l)	7762	7861	4325	4133	1896	907	332
Inlet P conc.(mgL^{-1})	5	5	5	5	5	5	5
	Average Amount of P(grams) removed per area, volume and mass of media per day						
gP m^{-2} day^{-1}	3.70	4.70	3.48	3.22	2.23	1.28	0.59
gP m^{-3} day^{-1}	6.20	7.89	5.83	5.40	3.74	2.14	0.99
gP kg^{-1} day^{-1}	1.08E-02	1.33E-02	9.51E-03	8.91E-03	5.74E-03	3.43E-03	1.64E-03

Table A.4 Final results from inlet concentration experiments

Col No..(Media, Contact,Rest))	25(GU,Al 6:6)	26(BS,Fe 6:6)	27(GU,Al, 12:6)	28(BS,Fe, 12:6)	29(Control 6:6)
Final g kg^{-1} of P on media	0.81	0.40	0.48	0.33	0.03
P input g/kg of media	0.99	0.59	0.60	0.45	0.19
Overall removal	82%	68%	81%	73%	14%
Bed Volumes	671	638	470	475	638
Volume of water treated(l)	1879	1404	1283	1045	1480
Inlet P conc.(mgL^{-1})	1	1	1	1	1
	Average Amount of P(grams) removed per area, volume and mass of media per day				
gP m^{-2} day^{-1}	0.71	0.46	0.46	0.33	0.10
gP m^{-3} day^{-1}	1.19	0.78	0.77	0.56	0.17
gP kg^{-1} day^{-1}	2.35E-03	1.26E-03	1.38E-03	9.24E-04	8.13E-08

Table A.5 Final results from RWW experiments

Col No..(Media, Contact,Rest))	30(GU,Al, 6:6)	31(GU,Al, 6:6)	32(BS,Fe, 6:6)	33(BS,Fe, 12:6)	34 (GU,Al, 12:6)	Bed 1(HO)	Bed 2(GU)
Final g kg^{-1} of P on media	3.48	3.27	0.76	1.12	1.46	2.92	2.66
P input g/kg of media	6.32	6.11	1.65	1.68	2.35	4.84	5.80
Overall removal	55%	54%	46%	66%	62%	60%	46%
Bed Volumes	742	742	742	493	493	703	703
Volume of water treated(l)	2226	2152	1039	724	1430	57725	54590
Inlet P conc.(mgL^{-1})	9.37±2.59	9.37±2.60	9.37±2.61	9.37±2.62	9.37±2.63	9.37±2.64	9.37±2.65
	Average Amount of P(grams) removed per area, volume and mass of media per day						
gP m^{-2} day^{-1}	3.92	3.68	1.52	1.54	2.86	0.97	0.69
gP m^{-3} day^{-1}	6.57	6.17	2.55	2.59	4.79	3.72	3.14
gP kg^{-1} day^{-1}	1.07E-02	1.00E-02	2.31E-03	3.13E-03	4.43E-03	9.47E-03	8.77E-03

The summary results reveal some interesting characteristic of the experiments. The calculated value for the largest amount of P adsorbed per kg of media was 7.7mg g^{-1} for Column 11(GU media with 0.5 hours contact and 5mgL^{-1}STP input), this column had the lowest contact time and removed only 40% of the phosphorus that entered the system. However, it treated almost 8m^3 of water when compared to only 330 litres treated by the columns operating with 24 hours contact time. The smallest amount of P adsorbed was 0.33 mg/g for Col 28 (BS media with 12 hours contact and 1mgL^{-1} STP).

The average removal rates across the systems in terms of loading rates varied between 0.33 and 8.58gP/m^2day with the highest amounts removed in the media with the shortest contact time, but this was due to the very high loading rate.

The columns passed between 332 and 7861 litres of water, and the meso beds passed approximately 55 000litres of water. The average amount of phosphorus removed per m^3 of media per day varied between 13.859 and 0.134 gP m^{-3} day^{-1} for column 11 and bed 2, respectively.

Appendix B: Design procedure for adsorption systems using isotherms.

The following design procedure and proof has been adapted from Crittenden and Thomas (1998)

B.1 Design procedure for stage wise contacting

Figure B.1 represents a simple adsorption system where:

V = volume of water which contains impurity (m^3)
C_0 = Initial concentration of TP (g m^{-3})
C_f = Desired concentration in effluent TP (g m^{-3})
M = Mass of adsorbent

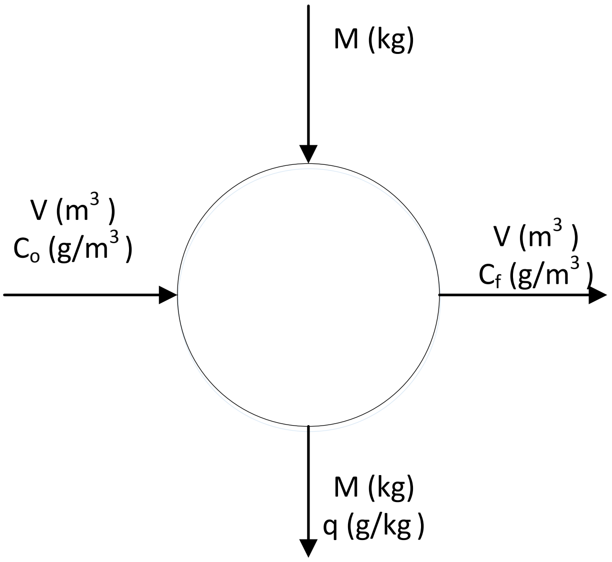


Figure B.1 Single stage contacting of a batch of adsorbent

If the adsorbent is initially free from impurity. The isotherm can be assumed linear and it will therefore follow Henry’s law and therefore.

$$q \quad = \quad Kc \qquad \textit{Equation B.1}$$

where q is the loading of TP on the adsorbent (g $kg^{-1}{}_{media}$) in equilibrium with the impurity concentration of TP in the wastewater c (g m^{-3}) and K is the equilibrium constant (m^3 kg^{-1}).

It is assumed that the water is not adsorbed and since the impurity concentration is always low relative to the mass of the adsorbent the volume of solution does not change. The mass balance for the impurity is therefore

$$V(C_0 - C_f) = Mq \qquad \textit{Equation B.2}$$

If the adsorbent were not initially free from the impurity but had a residual loading of q_0 then the equation becomes

$$V(C_0 - C_f) = M(q - q_0) \qquad \textit{Equation B.3}$$

where $q = KC_f$

Simultaneous solutions of equation B.2 and B.3 lead to the useful design equation of:

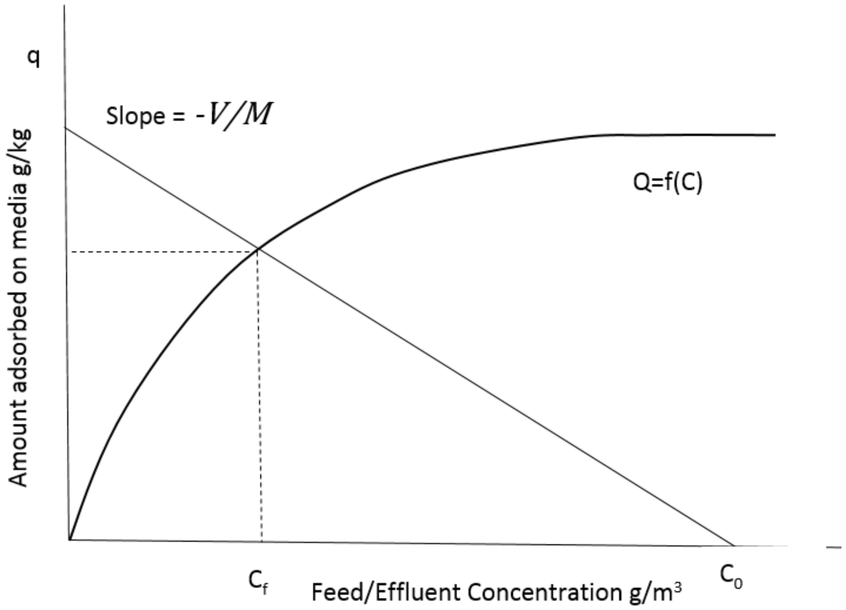
$$M = \frac{V}{K}\left(\frac{C_0}{C_f} \; - \; 1\right) \qquad \textit{Equation B.4}$$

This equation shows that the mass of adsorbent can be reduced if higher equilibrium constant can be found.

The equation can be usefully rearranged to give a liner relationship between q and C_F assuming that q=Kc

$$q = \frac{V}{M}\left(C_0 - C_f\right) \qquad \textit{Equation B.5}$$

In the case of a nonlinear isotherm the solution to the equation can be found graphically as shown in Figure B.2



`

Figure B.2 Graphical solution to single stage contacting

In other words for a fixed inlet concentration of TP a known outlet concentration requirement and a known mass of media the approximate volume of water that can be treated can be calculated from the slope of the line.

B.2 Multistage systems (why 2 is better than 1)

To make more efficient use of the media the system can be use beds in series as shown in Figure B.3.

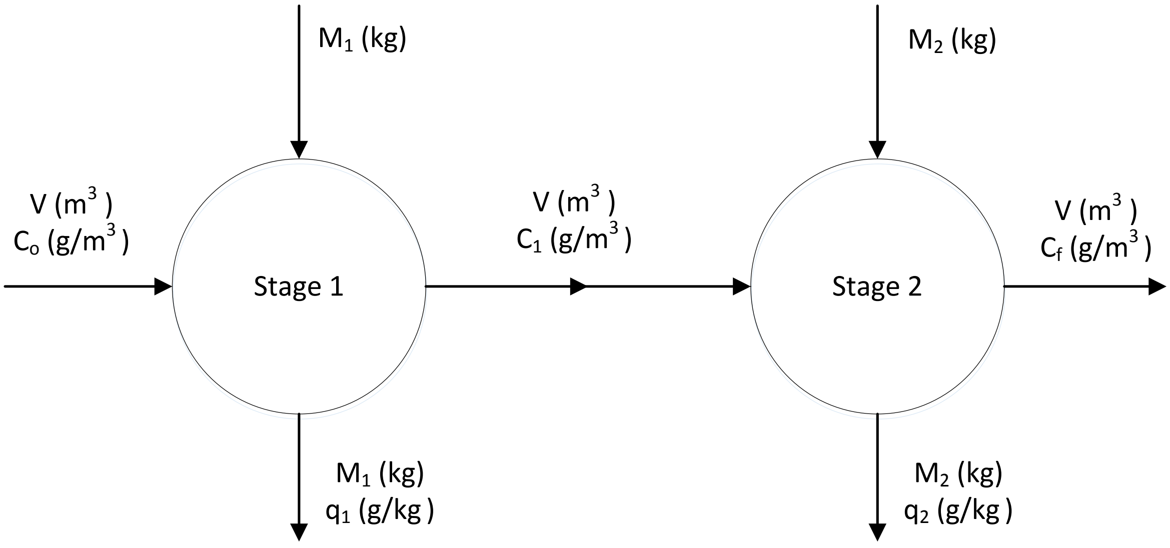


Figure B.3 Stagewise contacting of a batch fluid with two batches of adsorbent

Here the total amount of media is split into two parts M_1 and M_2. The feed enters stage one with a concentration of C_0 and leaves the first stage with a concentration of C_1. The fluid then passes on to the new fresh batch of adsorbent. In multi batch systems each subsequent batch of adsorbent removes less impurity as the impurity concentration decreases.

Simultaneous solution of the impurity mass balance with the equilibrium relationship for the first batch yields

$$\boldsymbol{M_1 = \frac{V}{K}\left(\frac{C_0}{C_1} - 1\right)} \qquad \textbf{\textit{Equation B.6}}$$

The loading q_1 is in equilibrium with the intermediate concentration C_1. Simultaneous solution of the impurity mass balance with the equilibrium relationship for the second batch vessel yields M_2.

$$\boldsymbol{M_2 = \frac{V}{K}\left(\frac{C_1}{C_f} - 1\right)} \qquad \textbf{\textit{Equation B.7}}$$

For the total mass of adsorbent to be a minimum the differential of (M_1 + M_2) with respect to the intermediate concentration C_1 needs to be zero, hence it can be shown that.

$$C_1 = (C_0 C_F)^{0.5} \qquad \textit{Equation B.8}$$

Substituting for earlier equations then the minimum amount of adsorbent needed for purification is given when.

$$M_1 = M_2 = \left\{\frac{V}{K}\left(\frac{C_0}{C_f}\right)^{0.5} - 1\right\} \qquad \textit{Equation B.9}$$

For a multistage process involving N stages the general result for a linear (Henry's law) isotherm is:

$$\sum(M_1 + M_2 \ldots. + M_N) = \frac{NV}{K}\left\{\left(\frac{C_0}{C_f}\right)^{\frac{1}{N}} - 1\right\} \qquad \textit{Equation B.10}$$

So finally comparing this multistage equation when N=2 with a single stage it can be shown that by splitting the adsorbent into two equal amounts the total amount of adsorbent required for the given purification is reduced from that required when all the adsorbent is used in one stage.

$$\frac{M_1 + M_2}{M} = \frac{2}{\left(\frac{C_0}{C_f}\right)^{0.5} + 1} \qquad \textit{Equation B.11}$$

Since C_0 is greater than C_f then from last equation

$$\frac{M_1 + M_2}{M} < 1 \qquad \textit{Equation B.12}$$

The reduction of adsorbent is achieved at the expense of more processing stages. And conversely better purification can be achieved with a given amount of adsorbent by increasing the number of stages.

The analysis above can be used in nonlinear isotherms (Figure B.4) although in such cases it would not be optimal to split the absorbent equally between stages.

:

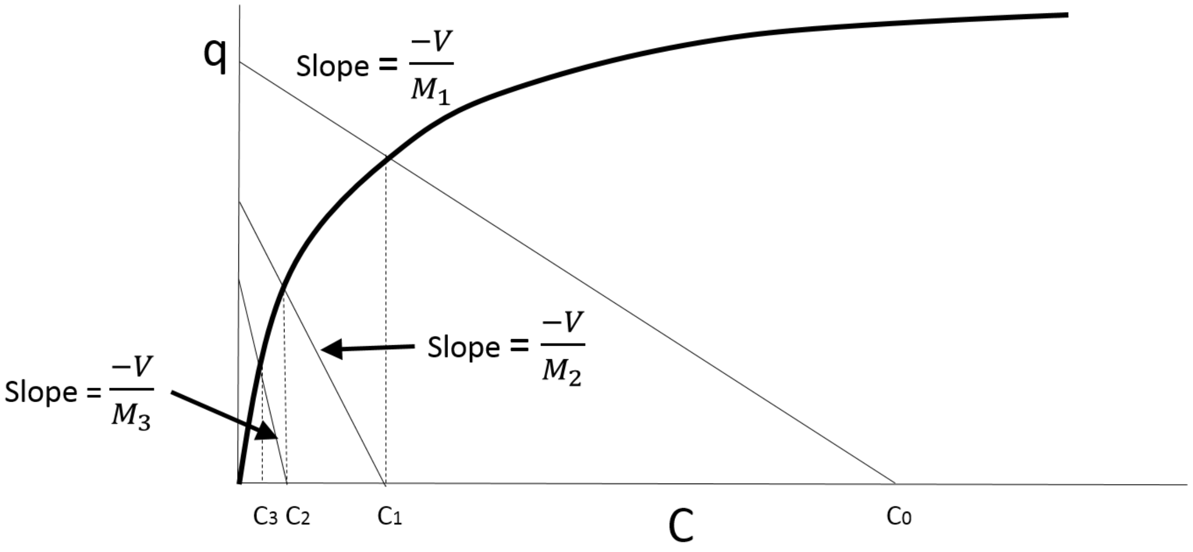


Figure B.4 Graphical solution to stage wise contacting fluid with three batches of adsorbent.

Appendix C: Results from principal component analysis

Table C.1 Principal component analysis of 28 physical and chemical properties of the media and raw water in feed to all the sites.

Principal Component	**PC1**	**PC2**	**PC3**	**PC4**
Eigenvalue	10.716	5.875	3.511	3.03
Proportion of variance (%)	36.69	21.76	13.00	12.232
Cumulative proportion of variance (%)	36.69	61.45	74.45	86.68
Rotated factor loading				
Fe	**.947**	-.159	.162	-.165
P_{ox}	**.936**	-.254	.007	-.191
Al_{ox}	**-.928**	.359	.003	.063
Voids ratio	**.924**	.159	.060	.197
Al	**-.924**	.362	-.003	.097
Al+Fe	**.918**	-.011	.264	-.204
SO_4	**.836**	-.141	-.399	-.128
Calculated Porosity	**.815**	-.067	-.023	.413
Particle Density	**.803**	.146	.429	.020
Ca	**.788**	.098	.483	.070
ph	**-.752**	.365	.498	.115
Moisture content	**.731**	-.140	-.189	.609
Particle Size	**-.587**	-.112	.540	.143
TC	-.060	**-.951**	-.001	-.011
Drysolids	.029	**-.906**	-.096	.265
Raw water pH	-.162	**.857**	.357	.243
Cl	.252	**-.757**	.271	.316
SSA	-.387	**.608**	.082	.531
Coagulant Dose	-.020	.162	**.909**	.114
Compression Index	.112	.000	**.797**	-.051
Raw water Turbidity	.435	.300	**.775**	.315
Raw water TOC	.020	-.396	**.610**	-.271
TP	.013	.253	.332	**.872**
Fe_{ox}	-.050	-.185	-.334	**.764**
Degree of Saturation	.074	-.307	.109	**.715**
EC	-.319	.627	-.035	**.678**
Alkalinity	-.328	.522	.306	**.595**

Appendix D: Matlab Program

The programme below has been appended as the vast majority of the code is related to the GUI and is therefore not shown.

```
%%----------------------------------------------------------------------
%set default values
set(handles.Pinput,'String','10');
set(handles.C_Time,'String','6');
set(handles.R_Time,'String','6');
set(handles.ReducPerform,'String','10');
set(handles.DaysOp, 'String','500');
set(handles.Porosity,'String','0.5');
set(handles.BulkDens,'String','1000');
set(handles.Width,'String','5');
set(handles.Depth,'String','0.6');
set(handles.NoBeds,'String','1');
set(handles.Slope,'String','-0.0005');
set(handles.Intercept,'String','.99');
set(handles.PopEq,'String','200');
set(handles.FlowPerPE,'String','200');
set(handles.Preq_mglLev1,'String','1'); %default level 1 P to get 2
set(handles.PreqLevel2,'String','5');  %default level 2 P to get 2
set(handles.OutleD,'String','100');% default pipe diameter mm
set(handles.OutletH,'String','50');% default outlet height diameter mm




%%THIS IS THE CALCULATION CODE
%% set the variables from GUI to variables used in code

clc
cla(handles.Days)            %clears graph for next run
cla(handles.Cycles)
cla(handles.Freundlich)
cla(handles.Cycles2ndOrder)
cla(handles.PercentRemoved2ndOrder)
cla(handles.CyclesCal)
cla(handles.DaysCal)

%% set variable names from on screen tags
contact_time = str2double(get(handles.C_Time,'string'));
rest_time = str2double(get(handles.R_Time,'string'));
inletPconc = str2double(get(handles.Pinput,'string')) %inlet P conc
mg/l
DaysOfOperation= str2double(get(handles.DaysOp,'string'));
ReductionInPerformance =
str2double(get(handles.ReducPerform,'string'));
ReductionInPerformance = ReductionInPerformance/100;    %convert
reduction in performance to percentage
Porosity = str2double(get(handles.Porosity,'string'));
BulkDens = str2double(get(handles.BulkDens,'string'));
Width = str2double(get(handles.Width,'string'));
Depth = str2double(get(handles.Depth,'string'));
NumBeds = str2double(get(handles.NoBeds,'string'));
Slopegraph= str2double(get(handles.Slope,'string'));
```

```
intercept= str2double(get(handles.Intercept,'string'));
PopEqu=str2double(get(handles.PopEq,'string'));  %population
equivalent
LperPopEqu = str2double(get(handles.FlowPerPE,'string'));  %population
equivalent%number of litres per population equivilent
HydraCond = str2double(get(handles.HydCond,'string')); %hydraulic
conductivity m/s
PolyD = str2double(get(handles.PolyDose,'string')); %poly dos in
unknown units
PartiDens = str2double(get(handles.PartDens,'string')); %Particle
Density kg/m3
Dry_Solids = str2double(get(handles.DrySolids,'string')); %Dry Solids
%
Prequ1 = str2double(get(handles.Preq_mglLev1,'string')); %Level1 of P
to measure days to
Prequ2 = str2double(get(handles.PreqLevel2,'string')); %Level 2 of P
to measure days to
PipeHeight = str2double(get(handles.OutletH,'string')); %Pipe height
above bed base mm
PipeDia = str2double(get(handles.OutleD,'string')); %Outlet pipe
diameter mm



%% Set variables from spread sheet of imported data
Fr_Kf = str2double(get(handles.Freund_Kf,'string'));
Fr_n = str2double(get(handles.Freund_n,'string'));
Cal_A = str2double(get(handles.Call_A,'string'));
Cal_B = str2double(get(handles.Call_B,'string'));
X1LnTime = str2double(get(handles.X1lntime,'string'));
X2LnTime = str2double(get(handles.X2lntime,'string'));
X1Const = str2double(get(handles.X1const,'string'));
X2Const = str2double(get(handles.X2const,'string'));
FirstOrd = str2double(get(handles.Firstorder,'string'));
SecondOrd = str2double(get(handles.SecondOrder,'string'));
SecOrdConst = str2double(get(handles.Constant,'string'));
MediaMassExp = str2double(get(handles.ExpMediaMass,'string'));
Gravity = 9.81;  % m/s/

%% calculations for p removal

cyclesperday=24/(contact_time+rest_time);  %calculates number of
cycles per day

Averagehourlyflow=(PopEqu*LperPopEqu)/24;   %calculates averega hourly
flow rate
InletPperday=24*((Averagehourlyflow*inletPconc)/1000);  %inlet p per
day in grammes

DaysofOP = 1:1:DaysOfOperation ;             %vector with each day
vertically
Cycleslist = DaysofOP.*cyclesperday ;        %vector with total cycles


%% calculations for bed area, and length------------------------------
---
TotflowperDay = (LperPopEqu*PopEqu)/1000 ;       %total flow per day
in m3
```

```
set(handles.CycleperDay,'string',round(cyclesperday,2)); %display
number of cycles per day
VolinBed = TotflowperDay/cyclesperday;           %amount of water in
m3 to be stored in bed to deal with flow
BedVol = VolinBed/Porosity;                      %actual vol of bed
required
Length = BedVol/(Width*Depth);                   %required length of
bed
set(handles.Length,'string',round(Length,2)) ;   %display length
TotArea = Length * Width;                        %calculate total area
of bed
set(handles.TotArea,'string',round(TotArea,2))   %display total area
WidthperBed = Width/NumBeds;                    %calculates the width
of each smaller bed depending on number of beds
set(handles.BedWidth2,'string',round(WidthperBed,2));
TotMediaVol = BedVol;                 %total volume of media required
set(handles.TotMediaVol,'string',round(TotMediaVol,2))
TotMediaMass = TotMediaVol*BulkDens;       %total mass of media KG
TotMediaMassTon =TotMediaMass/1000;
set(handles.TotMediaMass,'string',round(TotMediaMassTon,3))
M2perPE = TotArea/PopEqu;             %m2 per populastion eqivilant
set(handles.m2perPE,'string',round(M2perPE,2))
PdosePerM2 = TotflowperDay*inletPconc*1000/TotArea; %mgof P per m2 per
day
set(handles.Pdoseperm2,'string',round(PdosePerM2,2))
PdosePerM3 = TotflowperDay*inletPconc*1000/BedVol;  %mg P dose per m3
set(handles.mgperm3,'string',round(PdosePerM3,2))
PdosePerKG = TotflowperDay*inletPconc*1000/TotMediaMass; %mgP perkg
media
set(handles.mgperkg,'string',round(PdosePerKG,4))
ContTimeperbed = contact_time/NumBeds;
set(handles.Ctimeperbed,'string',round(ContTimeperbed,2))
RestTimeperbed = rest_time/NumBeds;
set(handles.Rtimeperbed,'string',round(RestTimeperbed,2))


%%calculation for drain down-------------------------------------------
 AreaOfOut =   (((PipeDia/1000)/2)^2)*pi;       %cross sectional area
of outlet pipe
 ActHeight = Depth - (PipeHeight/1000);         %actual head driving
drain
 AreaEachBed = WidthperBed * Length;            %individual area of
each bed
 DrainTimeSec =
(AreaEachBed/AreaOfOut)*((sqrt(ActHeight))/(sqrt(Gravity/2)));
%calculation using simplified bernoulli
 DrainTimeMin = DrainTimeSec/60;
 DrainTimeHrs = DrainTimeMin/60;

 if DrainTimeHrs > rest_time
    set(handles.NoTime,'string','NOT ENOUGH TIME  RESET REST TIME') ;
 elseif    DrainTimeHrs < rest_time
    set(handles.NoTime,'string','    ') ;
 end

 set(handles.DrainTime,'string',round(DrainTimeMin,2));
```

```
%%P removal and flow results-----------------------------------------
set(handles.TotFlowPerDay,'string',TotflowperDay);  %display total
flow per day m3
TotalFlow = TotflowperDay * DaysOfOperation;        %calculate total
flow in m3
set(handles.TotFlow,'string',TotalFlow);             %Display total
flow m3
TotPinKg = (TotalFlow * inletPconc)/1000;            %calculate total
amount of P in
set(handles.TotPin,'string',TotPinKg);               % display total
amount of P in
set(handles.TotPperDay,'string',InletPperday) ;      %display inlet P
per day in grammes


%% Freundlich graph plot

FreundInlet = [0:0.1:20]  ;                         %%inlet P
concnetration  mg/l
FreundOut  = Fr_Kf*(FreundInlet.^(1/Fr_n)) ;        %freund preidcted
out mg/kg
FreundOutCalc = Fr_Kf*(inletPconc^(1/Fr_n));        % Calculate max P
adsorbed predicted by freundlich at inlet concnetration
set(handles.Freund_res,'string',FreundOutCalc);      % display total
amount of P in

% Freundlich calculation for volume treated
Freundqt = Fr_Kf*(Prequ1^(1/Fr_n));                     % Calculates
value of qt on graph at  outlet concnetration of level 1
ConcDiff = inletPconc-Prequ1;                            %calculates
inlet - outlet concntration
VolMassSlope1 = Freundqt/ConcDiff;                          %slope of
volme/Mass line of freundlich isotherm
MaxVoltreated = VolMassSlope1*TotMediaMass;                  %volume
of water trated in m3 (as mg/l = g/m3 of water treated
set(handles.FreundVolTreat,'string',MaxVoltreated);         % display
max volume treatable in m3
Freund_Days_Lev1 = MaxVoltreated/TotflowperDay;
%calculate maximum number of days of treatment with predicted flow
set(handles.Freund_daystoLev1,'string',Freund_Days_Lev1);
%display max number of days treatable with frendlich calc at 1 level

%% Freundlich calc for multiple beds

Freundvect=1:1:NumBeds;         %create vertical vector with number of
beds
ConcStep = (inletPconc-Prequ1)/NumBeds  ;           %Calucltaes size
of ezch concnetration drop
ConcVect= inletPconc-(ConcStep.*Freundvect) ;        %concentration
required at each step
FreundQtVect= Fr_Kf*(ConcVect.^(1/Fr_n));            %freundlich qt at
each concnetration
VolMassSlopeAll = FreundQtVect./ConcStep    ;          %slope for each
freundlich mass line
MaxVoltreatedAll= VolMassSlopeAll.*(TotMediaMass/NumBeds);   %volume
each bed can treat
SumVoltreatedAll = sum(MaxVoltreatedAll) ;       %total of volume
treated
```

```
Freund_Days_Lev1_All = SumVoltreatedAll/TotflowperDay ;   % length of
time to saturation
set(handles.VolMultiBed,'string',SumVoltreatedAll);         %display
vol treated
set(handles.DaysMultiBed,'string',Freund_Days_Lev1_All);
%display days to sturation

%   plot Freundlich graph
    plot(handles.Freundlich, FreundInlet,FreundOut)
    xlabel(handles.Freundlich,'P conc mg/l')
    ylabel(handles.Freundlich, 'P adsorbed  mg/g')

    grid off

%%-------------------------------------------------------------
% calculation for p removal loop

%calculation using first order constants


if NumBeds==1       %run if number of bed =1 have to have a seperate
case as first run has constant inlet concentration
%
    PadsorbedRun1=((Cycleslist*Slopegraph)+(intercept)).*inletPconc;
% calculate vector amount of P absorbed in run 1 mg/l
    PremainingRun1=inletPconc-PadsorbedRun1;

%   plot cylces graph
    plot(handles.Cycles, Cycleslist,PremainingRun1)
    xlabel(handles.Cycles,'Cycles')
    ylabel(handles.Cycles, 'Pconc mg/l')

    grid off
%

%     % plot days graph
    plot(handles.Days,DaysofOP,PremainingRun1)
    set(handles.Days,'XminorTick', 'on')
    xlabel(handles.Days, 'Days')
    ylabel(handles.Days, 'Pconc mg/l')

 %--------------------------------------------------------
    %%%%     Calculation using second order constatnts

FlowPerCycle = TotflowperDay/cyclesperday ;        %flow per cycle in
m3
PinPerCycle = FlowPerCycle*Cycleslist*inletPconc;  %P input in g per
cycle
PingPerKgCycleVector = PinPerCycle/TotMediaMass    ; %vector of g/kg
input in cycles
PadsPerKgCycleVector = ((PingPerKgCycleVector.^2)*SecondOrd)+
(PingPerKgCycleVector.*FirstOrd) + SecOrdConst ; %vector with to P
adsorbed g/kg
PercentRem = PadsPerKgCycleVector./PingPerKgCycleVector;   %second
order percentage removal calc
Padsorbed2ndOrder = PercentRem * inletPconc   ;            %amount of
P adsorbed second order in mg/l
```

```
Premaining2ndOrder = inletPconc-Padsorbed2ndOrder ;        %P conc
remaining in solution in mg/l
Premaining2ndOrder(Premaining2ndOrder<0) = 0    ;
%%%% %plot cycles graph
    plot(handles.Cycles2ndOrder,Cycleslist, Premaining2ndOrder)
    xlabel(handles.Cycles2ndOrder,'Cycles')
    ylabel(handles.Cycles2ndOrder, 'P Conc mg/l')
hold on
    grid off
%%%% %plot P days graph
    plot(handles.PercentRemoved2ndOrder,DaysofOP,Premaining2ndOrder)
    xlabel(handles.PercentRemoved2ndOrder,'Days')
    ylabel(handles.PercentRemoved2ndOrder, 'P conc mg/l')

    grid off
%----------------------------------------------------------------------
%%%%%       Calculation using callery model

        CumFlowCyclVector=FlowPerCycle*Cycleslist *1000  ;
%vector with cummulative flow against cycles in litres
        MassMediaGrams = TotMediaMass*1000 ;
%mass of media in grams
        OutPconcCal = inletPconc -
(((Cal_A*MassMediaGrams*(CumFlowCyclVector.^((1/Cal_B)-
1)))/Cal_B)/(TotMediaMass/MediaMassExp)) ; %%outlet P conc mg/l
        PadsorbedCal=
(((Cal_A*MassMediaGrams*(CumFlowCyclVector.^((1/Cal_B)-
1)))/Cal_B)/(TotMediaMass/MediaMassExp))  ;    %Padsorbed mg/l


   %   plot cylces graph
    plot(handles.CyclesCal, Cycleslist,OutPconcCal)
    xlabel(handles.CyclesCal,'Cycles')
    ylabel(handles.CyclesCal, 'Pconc mg/l')

    grid off
%

%     % plot days graph
    plot(handles.DaysCal,DaysofOP,OutPconcCal)
    set(handles.Days,'XminorTick', 'on')
    xlabel(handles.DaysCal, 'Days')
    ylabel(handles.DaysCal, 'Pconc mg/l')



%----------------------------------------------------------------------
%     %Premoval stuff  for first order
     TotPremovedRun1 = PadsorbedRun1.* (TotflowperDay*1000);
%vector with amount of P removed each day in mg
     GrandTotPremovedrun1=sum(TotPremovedRun1)/1000000 ;
%total P removed run1 kg
      set(handles.TotPrem,'string',GrandTotPremovedrun1) ;
%display total P removed by run 1
     PercentPrem_Run1= (GrandTotPremovedrun1/TotPinKg)*100;
      set(handles.PercPremRun1,'string', PercentPrem_Run1)


      TotPadsmgkg = (GrandTotPremovedrun1*1000)/TotMediaMass;
%amount of P adsorbed mg/kg at finish
```

```
      set(handles.FinPad_mgkg,'string',TotPadsmgkg) ;
%display tot mg/kg


      %days to level calculation for first order
      DaystoLev1 = find(PremainingRun1 >=Prequ1,1) ;
%find number of days until output>1
        if max(PremainingRun1) < Prequ1
% decide id P concentration is reached
            set(handles.Daysto1mg,'string','P conc not reached') ;
%display P conc not reached
                elseif  max(PremainingRun1) >   Prequ1
%otherwise do calc
            set(handles.Daysto1mg,'string',DaystoLev1) ;
%display output in days
        end

         if max(PremainingRun1) < Prequ2
            set(handles.DaysToLevel2,'string','P conc not reached') ;
                 elseif   max(PremainingRun1) > Prequ2
            DaystoLev2 = find(PremainingRun1 >=Prequ2,1);
%find number of days until output>1
         set(handles.DaysToLevel2,'string',DaystoLev2) ;
%display output in days
         end

         if max(PremainingRun1) < inletPconc
             set(handles.DaysToSat,'string','not saturated')
%time to saturation
         elseif max(PremainingRun1) > inletPconc
         DaysToSatu = find(PremainingRun1 >=inletPconc,1);
         set(handles.DaysToSat,'string',DaysToSatu)

        end
 %--------------------------------------------------------------------
----------------------------------------------------------------------
-
 % removal stuff  for second order

  TotPremovedRun1_2nd = Padsorbed2ndOrder.* (TotflowperDay*1000) ;
%vector with amount of P removed each day in mg
     GrandTotPremovedrun1_2nd = sum(TotPremovedRun1_2nd)/1000000   ;
%total P removed run1 kg
     PercentPrem_2nd= (GrandTotPremovedrun1_2nd/TotPinKg)*100;
      set(handles.PercPrem_2nd,'string', PercentPrem_2nd);

      set(handles.TotPrem_2nd,'string',GrandTotPremovedrun1_2nd) ;
%display total P removed by run 1
     TotPadsmgkg_2nd = (GrandTotPremovedrun1_2nd*1000)/TotMediaMass;
%amount of P adsorbed mg/kg at finish
      set(handles.FinPad_mgkg_2nd,'string',TotPadsmgkg_2nd)


      %days to level calculation for second  order
       DaystoLev1_2nd = find(Premaining2ndOrder >=Prequ1,1)      ;
%find number of days until output>1
        if max(Premaining2ndOrder) < Prequ1
% decide id P concentration is reached
```

```
            set(handles.Daysto1mg_2nd,'string','P conc not reached') ;
%display P conc not reached
                elseif  max(Premaining2ndOrder) >   Prequ1
%otherwise do calc
            set(handles.Daysto1mg_2nd,'string',DaystoLev1_2nd) ;
%display output in days
        end

         if max(Premaining2ndOrder) < Prequ2
            set(handles.Daystolevel2_2nd,'string','P conc not
reached') ;
                 elseif   max(Premaining2ndOrder) > Prequ2
            DaystoLev2_2 = find(Premaining2ndOrder >=Prequ2,1);
%find number of days until output>1
         set(handles.Daystolevel2_2nd,'string',DaystoLev2_2) ;
%display output in days
         end

         if max(Premaining2ndOrder) < inletPconc
             set(handles.DaystoSat_2nd,'string','not saturated')
%time to saturation
         elseif max(Premaining2ndOrder) > inletPconc
         DaysToSatu_2nd = find(Premaining2ndOrder >=inletPconc,1);
         set(handles.DaystoSat_2nd,'string',DaysToSatu_2nd)

         end

          %% calculates stuff for 3d time plot
      time=[0.5:0.5:24] ;
%time loop



        [xx yy]=meshgrid(Cycleslist,time);
       FirstOrd = (X1LnTime * log(yy))+ X1Const    ;
%define first order constant
        SecondOrd = (X2LnTime * log(yy))+ X2Const   ;
%define second order constant

 PinPerCycle = FlowPerCycle*xx*inletPconc;  %P input in g per cycle
 PingPerKgCycleVector = PinPerCycle/TotMediaMass   ; %matrix of g/kg
input in cycles
 PadsPerKgCycleVector = ((PingPerKgCycleVector.^2).*SecondOrd)+
(PingPerKgCycleVector.*FirstOrd) + SecOrdConst ; %vector with to P
adsorbed g/kg
 PercentRem = PadsPerKgCycleVector./PingPerKgCycleVector;   %second
order percentage removal calc
Padsorbed2ndOrder = PercentRem * inletPconc   ;            %amount of
P adsorbed second order in mg/l
 Premaining2ndOrder = inletPconc-Padsorbed2ndOrder  ;       %P conc
remaining in solution in mg/l
  Premaining2ndOrder(Premaining2ndOrder<0) = 0    ;
    figure
    mesh(xx,yy,Premaining2ndOrder)
   xlabel('Cycles')
    ylabel('Contact time hrs')
    zlabel('Outlet P concnetration mg/l')
    title (['Outlet P conc.against contact time with inlet P'
num2str(inletPconc) 'mg/l and' MedType  'media'])
```

```
 %%%-----------------------------------------------------------------------
-----------------------------------------------------------------------
---
 % removal stuff  for Callery

  TotPremovedRun1_Cal = PadsorbedCal.* (TotflowperDay*1000) ;
%vector with amount of P removed each day in mg
     GrandTotPremovedrun1_Cal = sum(TotPremovedRun1_Cal)/1000000    ;
%total P removed run1 kg
     set(handles.TotPrem_Cal,'string',GrandTotPremovedrun1_Cal) ;
%display total P removed by run 1
   PercentPrem_Cal=(GrandTotPremovedrun1_Cal/TotPinKg)*100;
      set(handles.PercPrem_Cal,'string', PercentPrem_Cal)

     TotPadsmgkg_Cal = (GrandTotPremovedrun1_Cal*1000)/TotMediaMass;
%amount of P adsorbed mg/kg at finish
      set(handles.FinPad_mgkg_Cal,'string',TotPadsmgkg_Cal)



      %days to level calculation for Callery
      DaystoLev1_Cal = find(OutPconcCal >=Prequ1,1)     ;
%find number of days until output>1
        if max(OutPconcCal) < Prequ1           ;
% decide id P concentration is reached
            set(handles.Daysto1mg_Cal,'string','P conc not reached') ;
%display P conc not reached
                elseif  max(OutPconcCal) >   Prequ1
%otherwise do calc
            set(handles.Daysto1mg_Cal,'string',DaystoLev1_Cal) ;
%display output in days
        end

         if max(OutPconcCal) < Prequ2
            set(handles.Daystolevel2_Cal,'string','P conc not
reached') ;
                 elseif   max(OutPconcCal) > Prequ2
            DaystoLev2_2 = find(OutPconcCal >=Prequ2,1);
%find number of days until output>1
         set(handles.Daystolevel2_Cal,'string',DaystoLev2_2) ;
%display output in days
         end

         if max(OutPconcCal) < inletPconc
             set(handles.DaystoSat_Cal,'string','not saturated')
%time to saturation
         elseif max(OutPconcCal) > inletPconc
         DaysToSatu_Cal = find(OutPconcCal >=inletPconc,1);
         set(handles.DaystoSat_Cal,'string',DaysToSatu_Cal)

        end



elseif NumBeds > 1
%% Create matrix with zeroes for P adsorbed, P remaining and P removed
in mg
```

```
    PadsoRunall = zeros(NumBeds,length(DaysofOP));                  %
create matrices of zeroes for P adsorbed results
    PremainingRunall = zeros(NumBeds,length(DaysofOP));             %
create matrices of zeroes for P remaining  results
    TotPremoved=zeros(NumBeds,length(DaysofOP));
%create matrix with Total amount of P removed each day in mg
   PercentRem=zeros(NumBeds,length(DaysofOP));

    %% P adsorption calc for run 1 repeated
   PadsoRunall(1,:) =
((Cycleslist*Slopegraph)+(intercept)).*inletPconc;  % builds first row
of P adsorbed matrices
   PremainingRunall(1,:) = inletPconc-PadsoRunall(1,:);
%builds first row of P remaining matrix



   %%%-----------------------------------------------------------------
-----------------------------------------------------------------



%% Create matrix with zeroes for P adsorbed, P remaining and P removed
in mg 2nd order
    PadsoRunall_2nd = zeros(NumBeds,length(DaysofOP));
% create matrices of zeroes for P adsorbed results
    PremainingRunall_2nd = zeros(NumBeds,length(DaysofOP));
% create matrices of zeroes for P remaining  results
    TotPremoved_2nd=zeros(NumBeds,length(DaysofOP));
%create matrix with Total amount of P removed each day in mg
    PingPerKgCycleVector=zeros(NumBeds,length(DaysofOP));
%create matrix with Ping/kg for each cycle
     PadsPerKgCycleVector=zeros(NumBeds,length(DaysofOP));
%creates P adsorbed per cycle matrix with zeros
     PinPerCycle=zeros(NumBeds,length(DaysofOP));
%creates P in percycle matrices
    %% P adsorption calc for run 1 repeated    2nd order

FlowPerCycle = TotflowperDay/cyclesperday   ;      %flow per cycle in
m3
PinPerCycle(1,:) = FlowPerCycle*Cycleslist*inletPconc ; %P input in g
per cycle
PingPerKgCycleVector(1,:) = PinPerCycle(1,:)./TotMediaMass ;   %first
row of matrix  of g/kg input in cycles
PadsPerKgCycleVector(1,:) =
(((PingPerKgCycleVector(1,:).^2)*SecondOrd)*ReductionInPerformance)+
(PingPerKgCycleVector(1,:).*FirstOrd) + SecOrdConst ; %first row
matrix   with to P adsorbed g/kg
PercentRem(1,:) = PadsPerKgCycleVector(1,:)./PingPerKgCycleVector(1,:)
;  %second order percentage removal matrix  calc


PadsoRunall_2nd(1,:) = PercentRem(1,:) * inletPconc ;    % builds
first row of P adsorbed matrices
   PremainingRunall_2nd(1,:) = inletPconc-PadsoRunall_2nd(1,:)  ;
%builds first row of P remaining matrix
   PremainingRunall_2nd(PremainingRunall_2nd<0) = 0           ;
%replace negatives with 0
   PremainingRunall_2nd( isnan(PremainingRunall_2nd))=0  ;
```

```
   %% P adsorption for runs set by number of beds  First
hold on

    for i = 2:1:NumBeds

        %%%%%   First order

 PadsoRunall(i,:)=((Cycleslist*Slopegraph)+(intercept-
ReductionInPerformance)).*PremainingRunall((i-1),:);  % calculates
next rows inP adsorbed
   PremainingRunall(i,:) = PremainingRunall((i-1),:)-PadsoRunall(i,:);
%calculates next row of matrix  P remaining

%% calculate mass of P removed and time to 1mg/l
   TotPremoved(1,:) = PadsoRunall(1,:) .* (TotflowperDay*1000);
%matric row 1 with amount of P removed each day in mg
   TotPremoved(i,:)= PadsoRunall(i,:).*(TotflowperDay*1000);
     GrandTotPremovedvect=sum(TotPremoved) ;                    %vector
with total P removed ech run mg
     GrandTotPremoved = sum(GrandTotPremovedvect)/1000000;
      set(handles.TotPrem,'string',GrandTotPremoved) ;
%display total P removed by run 1
       PercentPrem_Run1= (GrandTotPremoved/TotPinKg)*100;
      set(handles.PercPremRun1,'string', PercentPrem_Run1)
         TotPadsmgkg = (GrandTotPremoved*1000)/TotMediaMass;
%amount of P adsorbed mg/kg at finish
             set(handles.FinPad_mgkg,'string',TotPadsmgkg) ;
%display tot mg/kg



   %% find number of days to get to set levels
        DaystoLev1 = find(PremainingRunall(i,:) >=Prequ1,1);
%find number of days until output>1
        if max(PremainingRunall(i,:)) < Prequ1
% decide id P concentration is reached
            set(handles.Daysto1mg,'string','P conc not reached') ;
%display P conc not reached
                elseif  max(PremainingRunall(i,:)) >   Prequ1
             set(handles.Daysto1mg,'string',DaystoLev1) ;%display
output in days
        end

        if max(PremainingRunall(i,:)) < Prequ2
            set(handles.DaysToLevel2,'string','P conc not reached') ;
                 elseif   max(PremainingRunall(i,:)) > Prequ2
            DaystoLev2 = find(PremainingRunall(i,:) >=Prequ2,1);
%find number of days until output>1
            set(handles.DaysToLevel2,'string',DaystoLev2) ;
%display output in days
        end


        if max(PremainingRunall(i,:)) < inletPconc
%check if saturated
             set(handles.DaysToSat,'string','not saturated')
%time to saturation
```

```
                elseif max(PremainingRunall(i,:)) > inletPconc
               DaysToSatu = find(PremainingRunall(i,:)
>=inletPconc,1);
         set(handles.DaysToSat,'string',DaysToSatu)

        end


         % plot cylces graph



  plot(handles.Cycles, Cycleslist,PremainingRunall(1,:))
   plot(handles.Cycles, Cycleslist,PremainingRunall(i,:))
 xlabel(handles.Cycles,'Cycles')
ylabel(handles.Cycles, 'Pconc mg/l')
grid on

  % plot days graph

    plot(handles.Days,DaysofOP,PremainingRunall(1,:))
     plot(handles.Days,DaysofOP,PremainingRunall(i,:))
    set(handles.Days,'XminorTick', 'on')
    xlabel(handles.Days, 'Days')
    ylabel(handles.Days, 'Pconc mg/l')

  %-------------------------------------------------------------------
------------------------------------------------------

   %%%%%   Second  order

PinPerCycle(i,:) = FlowPerCycle*Cycleslist.*PremainingRunall_2nd((i-
1),:);  %P input in g per cycle
PingPerKgCycleVector(i,:) = PinPerCycle(i,:)/TotMediaMass ;  %next row
of matrix  of g/kg input in cycles
PadsPerKgCycleVector(i,:) =
((PingPerKgCycleVector(i,:).^2).*SecondOrd)+
(PingPerKgCycleVector(i,:).*FirstOrd)+SecOrdConst  ;%first row matrix
with to P adsorbed g/kg
PercentRem(i,:) = PadsPerKgCycleVector(i,:)./PingPerKgCycleVector(i,:)
;  %second order percentage removal matrix  calc

PadsoRunall_2nd(i,:) = PercentRem(i,:) .*PremainingRunall_2nd ((i-
1),:);    % builds first row of P adsorbed matrices
  PremainingRunall_2nd(i,:) = PremainingRunall_2nd((i-1),:)-
PadsoRunall_2nd(i,:)  ;                      %builds first row of P
remaining matrix
      PremainingRunall_2nd( PremainingRunall_2nd<0)=0
;   %replace negative values with 0
        PremainingRunall_2nd( isnan(PremainingRunall_2nd))=0
;  %replace nan with 0



%%%% %plot cycles graph

   axes(handles.Cycles2ndOrder)
```

```
  plot(handles.Cycles2ndOrder,Cycleslist,PremainingRunall_2nd(1,:))
    plot(handles.Cycles2ndOrder,Cycleslist,PremainingRunall_2nd(i,:))



    xlabel(handles.Cycles2ndOrder,'Cycles')
    ylabel(handles.Cycles2ndOrder, 'P Conc mg/l')

    grid on
  hold (handles.Cycles2ndOrder,'on')


%%%% %plot P days graph

plot(handles.PercentRemoved2ndOrder,DaysofOP,PremainingRunall_2nd(1,:)
)

plot(handles.PercentRemoved2ndOrder,DaysofOP,PremainingRunall_2nd(i,:)
)
    xlabel(handles.PercentRemoved2ndOrder,'Days')
    ylabel(handles.PercentRemoved2ndOrder, 'P conc mg/l')

    grid off

% Amount of P removed  for second order in loop

   TotPremovedRunall_2nd(1,:) =  PadsoRunall_2nd(1,:).*
(TotflowperDay*1000) ;      %vector with amount of P removed each day
in mg
    TotPremovedRunall_2nd(i,:) =  PadsoRunall_2nd(i,:).*
(TotflowperDay*1000) ;
      GrandTotPremovedvect_2nd = sum(TotPremovedRunall_2nd) ;
       GrandTotPremovedvect_2nd ( isnan(GrandTotPremovedvect_2nd ))=0
;             %remove nan and replace with 0

%sum the vector
             GrandTotPremoved_2nd = sum(
GrandTotPremovedvect_2nd)/1000000;


                 PercentPrem_2nd= (
GrandTotPremoved_2nd/TotPinKg)*100;
      set(handles.PercPrem_2nd,'string', PercentPrem_2nd);
        set(handles.TotPrem_2nd,'string',GrandTotPremoved_2nd) ;
%display total P removed by run 1
             TotPadsmgkg_2nd =
(GrandTotPremoved_2nd*1000)/TotMediaMass;            %amount of P
adsorbed mg/kg at finish
                set(handles.FinPad_mgkg_2nd,'string',TotPadsmgkg_2nd)

     %days to level calculation for second  order
       DaystoLev1_2nd = find(PremainingRunall_2nd(i,:) >=Prequ1,1)    ;
%find number of days until output>1
        if max(PremainingRunall_2nd(i,:)) < Prequ1
% decide id P concentration is reached
            set(handles.Daysto1mg_2nd,'string','P conc not reached') ;
%display P conc not reached
```

```
                 elseif  max(PremainingRunall_2nd(i,:)) >   Prequ1
%otherwise do calc
            set(handles.Daysto1mg_2nd,'string',DaystoLev1_2nd) ;
%display output in days
        end

         if max(PremainingRunall_2nd(i,:)) < Prequ2
            set(handles.Daystolevel2_2nd,'string','P conc not
reached') ;
                  elseif   max(PremainingRunall_2nd(i,:)) > Prequ2
            DaystoLev2_2 = find(PremainingRunall_2nd(i,:) >=Prequ2,1);
%find number of days until output>1
            %%
            %
            %   for x = 1:10
            %       disp(x)
            %   end
            %
         set(handles.Daystolevel2_2nd,'string',DaystoLev2_2) ;
%display output in days
         end

         if max(PremainingRunall_2nd(i,:)) < inletPconc
             set(handles.DaystoSat_2nd,'string','not saturated')
%time to saturation
         elseif max(PremainingRunall_2nd(i,:)) > inletPconc
         DaysToSatu_2nd = find(PremainingRunall_2nd(i,:)
>=inletPconc,1);
         set(handles.DaystoSat_2nd,'string',DaysToSatu_2nd)

        end



    end          % end for for loop
  %% calculation for 3d plot of num beds against cycles P removal
  BedNum=[1:1:NumBeds]
   [CC BB]=meshgrid(Cycleslist,BedNum);
    figure                                                  %create
figure window
    mesh(CC,BB,PremainingRunall_2nd);
%create mesh plot
    xlabel('Cycles')
    ylabel('Number of beds')
    zlabel('Outlet P concnetration mg/l')
    title (['Outlet P conc.against contact time with inlet P'
num2str(inletPconc) ' mg/l and '   'GU(1-1) media'])




end             %end for if statement
 hold off

%output table
InputVariables = [  inletPconc; contact_time; rest_time;
ReductionInPerformance;DaysOfOperation;PopEqu;LperPopEqu; Width;Depth;
NumBeds;Prequ1;Prequ2   ]
```

```
BedOutputVariables=
[ContTimeperbed;RestTimeperbed;TotArea;WidthperBed;Length;cyclesperday
;TotMediaVol;TotMediaMassTon;M2perPE;PdosePerM3;PdosePerKG;PipeDia;Pip
eHeight;DrainTimeMin]
Totpflowinputs = [TotflowperDay;TotalFlow;InletPperday;TotPinKg]
Foutputs=
[FreundOutCalc;MaxVoltreated;Freund_Days_Lev1;SumVoltreatedAll;Freund_
Days_Lev1_All]


%% Pop up box to populate media data from spread sheet

% --- Executes on selection change in MediaType.
function MediaType_Callback(hObject, eventdata, handles)
% hObject    handle to MediaType (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = cellstr(get(hObject,'String')) returns MediaType
contents as cell array
%        contents{get(hObject,'Value')} returns selected item from
MediaType


% --- Executes during object creation, after setting all properties.
contents = cellstr(get(hObject,'String')) ;    %get the value out of
the pop up list
popChoice = contents{get(hObject,'Value')};
%%--------------------------------------------------------------------
-----
%bring in data from spreadsheet

[maindata_physmedia,textdata_physmedia,rawdata_physmedia]=xlsread('Med
iaSummaryTable.xlsx');  %import file rawdat has all data as a cell
[maindata_chemmedia,textdata_chemmedia,rawdata_chemmedia]=xlsread('Med
iaChemTable.xlsx');  %import file rawdat has all data as a cell


%if else loop to populate data in gui from popup menu
if (strcmp(popChoice,'BS'))          %if it=GU
    R = find(strcmp('BS',rawdata_physmedia));

     elseif (strcmp(popChoice,'FO'))
        R = find(strcmp('FO',rawdata_physmedia));

    elseif (strcmp(popChoice,'FO*'))
        R = find(strcmp('FO*',rawdata_physmedia));

    elseif (strcmp(popChoice,'GU'))
        R = find(strcmp('GU',rawdata_physmedia)) ;

    elseif (strcmp(popChoice,'HH'))
        R = find(strcmp('HH',rawdata_physmedia));

    elseif (strcmp(popChoice,'HH*'))
        R = find(strcmp('HH*',rawdata_physmedia)) ;

     elseif (strcmp(popChoice,'HO'))
```

```
        R = find(strcmp('HO',rawdata_physmedia));

      elseif (strcmp(popChoice,'LA'))
        R = find(strcmp('LA',rawdata_physmedia));

      elseif (strcmp(popChoice,'MO'))
        R = find(strcmp('MO',rawdata_physmedia));

      elseif (strcmp(popChoice,'WD'))
        R = find(strcmp('WD',rawdata_physmedia));

     elseif (strcmp(popChoice,'GU_Bed2'))
        R = find(strcmp('GU_Bed2',rawdata_physmedia));

         elseif (strcmp(popChoice,'GU_1_1'))
        R = find(strcmp('GU_1_1',rawdata_physmedia));

        elseif (strcmp(popChoice,'BS_1_1'))
        R = find(strcmp('BS_1_1',rawdata_physmedia));

         elseif (strcmp(popChoice,'HO_Bed_1'))
        R = find(strcmp('HO_Bed_1',rawdata_physmedia));
end
%% write the correct variable values into GUI

set(handles.HydCond,'String',rawdata_physmedia{R,6}) %bring in data
from set row
set(handles.PolyDose,'String',rawdata_physmedia{R,7})
set(handles.AlorFe,'String',rawdata_physmedia{R,10})
set(handles.Porosity,'String',rawdata_physmedia{R,5})
set(handles.BulkDens,'String',rawdata_physmedia{R,2})
set(handles.PartDens,'String',rawdata_physmedia{R,3})
set(handles.DrySolids,'String',rawdata_physmedia{R,4})
set(handles.Slope,'String',rawdata_physmedia{R,8})
set(handles.Intercept,'String',rawdata_physmedia{R,9})
set(handles.Freund_Kf,'String',rawdata_physmedia{R,12})
set(handles.Freund_n,'String',rawdata_physmedia{R,13})
set(handles.Call_A,'String',rawdata_physmedia{R,14})
set(handles.Call_B,'String',rawdata_physmedia{R,15})
set(handles.Call_Notes,'String',rawdata_physmedia(Guest et al., 2009))
set(handles.X1lntime,'String',rawdata_physmedia(Anderson and Magdoff,
2005))
set(handles.X1const,'String',rawdata_physmedia{R,26})
set(handles.X2lntime,'String',rawdata_physmedia{R,27})
set(handles.X2const,'String',rawdata_physmedia{R,28})
set(handles.Firstorder,'String',rawdata_physmedia{R,21})
set(handles.SecondOrder,'String',rawdata_physmedia{R,22})
set(handles.Constant,'String',rawdata_physmedia{R,23})
set(handles.notes2ndOrder,'String',rawdata_physmedia{R,24})
set(handles.ExpMediaMass,'String',rawdata_physmedia(Sim et al., 2013))
```

The remainder of the programme has not been displayed and as it is just call backs to the GUI.

T