Phosphorus Removal from Wastewater Using Carbonated Biochar/Steel Slag Composites

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Abstract. Phosphorus (P) pollution is a major contributor to eutrophication, while the accumulation of solid wastes such as steel slag and biomass without proper disposal poses significant environmental risks. To address these challenges, biochar/steel slag (BC/SS) composites were synthesised via the carbonation of BC and SS as a novel adsorbent to remove P from simulated wastewater. In this study, the carbonated BC/SS effectively captured P and reduced the pH and conductivity of the treated solutions. Different proportions of BC and SS were tested to optimise the adsorptive performance of the composites. Results show that BC10 (containing10 wt.% of BC) exhibited the highest adsorption capacity for P in the batch experiments. The adsorption process followed the pseudo-second-order kinetics and conformed closely to the Langmuir isotherm, with a maximum adsorption capacity (q_m) of 5.36 (mg/g) in 48 h. Column experiments further confirmed the strong P removal efficiency of the composite. Material characterisations revealed that carbonation primarily led to the formation of calcium carbonate from Ca-species, and the addition of BC enhanced the carbonation reaction. This study highlights the potential of carbonated BC/SS composites as an effective adsorbent for P removal from wastewater, offering a sustainable method for the utilisation of solid wastes.

Keywords: Biochar; Steel slag; Phosphorus; Carbonation; Adsorption

1. Introduction

Excess phosphorus (P) contamination from agricultural runoff has become a critical environmental concern, triggering eutrophication of watersheds [1]. Elevated P loading also promotes the growth of aquatic bacteria, which can adversely affect ecosystem functions and pose microbiological risks to human health [2]. Concurrently, evolving regulatory frameworks on waste management regulations and circular economy principles have intensified the exploration of industrial byproducts such as basic oxygen furnace steel slag (SS) as sustainable remediation materials [3].

SS has emerged as a promising P removal candidate due to its inherent chemical/mineral composition [4, 5]. SS contains Ca-, Fe-, and Al- rich mineral phases, making it a cost-effective and efficient material for wastewater treatment, especially for P removal through synergistic chemisorption-precipitation mechanisms over a wide range of water characteristics [6]. However, the high pH and conductivity of the outflow solution attributed to the alkaline leaching pose significant challenges for the practical implementation such as accelerated corrosion of the equipment [7]. Furthermore, the high density and low porosity of SS limit its adsorption efficiency by diminishing hydraulic permeability, and restricting contaminant diffusion and active site accessibility [8].

Carbonation technology involves the reaction of calcium-bearing minerals with CO_2 to form stable calcium carbonate, which can reduce the leaching of constituents and lower the pH and conductivity [9, 10]. In order to further improve its properties, researchers have found that the incorporation of porous materials such as biochar (BC) can enhance the carbonation efficiency and hydraulic performance of the material [11, 12]. BC is a carbon-rich material derived from pyrolysis of biomass in an oxygen-limited environment. BC is a promising sorbent for removing organic and inorganic contaminants from wastewater due to the excellent porous structure and various functional groups [13]. The modification with BC including impregnating with metal containing minerals to optimise the physical and chemical properties has been proved can meet practical environmental application requirements [14].

BC/SS has been designed to remove P from aqueous solution [15], but the composites are usually manufactured by co-pyrolysis of biomass and raw slag, which is associated with energy consumption and potentially harmful gas emissions [16, 17]. This study proposed the combination of SS and BC fabricated by carbonation as a porous sorbent in P removal from the aqueous solution. Carbonation-induced calcite precipitation binds the powders together while simultaneously stores CO_2 in the composite. It also reduces the potential risks of applying raw SS for water treatment, and the addition of BC would enhance carbonation efficiency, improve hydraulic performance, as well as adjust the microstructure of the composites. This work aims to: 1) evaluate the P sequestration performance of the composites with different proportions of BC and SS; 2) determine the P removal kinetics and isotherms with the batch adsorption test; and 3) investigate the long-term P removal performance using the column adsorption test.

2. Materials and methods

2.1 Fabrication of BC/SS composites

Table 1. Mixing ratios of SS and BC

Samples	Steel slag	Biochar	Carbonation
BC0	100	0	Yes
BC10	90	10	Yes
BC20	80	20	Yes
BC50	50	50	Yes
SS	100	0	No
BS	90	10	No

BC used in this study was purchased from Oxford biochar Ltd. It was produced from the pyrolysis of mixed hard woods at 400 °C. SS is a basic oxygen furnace slag supplied by Tarmac Ltd. The raw BC and SS were crushed and sieved to obtain particles with sizes of 75-150 μm and then stored in sealed plastic bags before use. The BC/SS composites were prepared by direct mixing and carbonation curing. Briefly, different proportions of SS and BC (Table 1) were firstly mixed in a blender at 800 rpm for 5 minutes while adding 30 wt.% deionised water during mixing to achieve homogeneity. The BC content varies from 0 to 50% by mass and the samples were denoted as BC0, BC10, BC20 and BC50, respectively. The obtained mixtures were then placed into polystyrene petri dishes (100 mm in diameter and 15 mm in height) and then moved into a carbonation chamber for CO_2 exposure with the duration of 7 days. The inner temperature and CO_2 concentration were maintained at 50°C and 20%, and the relative humidity was kept at around 70% by saturated sodium chloride solution. After carbonation, the specimens were dried in an oven at 75°C for 24 hours to remove the excess water and then crushed into less than 0.25 mm for batch adsorption test and between 0.25 and 2 mm for column test. The smaller particles in batch tests maximise the adsorbent's reactivity due to the larger surface area, but they do not perform well in column tests due to their poor permeability and potential clogging issues. Thus, for the column test, larger particles are preferred to ensure proper flow and better simulate what really happened in the field for contaminated groundwater remediation.

2.2 Batch adsorption test.

The phosphorus removal performance of the composite was investigated by batch tests. For comparison, pristine BC, SS, and non-carbonated BC (10 wt.%) + SS (90 wt.%) mixture (BS) were also included in the experiments. Phosphorus stock solution (1 g/L) was prepared by dissolving dipotassium hydrogen phosphate (K_2HPO_4) in deionised water. Subsequent solutions with desired concentrations were obtained by diluting the stock solution. All batch tests were carried out in triplicates and the average values were reported here (with coefficient of variation <8.12%).

Based on preliminary trials and literature, approximately 0.16 g of solid samples was added into 50 mL centrifuge tubes containing 40 mL of P solution (solid/liquid ratio of 0.04 mg/mL) with an initial P concentration of 10 mg/L. This ratio allows effective interaction between the adsorbent and the solution. The P concentration of 10 mg/L is similar to that in the agricultural runoffs and some industrial water. The mixture was shaken at 200 rpm for 48 h at room temperature. After reaching equilibrium, 2 mL of solution was extracted, filtered through 0.45 μm filter, and analysed for P concentration using ICP-OES.

BC10 was selected to evaluate the adsorption kinetics and isotherms of P removal. The adsorption kinetics were assessed by measuring the P concentration at different time intervals (5 min, 30 min, 2 h, 5 h, 10 h, 24 h, and 48 h) using an initial P concentration of 10 mg/L. The kinetic data were fitted with nonlinear pseudo-first-order (1) and pseudo-second-order (2) models. Adsorption isotherms were determined by equilibrating the prepared samples with initial P concentration solutions ranged from 1 to 100 mg/L for 48 h. The equilibrium results were analysed using the Langmuir (3) and Freundlich (4) models.

$$y = \mathrm{q}_e\left(1 - e^{-\mathrm{k}_1\mathrm{x}}\right) \qquad (1)$$

$$y = \frac{k_2 q_e^2 x}{1 + k_2 q_e x} \qquad (2)$$

$$q_e = \frac{q_m k_l c_e}{1+k_l c_e} \qquad (3)$$

$$q_e = k_f c_e^{\frac{1}{n}} \qquad (4)$$

where y represents the amount of adsorbate at time x, q_e is the equilibrium adsorption capacity, k_1, k_2 are the rate constants, q_m is the maximum adsorption capacity, c_e is the equilibrium concentration of the adsorbate, k_l, k_f are the Langmuir and Freundlich constant respectively, and n is the heterogeneity factor.

2.3 Column test

In order to compare the effects of carbonation and BC modification on the wastewater treatment performance, a column study was conducted to evaluate the long-term P removal performance [18]. Columns (300 × ø40 mm) were packed with 150 mm of B0, B10, SS, and BS with a 30 mm of glass beads placed at both top and bottom. The choice of the size of the column is to ensure the diameter of the column (40 mm) is more than 10 times the maximum size of the composite (2 mm) to minimise the boundary effect. A peristaltic pump was employed to inject a synthesised P solution (12.5 mg/L) at a steady flow rate of 1 mL/min through the column, which is simulating the slow groundwater flow in a low-gradient sandy aquifer. Prior to the experiment, columns were equilibrated in a deionised water bath for approximately 18 h to eliminate impurities in the samples. At specific time intervals, a certain volume of the filtered solution was collected and stored in a plastic vial in a fridge for subsequent analysis.

2.4 Analytical and characterisation methods

The crystalline phases were identified by X-ray diffraction (XRD) analysis using a Siemens D5000 Diffractometer operating at 40 kV and 30 mA. During the adsorption experiments, the pH and conductivity of the solutions were detected by a Multiparameter (Mettler Toledo, S479-K). P concentrations were measured by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) on a Perkin Avio 220 Max instrument.

3. Results

3.1 Characterisation of adsorbents

According to X-ray diffraction (XRD) analysis (Fig. 1), the primary mineral phases in SS consist of dicalcium silicate (C_2S), $Ca_2Fe_2O_5$, and the RO phase (continuous solid solution formed by iron oxide, magnesium oxide, and manganese oxide). After carbonation, $CaCO_3$ was generated through the reaction between Ca ions and dissolved CO_2. The diffraction peak intensity of C_2S decreased after the addition of BC, and as the BC content increased, the intensity of $CaCO_3$ peaks became more pronounced, indicating that BC promoted the carbonation of Ca-containing phases. This can be attributed to its hydrophilic property and porous structure. When combined with SS, BC functions as an internal curing agent, suppling absorbed free and bound water, as well as CO_2, thereby enhancing the carbonation reaction [12].

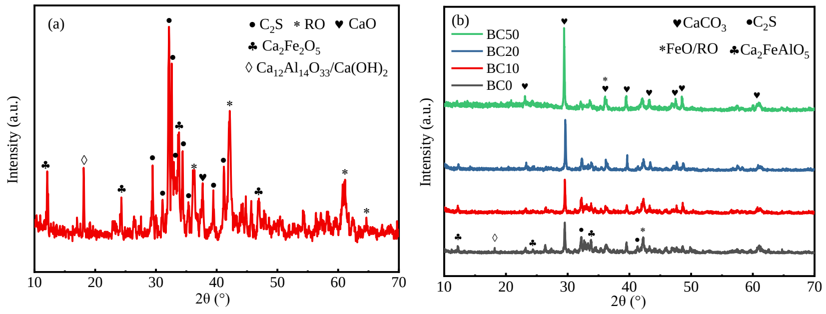

Fig. 1. XRD spectra of the: (a) raw SS and (b) composites after carbonation

3.2 Batch results

The P removal performance among different adsorbents is shown in Fig. 2. Results indicated that P removal by pristine BC was almost negligible (BC=0). This is because the surface of BC is often negatively charged and repel negatively charged ions such as phosphate [19]. The uncarbonated samples exhibited a strong affinity for P adsorption; however, the pH and the conductivity of the solution after treatment were significantly elevated, with pH exceeding 11 and conductivity surpassing 1000 μS/cm. This poses a major challenge for the application of pristine SS as a substrate for wastewater treatment directly [4, 7]. The P removal efficiency of SS decreased after carbonation, primarily due to the precipitate of carbonate compounds on the surface, blocking or alter the active sites for P adsorption. Additionally, the less dissolved Ca^{2+} in the solution reduced the P removal efficiency via precipitation. Compared to BC0, the addition of 10 wt.% of BC greatly improved the adsorption efficiency, reaching approximately 99%, similar to that observed with uncarbonated samples. The incorporation of BC may have improved the pore structure and provide additional adsorption sites. Nevertheless, when BC was added in higher amounts (20 wt.% and 50 wt.%), it reduced the reactive components present in SS, resulting lower overall P removal efficiency. Therefore, the combination of carbonation and BC modification can effectively lower the pH and conductivity, while maintaining a high P removal efficiency, ultimately leading to improved water quality after treatment.

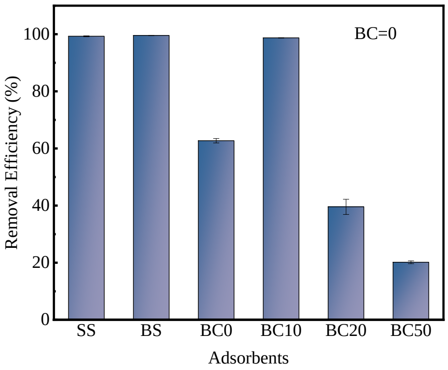

Fig. 2 P removal efficiency of different adsorbents

Since BC10 exhibited the best P removal performance compared to other carbonated composites, it was chosen for further evaluation of kinetics and isotherms as shown in Fig. 3. This was consistent with the decision to choose BC10 for the column test as well. Unlike other adsorbents that exhibited rapid P removal efficiency in the initial stages [7, 20], the P adsorption performance of the carbonated material was much slower, with adsorption equilibrium being reached after 40 hours. Although the addition of BC may enhance the physical adsorption of P, the carbonation process lowered the availability of Ca^{2+} in SS, thereby limiting the chemical precipitation rate of P. While SS primarily removes P through chemical adsorption [3], the slow dissolution process of calcium carbonate formed after carbonation results in an overall sluggish adsorption behaviour. Fig. 3b. shows that the P removal capacity of BC10 increased with the rise in initial P concentration, stabilising at around 5.3 mg/g beyond 60 mg/L, as adsorption saturation had been reached.

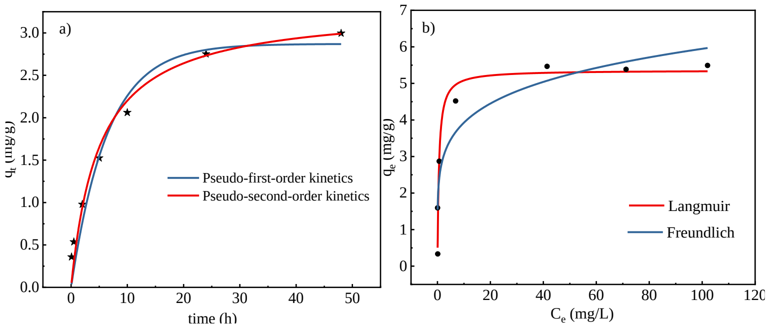

Fig. 3. The P adsorption kinetics and isotherms for sample BC10

To better understand the P sorption performance of BC10, two adsorption kinetic models were used for evaluation. The pseudo-first-order model fit resulted in $R^2 = 0.94$, while the pseudo-second-order model had $R^2 = 0.98$, suggesting that the pseudo-second-order model better describe the P removal process. Fig. 3b compares two isotherm models to further fit the P adsorption data on BC10. Results indicate that Langmuir isotherm showed a better fit ($R^2 = 0.93$) than the Freundlich model ($R^2 = 0.85$). The maximum adsorption capacity q_m=5.36 (mg/g) reflects the P adsorption potential of BC10 under optimal conditions.

Table 2. Fitting parameters for adsorption kinetics and isotherms

Adsorption model	Fitted parameters		R^2
Pseudo-first-order kinetics	q_e=2.88 (mg/g)	k_1=0.15 (h^{-1})	0.94
Pseudo-second-order kinetics	q_e=3.30 (mg/g)	k_2=0.0604 (g/(mg•h))	0.98
Langmuir	q_m=5.36 (mg/g)	k_l=1.82 (L/mg)	0.93
Freundlich	1/n=0.18	k_f=2.59 (mg/g)(L/mg)$^{1/n}$	0.85

3.3 Column results

Fig. 4 presents the changes in P removal efficiency, pH, and conductivity over time for different adsorbents (BC0, BC10, SS, and BS) to compare the effects of carbonation (SS vs. B0 & BS vs. BC10) and the modification of steel slag with biochar (B0 vs. B10) on the wastewater treatment performance. As shown in Fig. 4 (a), all adsorbents exhibited high P removal efficiency (~100%) and remained stable during the column experiments. Fig 4 (b) illustrates that the carbonation of SS lowered the pH of the solution, and the addition of BC further intensified this reduction. As for the conductivity, the SS and BS samples showed higher initial conductivity, suggesting greater ion release. The B10 sample showed a smaller fluctuation and lower values in both pH and conductivity, implying better chemical stability. This is due to the more developed pore structure and increased specific surface area of modified composite, which limited the diffusion of conductive ions. During the course of experiment, white precipitates were observed in the effluent water collected in the SS sample column, suggesting that the more Ca^{2+} dissolved and subsequently formed $CaCO_3$ upon exposure to air. These precipitates may interfere with filtration process by clogging the pores and reducing the permeability of the column.

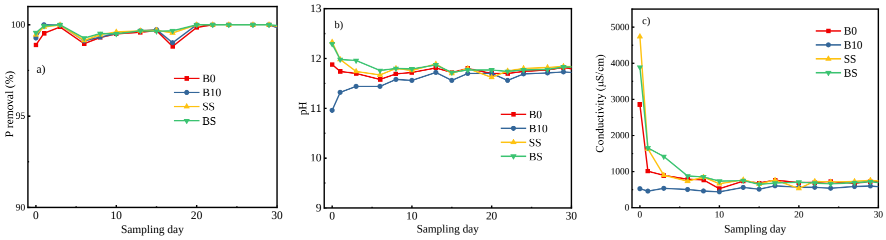

Fig. 4. Effect of adsorbents on P removal, pH, and conductivity

4. Conclusion

The results of this study indicate that the carbonated BC/SS composite is a promising adsorbent for P removal. XRD analysis revealed that BC facilitated the carbonation of calcium-containing phases. Batch experiments demonstrated that carbonation lowered the pH and conductivity, while BC addition improved P sequestration efficiency. The superior performance of BC10 made it the most suitable candidate for further evaluation and modelling. The adsorption process of BC10 followed pseudo-second-order kinetics and fitted well with the Langmuir isotherm. Column study further confirmed that BC10 not only exhibited excellent P removal efficiency, but also effectively reduced and stabilised the effluent's pH and conductivity, which may be advantageous for long-term water treatment applications. Future studies will focus on characterisation of column media after adsorption to investigate the mechanism of P removal. In addition, more parametric studies will be conducted by varying the flow rate, and pH value etc. to achieve the breakthrough points and model the dynamic adsorption behaviour of the materials.

Reference

1. Goyette, J.O., E.M. Bennett, and R. Maranger.: Low buffering capacity and slow recovery of anthropogenic phosphorus pollution. Nature Geoscience, 11(12), 921-925 (2018).

2. Mallin, M.A. and L.B. Cahoon: The Hidden Impacts of Phosphorus Pollution to Streams and Rivers. BioScience, 70(4), 315-329 (2020).

3. Bowden, L.I.: Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag. Environmental Science & Technology, 43(7), 2476-2481(2009).

4. Johansson, L.: Blast furnace slag as phosphorus sorbents — column studies. Science of The Total Environment, 229(1), 89-97 (1999).

5. Barca, C.: Steel slag filters to upgrade phosphorus removal in small wastewater treatment plants: Removal mechanisms and performance. Ecological Engineering, 68, 214-222 (2014).

6. Edgar, M.: Phosphorus removal by steel slag from tile drainage water: Lab and field evaluations. Chemosphere, 307, 135850 (2022).
7. Blanco, I.: Basic Oxygen Furnace steel slag aggregates for phosphorus treatment. Evaluation of its potential use as a substrate in constructed wetlands. Water Research, 89, 355-365 (2016).
8. Li, J., et al.: Preferential removal of phosphorus using modified steel slag and cement combination. Environmental Technology & Innovation, 10: 264-274 (2018).
9. Huijgen, W.J.J. and R.N.J. Comans.: Carbonation of Steel Slag for CO2 Sequestration, Environmental Science & Technology, 40(8): 2790-2796 (2006).
10. Zhang, Q.: Comparative analysis of carbonation strengthening mechanisms in full solid waste materials. Cement and Concrete Composites, 157,105927 (2025).
11. Jiang, X., et al.: Cold-bonded biochar-cement lightweight aggregates for evaporation-enhanced permeable bricks. Journal of Cleaner Production, 144886 (2025).
12. Xu, M., et al.: Effects of internal CO_2 curing provided by biochar on the carbonation and properties of steel slag-based artificial lightweight aggregates (SALAs). Cement and Concrete Composites, 142, 105197 (2023).
13. Ahmed, M.B.: Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresource Technology, 214: 836-851 (2016).
14. Zhang, P.: Functional Biochar and Its Balanced Design. ACS Environmental Au, 2(2): 115-127 (2022).
15. Zhou, Y., et al.: Facile synthesis of magnetic biochar from an invasive aquatic plant and basic oxygen furnace slag for removal of phosphate from aqueous solution. Biomass and Bioenergy, 173, 106800 (2023).
16. Wang, M., et al.: Treatment of Cd and As co-contamination in aqueous environment by steel slag-biochar composites. Journal of Hazardous Materials, 447, 130784 (2023).
17. Kan, T., et al.: Catalytic pyrolysis of biomass impregnated with elements from steelmaking slag leaching and simultaneous fabrication of phosphorus adsorbent. Journal of Cleaner Production, 328, 129490 (2021).
18. El Barkaoui, S., et al.: Optimizing biochar-based column filtration systems for enhanced pollutant removal in wastewater treatment: A preliminary study. Chemosphere, 372, 144067(2025).
19. Yao, Y.: Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. Bioresource Technology, 102(10), 6273-6278 (2011).
20. Yin, H., X. Yan, and X. Gu: Evaluation of thermally-modified calcium-rich attapulgite as a low-cost substrate for rapid phosphorus removal. Water Research, 115 329-338 (2017).