Article

Towards Greener Lixiviants in Value Recovery from Mine Wastes: Efficacy of Organic Acids for the Dissolution of Copper and Arsenic from Legacy Mine Tailings

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Abstract: In many cases, it may be possible to recover value (e.g., metals, land) from legacy mine wastes and tailings when applying leaching-based remediation such as dump/heap leaching or in-vessel soil washing. However, if the lixiviant used has the potential to cause environmental damage upon leakage, then this approach will have limited practicability due to actual or perceived risk. This study focused on comparing the efficacy of organic acids, namely methanesulfonic (CH_3SO_3H) and citric ($C_6H_8O_7$) acid, with mineral acids, namely sulfuric (H_2SO_4) and hydrochloric (HCl) acid, for the dissolution of Cu and As from mine tailings. The advantage of the former acid type is the fact that its conjugate base is readily biodegradable which should thereby limit the environmental impact of accidental spill/leakage (particularly in non-carbonate terrain) and might also be directly useful in capture/recovery systems coupled with percolation leaching (e.g., as an electron donor in sulphate-reducing bioreactors). The operational factors acid concentration, leaching time, mixing intensity and solid–liquid ratio, were tested in order to determine the optimum conditions for metal dissolution. HCl, H_2SO_4, and CH_3SO_3H typically exhibited a relatively similar leaching ability for As despite their different pKa values, with dissolutions of 58%, 56%, 55%, and 44% recorded for H_2SO_4, HCl, CH_3SO_3H, and $C_6H_8O_7$, respectively, after 48 h when using 1 M concentrations and a 10:1 L:S ratio. For the same conditions, H_2SO_4 was generally the most effective acid type for Cu removal with 38% compared to 32%, 29% and 22% for HCl, CH_3SO_3H and $C_6H_8O_7$. As such, CH_3SO_3H and $C_6H_8O_7$ demonstrated similar performances to strong mineral acids and, as such, hold great promise as environmentally compatible alternatives to conventional mineral acids for metal recovery from ores and waste.

Keywords: valorisation; mine waste; soil washing; heap leaching; dump leaching; mine drainage; remediation

1. Introduction

Legacy mining wastes have polluted and continue to pollute the environment on decadal to millennial timescales [1–3]. For example, in the UK, one of the most significant metal pollution contributors to fresh waters is legacy non-ferrous metalliferous mines [4,5]. Several thousand mines are known to be discharging environmentally deleterious quantities of metal/metalloid pollutants into surrounding watercourses [4]. It has been estimated that nine percent of rivers in England and Wales, and two percent in Scotland are at risk of failing to meet their European Water Framework Directive

targets of chemical and ecological quality because of legacy mines [4]. These rivers carry some of the largest quantities of contaminant metals, such as As, Cu, Cd, Pb, and Zn, into the seas surrounding the UK each year. Similar situations exist in most other locations with a metal mining legacy worldwide. Some examples include the USA and Canada, which have approximately 35,000 and 10,000 legacy metal mine sites, respectively, Japan with approximately 5500 legacy metal mines, and Sweden with around 1000 legacy metal mines [6].

As well as causing environmental degradation, mine sites can also represent opportunities for resource recovery [7]. Resources can be present in many forms, including as metals that can be leached and recovered; decontaminated residue that can be reused (for example as aggregate); or as a landscape resource. This latter resource value is recognised by planning designations based on its cultural or ecological value and the increase in heritage tourism [8]. These unique geological, ecological and cultural designations would act as significant constraints to mine waste remediation and site reclamation if the existence of these features was to be adversely affected by such activities [5]. The metal resources in these historical deposits are often not insubstantial but are generally not sufficient to present (planning issues aside) a justification for intervention for resource recovery alone [8]. However, if designed correctly, remediation of such sites could be implemented where economically valuable metals are also recovered and used to offset the costs of such remediation activity.

Leaching-based technology can be applied to achieve the removal of metals and metalloids (hereafter, "metals") for the purpose of remediation and/or recovery of resource(s), either through ex situ in-vessel soil washing or via in situ percolation leaching, with the latter technology being preferable to reduce capital and operational costs (e.g., of material handling). Percolation leaching could be carried out on the waste in situ (dump leaching), or the waste could be excavated, agglomerated, and placed on an engineered liner for leaching (i.e., heap leaching).

However, if the lixiviant used has the potential to cause environmental damage through leakage or run-off from residues, then heap leaching and soil washing might have limited practicability due to actual or perceived risk. Towards the goal of leaching with more environmentally acceptable ("greener" see for example (e.g., [9–11]) lixiviants, this study focused on the efficacy of organic acids in remediation/value recovery (e.g., reference [12]) because of the advantage that the conjugate base is biodegradable which should limit the environmental impact of accidental spill/leakage (e.g., references [13–15]) and might be directly useful in capture/recovery systems (e.g., to alleviate metal toxicity and act as an electron donor in sulphate-reducing bioreactors (e.g., references [16,17]) or microbial electrochemical systems.

There are several reasons why a biodegradable lixiviant is preferable for in-vessel soil washing, in situ and/or in heap leach scenarios. For soil washing, whilst the main process is contained within tanks, leaks/spills can occur, but more perhaps more importantly, when waste is replaced, there is the risk of environmental degradation from residual acidic leachate run-off. With in situ leaching of legacy mine wastes, it is highly unlikely that there is an engineered liner under the waste. Thus, for in situ dump leaching of waste piles, either there has to be a high-level of confidence that the underlying rock is impermeable, or a liner needs to be retrospectively installed. This is possible through the injection of cement-based grouts and chemical grouts or jet grouting. However, given that the use of such a technique for creating an impermeable barrier should ideally be limited to homogenous soils [18] and that even well engineered liner systems can leak, the use of biodegradable lixiviant would add confidence that should leakage occur, biodegradation will retard the transport of the escaping plume. This is particularly the case in areas of non-carbonate rocks where the effect of acid escape is far more serious because of the lack of acid-neutralisation. Furthermore, even if the mine waste is placed on to a highly engineered liner, leakage can still occur through pinholes and shrinkage cracks in geomembrane and clay liners, respectively. The strong mineral acids hydrochloric (HCl) and sulfuric acid (H_2SO_4) are conventional hydrometallurgical reagents, and the latter, in particular, is extensively used as a lixiviant in heap leaching of Cu and U ores. Environmental concerns have arisen from the failure to contain process solutions within

the heap leach circuit, which is compounded by large surface areas, the use of open drainage trenches (rather than enclosed in pipework) [19]. Its strong acidity and environmental persistence also dictates that even after leach pad decommissioning, the leachate from the spent ore (ripios) has to be carefully managed for many years until residual acidity has been fully flushed by meteoric water.

A further disadvantage of using sulfuric acid as a lixiviant is the subsequent formation of sulfate precipiates (e.g., jarosite and gypsum) that consume sulfuric acid whilst simultaneously resulting in unwanted permeability loss.

Strong organic acids, such as some sulfonic acids, are a class of strong acids with readily (bio)degradable conjugate bases that have been demonstrated as generally less environmentally persistent than mineral acids, such as sulfuric acid. Methanesulfonic acid, CH_3SO_3H (pKa = -1.9), has been demonstrated as being highly efficient for the dissolution of a number of different heavy metals via the formation of soluble methanesulfonate complexes [20]. Furthermore, the properties of methanesulfonic acid, such as its high conductivity, stability against volatilisation and hydrolysis, and low corrosiveness [20] are advantageous for its widespread use in hydrometallurgy and chemical engineering. Another advantageous property of methanesulfonic acid is the stability of reduced metal ions in methanesulfonic acid solutions, which is best known in the Sn^{2+}/Sn^{4+} system. Furthermore, methanesulfonic acid has a comparable conductivity to hydrochloric and sulfuric acid (299.6, 346.1 and 444.9 S cm^2 mol^{-1}, respectively) allowing for efficient recovery of metals from solution using electrowinning. Despite these attributes, the application of methanesulfonic acid to metal recovery from tailings has not been widely explored, aside from leaching of rare earth elements from bauxite residue [21].

As a weak acid, citric acid ($C_6H_8O_7$) partially dissociates in water to form hydrogen ions and its conjugate base, citrate, which is readily biodegradable in aerobic and anaerobic environments [12,14,15] and is commonly used as a raw material in the manufacturing/food and beverage industry and thus, is readily available as a bulk commodity and may be public acceptable due to common use in food products. The role of citric acid in metal mobilisation from tailings has been investigated more widely than methanesulfonic acid, for example, by Burckhard et al. [22], and the efficacy of citric acid in remedial application has been previously investigated in relation to the leaching of metal-contaminated soils, e.g., in references [12,23], and for hydrometallurgical application in Ni-bearing lateritic/saprolitic ores [24–26].

Here, we present a preliminary study that assesses the comparative efficacy of citric, hydrochloric, methanesulfonic and sulfuric acids for the recovery of economically valuable and/or contaminant metals from mine tailings waste taken from a legacy Cu/As mine in the southwest England. The work was established in order to demonstrate the feasibility of using such lixiviants for the recovery of toxic and/or economically valuable metals from metalliferous mine waste.

2. Methodology

2.1. Site Description

The Devon Great Consols (DGC) mine is a disused Cu/As mine located in Devon, England (50°32′16″ N, 04°13′17″ W). It was selected for study here because as a member of the UK mine water directive sites, it is known to release significant quantities of heavy metals into the surrounding environment each year [4,27]. The principal minerals extracted at the DGC mine were chalcopyrite ($CuFeS_2$) and arsenopyrite (AsFeS) and at its peak in the late 19th century it was the largest producer of both Cu and As in the world [28]. Its output for the period spanning 1844–1902 is estimated to have been approximately 736,200 tons of Cu ore and 72,300 tons of refined As [29]. The on site processing of both Cu and As ores has resulted in the accumulation of large quantities of mine tailings which are currently predominantly located in two piles with an estimated total volume of approximately 258,600 m^3 [8].

2.2. Mine Tailing Collection Procedure

This study focuses on two major mine tailing piles at the DGC site. The larger Northern pile (50°32′16″ N, 4°13′14″ W) is predominantly composed of sand and silt sized particles, and the smaller Southern pile (50°32′13″ N, 4°13′09″ W) is finer grained, because it was reworked during the period from 1902–1925 to extract As. A total of 18 mine tailing samples were collected (15 from the Northern heap and 3 from the Southern heap) following the methodology of ASTM D6009-12 [30]. Samples were collected using a stainless-steel trowel at equal distances around the base of each tailing pile at a depth of 0.3 m. Each sample had a volume of approximately 5 L with a mass typically between 6 and 8 kg (depending on bulk density). Once collected, the samples were heated at 105 °C for 24 h in order to remove any moisture present.

2.3. Physical and Chemical Characterisation of the Mine Tailings

A composite sample was created by riffling each sample 6 times and then thoroughly mixing each final subsample together using a mixing pad. Each composite sample was then riffled to yield an appropriate mass for each analysis technique. All analysis methods were performed using duplicate samples with the average taken. Particle size distribution (PSD) measurements were performed via dry sieving and sedimentation (ISO 11277:2009) [31] using approximately 200 g of the composite. Uncompacted aggregate bulk density measurements were performed in accordance with BS 812: 1995 [32] using a cylinder of 1876 mL in volume and a tamping rod of 16 mm in diameter. Paste pH measurements were preformed via ASTM D4972-13 [33] using 40 g from each composite and 40 mL of Milli-Q water (resistivity > 18.2 MΩ cm). Samples were prepared for X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), total organic carbon (TOC) analysis, and total inorganic carbon (TIC) analysis by crushing (to particle size <75 μm) a riffled (approximately 200 g) subsample of the composite sample using a Labtech Essa LM1-P puck mill crusher at 935 RPM for 120 seconds. The XRD analysis was performed using a Phillips Xpert Pro diffractometer with a CuKα radiation source (λ = 1.5406A; generator voltage of 40 keV; tube current of 30 mA). Spectra were acquired between 2θ angles of 5–90° with a step size of 0.02° and a 2 s dwell time. The sample was prepared by packing approximately 2 g of the material into an aluminium XRD stub. ICP-OES analysis was performed using a Perkin Elmer Optima 2100 DV ICP-OES. The sample was prepared for analysis via the 4 acid digest method (EPA 3052-12) [34]. Firstly, 0.01 g was placed in a PTFE lined microwave digest cell, and 3 mL of analytical grade 45.71% hydrofluoric acid (HF) was then added and left for 12 h. Six millilitres of aqua regia solution (1:1 ratio of analytical grade 32% hydrochloric acid (HCl) and 70% nitric acid (HNO_3)) was then added, and the container was then placed in a microwave digest oven (Anton Paar Multiwave 3000) and heated at 200 °C (1400 watts) for 30 min (after a 10 min up ramp time period) and then allowed to cool for 15 min. The resultant solution was then neutralised using 18 mL of analytical grade 4% Boric acid (H_3BO_3) at 150 °C (900 watts) for 20 min (after a 5 min up ramp time period) and then allowed to cool for 15 min. Total carbon (TC) measurements were performed using a Leco SC-144DR sulfur/carbon analyser. Samples of 0.35 g mass were loaded into the instrument and heated at 1350 °C in a pure O_2 (>99.9%) atmosphere. The concentration of CO_2 released by each sample was then measured using an infrared detection cell at a constant flow rate. Total inorganic carbon (TIC) measurements were performed using a Shimadzu (Kyoto, Japan) SSM-5000A using 99.9% O_2 at 500 mL/min and catalytically aided combustion oxidation performed at 900 °C. Total organic carbon (TOC) was calculated by subtracting each TIC measurement from the corresponding TC measurement for each sample. SEM-EDX maps of the mine tailings were acquired using a Zeiss Sigma HD Field Emission Gun SEM outfitted with 2*Oxford Instruments (Abingdon, UK) 150 mm^2 X-Max EDS detectors. The sample was first mounted onto an aluminium stub using an adhesive carbon tab. A 15 nm thick conductive carbon layer was applied by thermal evaporation using an Agar Turbo Carbon Coater to prevent charging effects. SEM-EDX data were obtained using a 20 kV accelerating voltage with a nominal beam current of 4.7 nA, a pixel dwell time of 10–20 ms, and a pixel size of 0.5 to 1.3 μm using Oxford Instruments Aztec acquisition

software. The shortest process time (time constant) was used to maximise counts in each pixel. Background and peak overlap corrections were applied within Aztec to provide semi-quantitative results for the samples.

2.4. Hydrometallurgical Extraction

Batch hydrometallurgical extraction experiments were conducted using an acid strength of 1 M, a solid liquid ratio of 1:10, a mixing speed of 200 RPM (using a Stuart SSL1 orbital shaker table), a solution volume of 200 mL, and an equilibration time of 24 h for all experiments, unless specified elsewhere. The following variables were investigated: acid strength (0, 0.01, 0.1, 1, 2, and 4 M), solid–liquid (S/L) ratio (1:5, 1:10, 1:20, and 1:40) and mixing speed (0, 50, 100, and 150 RPM) using separate batch systems (sealed glass jars that were 250 mL in volume). Aqueous samples of 5 mL volume were extracted from each batch system using a 10 mL syringe and then filtered through a 0.45 μm PTFE membrane. Experiments were conducted at room temperature which was measured to be 21.0 °C ± 1.5 °C.

3. Results and Discussion

3.1. Physical and Chemical Characterisation of the Mine Tailings

Table 1 displays the volume, bulk density, paste pH, TOC, and TIC data for the mine tailing composite along with the calculated total mass of the tailing piles. It was noted that the paste pH was 3.33, which indicates that the tailings are acid-producing and therefore, likely to represent a source of metals into the surrounding environment when flushed by meteoric water. In addition, the TIC was recorded as <0.00%, which indicates that the tailings have no appreciable carbonate content; thus, the materials are not strongly acid-consuming and are thus amenable to acid leaching. Table 2 displays notable metal and metalloid concentration data for the composite sample. It can be seen that the Cu, Zn, and Pb levels were recorded as exceeding the screening levels for ecological health. As levels were above the guideline levels for human health, and Cr levels exceeded both parameters. In addition, relatively high concentrations of Al (4.60%) and Fe (9.99%) were recorded. Figure 1 displays the XRD spectra for the composite sample, which indicate quartz (α-SiO$_2$) as the major crystalline component present with a relatively minor contribution from muscovite (H$_2$KAl$_3$(SiO$_4$)$_3$). The original primary ore minerals, arsenopyrite and chalcopyrite, were not detected. Figure 2 displays SEM-EDX data for the mine tailings and indicates that As and Cu are both relatively widely distributed in the mine tailings but in varying concentrations. Moreover, where present, both elements are often located in discrete regions on each particle. In general, As, Cu, and Fe are distributed in relatively similar locations, whereas no clear correlation with S was observed. This suggests that As, Cu, and Fe are unlikely to be still present as the original ore minerals (chalcopyrite and arsenopyrite) with S likely to have been removed during the original ore processing and/or subsequent weathering of the tailings (possibly via dissolution). This result is in contrast to previous work where arsenopyrite was detected using SEM-EDX, but it was also commonly recorded as partially altered to iron oxyhydroxides [35].

Figure 3 displays the particle size as a function of percentage passing by mass for the composite mine tailing sample. It can be noted that the majority of the mass of particles was recorded within the size fraction range of sand (particle sizes 0.063–2 mm) with 78.82% recorded, compared to 18.78 and 2.41% recorded for gravel (particle sizes 2–64 mm), silt, and clay sized particles (particle sizes < 0.063 mm) respectively. The D$_{50}$, D$_{10}$, and D$_{90}$ were 0.99, 0.18, and 2.80 mm, respectively, indicating that the median particle mass is approximately 1 mm in diameter. Figure 4 shows that, in general, the greatest concentrations of Cu and As are in the largest particle size fractions. In addition, a slight increase in both Cu and As concentrations was recorded for the finest size fractions of the tailings.

Table 2 displays the notable metal concentrations recorded for the composite mine tailings sample, Table 3 displays their values per ton and subsequent estimated total values in the tailings pile. It can

be observed that Cu and As had relatively high concentrations, with 0.183 and 1.92 wt % recorded respectively. Although cut-off values are invariably specific to the ore, mine setting, and reserve tonnage, a survey of typical cut-off grades (percentage w/w) for a range of heavy metals indicated that Cu is economic at grades of approximately >0.5% [36], and Sn is economic at grades of >0.15% [37]. It is therefore unlikely that such metals would be considered to be suitable targets at present for extraction (i.e., when compared to conventional ore deposits). However, if combined with site remediation, then the value of such metals could be used to offset the remediation cost. In particular, As concentrations were recorded as being significantly high. Therefore, conceivably, a site remediation strategy could be designed whereby As is removed along with any economically valuable metals present which would enable clean-up to be conducted at a significantly lower cost.

Table 1. Volume, bulk density, paste pH, TOC, and TIC data for the composite mine tailings sample along with the total mass of the tailing piles.

Volume (m^3)	Bulk Density (g/cm^3)	Mass (Tonnes) [6]	Paste pH	TOC (wt %)	TIC (wt %)
198.923 [6]	1.30	258,600	3.33	0.16	0.00

Table 2. Notable metal and metalloid concentration data (wt %) for composite samples from all sites [†] indicates concentrations above screening levels for ecological risk (1); [‡] indicates those above guideline levels for human health risk (2,3).

Li	Na	Mg	Al	K	Ca	Ti	Cr	Mn
0.0135	0.4312	0.5295	4.6035	0.8871	1.1426	0.2207	0.0315 [‡†]	0.0610

Fe	Ni1	Cu	Zn	As	Ag	Cd	Sn	Pb
9.9893	0.0019	0.1833 [†]	0.0101 [†]	1.9176 [‡]	<DL	0.0012 [†]	0.0290	0.0067

[1] Proposed Soil Screening Values under the framework for Ecological Risk Assessment [38]; [2] Category 4 Screening Values for public open space where there is considered to be a "negligible tracking back of soil" [39]; [3] Soil Guideline Value for commercial land use [40–42].
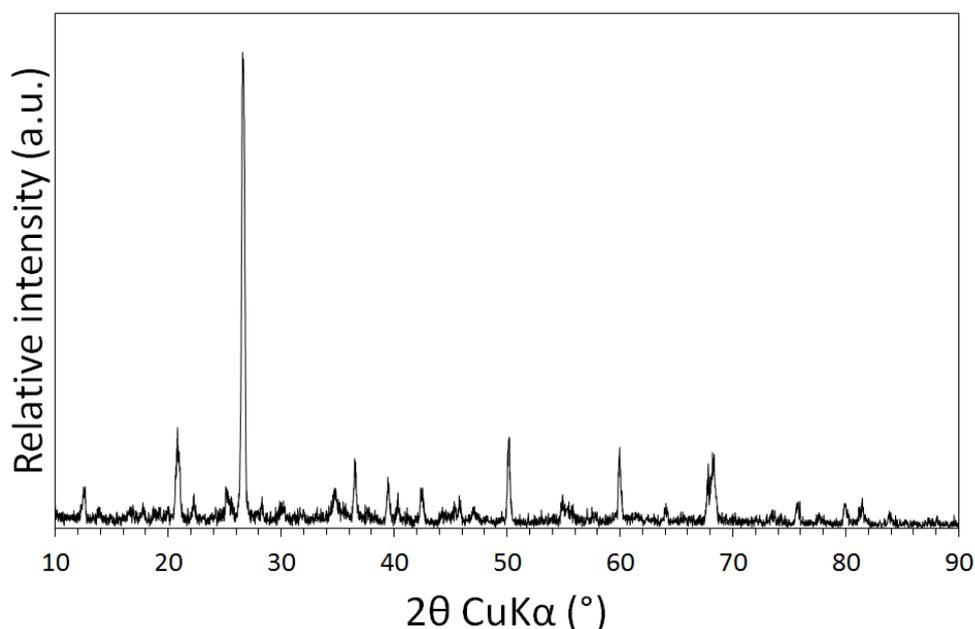

Figure 1. XRD spectra of the composite mine tailings sample.
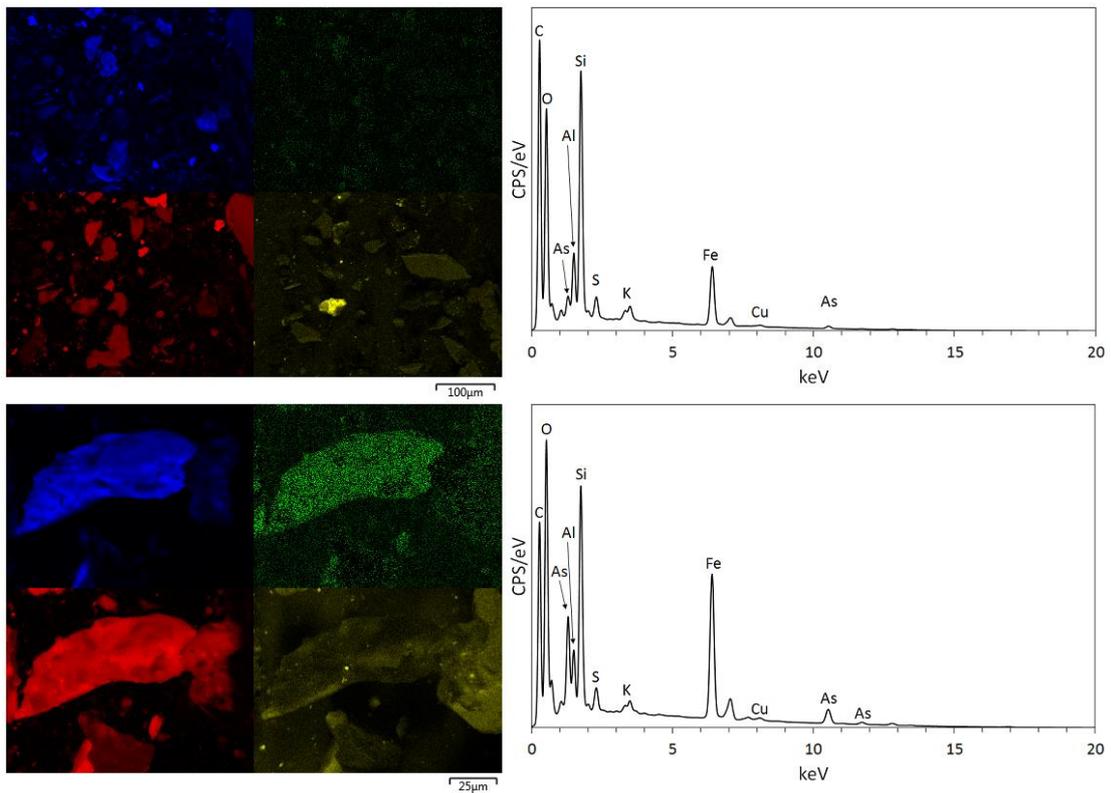
Figure 2. SEM-EDX maps for As (blue), Cu (green), Fe (yellow), and S (red) for the mine tailings along with corresponding spectra for CPS/eV detected for each element within the detection range of 0–20 keV.
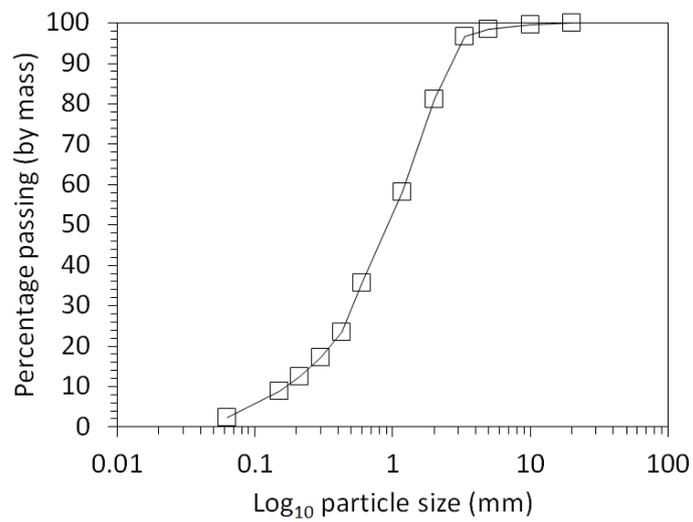

**Figure 3.** Particle size as a function of percentage passing (by mass) for the composite mine tailing sample.
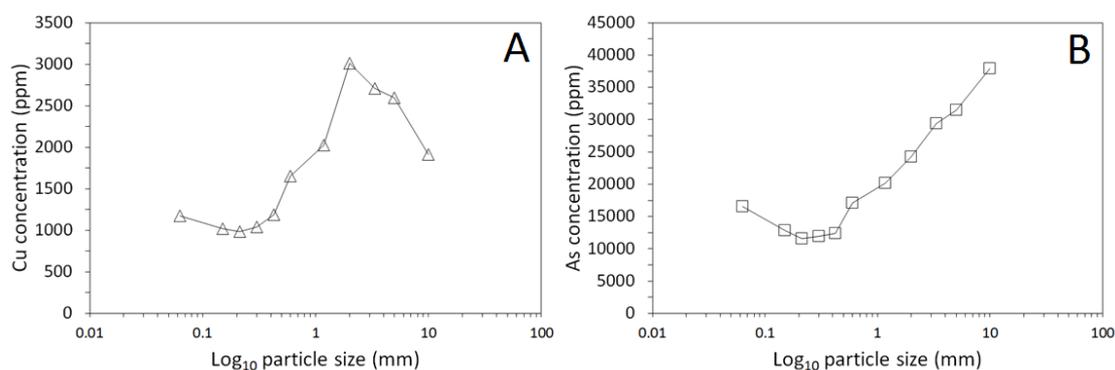
Figure 4. Cu (**A**) and As (**B**) concentrations as a function of particle size.

Table 3. Notable metal value per ton and subsequent estimated total value in the tailings pile. * Value per ton was calculated by multiplying the current metal price (26/07/2018) of each metal by their concentrations in the mine waste composite. The metal prices used were as follows: Cu = £4635/ton, Zn = £2010/ton, Sn = £14,683/ton, and Pb = £1601/ton. † The estimated value in the tailings pile was calculated by multiplying the metal value per ton by 258,600 (estimated total mass in tons of the tailings pile [8]) and rounded to the nearest thousand.

Element	Value Per Ton (£) *	Estimated Value in Tailings Pile †
Cu	8.50	1,511,000
Zn	0.20	36,000
Sn	4.26	757,000
Pb	0.11	19,000

3.2. Influence of Acid Concentration on Cu and As Dissolution

The influence of the acid concentration on the extent of metal leaching (after 48 h) is displayed in Figure 5. It can be observed that all acid types are relatively non-selective for metal recovery from the tailings, with simultaneous removal of a wide range of different metals. The quantity of leached metals was recorded as being dependent on the acid concentration at <1 M concentration with relatively limited additional metal recovery recorded for greater acid concentrations. The extent of Cu and As leaching as a function of time is shown in Figures 6 and 7 with Cu and As recovery after 48 h as a function of the acid concentration displayed in Figure 8. The recovery of Cu and As was shown to depend strongly on the acid concentration and increased as a function of time. The greatest Cu and As recovery was typically recorded for 4 M acid concentration after 48 h reaction time, however, relatively similar recovery was also often recorded for 1 M acid concentrations and a 24 h reaction time. The recovery of As was typically higher than Cu for all acid types with removal of 59.32%, 61.53%, 59.35%, and 43.71% of As recorded for 4 M solutions of H_2SO_4, HCl, CH_3SO_3H, and $C_6H_8O_7$, respectively, after a 48 h reaction, compared to 47.41%, 54.23%, 32.34%, and 23.24% removal of Cu. H_2SO4 and HCl were generally shown to bethe most effective acid types for Cu removal, and H_2SO_4, HCl and CH_3SO_3H were generally shown to be the most effective for As removal.
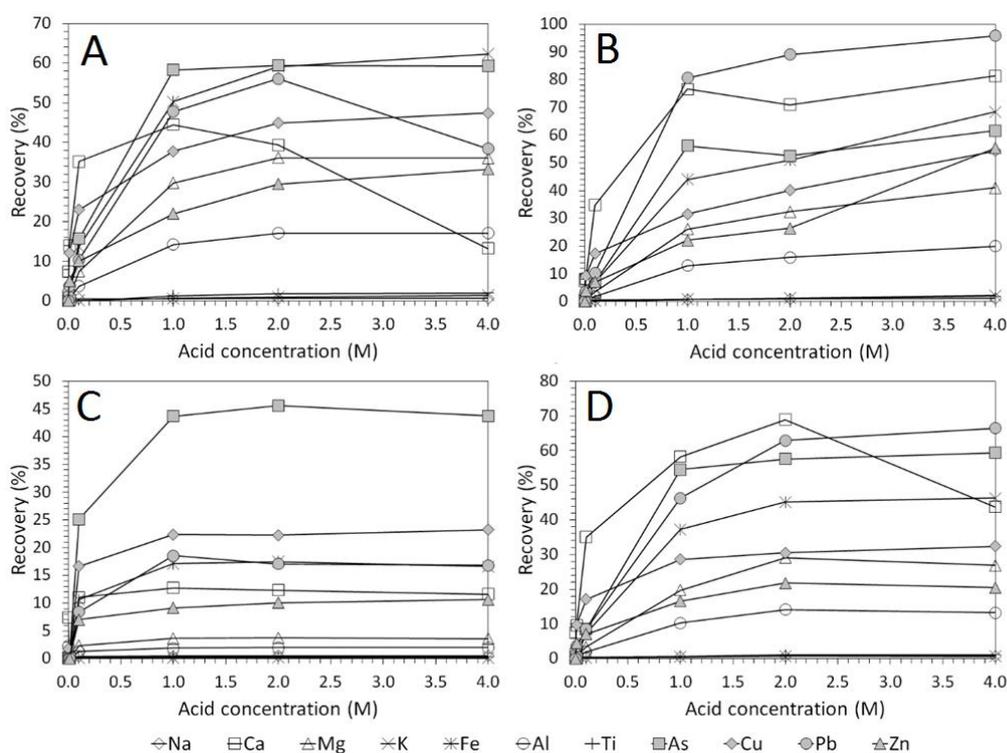
Figure 5. Metal recovery as a function of acid concentration after 48 h for each acid type: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**) A solid–liquid ratio of 0.1 and lixiviant volume of 200 mL were used for each experiment.
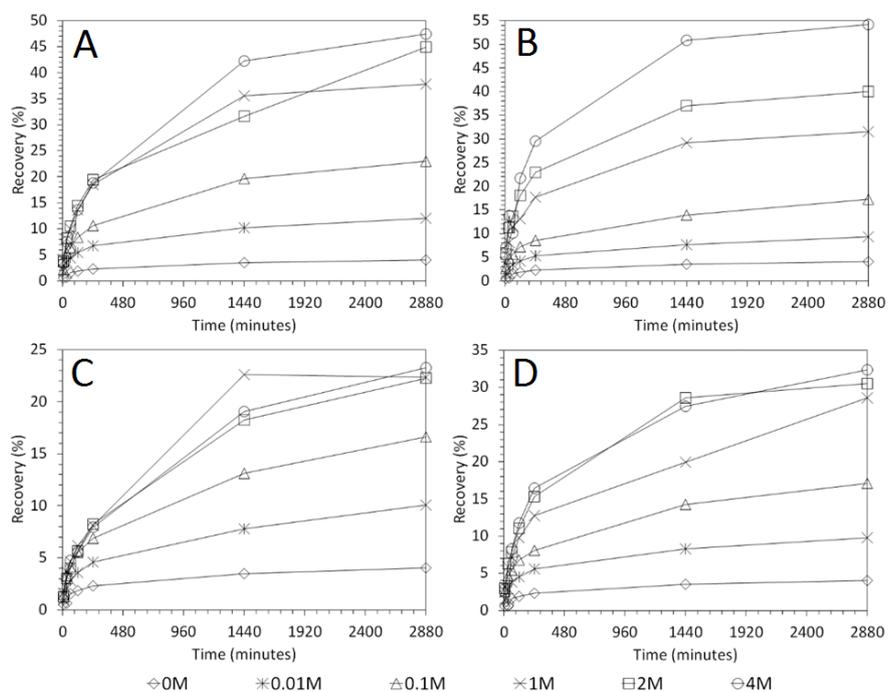
Figure 6. Cu recovery as a function of time and acid concentration for: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). A solid–liquid ratio of 0.1 and lixiviant volume of 200 mL were used for each experiment.
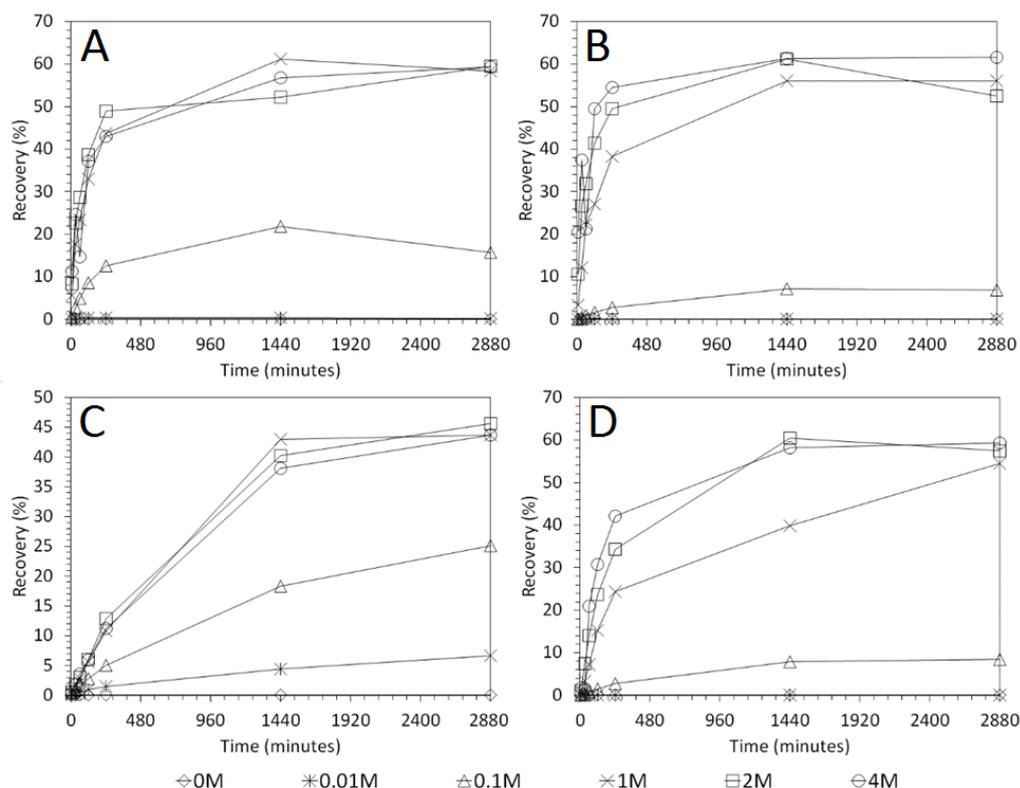
Figure 7. As recovery as a function of time for each acid concentration for each acid type: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). A solid–liquid ratio of 0.1 and lixiviant volume of 200 mL were used for each experiment.

3.3. Influence of Solid–Liquid Ratio for Cu and As Dissolution

The influence of the S/L ratio on the leaching degrees of Cu and As is displayed in Figures 8 and 9. An inverse correlation can be observed between the S/L ratio and both Cu and As recovery, with 32.28%, 28.04%, 23.77%, and 14.96% Cu recovery recorded for H_2SO_4, HCl, CH_3SO_3H, and $C_6H_8O_7$, and a S/L ratio of 0.025, respectively, compared to 21.49%, 23.94%, 18.17%, and 12.93% respectively recorded for a S/L ratio of 0.2. Similarly, As recovery levels of 59.86%, 59.60%, 57.27% and 35.93% were recorded for an S/L ratio of 0.025 compared with 36.50%, 34.96%, 28.03%, and 20.37%, respectively, for an S/L ratio of 0.2. The results therefore demonstrate that the recovery efficacy of Cu and As can be improved by lowering the S/L ratio when within the range of 0.025–0.2, which is likely to be due to greater acid consumption (neutralisation) at higher S/L ratios.
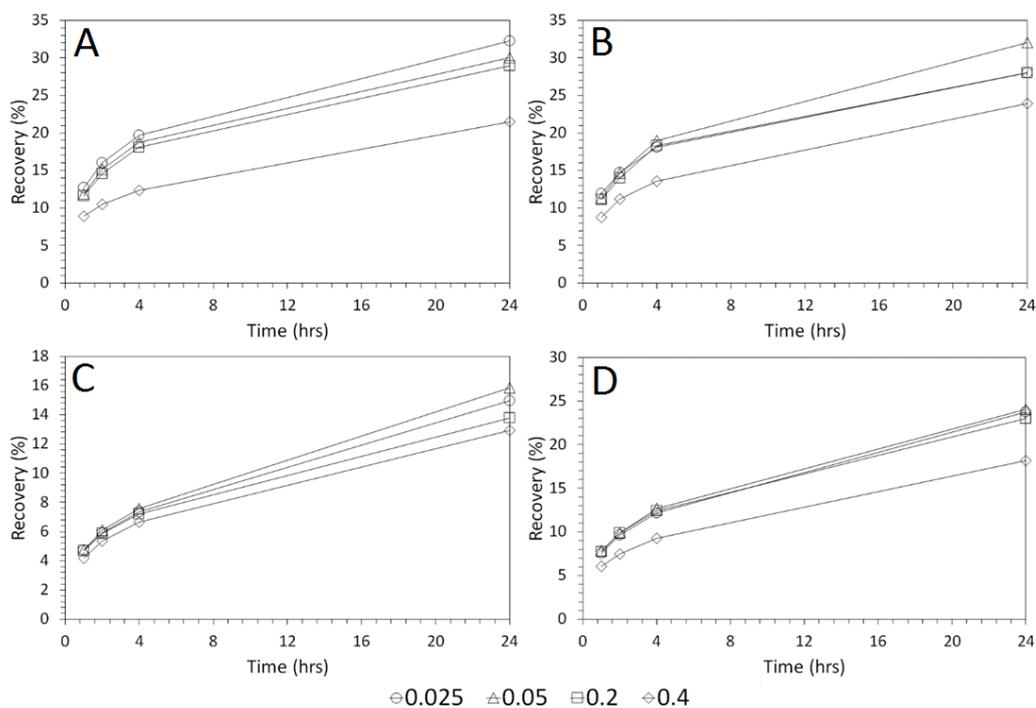
Figure 8. Cu recovery as a function of time for solid–liquid ratios of 0.025, 0.05, 0.2, and 0.4 using: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). The acid concentrations were 1 M and lixiviant volumes were 200 mL.
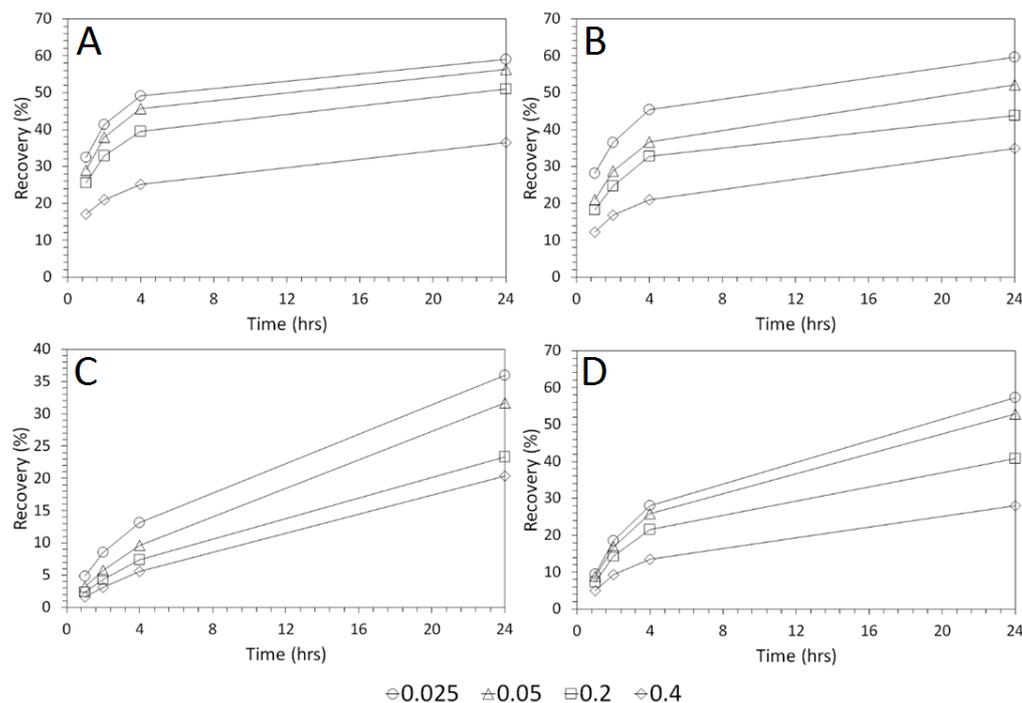
Figure 9. As recovery as a function of time for solid–liquid ratios of 0.025, 0.05, 0.2, and 0.4 using: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). The acid concentrations were 1 M and the lixiviant volumes were 200 mL.

3.4. Influence of Mixing Speed on Cu and As Dissolution

The influence of the mixing speed (0 to 150 RPM) on the As and Cu leaching degrees are displayed in Figures 10 and 11. It can be observed that the stirring speed has a clear positive influence on both As and Cu dissolution with greater dissolution occurring at a greater stirring speed. This is attributed to a decrease in the thickness of the diffusion layer surrounding the mine tailing particles, which, in turn, increases the metal dissolution rate [43].
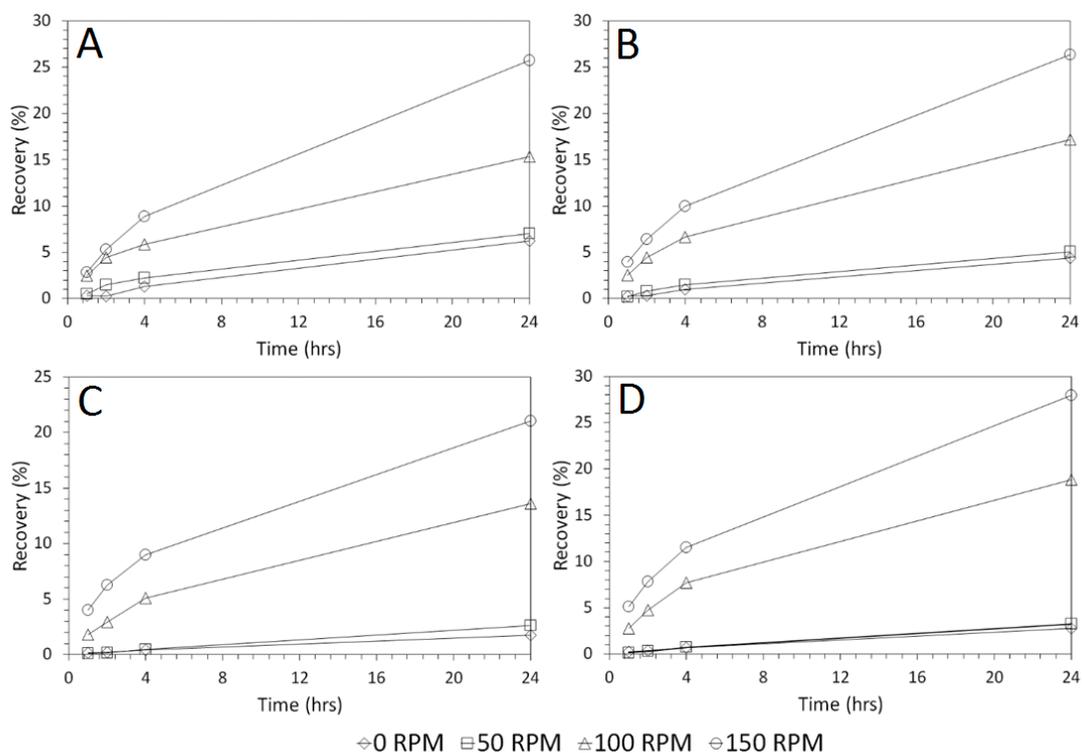
Figure 10. Cu recovery as a function of time for mixing speeds of 0, 50, 100, and 150 RPM using: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). The acid concentrations were 1 M and the lixiviant volumes were 200 mL.
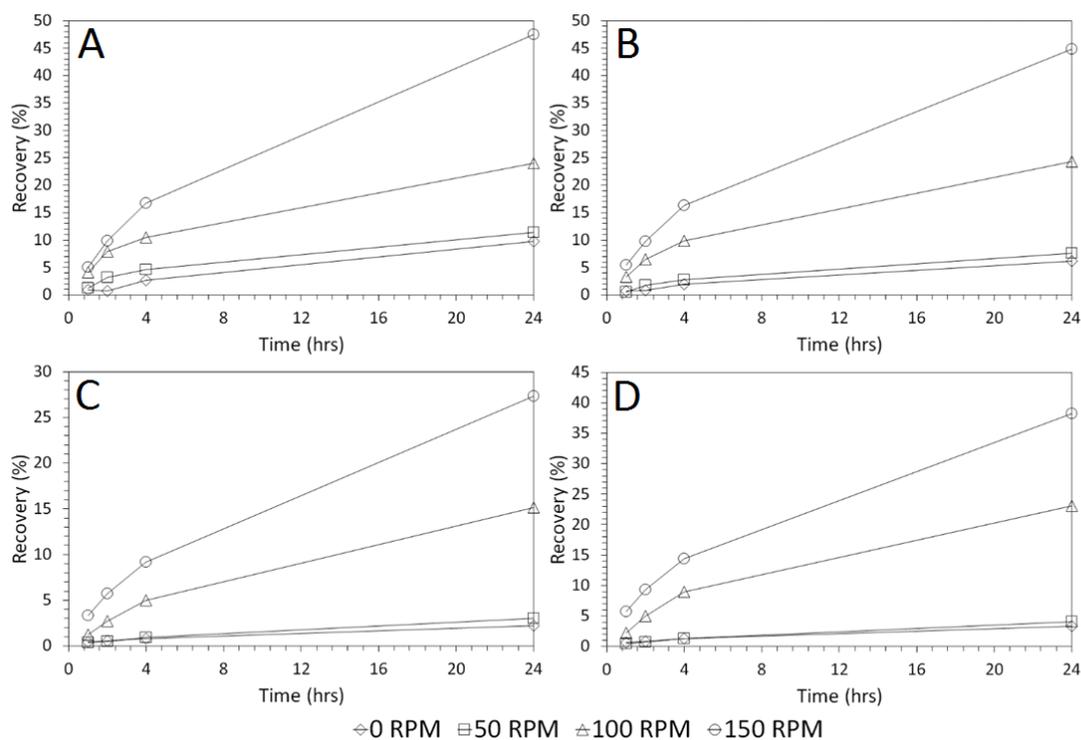
Figure 11. As recovery as a function of time for mixing speeds of 0, 50, 100, and 150 RPM using: H_2SO_4 (**A**), HCl (**B**), $C_6H_8O_7$ (**C**) and CH_3SO_3H (**D**). The acid concentrations were 1 M and the lixiviant volumes were 200 mL.

4. Discussion

The results demonstrate that CH_3SO_3H has relatively similar ability to remove Cu and As from mine waste as H_2SO_4 and HCl. As such, it is suggested that CH_3SO_3H is a suitable alternative for soil washing and heap leaching. $C_6H_8O_7$ is a relatively weak organic acid (pKa = 2.79) and complexing agent, and has been demonstrated as secondary to the other acids but is still effective for the dissolution of Cu. However, it was demonstrated as being able to exhibit relatively high removal of As from mine tailings. This result is of particular significance because weak organic acids, such as $C_6H_8O_7$, are an attractive alternative to stronger acids due to their lower acidity and subsequent lower environmental impact.

In soil washing and dump/heap leaching applications, the recovery of economically valuable and/or contaminant metals and metalloids is the primary objective. Such interventions must be conducted, however, whilst also ensuring that the treated residue is chemically stable (e.g., a low tendency to release aqueous contaminants). Certain mineral acids, such as HCl and H_2SO_4, which have strong acidity and persistence in the environment are therefore not ideal lixiviants for such applications. In contrast, the use of organic acids, such as CH_3SO_3H and $C_6H_8O_7$, which exhibit lower acidity, but also lower environmental persistence, could provide an alternative which would enable targeted metal recovery with a lower detrimental impact on the environment, particularly for non-carbonate lithologies, such as in this study, which are very susceptible to acidification. An assessment of the feasibility of any proposed percolation or in-vessel leaching process based on the lixiviants studied herein would have to be made in light of (i) the ability of the lixiviant to achieve the site-specific remedial target concentrations in the residue, and (ii) a site-specific environmental risk assessment.

5. Conclusions

This study has demonstrated that H_2SO_4, HCl, CH_3SO_3H, and $C_6H_8O_7$ solutions can be applied for the recovery of both Cu and As from mine tailings taken from the Devon Great Consols mine in southwest Devon, England. The leaching potential of each acid was investigated under changing operational factors—acid concentration, leaching time, mixing intensity, and solid–liquid ratio—in order to determine the optimum conditions for metal recovery. The following can be concluded:

(a) Cu and As dissolution rates were determined to typically increase with an increase in the acid concentration, mixing speed, and liquid to solid ratio.

(b) HCl, H_2SO_4 and CH_3SO_3H generally exhibited relatively similar leaching abilities for As despite their different pKa values, with removal percentages after 48 h of 58%, 56%, and 55% recorded for 1 M H_2SO_4, HCl and CH_3SO_3H respectively, compared to 44% exhibited by $C_6H_8O_7$.

(c) H_2SO_4 was generally shown to be the most effective acid type for Cu removal with 38% removal for 1 M solutions after 48 h, compared to 32%, 29%, and 22% recorded for HCl, CH_3SO_3H, and $C_6H_8O_7$ respectively.

(d) Overall the optimum leaching conditions was found to be 1 M acid concentration, 200 RPM mixing speed and a mixing time of 24 h, with only minor improvements in leaching efficacy recorded for concentrations greater than 1 M or time periods greater than 24 h.

The results therefore suggest that processes, such as in-vessel soil washing or percolation leaching, could be relatively low-cost, and in the case of percolation leaching, non-invasive metal recovery techniques that enable simultaneous contaminant and/or economically valuable metal recovery from mine tailing waste. In particular, the use of organic acids, such as CH_3SO_3H and $C_6H_8O_7$, could provide similar As and Cu removal efficacies to H_2SO_4 and HCl but with a potentially lower environmental impact, especially in dump and heap leaching applications for environmental remediation and particularly, in cases where host rocks have low neutralising potential, which are more susceptible to acidification by non-degrading mineral acids. This work also provides a foundation which substantiates further research into the relative environmental performances and other co-benefits of the application of organic acids in metal mine waste remediation and value recovery, particularly for methanesulfonic acid, which, to the authors' knowledge, has not previously been applied to metal recovery from mine tailings.

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