Investigations into the closed-loop hydrometallurgical process for heavy metals removal and recovery from biosolids via mild acid pre-treatment

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A B S T R A C T

Biosolids contain heavy metals (HMs), restricting their beneficial reuse in agricultural land. However, these metals can be a valuable resource in many applications if recovered efficiently. Therefore, the removal and recovery of HMs and other limiting contaminants in biosolids without degrading the organic nutrients of the resulting treated biosolids demands holistic investigations. A closed-loop hydrometallurgical treatment process for metal removal and recovery from biosolids was developed in this study. Firstly, mild acid treatment using 3% v/v H_2SO_4 at 25 °C, 600 rpm for 30 min was performed in a 1 L continuous stirred tank reactor to extract common HMs (such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) from biosolids into the aqueous phase. The effects of solids concentration and acid types on the HMs extraction efficiency were studied. Then, the primary acid leachate stream was continuously recycled for metal extraction from biosolids until the dissolved metals in the solution reached saturation concentration. After that, the dissolved metals were recovered in staged NaOH precipitation and adsorption. Low solids contents (<5% w/v) using mineral acids having pH <2 and oxidation-reduction potential (ORP) ~500 mV (versus SHE) favoured HMs solubilisation from biosolids with an average extraction efficiency of 70%. The dissolution of ferric iron (Fe^{3+}) by H_2SO_4 and subsequent in-situ formation of ferric sulfate enhanced the metal extraction strength of the spent leachate stream during recycling. However, the solids loading in each leaching process must be kept low to prevent ferric concentration build-up and precipitation as the leachate pH steadily increases above 2 during recycling. Amongst the metal recovery methods investigated, H_2O_2 oxidation prior to 2-stage NaOH precipitation had the highest efficiency with 75–95% HMs recovery. The clarified stream was used to neutralise the acidic treated biosolids to close the process loop. The complete process flowsheet was developed with mass balances, and the fate of nutrients (mainly C, N, and P) and major *per*- and polyfluoro alkyl substances (PFAS) were overviewed.

1. Introduction

Biosolids, also known as stabilised sewage sludge, are the by-product of the wastewater treatment process. Biosolids contain valuable organic and inorganic components (mainly N, P, and K) that constitute important plant nutrients. These nutrients facilitate the application of a substantial volume of biosolids in agricultural soils in many countries, including Australia (Paz-ferreiro et al., 2018). However, heavy metals (HMs) and other contaminants such as pesticides, microbial pathogens, microplastics, and surfactants are limiting the attractiveness of biosolids for direct land application with increasingly stringent regulations (EPA Victoria, 2004; LeBlanc et al., 2009). Thermochemical treatment of sub-grade biosolids via pyrolysis, gasification, hydrothermal carbonisation/liquefaction or incineration process can effectively degrade the organic and microbial contaminants (Kundu et al., 2021; Ross et al., 2016). However, HMs remain a persistent pollutant in biosolids and their

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thermally-derived products due to the low thermal degradation as well as the formidable bioaccumulation and high environmental toxicity of HMs (Feng et al., 2018).

The pre-treatment of biosolids is considered an effective process for removing the HMs before land application or thermal processing. Several pre-treatment methods, including chemical leaching with acids (Gaber et al., 2011; Stylianou et al., 2007), chelating agents (Gheju et al., 2011; Leštan et al., 2008), ferric salts (Bayat and Sari, 2010; Ito et al., 2000), ionic liquids (Abouelela et al., 2022; Yao et al., 2021), surfactants (Guan et al., 2017; Tang et al., 2017), and microbial agents (Pathak et al., 2009; Xiang et al., 2000) have been investigated for this purpose. Amongst all, leaching with acids is the most common, efficient with short operation times, and cost-effective with high industrial maturity (Babel and del Mundo Dacera, 2006; Gunarathne et al., 2020; Hakeem et al., 2022a). The high oxidising potential, as well as the low pH of acids, are favourable for metal dissolution (Ma et al., 2020). In addition, most metal cations are basic and readily ion-exchangeable with protons from acids (Persson et al., 2017). Therefore, acid leaching plays a leading role in hydrometallurgical processes for metals recovery from different materials, including biosolids (Gunarathne et al., 2020; Montenegro et al., 2016). In a typical acid leaching process, a high liquid-to-solid ratio is desired to achieve high HMs dissolution by overcoming thermodynamic equilibrium, which occurs when the solid dissociates to such an extent that the metal species are fully saturated in the solution (Lee et al., 2006). Hence, acid leaching is usually accompanied by a large volume of aqueous waste stream with dilute metal concentrations. Metal recovery from this dilute stream is unattractive and improper disposal poses environmental threats.

One of the potential ways to manage the resulting leachate stream from biosolids pre-treatment is to reuse and recycle the stream for another leaching process until the leachate stream gets saturated with HMs. The heavily concentrated leachate stream can be a precursor for recovering valuable metals. Recycling the aqueous acidic leachate stream can be attractive for metal extraction due to its low pH, high oxidation-reduction potential (ORP), and presence of surrogate leaching components such as dissolved ferric sulfates or chlorides (Beauchesne et al., 2007; Ito et al., 2000; Strasser et al., 1995). In addition, recycling the acidic waste stream can reduce the overall acid solution requirements during the metal extraction process, with the potential to favour the techno-economics of the process. The effect of process variables such as temperature, acid concentration, solids contents, agitation speeds, and contact time on HMs removal efficiency has been elucidated in previous studies (del Mundo Dacera and Babel, 2006; Gaber et al., 2011; Hakeem et al., 2022b; Yang et al., 2021). However, there is a limited investigation on the recyclability of the acidic leachate stream as a solvent for metal extraction from raw biosolids (Shim, 2023). Particularly, the effects of solids loading on the recycling performance of the leachate stream have not been reported in extant literature.

The overall hydrometallurgical process can be grouped into three sequential stages: metal extraction, leachate concentration and purification, and metal recovery (Gunarathne et al., 2020). The growing interest in resource recovery has increased the prospect of critical element extraction and recovery from biosolids via hydrometallurgical operations (Tyagi and Lo, 2013). However, metal recovery from biosolids has not been fully explored in the literature beyond the acid leaching stage, which removes the metals from biosolids to the liquid phase, as described earlier. Therefore, developing a comprehensive hydrometallurgical process chain to understand the feasibility of metal recovery from biosolids through the production of less contaminated biosolids is desired. While the metal extraction stage is the most critical in the overall hydrometallurgical process, leachate purification and metal recovery are the most challenging because acidic solvents have poor selectivity during metal solubilisation. Moreover, biosolids have many metal and non-metal components that elute simultaneously into solution during acid leaching. For example, the co-solubilisation of iron, aluminium, and alkali and alkaline earth metals (AAEMs) alongside HMs

usually complicates the selective recovery of valuable metals from the leachate stream (Lee et al., 2002). In some cases, elements such as carbon (C), nitrogen (N), and phosphorous (P) are dissolved in the acidic stream, interfering with the purification and recovery of desired metals.

The main techniques for metal recovery from aqueous streams are chemical precipitation (Liang et al., 2019; Marchioretto et al., 2005), electrodeposition (Yao et al., 2021), adsorption (Singh et al., 2020), ion exchange (Yoshizaki and Tomida, 2000), and solvent extraction (Montenegro et al., 2016). Chemical precipitation using caustic soda (NaOH) or slaked lime (Ca(OH)$_2$) and adsorption are the most common, less laborious, and suitable for multi-components metal streams typical of biosolids leachate (Li et al., 2021; Marchioretto et al., 2005). However, the efficacy of alkali precipitation of HMs is challenged by the amphoteric nature of some metal ions having different optimum hydroxides solubility as well as interferences from other metal species, particularly iron (de Fátima da Silva et al., 2020). Given the number of metal in a biosolids leachate stream, identifying suitable metal recovery methods will depend on the final composition, metal concentration, and pH (Sethurajan et al., 2017). Studies involving the chemical precipitation of multiple metal from real biosolids leach solutions are limited in the literature (Marchioretto et al., 2005). Chemical precipitation and adsorption have only been extensively applied on metal ores leachate or simulated wastewater containing single or dual metal components (Ait Ahsaine et al., 2017; Ni et al., 2019; Xu et al., 2009).

In summary, the full spectrum of chemical treatment of biosolids for HMs removal involving metal extraction, separation of solids from the leach liquor, leachate concentration and purification, and metal recovery is missing in the literature. Hence, this study explored a comprehensive mild acid treatment of biosolids for HMs extraction and the subsequent recovery of the metal from the concentrated leachate stream. The specific objectives of the work were to (i) study the effect of acid solution and solids concentration on the extraction efficiency of metals from biosolids, (ii) investigate the reusability and extraction performance of the primary leachate stream through partial and complete recycling at optimum solids concentrations, (iii) examine the efficacy of staged NaOH co-precipitation, H$_2$O$_2$ oxidation followed by NaOH co-precipitation, and biochar adsorption for the purification and recovery of HMs from the concentrated leachate stream, (iv) understand the fate of dissolved nutrients (mainly C, N, K, and P) and *per*-and poly-fluoro alkyl substance (PFAS) compounds in the process streams, and (v) develop and propose optimum process flow diagrams with mass balances for biosolids metal removal and recovery. This detailed investigation will help to understand the feasibility of developing an in-situ or ex-situ hydrometallurgical process for biosolids HMs decontamination with potential for nutrient and critical metal recovery within the existing wastewater treatment facilities.

2. Materials and methods

2.1. Biosolids preparation and analyses

Biosolids used in this study were obtained from Mount Martha Water Recycling Plant, South East Water Corporation, Victoria, Australia. The biosolids production process was described in our previous study (Hakeem et al., 2022b). Before use in the pre-treatment experiments, biosolids were dried overnight in an oven at 105 °C and sieved to 100–300 μm particle size. The elemental composition was determined by X-ray Fluorescence (XRF, S4 AXS Bruker), ultimate analysis was performed using a CHNS Series II Perkin Elmer instrument, and the metal concentration was measured using Inductive Coupled Plasma-Mass Spectrometry (ICP-MS 2200 series, Agilent Technologies). The chemicals used in this work were of analytical grades. They include 98% H$_2$SO$_4$ (Chem-Supply Pty Ltd), 65% HNO$_3$ (Univar Pty Ltd), 35% HCl (Emplura Pty Ltd), 99% glacial acetic acid (Sigma Aldrich), 99.5% citric acid (Sigma Aldrich), 21–23% ferric sulfate pentahydrate (Chem-Supply) and 30% hydrogen peroxide (Rowe Scientific Pty Ltd). Milli-Q

water with a resistivity of 18.2 MΩ cm was used throughout this study. Table 1 shows the composition of the biosolids. The concentration of some of the HMs, such as Cu, Zn, and Cd, is higher than that prescribed for the least contaminant grade (C1) for unrestricted beneficial reuse of biosolids according to Victoria EPA biosolids guidelines (EPA Victoria, 2004).

2.2. Heavy metals fractionation in the biosolids

The efficacy of acid leaching for metal extraction depends on the chemical fractionation of the metal in the biosolids matrix (Geng et al., 2020). Therefore, according to previous literature, a modified three-step Community Bureau of Reference (BCR) sequential extraction technique was used to determine the distribution of metal in the biosolids (Liu et al., 2021, 2018; Wang et al., 2019). This method allows the chemical classification of HMs species in biosolids, soils, and sediments into four major fractions: exchangeable (F-1), reducible (F-2), oxidisable (F-3), and residual (F-4) based on the ease of extraction with standard reagents (Zhao et al., 2018). The F-1 refers to acid-ionisable metals, F-2 are metals bound to carbonates and Fe—Mn oxides, F-3 are metals bound to organic matter and sulfides, and F-4 are bound to silicates and recalcitrant organics. Depending on the severity of the acid leaching conditions, such as acid concentration (or pH), temperature, and time, F-1, F-2, and F-3 metals can be removed at various rates in decreasing order, while F-4 metals are hardly removed via chemical leaching. The result of this analysis is presented in Fig. S1. From Fig. S1, the potential mobility of the metals in the biosolids can be estimated by adding F-1 and F-2 metal percentages (Geng et al., 2020), and this can be ranked as Mn > Zn > Cd ≈ Ni ≈ Co > Cr > As>Pb > Cu ≈ Fe. Copper has the highest F-3 percentage due to the higher affinity of Cu to organic matter (Beauchesne et al., 2007), while Fe and Pb have the highest F-4 percentages. Copper is the most challenging HM to remove in biosolids via acid leaching; this observation has been widely reported in other works (Beauchesne et al., 2007; Blais et al., 2005; Mercier et al., 2002). Therefore, the extraction of Cu under mild acid leaching conditions may be limited.

2.3. Biosolids metals extraction

The batch pre-treatment procedure was as described previously (Hakeem et al., 2022b). All leaching experiments were conducted at room temperature (25 ± 2 °C) using 3% (v/v) acid concentration under continuous stirring at 600 rpm for 30 ± 2 min in a 1 L continuous stirred tank reactor. These are the optimised conditions from our previous investigation (Hakeem et al., 2022b). The effect of acid types was studied by using three mineral acids (H_2SO_4, HCl, HNO_3) and two organic acids (acetic and citric) to extract HMs (such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) from biosolids at 5% (w/v) solids loading using 3% (v/v) acid solution. Similarly, the effect of solids concentration was studied by leaching biosolids at 1, 3, 5, 10, 15 and 20% (w/v) solids using 3% (v/v) H_2SO_4 solution. At the end of each metal extraction experiment, the slurry was transferred into Eppendorf tubes and centrifuged at 4000 rpm for 30 min. The leachate stream was carefully decanted into sample vials, and the residue (treated biosolids) was dried and stored for further analysis. The pH and ORP of the leachate stream

were measured, and 1 mL aliquot of the well-mixed leachate was filtered, diluted, and quantified for metals by ICP-MS. All leaching experiments were performed in triplicates, and average results were reported with errors expressed as the standard deviation of the measurements. A schematic illustration of the metal extraction process including the downstream separation and metal recovery processes is shown in Fig. 1.

2.4. Concentration of the leachate stream

2.4.1. Total recycling of the leachate

The recovered aqueous stream from the parent (primary) pre-treatment was reused fully for another extraction process at 5% and 10% (w/v) fresh biosolids loading; all other conditions remain unchanged. The process was repeated for five leaching cycles (after the parent leaching) using 100% spent leachate stream and fresh biosolids in each cycle. The volume of the leachate stream and mass of the fresh biosolids were adjusted to achieve 5% or 10% solids loading in each cycle. It is assumed that the metals dissolved in the leachate will remain in the solution all the time unless the pH ≥2.5, where ferric precipitation will be initiated. During the recycling, precipitate from poorly soluble metals such as Ca and Pb is partitioned in the treated solids. The parent (primary) leachate stream and leachate stream after each successive recycle are denoted by R0 and Rn, where $n = 1, 2, 3$ etc., denotes the number of cycles.

2.4.2. Partial recycling of the leachate

A constant volume pre-treatment experiment was performed with biosolids to liquid (g/mL) ratio of 1:10 (10% solids) and 1:20 (5% solids) using the recovered leachate. A fixed mass of biosolids (10 g or 5 g) and a solution volume of 100 mL were maintained for this experiment. The recycled stream was topped with fresh 3% (v/v) H_2SO_4 to maintain the solution volume at 100 mL for each leaching experiment. The added fresh lixiviant (FL) volume replaced the lost solution volume during each leaching cycle, including aliquots taken for analysis. Thus, the make-up ratio (volume of FL to volume of spent leachate) was ~15 vol% and ~20 vol% at 5% and 10% solids, respectively. The number of effective leaching cycles (n) was determined by continuously reusing the spent stream with make-up solution until the solution became saturated with dissolved metals. At the end of each leaching cycle, the recovered leachate stream was filtered to reduce suspended solids carryover before reusing it in another leaching cycle. All pre-treatment expriment with leachate recyling was repeated at least two times, and average data was reported.

2.5. Metals recovery

Most HMs precipitate out of solution at a pH range of 7–12 (Fu and Wang, 2011); however, the concentrated leachate stream obtained from the partial leachate recycling experiment was in the acidic pH (2.45). Therefore, an alkaline solution is required to adjust the solution pH to the metal precipitation region. Since each metal has different optimal precipitation pH depending on the metal ion concentration in the solution (Sethurajan et al., 2017), a typical pH of 9 was chosen for the precipitation experiment. A concentrated NaOH (6 M, pH 14) solution

Table 1
Metals composition of biosolids.

Metal type	Source	Metals composition (mg/kg)								
Major and trace metals	This study	Ca	Mg	Na	K	Al	Fe	Mn	Mo	Ba
		35,600	3630	2790	3530	5180	13,440	210	6	185
Heavy metals		Cr	Ni	Pb	Cd	As	Co	Cu	Zn	
	This study	22	14	17	1.3	2	3	825	815	
	C1 grade[*]	400	60	300	1	20	–	100	200	
	C2 grade[*]	3000	270	500	10	60	–	2000	2500	

[*] Biosolids contaminant grade as prescribed by Victoria EPA biosolids guidelines (EPA Victoria, 2004).
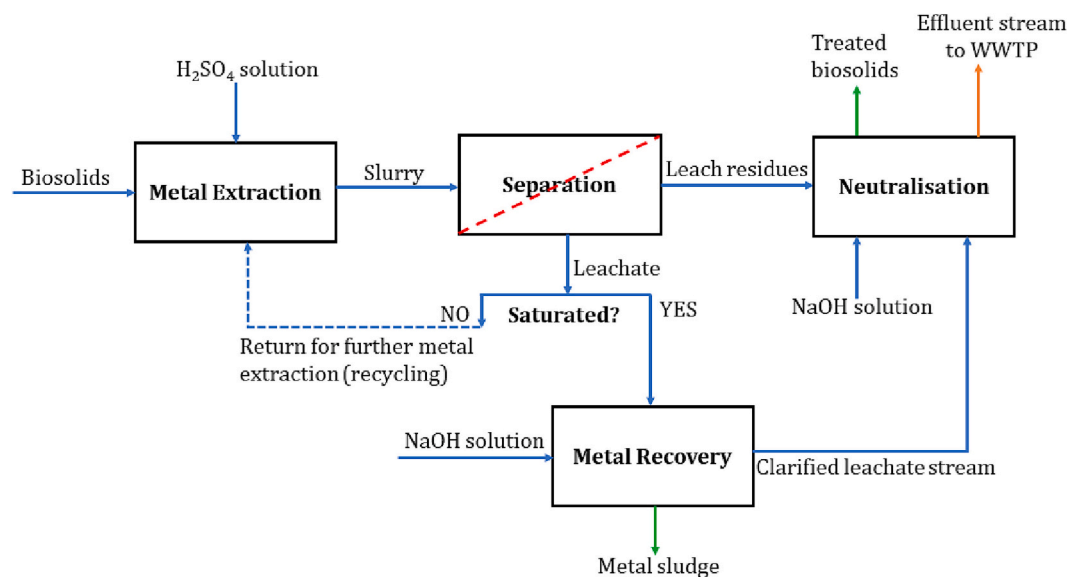
Fig. 1. Schematic of biosolids hydrometallurgical process for metal removal and recovery.

was used for the precipitation of metal ions to reduce the dilution effect on the concentration of the metals. The metal ion precipitation experiment was designed in the following ways to maximise the recovery of the HMs from other metal and non-metal contaminants.

1) Two-step NaOH precipitation when Fe/Al precipitation was considered: 20 mL of well-mixed and filtered leachate stream was measured in a conical flask, and 6 M NaOH was added in drops under continuous stirring until the solution pH was 4.5 ± 0.2. The pH of the solution was monitored via a well-calibrated pH meter, and the amount of NaOH added was noted. The sample was left to stay still for 2 h and centrifuged at 4000 rpm for 30 min to recover the precipitates. Then, 5 mL of the clarified stream was treated in the second step with NaOH in drops until the solution pH was 9.0 ± 0.5; the solution was left to settle for 2 h and centrifuged to recover the precipitates. The concentration of metal in the treated liquid after each step was measured by ICP-MS.

2) Single-step NaOH precipitation when Fe/Al precipitation was not considered: 10 mL of the leachate stream was treated with NaOH until the final pH was 9.0 ± 0.5. The presence of Fe and Al in the stream may help in the co-precipitation reaction with HMs since Fe^{3+} and Al^{3+} salts are common coagulants used in the wastewater treatment process.

3) Fenton reaction by adding H_2O_2 when oxidation of Fe and dissolved organics were considered: Ferric iron is known to precipitate at low pH <4, whereas ferrous has a high precipitation pH >8.5, so H_2O_2 can oxidise ferrous to ferric for recovery at stage 1 (pH 4.5). Moreover, dissolved organics in the form of COD (chemical oxygen demand) can limit HMs recovery, so the oxidation of dissolved organic by H_2O_2 was considered before NaOH precipitation. Briefly, a few drops of 30% v/v H_2O_2 (<0.5 mL) were added to 10 mL of well-filtered leachate stream. Then, the pH of the stream was adjusted to 4.5 with the addition of NaOH in drops to recover Fe/Al. The clarified stream was treated in a second stage to co-precipitate all other metals at pH 9.0 by adding NaOH.

4) Adsorption: An attempt to use biochar for adsorption when the leachate stream was at acidic pH (2.45) caused the leaching of metals from the biochar to the liquid, so adjustment of the leachate pH is necessary. Ten mL of clarified leachate (pH 4.5) obtained after the first step of Fe/Al precipitation was used for the adsorption experiment. Biochar produced from raw biosolids at 500 °C for 3 h residence time in a muffle furnace was used as the adsorbent and

charged at a dose of 0.05 g per mL leachate (0.048 g/g leachate). The adsorption was carried out at room temperature overnight under a constant agitation speed of 250 rpm. The mixture was filtered to separate the biochar and the aqueous stream, which was analysed for metal contents by ICP-MS. It should be noted that the presence of HMs in biosolids-biochar is a major concern only for land application of biochar. Metal-loaded biochar can have many valuable applications in catalysis and energy storage (Shen and Chen, 2022; Wang et al., 2017). Besides, biochar adsorption could be an effective and cheaper alternative than alkali precipitation for recovering dissolved metals from the acidic leachate stream.

2.6. Process configurations and the fate of nutrients and PFAS

The process flow diagram was developed to capture the entire hydrometallurgical treatment chain from metal extraction via acid leaching to metal recovery via alkali precipitation and, finally, the neutralisation of treated solids. Material balances were performed assuming a steady-state operation. The flow of C, N, and P in the process streams from the biosolids feed to the leachate stream and treated biosolids was overviewed. Similarly, twenty-eight compounds of PFAS (per- and polyfluoroalkyl substances) were measured in the raw biosolids, neutralised treated biosolids, the acidic leachate, and the final liquid effluent. The change in pH of both solid and liquid streams along the treatment chain might influence the leachability and the final fate of PFAS compounds (Kabiri et al., 2022). The C and N content in the raw and treated biosolids was determined using a CHN Series II Perkin Elmer instrument, while P content was measured by XRF analysis. Total organic carbon dissolved in the leachate stream was measured using TOC-L (Shimadzu Corporation). Total N representing the sum of t*otal Kjeldahl nitrogen* (TKN) and NOx and total P analysis, as well as PFAS analysis, were performed externally at ALS Water Resource Group, Melbourne, Australia.

3. Results and discussions

3.1. Effect of acid types

The efficiency of three minerals acids (sulfuric, nitric and hydrochloric) and two organic (acetic and citric) acids at the same volume concentration of 3% (v/v) and 5% (w/v) solids were studied on HMs extraction (Fig. 2). Mineral acids outperformed organic acids, and
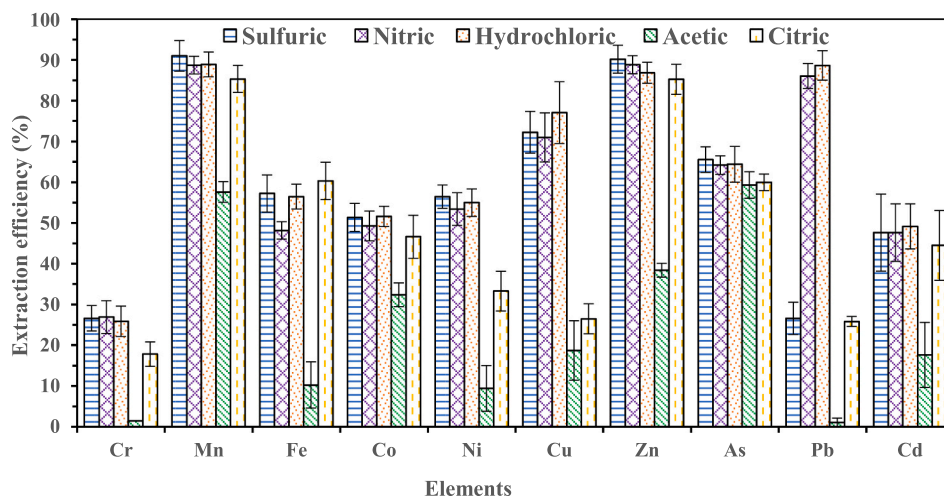
Fig. 2. Effect of mineral and organic acid solutions on the metal extraction efficiency from biosolids (conditions: 5% (*w/v*) solids, 3% (*v/v*) acid concentration, 25 °C, 30 min, and 600 rpm).

except for Pb, all mineral acids perform similarly in the metal extraction process. The high ionising power and extremely low pH of the mineral acids (~1.7) compared to the organic acids (~2.7) favoured the solubilisation of HMs (Gaber et al., 2011). Most sulfate, nitrate, and chloride salts are highly soluble in water and dilute acids, which may explain the similar metal extraction efficiencies of the three mineral acids. Sulfuric acid performed poorly in removing Pb owing to the low solubility (0.038 g/L) of PbSO$_4$ in water ($Ksp_{@298\ K}$ 1.6 × 10^{-8}). Generally, organic acids are considered weak acids (pK$_a$ > 1) as the ionised hydrogen concentration is typically lower than strong acids (pK$_a$ < 0) at the same molar concentration. For instance, the ionised hydrogen concentration of nitric acid is 100% of the acid concentration, whereas the ionised hydrogen concentration of citric acid is equivalent to 1.3–2.1% of nitric acid concentration (Lee et al., 2005). Therefore, it is expected that both organic acids have weaker ionic strength to desorb HMs ions in the biosolids, especially at low acid concentrations. However, of the two organic acids, citric acid was competitive with mineral acids despite having a similar pH to acetic acid in the metal extraction process. Citric acid is a natural chelating agent, and citrate ions form soluble complexes with cations of metals (Ma et al., 2020). Moreover, acetic acid is dicarboxylic while citric acid is tricarboxylic; the presence of an extra carboxylic group in citric acid also favours the number of available chelating sites for metal extraction (Gheju et al., 2011). Therefore, the chelating mechanism of citric acid was responsible for the high metal extraction rather than the acidolysis (reaction with H$^+$) mechanism for the mineral acid-based leaching. Studies have demonstrated that the oxidation-reduction potential (ORP) of the leaching solvents can affect their metal extraction ability since metal solubilisation usually involves an ion-exchange reaction with protons from acid (Babel and del Mundo Dacera, 2006; Bayat and Sari, 2010; Blais et al., 2005; Pathak et al., 2009). In this work, 3% nitric acid had the highest ORP of 611 mV, followed by sulfuric acid (590 mV) and hydrochloric acid (473 mV). This ORP value can be related to the amount of dissolved oxygen each solvent can donate to participate in redox reactions involving metal ions and H$^+$. However, there is no obvious difference in the removal efficiency of the three mineral acids for all metal ions (except Pb), irrespective of the ORP of the slurry/solution. Hence, the metal leaching process observed in this study can be stated to be largely controlled by the solution pH. This observation is contrary to a few studies reporting that both the leaching solution pH and ORP influence HMs solubilisation in biosolids (Beauchesne et al., 2007; Blais et al., 2005; Mercier et al., 2002). In particular, Cu dissolution was found to be driven by the redoxolysis mechanism rather than acidolysis due to the higher affinity of Cu to organic matter in sludge (Blais et al., 2005; Strasser et al., 1995). Based on this, the

leaching of biosolids was further tested with strong oxidising solutions such as 3% acidified ferric sulfate (670 mV) and ferric sulfate added hydrogen peroxide (603 mV). However, no significant improvement in metal extraction was observed, particularly for Cu and Cr, compared to mineral acids (data not shown). A previous study has reported that there was an optimum pH at which ORP of slurry becomes influential on HMs extraction efficiency (Beauchesne et al., 2007). Also, different washing agents may have various degrees of affinity and selectivity for different HMs. The removal efficiencies of multiple HMs in biosolids can be greatly improved by composite or sequential treatment (Shi et al., 2020). From these results, sulfuric acid was selected for subsequent experiments due to the relatively low cost of H$_2$SO$_4$, industrial maturity, and lesser toxicity of sulfates of HMs than their corresponding nitrates or chlorides salts at the same molar concentration (Erichsen Jones, 1934; Nie et al., 2015).

3.2. Effect of solids concentration

The effect of solids concentration on the metal extraction from biosolids using 3% v/v H$_2$SO$_4$ at 25 °C, 600 rpm for 30 min was investigated, and the results are presented in Fig. 3. The solids concentration significantly influenced the extraction of the metals (p < 0.05). The extraction of all metals (except Pb and Cr) at lower solids contents (1–3%) achieved ~60–95% removal compared to 30–80% removal at higher solids content (5–15%). This behaviour is expected from the stoichiometry of the leaching/desorption reaction. Notably, Mn and Zn had the least variation in extraction efficiency with the change in solids concentration because they have the highest proportion (75–90%) of acid-leachable metal fractions (F-1 + F-2) in the biosolids used in this study (Fig. S1). The change in solids concentration was largely inconsequential on Cr and Pb extraction. The consistent low solubilisation of Cr in biosolids can be attributed to the poor mobility of Cr; the trivalent metal ions such as Fe and Cr are more difficult to extract than the divalent ions such as Zn, Ni, and Cd due to the competitive uptake of protons by the more reactive species. Lead has the highest residual (inert) fraction (F-4) of all metals in the biosolids (Fig. S1); therefore, its extraction is usually limited by common acids (Gheju et al., 2011; Xiao et al., 2015). Moreover, H$_2$SO$_4$ is not a suitable lixiviant for Pb extraction due to the low solubility of PbSO$_4$ in water (see Fig. 2). The removal efficiencies of all other metals increased with decreasing solid/liquid ratio, and the maximum extraction efficiency for all metals was observed at the lowest solids content (1%). The result agrees with previous literature on the effect of solids concentration on metal extraction (Bayat and Sari, 2010; Kuan et al., 2010; Wu et al., 2009). Low solids content is
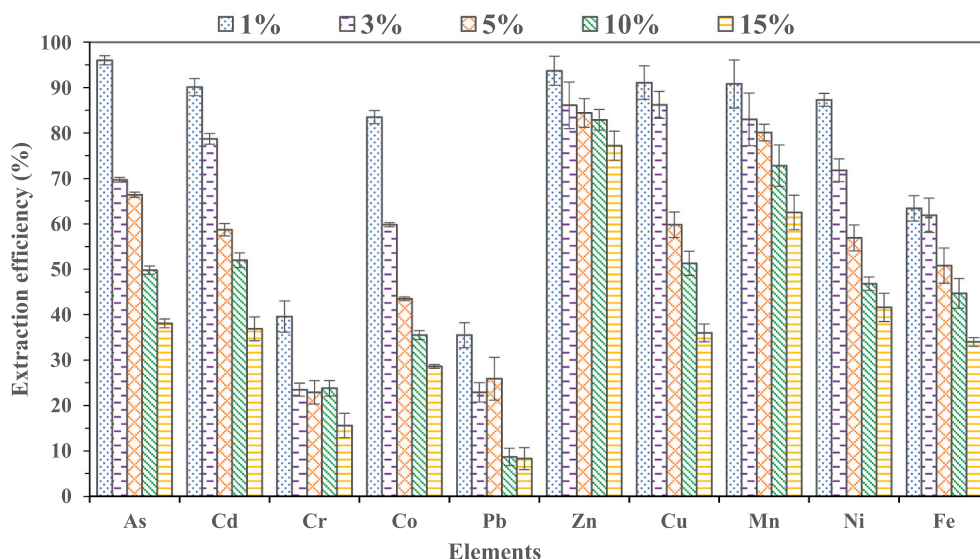
Fig. 3. Effect of solids concentration (w/v) on metal extraction efficiency from biosolids (conditions: 3% (*v/v*) H$_2$SO$_4$, 25 °C, 30 min, and 600 rpm).

associated with a higher volume of lixiviant and higher proton (H$^+$) concentration, benefiting the dissolution of acid-exchangeable HMs fraction (F-1) in the biosolids. Since there are more H$^+$ than available surface chelating sites on the biosolids, the excess H$_2$SO$_4$ can penetrate the biosolids pores and react with more metal ions, particularly the reducible (F-2) and oxidisable (F-3) HMs fractions, leading to overall higher extraction efficiency (Yang et al., 2021).

Table S1 shows the dissolved metal ion concentration in the leachate at different solids loading. The dissolved metal ion concentration in mg/

L liquid increased with increasing solids contents, while the metal ion concentration in mg/kg solids decreased with increasing solids contents (Table S1). Treatment using 1% (*w/v*) solids concentration produced cleaner biosolids, while the 15% (w/v) solids produced a highly concentrated metal-laden leachate stream which can make the recovery of metals more attractive. On the other hand, lower solid loading produced a dilute liquor stream. Moreover, 1% solids concentration appears unrealistic in practical scenarios in wastewater treatment plants (WWTPs). Besides, lower solids concentration is associated with higher
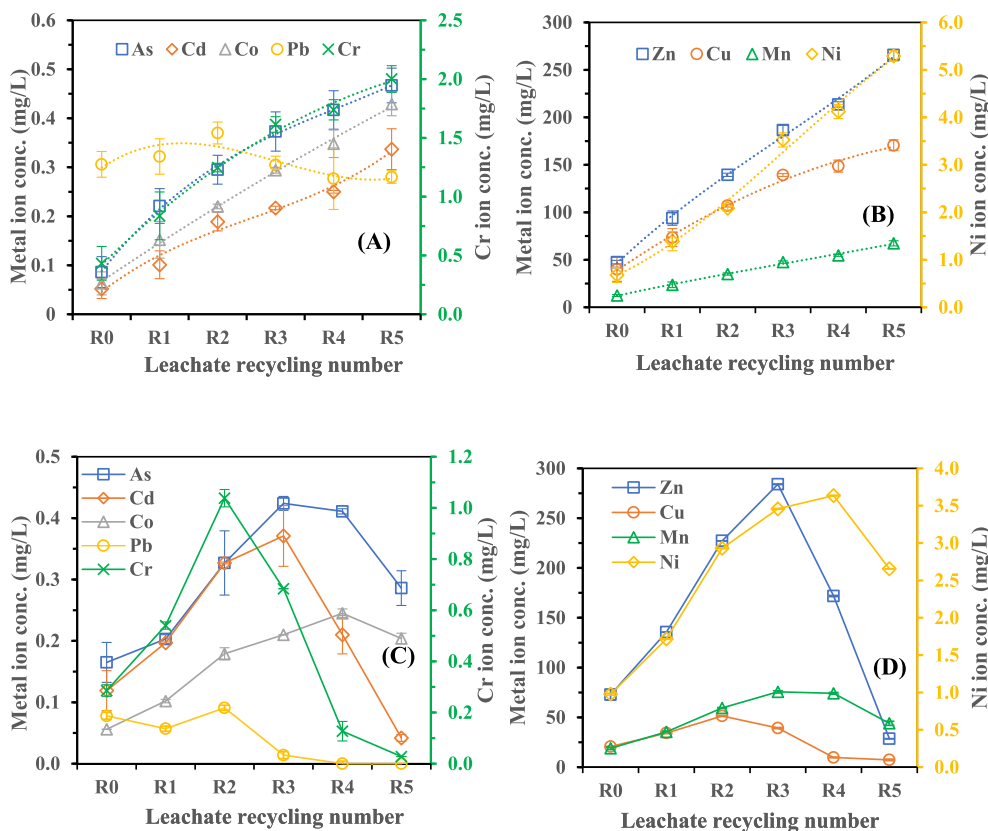

Fig. 4. Effect of fresh biosolids concentration on 100% recycling of the leachate stream (A) & (B) 5% solids (C) & (D) 10% solids (conditions: 3% (*v/v*) H$_2$SO$_4$, 25 °C, 30 min, and 600 rpm).

lixiviant consumption, and dewaterability can be challenging (Vesilind and Hsu, 1997). Similarly, at 15% solids, the mass transfer limitation was significant, negatively impacting mixing and liquid recovery, and the overall metal ion removal efficiency was the lowest. In fact, at 20% solids, mixing and separation became difficult, and the leaching process was not successful (data not reported). Hence, a moderate 5–10% solids loading may be a good balance and are the typical value in most biosolids leaching operations (Gheju et al., 2011; Wang et al., 2015; Wu et al., 2009).

3.3. Recyclability of the leachate stream

3.3.1. Metal saturation concentration and the leachate recycling efficiency

The cumulative metal concentration in the leachate stream after five successive leaching cycles at 5% and 10% solids using 3% v/v H_2SO_4 solution, 25 °C, 30 min, and 600 rpm is presented in Fig. 4(A-D). It is obvious that the primary leachate stream (R0) from the parent leaching experiment has not reached its maximum extraction capacity as more metals were extracted from fresh biosolids using the R0 stream five times. At 5% solids, the R0 stream had higher extraction strength than that at 10% because of the higher liquid-to-solid ratio and the dilute concentration of the dissolved metal. A higher liquid-to-solid ratio slowed the attainment of thermodynamic equilibrium between the dissolved metal species and the acidic solution (Lee et al., 2006). The leachate streams obtained at 10% solids were saturated faster compared to 5% solids. The primary leachate at 5% solids was recycled up to five times without reaching saturation point (Fig. 4(A&B)), while the leachate at 10% solids can only be reused up to three times, beyond which a rapid decline in cumulative concentration was observed (Fig. 4 (C&D)). There was at least a 3-fold increase in the concentration of all metals (except Pb) by completely reusing the primary leachate stream from R0 to R5 (Fig. 4(A&B)). At 5% solids, the percentage increase in metal ion concentration in the leachate from R0 to R3 can be ranked as Cu(II) (249) < Cr(III) (273) < Mn(II) (284) < Zn(II) (293) < Cd(II) (317) < As(III) (334) < Co(II) (367) < Ni(II) (419). However, at 10% solids (Fig. 4(C&D)), there was a lesser increase in the cumulative concentration from R0 to R3, and the percentage increase was Cu(II) (90) < Cr (III) (139) < As(III) (157) < Cd(II) (212) < Ni(II) (254) < Co(II) (275) < Zn(II) (290) < Mn(II) (300). The percentage increase in cumulative concentration for Mn and Zn was similar at 5% and 10% solids, whereas there was a substantial decrease in the accumulation of other metals at 10% solids compared to 5% solids. Expectedly, higher solids loading limited the efficiency of metal accumulation during leachate recycling at the same extraction cycle with 5% solids. In particular, the cumulative Cu loading during recycling was severely impacted at 10% solids, possibly due to the dominant redox reaction between soluble Cu(II) and iron(II) sulfate, the mechanism which has been elucidated in previous literature (Matocha et al., 2005). The 100% recycling of the leachate stream at 10% solids performed competitively with 5% solids only in removing easily leachable metal fractions (F-1 and F-2) such as Zn and Mn, while the removal of other metal species dominant in F-3 was largely difficult. The removal of metal ions in F-3 fractions will require abundant protons from fresh H_2SO_4 solution as well as harsh oxidising conditions to break the organometallic bond (Beauchesne et al., 2007). The monotonic decline in the extraction efficiency after the third recycling at 10% solids (Fig. 4(C&D)) was due to Al/Fe-induced co-precipitation of metal from the leachate to the solid phase as the solution pH approaches 3, which is conducive for ferric precipitation (Marchioretto et al., 2005). The pH of the R5 stream at 10% solids was 4.5, while it was 2.4 at 5% solids.

Furthermore, it was observed that all metal extraction profiles followed closely that of Fe, and the improved extraction of HMs using the spent leachate stream can be attributed to the role of ferric sulfate hydrates in the metal desorption process. The iron source in the biosolids is the ferric salt coagulant used during the wastewater treatment process. Sulfuric acid solution can partly dissolve ferric-containing salts (such as

FeCl$_3$ or FeOOH), and then dissolved ferric ion can form ferric sulfate through ion exchange reaction with SO_4^{2-} or HSO_4^- from H_2SO_4 (Demol et al., 2022). Ferric sulfate is a well-known leaching agent which acidifies by hydrolysis ($Fe^{3+} + H_2O = FeOH^{2+} + H^+$) and increases the elution efficiency of HMs from soils and biosolids (Bayat and Sari, 2010; Ito et al., 2000; Shi et al., 2020; Strasser et al., 1995). X-ray photoelectron spectra of the metal precipitates confirmed the presence of ferric sulfate (Fig. S2). The effective extraction of HMs by dissolved Fe^{3+} is due to its ability to oxidise metal sulfides to soluble metallic ions and the release of more protons through the hydrolysis of ferric hydrates (Pathak et al., 2009). The dissolution of inherent ferric-containing components in biosolids and the subsequent formation of ferric sulfates extended the overall extraction strength of the leachate stream during recycling. The presence of native ferric salts was beneficial for the reuse of the leachate stream; however, there is a critical Fe^{3+} concentration beyond which it counteracts the HMs extraction as Fe^{3+} precipitates at a low pH value (<4). It was observed that the higher the concentration of Fe in the stream, the better the extraction efficiency of other metals up to a certain Fe concentration (~1400 mg/L). This is consistent with the study of Ito et al. (2000), who observed that the higher the amount of ferric iron added, the lower the pH of the lixiviant and the higher the extraction efficiency of HMs (~80%) from digested biosolids at low solids concentration (2% w/w). In other studies, leaching at pH 2 with acidified ferric iron outperformed H_2SO_4 in extracting common HMs from biosolids (Bayat and Sari, 2010; Ito et al., 2000). The combination of ferric sulfate and acid solutions at different dosage had positive synergistic interactions for the solubilisation of multiple HMs from biosolids and soils (Beauchesne et al., 2007; Shi et al., 2020).

3.3.2. Effect of make-up solution on the leachate recyclability

The cumulative metal ion concentration in the leachate stream after ten successive cycles with the addition of make-up lixiviant between each cycle is shown in Fig. 5. A constant feed rate of 5 g or 10 g of dry biosolids per 100 mL liquid for a 30 min leaching cycle was maintained. Contrary to the observation at 100% leachate recycling, without adding make up lixiviant (Fig. 4), the continuous addition of 3% H_2SO_4 as FL prolonged the extraction strength of the spent leachate until R8 stage (Fig. 5). At 5% solids (Fig. 5), there was a substantial increase (at least 250%) in the cumulative metal ion concentration (except for Pb) from R0 to R10. For instance, Ni(II) was concentrated from 0.5 to 3.5 mg/L, Zn(II) from 38.9 to 277 mg/L, Cu(II) from 11.5 to 100 mg/L, As(III) from 0.14 to 0.51 mg/L, Cd(II) from 0.04 to 0.34 mg/L, Cr(III) from 0.12 to 1.2 mg/L, Co(II) from 0.04 to 0.22 mg/L, and Mn(II) from 10.3 to 71.5 mg/L. There was a steady increase in the cumulative metal ion concentration from R0 to R4 due to the low make-up ratio of the FL in the total leachate stream (<25%). The addition of FL to the leachate stream possibly aided the dilution of the metal ion concentration and hence enhanced the extraction strength (and capacity) of the stream. Up to R7, the increase in the metal ion concentration far outweighed the dilution effect of the added fresh solution. Nevertheless, adding FL was not beneficial beyond R6 as the leachate had been fully saturated with the metal ions. This observation was due to the similar extent of metal ions dilution and extraction efficiency in the stream by the added FL beyond R6. At R6, increasing the make-up ratio above 15 vol% would likely enhance the metal extraction strength of the stream further. The overall extraction trend of the HMs was largely governed by Fe, which reached saturation at R6. Contrary to the observation for 100% leachate recycling without adding make up lixiviant (Fig. 4), the continuous addition of the FL and the acidifying effect of Fe^{3+} kept the pH of the leachate stream at <2 throughout the process, limiting ferric precipitation.

The addition of make-up acid lixiviant was less beneficial in enhancing the recyclability of the leachate stream at 10% solids compared to 5% solids (Fig. S3). There was no monotonic increase in the concentration of metal ions, and the irregular increase and decrease in the cumulative concentration across the ten leaching cycles can be
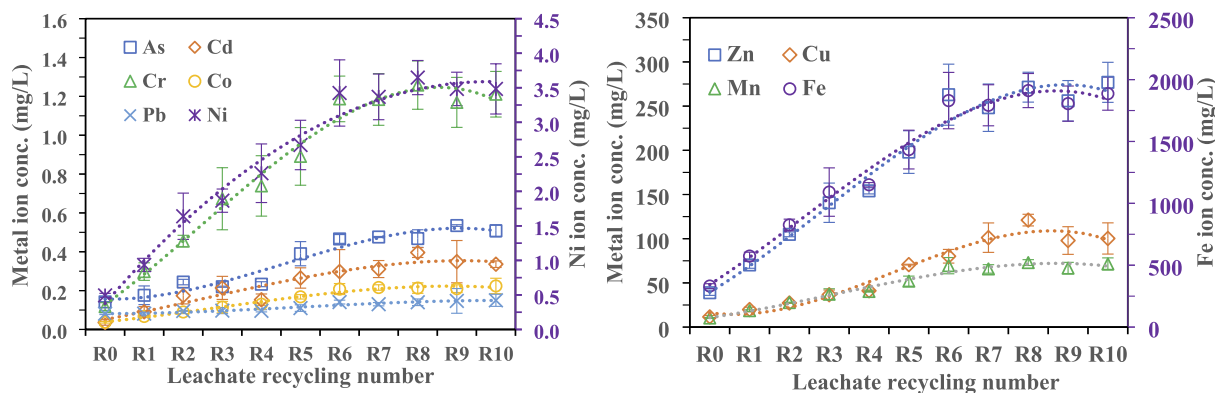
Fig. 5. Effect of make-up lixiviant on the recyclability strength of the leachate stream at 5% fresh biosolids concentration (conditions: 3% (v/v) H_2SO_4, 25 °C, 30 min, and 600 rpm).

attributed to Fe(III) precipitation. The leachate at 10% solids saturated faster than at 5% solids, and pH increased rapidly, thus facilitating Fe(III) precipitation much earlier. Iron(III) co-precipitated other metals in the stream. Contrary to the observation at 5% solids, adding FL between successive leaching could not suppress Fe precipitation (Fig. S3) at 10% solids. The dilution and acidifying effect of the FL on the metal ion concentration in the leachate stream were minimal at higher solids loading. The sharp rise in solution pH rather than the increase in Fe concentration stimulated Fe co-precipitation reaction at 10% solids. For instance, at 10% solids, Fe precipitation began at a maximum concentration of ~1400 mg/L (pH 2.45), whereas, at 5%, no Fe precipitation occurred even at the maximum concentration of 1830 mg/L (pH 1.85). At low pulp density (5% solids), the overall extraction efficiency of the spent stream was competitive with the FL, and the performance improved with increasing Fe concentration in the stream. Acidified ferric salt leaching is optimally performed at low solids concentration (<5% w/v) to avoid a rapid increase in pH and minimise ferric precipitation, which is counterproductive for HMs solubilisation (Bayat and Sari, 2010; Ito et al., 2000).

Leachate recycling could bring significant cost savings for H_2SO_4 lixiviant besides environmental benefits. The 100% recycling of the spent leachate at 5% solids loading for five leaching cycles (Fig. 4) could save 4.5 times the required H_2SO_4 volume at 90% liquid recovery per leaching cycle. Similarly, for the partial recycling of the leachate with 15% make-up lixiviant at 5% solids for six leaching cycles (Fig. 5), there

could be ~5 times reduction in the volume of H_2SO_4. Assuming a linear relationship between H_2SO_4 volume and cost, around 400% cost savings can be achieved with leachate recycling with make-up lixiviant, which may substantially lower the cost of acid leaching.

3.4. Metal recovery from the concentrated leachate stream

A single-step or two-step NaOH co-precipitation and biochar adsorption were investigated for recovering HMs from the saturated leachate stream. Metals like Cr, Cu, Pb, and Zn do not form hydroxide precipitates at pH <6, allowing the separation from ferric iron and aluminium, which precipitate at pH <5 (Marchioretto et al., 2005). Table S2 shows the metal ion composition of the leachate stream used for the metal recovery experiments. It was observed that the concentration of Zn, Mn, and Cu in the leachate was up to 100 mg/L. Concentrations of all other HMs were < 5 mg/L, while Fe, Al, and alkali and alkaline earth metals (AAEMs: Na, K, Mg, and Ca) were highly concentrated in the stream (>500 mg/L). The metal recovery at each precipitation stage is shown in Table 2, while the overall metal recovery from the different methods is shown in Fig. 6.

The single-stage NaOH precipitation at pH 9 recovered about 9–99% of the HMs. The recovery efficiency of the metals can be ranked as Zn (99%) ≈ Cd (99%) > Cr (97%) > Pb (79%) > Co (33%) > Ni (31%) > As (11%) > Cu (9%). The precipitation of these HMs was accompanied by the precipitation of >90% for Fe, Al, Ca, Mg, and Mn. The precipitation

Table 2
Metals recovery from the leachate stream under different methods.

Description	Metals	NaOH consumption, pH, and metal removal efficiency in different methods					
		Single-stage co-precipitation	2-stage co-precipitation		H_2O_2 pre-2-stage co-precipitation		Biochar sorption
		One stage	1st	2nd	1st	2nd	One stage
Stages	–	One stage	1st	2nd	1st	2nd	One stage
NaOH (g/mL)[a]	–	0.11	0.04	0.08	0.05	0.06	0.04
pH range	–	2.5–9.0	2.5–4.5	4.5–9.0	2.5–4.5	4.5–9.0	2.5–4.5
Heavy metals (%)[b]	As	11.4	20.4	8.4	13.0	60.6	19.0
	Cd	98.9	32.7	94.3	35.5	97.2	46.8
	Co	32.9	3.2	32.3	13.4	51.5	32.1
	Cr	97.4	72.7	85.5	82.6	57.3	47.1
	Cu	9.30	15.1	31.3	24.5	49.0	56.0
	Ni	30.7	3.50	33.2	33.2	73.8	70.5
	Pb	78.7	34.0	78.7	80.9	26.6	3.80
	Zn	99.3	35.5	96.3	50.0	99.0	56.8
Other metals (%)[b]	Al	97.4	91.4	77.9	95.4	96.6	95.8
	Ca	91.0	2.30	88.9	23.8	76.9	20.9
	Fe	98.5	99.0	59.5	99.1	96.1	46.6
	K	18.7	16.8	22.3	24.7	46.2	22.6
	Mg	98.0	3.40	99.0	13.3	92.2	29.6
	Mn	99.3	11.4	99.2	22.1	94.4	35.6

[a] 6 M NaOH consumed (g/mL leachate).
[b] The metal removal efficiency in the second stage refers to the percentage removal of the remaining metal in solution after the first stage.
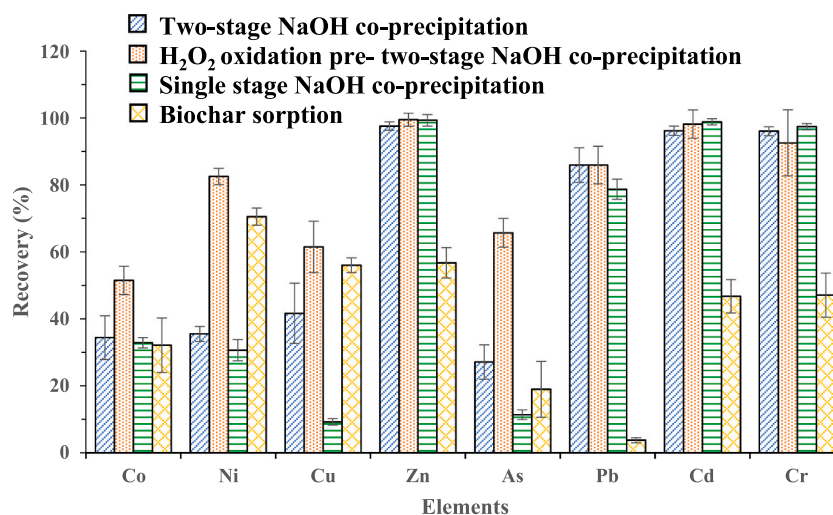
Fig. 6. Overall removal efficiency of HMs under different recovery techniques.

of Co, Ni, As, and Cu was low under this condition due to the high solubility of their respective metal hydroxide at pH 9 (see Fig. S4). It was hypothesised that the presence of Fe and Al would facilitate the precipitation of HMs in the stream. However, the presence of both metal salts did not improve HMs recovery at the basic pH 9 relative to the observation at acidic pH 4.5. The co-precipitating effect of Fe and Al on the other metals cannot be observed under the single-stage recovery, and only the solubility of the various metal hydroxides at pH 9 can be assessed. The single-stage precipitation resulted in a low recovery efficiency of some HMs and, at the same time, produced a highly contaminated HMs sludge stream. This may reduce the attractiveness of the recovered metal sludge for downstream separation and subsequent applications in catalysis or smelting.

The staged recovery of the metals at pH 4.5 (stage 1) and pH 9.0 (stage 2) effectively precipitated Fe and Al from the leachate stream in the first stage, while most of the HMs were recovered in the second stage (Table 2). About 99% Fe and 91% Al were recovered in the first stage (pH 4.5); however, 3–73% of some HMs were co-precipitated. For example, 73% Cr, 36% Zn, 34% Pb, 33% Cd, 20% As, 15% Cu, 4% Ni and 3% Co were co-precipitated with Fe/Al at pH 4.5. The removal of these HMs at pH 4.5 was due to the sorption capacity and co-precipitating ability of Fe and Al hydroxides (Lee et al., 2002). No precipitation of these metals was observed at pH 4.5 in the absence of Fe and Al when the solution of their pure salts was treated with NaOH (data not shown). Only Cd and Zn had the highest removal efficiency of >94% in the second stage. In comparison, other HMs' removal efficiency was 8–79%, similar to the single-stage precipitation from solutions of same pH value of 9 (Table 2). The recovery of As was minimal in the staged NaOH co-precipitation; the highest recovery of 20% occurred at pH 4.5, which could be attributed to the formation of ferric arsenate (Hao et al., 2018). The major benefit of the dual-stage precipitation, aside from the selective recovery of Al, Fe and Cr, was the improvement in Cu recovery from 9% in the single-stage to 31% in the two-stage at pH 9. The mechanism involving the precipitation of ferric iron and the associated Cu loss from solution has been elucidated elsewhere (Javed and Asselin, 2020). The chosen pH 9 is a compromise for the recovery of all the HMs; further optimisation studies are required to identify the optimum recovery pH for each metal species in the solution. From the theoretical solubility curve for metal hydroxides (Fig. S4), Cu has the lowest solubility (<0.1 mg/L) at pH 9 relative to other HMs. However, this theoretical solubility behaviour contradicts the low recovery of Cu (<50%) at pH 9 with a solubility concentration of 36 mg/L. Probable explanations for this include the affinity of Cu(II) to dissolved organic ligands making complexes and the crystal growth vs (super)saturation level of the various metals in the solution (Weng et al., 2002). Moreover, the leachate

stream contains many metal and non-metal species, which may cause significant deviation from the theoretical solubility behaviour of pure metal in aqueous systems.

Adding H_2O_2 prior to NaOH precipitation improved the recovery of some HMs from the leachate. For example, without adding H_2O_2, the overall recovery of As was 27%; however, it increased to 66% when H_2O_2 was added. Similarly, Cu recovery increased by 47%, Co recovery improved by 53%, and Ni recovery increased by 130%. In fact, increasing the amount of H_2O_2 added by a unit volume before the staged NaOH precipitation further increased the recovery of As, Co, Cu, and Ni by 48%, 22%, 18%, and 68%, respectively (Fig. S5). The addition of H_2O_2 had no improvement on the recovery of Zn, Pb, Cd, and Cr compared to the sole 2-stage NaOH co-precipitation. The oxidation of dissolved organics by H_2O_2 enhanced the desorption of metal species. The biosolids used in this study contain organically bonded HMs (F-3 fraction; Fig. S1), where the bonding strength can be ranked as Cu > As > Co > Ni. The complexation of HMs with dissolved organic matter in aqueous solutions has been reported to influence the solubility and mobility of metals (Weng et al., 2002).

The removal efficiency of the HMs via biochar adsorption was poor compared to the alkali precipitation and did not follow any specific trend. Only a modest 3–70% uptake was achieved, with the highest for Ni and the lowest for Pb. The performance of biochar adsorption for HMs uptake from aqueous solutions is influenced by many factors, including the adsorbent properties, pH, adsorbate concentration, temperature, and solution chemistry of the metal species (Ni et al., 2019). Most of these factors have not been optimised in this study and may contribute to the relatively poor removal efficiency of the biochar sorption process. The FTIR spectra of the biochar before and after the sorption (Fig. S6) confirmed the non-depletion of the surface functional group of the biochar, suggesting the dominance of physisorption. Chemisorption usually involves the chemical reaction between the charged surface functional group of the biochar adsorbent and the metal ions via electrostatic precipitation, organo-metallic complexation, and deprotonation phenomena (Yang et al., 2021).

3.5. Process configurations and mass balances

The various unit operations were put together in a process flow diagram (Fig. 7) to provide an insight into the materials requirement of the treatment process demonstrated in this work. Based on our findings, leachate recycling is only attractive at 5% solids which can considerably lower acid and alkali consumption. However, processing 10% solids with no leachate recycling may be favourable commercially. Fig. 7(A) shows the mass balance for processing 10% solids with no leachate
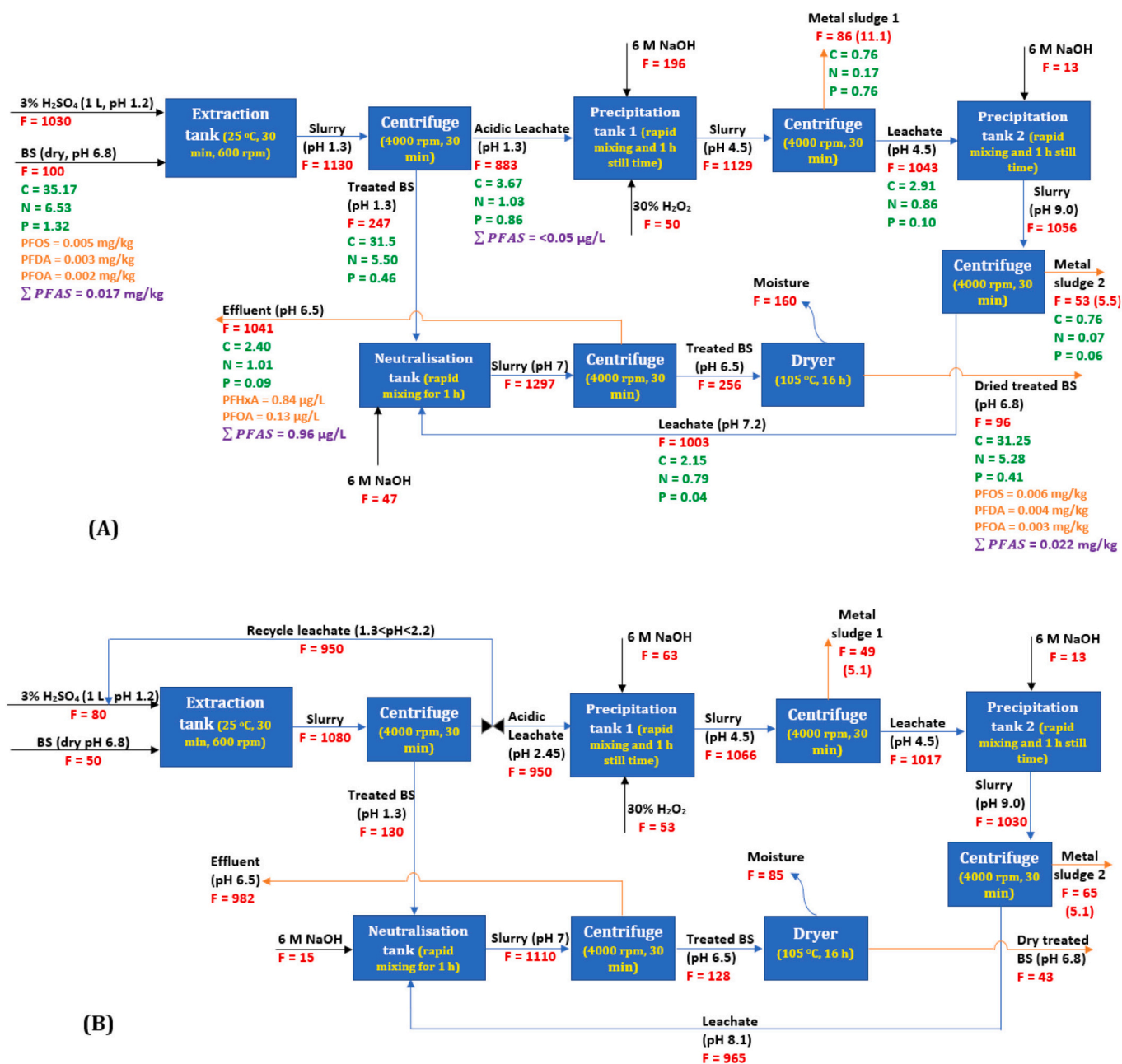
Fig. 7. Process block flow diagram for HMs removal and recovery from biosolids. (A) for processing 10% solids with no leachate recycling (B) for processing 5% solids with leachate recycling (with top-up lixiviant). *Red font (F) denotes mass flow in grams; the flowrate in parenthesis corresponds to the dry weight of the metal sludge; green font (C, N, and P) denotes carbon, nitrogen, and phosphorous mass flows in grams, while the purple font denotes total PFAS concentration in the major streams.* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

recycling, while Fig. 7(B) shows the balance for processing 5% solids with leachate recycling with make-up lixiviant. The separation of solids from the leachate produced acidic treated biosolids (pH 1.3), which cannot be used directly for land application or thermal processing without prior neutralisation or conditioning. A considerable volume of water is required to wash off residual acid in the treated biosolids and raise the pH to near neutral values. It is proposed that the clarified alkali stream be used to neutralise the acidic treated biosolids in an attempt to close the process loop and reduce the volume of aqueous waste generated. In Fig. 7, the total mass flow of streams (grams) in and out of each unit operation is denoted as F, and carbon, nitrogen and phosphorous mass flows (in grams) are denoted as C, N, and P, respectively. For a 1:10 *w/v* (biosolids to H_2SO_4 solution ratio) feed rate (Fig. 7(A)), the

overall liquid recovery was 77%, while overall solids recovery was 96% (dry biosolids basis). When the feed ratio was changed to 1:20 w/v (5% solids) with leachate recycling, the mass balance is shown in Fig. 7(B). Overall liquid and solids recovery was 84% and 86%, respectively. Notably, the leachate recycling yielded about a 92% and 43% decrease in H_2SO_4 and NaOH consumption, respectively. The lixiviant consumption changes remarkably when processing 5% solids with no leachate recycling (Fig. S7). The total H_2SO_4 consumption (g/g biosolids) doubled, and total NaOH consumption increased by 25% relative to processing 10% solids. The overall results with respect to solids and liquid recovery, metal sludge recovery as well as H_2SO_4 and NaOH consumption at different process configurations are summarised in Table 3. At 10% solids processing, the major composition (wt%) of

Table 3

Summary of process performance at different configurations.

Indicators	Unit	Process configurations		
		10% solids with no leachate recycling	5% solids with no leachate recycling	5% solids with leachate recycling with make-up lixiviant
Overall solids recovery	wt% dry basis	96	87.6	85.8
Overall liquid recovery	wt%	76.7	80.3	82.4
Total metal sludge recovery	g/g dry biosolids	0.17	0.19	0.21
H_2SO_4 consumption[a]	g/g dry biosolids	0.57	1.14	0.09
NaOH consumption[b]	g/g dry biosolids	0.50	0.63	0.36

[a] H_2SO_4 stock solution (98% Assay, SG = 1.84).

[b] NaOH (Analytical reagent grade pellets, SG = 2.13).

recovered metal sludge 1 is 10.7% Fe, 8.8% Na, 8.2% S, 7.9% P, and 5.5% Al while that of metal sludge 2 is 13.1% Na, 12.5% S%, 12.4% Ca, 6.0% P, and 3.3% Mg. The detailed composition is provided in Table S3, and the thermal stability profile of the recovered metal sludge is shown in Fig. S8. The recovered metal can be employed in a number of potential applications in catalysis, smelting, and materials production, such as metal-based adsorbents/nanomaterials depending on the required purity and properties (Tawalbeh et al., 2021; Yu et al., 2022).

3.6. Fate of nutrients and PFAS

Considering the processing of 10% solids with no leachate recycling, the balance around organic nutrients (C, N, and P) is presented in Fig. 7 (A). The overall process modestly preserved the organic matter in the biosolids as the reduction in C, N, and P contents from raw biosolids to treated biosolids was 11%, 19%, and 65% (*w*/w), respectively. This observation on nutrient dissolution is comparable to other studies. For example, Mercier et al. (2002) reported about 19% decrease in dissolved organic carbon in treated sludge compared to raw sludge. Similarly, Beauchesne et al. (2007) and Shiba and Ntuli (2017) observed about 77% P and 82% P solubilisation, respectively, from biosolids treatment using H_2SO_4 (pH <2). The excessive dissolution of P in biosolids is a typical limitation of mineral acid leaching. The joint use of ferric salts and/or H_2O_2 with H_2SO_4 has been reported to enhance P retention in biosolids as ferric phosphate (Beauchesne et al., 2007). However, unlike C and N, which largely remain in the dissolved form in the liquid streams, >90% of the total dissolved P was recovered at the metal precipitation stages. Phosphorous has a high affinity for metal ions (particularly Fe) in aqueous media which can be recovered as metal phosphate precipitates (Vardanyan et al., 2018). The dissolution and recovery of P is more sensitive to pH compared to C and N. In the neutralisation stage, where the acid-leached biosolids are treated with NaOH, about 1% C, 4% N and 11% P were further lost from the solids to the liquid phase. The final effluent stream contains about 0.23% C, 0.10% N and 0.009% P (*w*/w). The guideline for the disposal of this effluent stream as trade wastewater was assessed with respect to the organic and metal concentration load (Table S4). All the metals and organic nutrient concentrations (except for N) are within the acceptable criteria set by South East Water Recycling Corporation, Melbourne, Australia. The excess nitrogen can be removed from the effluent stream by adsorption, and the final liquid can be safely discharged.

Per- and poly-fluoroalkyl substances (PFAS) are rapidly becoming a limiting contaminant for biosolids reuse in agricultural land. Therefore, there is interest in understanding the fate of the plethora of PFAS compounds during the hydrometallurgical treatment process. Twenty-eight common PFAS compounds, the major ones being PFOA ($C_8HF_{15}O_2$), PFOS ($C_8HF_{17}O_3S$), PFDA ($C_{10}HF_{19}O_2$), PFBS ($C_4HF_9O_3S$), and PFHxA ($C_6HF_{11}O_2$), were measured in the raw biosolids, treated biosolids (with leachate neutralisation), acidic leachate, and the final effluent stream. The representative PFAS compounds detected in the

selected process streams and the total sum of PFAS are shown in Fig. 7 (A). The overall PFAS result is presented in Table S5. The acid extraction (at pH <2) did not leach out the PFAS compounds in the raw biosolids (0.0165 mg/kg), as the concentration of the PFAS in the acidic leachate stream was <0.05 μg/L. However, there appears to be an increase in the leachability of PFAS compounds with a carboxylic head group (particularly PFHxA and PFOA) at the neutralisation stage at pH > 7. The leaching of these PFAS compounds from the acidic treated biosolids (pH 1.3) slightly increased the concentration of the PFAS compounds in the final effluent to 0.96 μg/L. Nevertheless, the PFAS compounds reaching the liquid stream are substantially negligible (<1 μg/L), and the PFAS are largely retained in the treated biosolids (0.0221 mg/kg). Further investigations into the mechanisms controlling the mobility and the final fate of the diverse PFAS compounds during biosolids acid pre-treatment are needed.

Lastly, the viability of the developed closed-loop process with respect to residual nutrients and HMs concentration in the treated biosolids was briefly assessed. The concentration of nutrients and HMs in the treated biosolids with leachate neutralisation was compared with treated biosolids obtained under two different neutralisation washing scenarios at the same pre-treatment conditions. The neutralisation washing scenarios were (i) treated biosolids with leachate neutralisation, (ii) treated biosolids with no neutralisation, and (iii) treated biosolids with deionised water neutralisation. The concentration of the residual nutrients, HMs, and PFAS in the three treated biosolids streams are presented in Table 4. The concentrations are further benchmarked with EPA Victoria prescribed concentration for contaminant-grade biosolids (C1-grade and C2-grade) (EPA Victoria, 2004). The C1-grade refers to the least contaminant grade biosolids with respect to HMs concentration which can be applied to land unrestrictedly. Except for Cu in all scenarios, all other HMs concentrations met the requirements of C1-grade biosolids, with the lowest concentration obtained in treated biosolids with water neutralisation step. Most metal sulfates are soluble in water; therefore, water neutralisation washing helped in the dissolution of metal sulfate salts as well as the removal of H_2SO_4-insoluble metal species. Hence it is proposed that the treated biosolids obtained with the leachate neutralisation step be neutralised in a second step with deionised water to reduce the residual metal concentration load further, particularly for Cu. There is largely an inconsequential difference in residual nutrient concentration in the treated biosolids with respect to neutralisation washing scenarios.

4. Conclusions

This work provided a detailed investigation into the hydrometallurgical process for extracting and recovering HMs from biosolids. The extraction performance of mineral acids (H_2SO_4, HNO_3 and HCl) was similar and only citric acid performed competitively with mineral acids in achieving ~70% extraction of HMs at 5% solids loading. Low solids content (1–5% *w*/v) favoured HMs extraction and produced a leachate

Table 4

Concentration of residual nutrients, metals, and PFAS in biosolids streams obtained under different neutralisation washing scenarios by processing 10% solids.

Content	Elements/ abbreviations	Streams, pH, and concentration					
		Raw biosolids	Treated biosolids (no washing)[a]	Treated biosolids (leachate washing)[b]	Treated biosolids (water washing)[c]	C1-grade biosolids[d]	C2-grade biosolids[d]
	pH	6.8	2.0	6.5	7.0	7.0	7.0
Nutrients (% w/w dry feed basis)	C	35.4	32.9	35.2	36.4	–	–
	N	5.6	5.5	6.2	5.6	–	–
	K	1.1	0.4	0.3	0.2	–	–
	P	1.3	0.5	0.4	0.5	–	–
Major metals (% w/w dry feed basis)	Na	0.1	BDL[e]	1.5	BDL	–	–
	Mg	0.5	0.1	0.1	0.1	–	–
	Al	0.7	0.6	0.4	0.5	–	–
	Ca	10.2	8.5	6.8	5.4	–	–
	Fe	4.2	2.3	2.9	4.1	–	–
Trace metals (mg/kg dry feed basis)	As	<5	<5	<5	<5	20	60
	Cd	1.3	0.5	0.4	0.3	1	10
	Co	<5	<5	<5	<5	–	–
	Cu	690	380	420	220	100	2000
	Cr	20	16	14	14	400	3000
	Hg	0.7	0.9	0.9	0.9	1	5
	Mn	210	53	39	17	–	–
	Mo	8	8	8	9	–	–
	Ni	18	12	14	8	60	270
	Pb	20	17	18	18	300	500
	Se	5	4	4	3	3	50
	Zn	850	160	160	48	200	2500
Major PFAS[f] (mg/kg dry feed basis)	PFBS	0.0005	–	0.0003	–	–	–
	PFDA	0.0028	–	0.0040	–	–	–
	PFHxA	0.0014	–	0.0014	–	–	–
	PFOS	0.0048	–	0.0060	–	–	–
	PFOA	0.0019	–	0.0029	–	–	–
	$\sum PFAS$	0.0165	–	0.0221	–	–	–

[a] Refers to the as-obtained acidic treated biosolids.

[b] Refers to the treated biosolids obtained from the closed-loop process developed in this study (see Fig. 7(A)).

[c] Refers to treated biosolids obtained from deionised water washing post the acid treatment step until neutral pH.

[d] Refers to contaminant-grade biosolids as prescribed in Victoria EPA biosolids management guidelines (EPA Victoria, 2004).

[e] BDL- Below detection limit.

[f] Abbreviations and chemical formulae–

PFBS: Perfluorobutanesulfonic acid, $C_4HF_9O_3S$.

PFDA: Perfluorodecanoic acid, $C_{10}HF_{19}O_2$.

PFHxA: Perfluorohexanoic acid, $C_6HF_{11}O_2$.

PFOS: Perfluorooctanesulfonic acid, $C_8HF_{17}O_3S$.

PFOA: Perfluorooctanoic acid, $C_8HF_{15}O_2$.

stream with dilute metal concentration suitable for recycling, whereas high solids content >5% w/v produced a highly concentrated leachate stream attractive for metal recovery. The leachate stream produced at 5 and 10% solids can be completely recycled at least two times to reach saturation levels of metal ion concentration. However, the recycling of the leachate stream was only attractive at 5% solids; the rapid build-up of ferric iron concentration and increase in solution pH limit the recycling performance of the leachate stream at 10% solids loading. The continuous addition of fresh H_2SO_4 solution as a make-up lixiviant during the partial recycling (85%) of the spent leachate stream enhanced the dilution of the metal ion concentration and suppressed the precipitation of ferric from the solution at 5% solids. The oxidation of dissolved organics by H_2O_2 before the 2-stage NaOH precipitation achieved the optimum metal recovery of ~75% from the concentrated leachate stream. The developed process modestly preserved the organic nutrient to a larger extent in the treated biosolids with about 11% loss of carbon and 19% loss of nitrogen. The leaching of PFAS from biosolids into the aqueous phase was limited under the investigated conditions. The findings of this work provide a framework for developing a hydrometallurgical process for biosolids treatment which may be implemented within the existing wastewater treatment facilities.

CRediT authorship contribution statement

Ibrahim Gbolahan Hakeem: Conceptualization, Methodology, Formal analysis, Investigation, Software, Writing – original draft. **Pobitra Halder:** Validation, Visualization, Data curation, Writing – review & editing. **Shefali Aktar:** Formal analysis. **Mojtaba Hedayati Marzbali:** Validation, Writing – review & editing. **Abhishek Sharma:** Writing – review & editing. **Aravind Surapaneni:** Resources, Supervision, Writing – review & editing. **Graeme Short:** Methodology, Supervision. **Jorge Paz-Ferreiro:** Supervision, Writing – review & editing. **Kalpit Shah:** Conceptualization, Validation, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2023.106044.

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