



Heavy metal dissolution mechanisms from electrical industrial sludge

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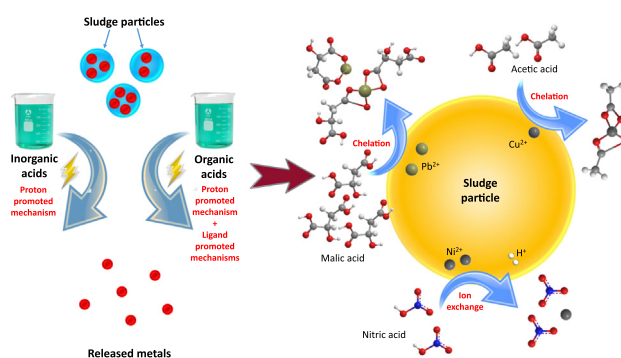
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HIGHLIGHTS

- Metal release of electrical industrial sludge via acid leaching has been studied.
- Efficiency of leaching depends on the characteristics of sludge and the acid type.
- Metal release from sludge is facilitated by proton- and ligand-promoted mechanisms.
- Inorganic acids containing ligands can increase the leaching efficiency of metals.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we investigate the release of heavy metals from sludge produced from an electrical industry using both organic and inorganic acids. Single and sequential extractions were conducted to assess heavy metals in different phases of the sludge. Metal release from sludge was investigated in the presence of three inorganic acids (nitric, sulfuric, and phosphoric) and three organic acids (acetic, malic, and citric) at concentrations ranging from 0.1 to 2.0 mol L⁻¹. Sequential extraction indicated the presence of Cu primarily in the carbonate fraction, Pb in the residual fraction, and Ni in the Fe—Mn oxide fraction. The cumulative release rates of heavy metals (i.e., Pb, Cu, and Ni) by 1.0 mol L⁻¹ of acid increased with the use of the following acids in the order of: malic < sulfuric < acetic < phosphoric < citric < nitric. Acetic acid exhibited the highest release of Cu, at a rate of 72.62×10^{-11} mol m⁻² s⁻¹ at pH 1, and malic acid drove the release of Pb at a maximum rate of 3.90×10^{-11} mol m⁻² s⁻¹. Meanwhile, nitric acid provided the maximum rate of Ni release (0.23×10^{-11} mol m⁻² s⁻¹) at pH 1. The high rate of metal release by organic acids is explained through ligand-promoted mechanisms that enhance the release of metal ions from

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1. Introduction

The accelerated development of industries has contributed to increased generation of contaminants-containing waste. For example, the electrical appliance industry is known to produce large amounts of waste that contain heavy metals (Hossain et al., 2015; Pérez-Belis et al., 2015; Terazono et al., 2006). However, among various types of industrial waste, sludge has been recognized as one of the most challenging to treat (Barakat, 2011; Ghorpade and Ahammed, 2017; Ried, 1988; Tsai et al., 2009). Most of the industrial sludge types are resistant to biodegradation as a result of their low solubility, non-optimal C/N ratio, and presence of high amounts of toxic heavy metals (Azbar et al., 2008). Therefore, landfill disposal is most widely used to handle industrial sludge, although it is not an environmentally friendly approach (Huyen et al., 2016). Nevertheless, anaerobic and aerobic digestion, vacuum filtration, elutriation, use of drying beds and sludge lagoons, wet combustion, atomized suspension, drying and incineration, and centrifugation are widely practiced treatment methods that involve reducing the quantity of final sludge prior to disposal into the ocean (sludge barging) or sanitary landfills (Nemerow, 2010; Al-Harabsheh et al., 2018; Lobato et al., 2015). As an example, galvanic sludge, which is generally produced by the precipitation of rinsing water and spent electrolytes in electrical and electroplating industries, exceeds 1,000,000 metric tons of global waste generation per year (Silva et al., 2008; Ghorpade and Ahammed, 2017). Industrial sludge contains elevated concentrations of heavy metals, particularly Cr, Ni, Zn, Cu, and Pb (Cui et al., 2010). The release of heavy metals into the natural environment through the direct disposal of non-treated or partially treated industrial waste may contribute to human and ecosystem health risks (Tou et al., 2017; Pecht et al., 2018). Therefore, selecting a proper method to treat industrial sludge before disposal is mandatory.

The increasing global demand for metals makes metal recovery from readily-available and continuously generated secondary resources and waste more appealing as compared to treatment and landfill disposal (Shemi et al., 2015). As a result, various kinds of alternative pyro and hydrometallurgical techniques, including bioleaching, alkaline leaching, and acid leaching, as well as combinations of these techniques are increasingly utilized (Seidel et al., 2001; Habashi, 2005; Shemi et al., 2015; Yao et al., 2014). However, pyrometallurgical techniques are associated with disadvantages and limitations due to high energy consumption and the poor quality of end products (Medi et al., 2006).

Among the methods currently in use, acid leaching is commonly utilized for heavy metal recovery due to its wide applicability. Sulfuric acid leaching has been effectively utilized together with electrowinning to recover Cu from galvanic sludge (Huyen et al., 2016). The study by Huyen et al. (2016) emphasized that the use of acid for leaching is more cost effective and efficient than leaching with bases. Vemic et al. (2016) focused on the recovery of heavy metals (i.e., Mo, Ni, and Co) from sludge generated from recycling plants, using several concentrated acids, including sulfuric, nitric, and hydrochloric acids, as well as an acid combination. The greatest recovery of metals resulted from concentrated sulfuric acid, reflecting its capability for leaching due to its strong oxidizing capacity as a diacidic compound. Alternately, Walawalkar et al. (2016) used sulfuric, nitric, and hydrochloric acids to recover rare earth elements from phosphogypsum and found that nitric and hydrochloric acids exhibited better leaching than sulfuric acid. The leaching efficiency is not only dependent on the type of acid used but

also on the type of the raw material or waste used. Although many studies to date have investigated the capacity of inorganic acids for acid leaching, experiments with organic acids are limited (Zhou et al., 2017; Battsengel et al., 2018; Liu et al., 2016). The studies of Hamer et al. (2003) and Rajapaksha et al. (2012) highlight the usability of organic acids for the dissolution of metals from minerals by increasing the rate of dissolution by both ligand-promoted and proton-promoted mechanisms.

As a developing country, industries in Sri Lanka make only minimal efforts for treatment of generated waste due to lack of treatment facilities and associated costs. The electrical appliances industries in Sri Lanka generate large quantities of heavy metal rich sludge. However, the limited availability of treatment facilities leads to the discharge of this sludge directly into surrounding habitats, including wetlands, posing serious threats to the environment and human health (Anjithan et al., 2015). Treating heavy metal-rich waste by acid leaching could be the best option for a developing country like Sri Lanka, because it involves the recovery of heavy metals alongside detoxification. However, industrial sludge types widely vary in terms of physicochemical characteristics, influencing the effectiveness of the treatment methods and processes. Further, due to the variation in chemical composition of various industrial sludges, the effectiveness of different types of acids for acid leaching may also vary. In this regard, an understanding of the types of metals present in the sludge and their fractionation among the different phases of sludge is useful in adopting the most suitable acid type for leaching. Additionally, an understanding of the mechanisms involved in the metal release from sludge can better inform the best and most cost-effective acid treatments for metal recovery. Therefore, the main objectives of this study are to 1) characterize the sludge, 2) determine the release rate of Cu, Pb and Ni by three organic and three inorganic acids to find out the most effective leaching solution, and 3) describe the mechanisms involved in the release of metals.

2. Material and methods

Electrical industrial sludge was collected from the wastewater treatment plant of one of the leading electrical product manufacturing companies in Western Province, Sri Lanka. The sludge was dried at ambient temperature (25–27 °C), mechanically crushed, and sieved through a 1-mm mesh.

2.1. Characterization of sludge

Chemical parameters, including pH, electrical conductivity (EC), available nitrogen and phosphorus, percentage of total organic carbon (TOC), and cation exchange capacity (CEC) were analyzed using the standard procedures presented in Anderson and Ingram (1989). The pH and EC of electrical industrial sludge were determined by analyzing the sludge in liquid suspension with deionized water at a 1:10 ratio. Plant-available nitrogen, phosphorus, and %TOC were estimated by colorimetric methods. To measure the CEC of electrical industrial sludge, an extraction of ammonium acetate was used. From the sludge, 2.0 g was shaken with 20 mL of ammonium acetate solution for 15 min at 100 rpm, and the solution was filtered through a 0.45- μ m syringe filter. The filtrate was analyzed for Na, K, Ca, and Mg using inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCAP 7600 ICP-OES), and the CEC value for electrical industrial sludge was calculated.

Scanning electron microscopy (Hitachi SU6600 Analytical Variable Pressure FE-SEM) was employed to analyze the surface characteristics of sludge particles. Energy-dispersive X-ray spectroscopy (SEM/EDS) was carried out to determine the elemental composition of electrical sludge sample using the same scanning electron microscope.

The structural mineralogy of the sludge sample was determined by the powder X-ray diffraction (PXRD) technique (Rigaku, Ultima IV-Japan). The PXRD patterns were obtained from Cu K α radiation at a wavelength of 1.54056 Å at 40 mA and 40 kV, scanning the range between 2 and 65° (2 θ). Fourier transform infrared spectrophotometry (FTIR), using the Thermo Scientific NICOLET iS10 (USA), was utilized to determine functional moieties present in the sludge particles. FTIR transmission mode was utilized to collect spectra between wavenumbers 4000–400 cm^{−1} at a resolution of 4 cm^{−1} and using 64 repeat scans. The Brunauer-Emmett-Teller (BET) method was employed to estimate the specific surface area of electrical industrial sludge.

2.2. Chemical extractions

2.2.1. Diethylene triaminepentaacetic acid (DTPA) extraction

The DTPA extraction method was utilized to determine the DTPA extractable concentrations of heavy metals, as this extraction is well-suited to determine the plant bioavailable fraction of metals in soil and sediments (Rajapaksha et al., 2012). A total of 20.0 mL of 0.005 mol L^{−1} DTPA and 0.01 mol L^{−1} CaCl₂ in 0.1 mol L^{−1} triethanolamine solution of pH 7.30 was used to extract metals from 10.0 g of air-dried electrical industrial sludge. The solution was shaken for 2 h at 100 rpm and filtered through a 0.45- μ m syringe filter. The bioavailable concentrations of metals in extracted solution were quantified by ICP-OES (iCAP 7600 ICP-OES).

2.2.2. TCLP test

The toxicity characteristic leaching procedure (TCLP) introduced by the United States Environmental Protection Agency (EPA) was employed to determine the ability of toxic metals in sludge to be released into the environment and groundwater. Extraction was done with TCLP extraction fluid # 2 (pH 2.88 $\pm$ 0.05) and a liquid:solid ratio of 20 in polypropylene tubes, using a rotary shaker for 18 h at 30 $\pm$ 2 rpm at ambient temperature (25–27 °C). Solutions were filtered through 0.45- μ m syringe filters and analyzed by ICP-OES (iCAP 7600 ICP-OES) for metals.

2.2.3. Sequential extractions of heavy metals

Sequential extraction for sludge was done through five consecutive extractions (Tessier et al., 1979; Armienta et al., 1996). A sample of 1.0 g of air-dried sludge was taken for the initial extraction step.

Extraction 1 (Exchangeable)

The sludge sample was treated with 20.0 mL of 1 mol L^{−1} magnesium chloride solution (pH 7.0) with continuous agitation for 1 h at ambient temperature (25–27 °C).

Extraction 2 (Bound to carbonates)

Residue that resulted from *Extraction 1* was leached with 20.0 mL of 1 mol L^{−1} sodium acetate (adjusted to pH 5.0 with acetic acid) for 2 h at ambient temperature (25–27 °C) with continuous agitation.

Extraction 3 (Bound to Fe—Mn oxide)

Residue from *Extraction 2* was reacted with 20.0 mL of 0.04 mol L^{−1} hydroxylamine hydrochloride in 25% (v/v) acetic acid with slow and continuous agitation at 90 °C for 2 h.

Extraction 4 (Bound to organic matter)

Residue from *Extraction 3* was treated with 3.0 mL of 0.02 mol L^{−1} nitric acid and 5.0 mL of 30% hydrogen peroxide, which was adjusted to pH 2 with the addition of nitric acid. The solution was heated at 85 °C for 2 h with occasional stirring. Then, a 3.0 mL aliquot of 30% hydrogen peroxide at pH 2 was transferred to the same solution and heated to 85 °C with intermittent agitation for 3 h. Afterwards, the solution was maintained at ambient temperature (25–27 °C), and 5.0 mL of 3.2 mol L^{−1} ammonium acetate in 20% (v/v) nitric acid was mixed. Then, the solution was diluted to 20.0 mL, with continuous agitation.

Extraction 5 (Residual)

From the *Extraction 4* residue, 0.2 g was digested by a microwave digester with 4.0 mL of concentrated nitric acid.

After each successive extraction, the solution was centrifuged for 15 min at 3500 rpm, and the supernatant was filtered through 0.45- μ m syringe filters and analyzed for metals using ICP-OES (iCAP 7600 ICP-OES).

2.3. Heavy metal dissolution with organic and inorganic acids

Acid leaching was done in batch experiments using three inorganic (i.e., nitric, sulfuric, and phosphoric) and three organic (i.e., acetic, malic, and citric) acids. Among the six acids, nitric and acetic are monobasic, sulfuric and malic are dibasic and phosphoric and citric are tribasic. These different acids were selected for leaching experiments in order to determine their effectiveness for heavy metal dissolution and to uncover related mechanisms. All metals were analyzed after the extraction step with ICP-OES (iCAP 7600 ICP-OES).

2.3.1. Solid to liquid ratio

To find the most suited solid to liquid (S/L) ratio for heavy metal recovery from sludge, 2 mol L^{−1} sulfuric and malic acid solutions were used. Three S/L ratios of 20, 60, and 100 g L^{−1} were employed. All the solutions were shaken with a linear shaker at 100 rpm at ambient temperature (25–27 °C) for 12 h.

2.3.2. Release rate and pH dependency

Five concentrations (i.e., 0.1, 0.5, 1.0, 1.5, and 2.0 mol L^{−1}) for each of the six acids were made and extractions were done with each sample of sludge using an S/L ratio of 20 g L^{−1}, which was determined to be the optimal S/L ratio from previous experiments. Each leachate was filtered through 0.45 μ m filters after shaking for 12 h at 100 rpm at ambient temperature (25–27 °C). All the filtrated samples were analyzed with ICP-OES (iCAP 7600 ICP-OES) to find out the released concentrations of metals.

The methodology described in Hamer et al. (2003) was incorporated to evaluate the rate of release of Pb, Cu, and Ni from sludge with varying concentrations of organic and inorganic acids.

$$R_T = K_T a_{acid}^{n_T} \quad (1)$$

where R_T (mol m^{−2} s^{−1}) is the total rate of metal dissolution with the action of a particular acid, K_T (mol m^{−2} s^{−1}) is the rate constant of the particular acid, n is the experimentally determined reaction factor, and a is the activity of the particular acid, based on its concentration.

Similarly, Eq. (2) was used to evaluate the pH dependency of the release rate of the total Pb, Cu, and Ni by a particular acid with the same variables as in Eq. (1).

$$\log R_T = \log k_T - n_T pH \quad (2)$$

Table 1
Chemical properties and elemental composition^a of electrical industrial sludge.

Parameter	pH (1:10)	EC ($\mu\text{s cm}^{-1}$)	Available N (mg kg^{-1})	Available P (mg kg^{-1})	TOC (%)	CEC ($\text{cmol}_c \text{ kg}^{-1}$)	BET ($\text{m}^2 \text{ g}^{-1}$)			
EC = Electrical conductivity, TOC = Total organic carbon, and CEC = Cation exchange capacity.										
Element	C	O	P	Ca	Mg	Si	Al	Fe	Cu	Zn
wt%	37.0	37.4	5.1	10.0	0.2	1.8	1.6	4.6	0.6	1.6

^a Elemental composition was obtained from SEM/EDS.

3. Results and discussion

3.1. Characterization of the sludge

Table 1 summarizes the basic chemical characteristics of electrical industrial sludge. The sludge was slightly alkaline in nature, and this probably resulted from the pretreatment of sludge before release from the industrial wastewater treatment plant or due to presence of carbonate compounds.

The electrical industrial sludge consists of heterogeneous particles, as revealed by SEM images (Fig. 1a(i)). The uneven surfaces of large sludge aggregates were comprised of nano-range (<100 nm) unorganized, minute particles (Fig. 1a(ii)).

The SEM/EDS results also provide elemental composition data of the sludge (Fig. 1b). The electrical industrial sludge was primarily composed of carbon, oxygen, and calcium (37.0, 37.4, and 10.0 wt%,

respectively), while P, Mg, Si, Al, Fe, Cu, and Zn were also present (Table 1). The presence of a relatively high weight percentage of C in the SEM/EDS results reveals the occurrence of organic compounds, which is also supported by the high percentage of total organic carbon observed in the sludge (Table 1). In addition, the occurrence of a high weight percentage of C and Ca indicates the existence of CaCO_3 , which may have contributed to the slight alkalinity of sludge.

The Fig. 2(a) reveals the PXRD pattern that was obtained for electrical industrial sludge. The peaks at 21.94° , 39.32° and 47.45° 2θ indicate Zn in the form of Zn(OH)_2 ; peak at 29.423° 2θ for PbO ; peaks at 32.29° and 36.55° 2θ for PbO_2 and the peaks obtained at 26.64° and 43.148° 2θ are attributed to Fe in the form of Fe_2O_3 . Furthermore, the presence of rare paramelaconite (Cu_4O_3) is indicated by the peak at 43.14° 2θ . Moreover, the intense PXRD pattern at 29.423° 2θ and peaks at 36.55° and 39.39° 2θ show the presence of CaCO_3 and peaks at 20.64° and 33.07° 2θ indicate SiO_2 .

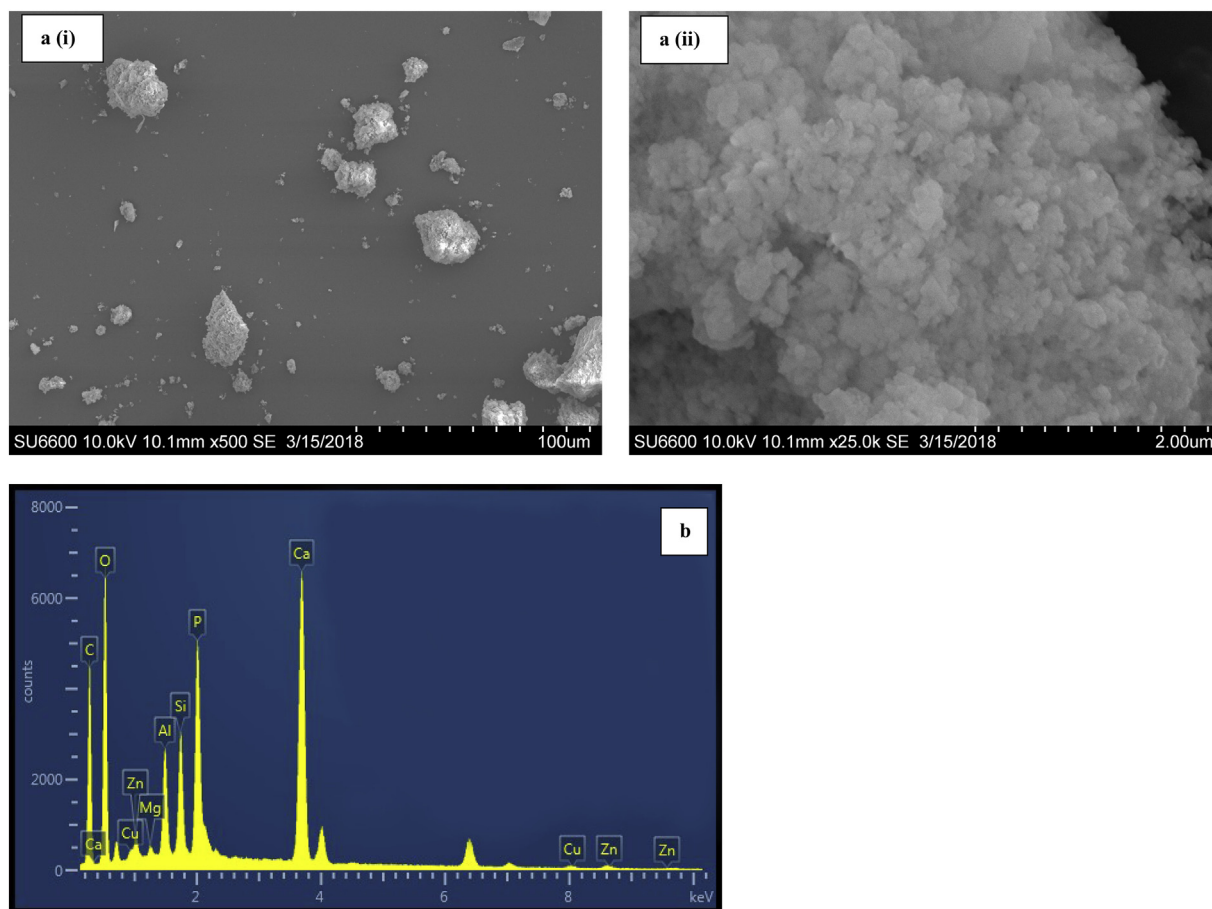


Fig. 1. SEM images (a) and SEM/EDS pattern (b) of electrical industrial sludge; magnification of (i) $\times 500$ and (ii) $\times 25,000$.

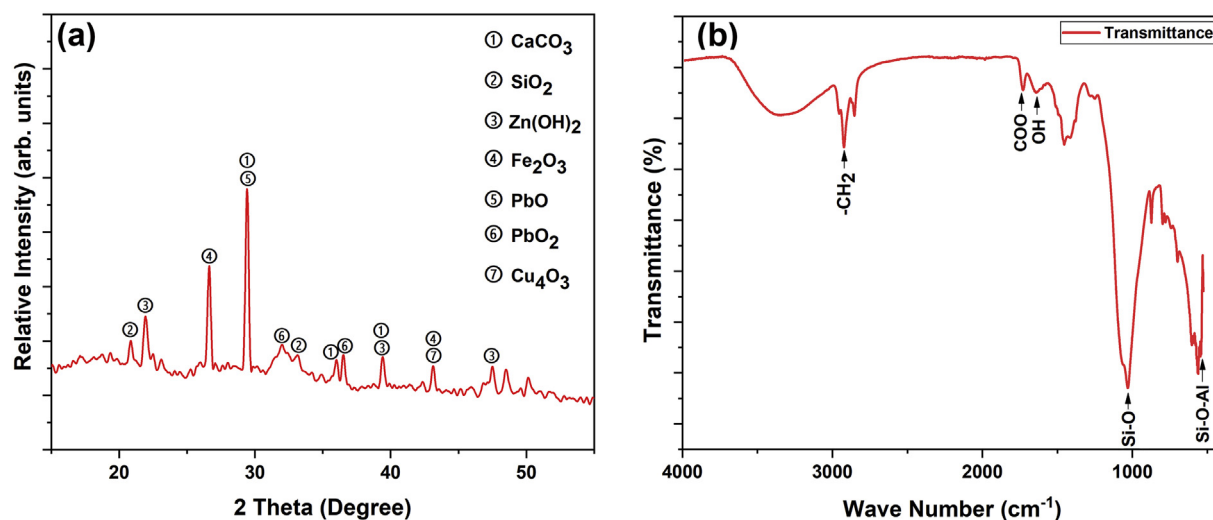


Fig. 2. (a) PXRD patterns and (b) FTIR spectrum for electrical industrial sludge.

The deep band at approximately 1030 cm^{-1} in the infrared spectrum of electrical industrial sludge (Fig. 2b) indicates the symmetric and antisymmetric stretching of Si—O bonds, among tetrahedral groups (Barrera et al., 2017). The small band at 542 cm^{-1} represents the presence of the Si—O—Al bond (Tireli et al., 2015). Similarly, the small band pattern at 1642 cm^{-1} indicates the stretching and bending vibrations of OH (Wang et al., 2018). Moreover, the band at 2922 cm^{-1} is generated by $-\text{CH}_2$, and that at 1727 cm^{-1} represent COO stretching (Lu et al., 2009), revealing that the sludge contains organic matter. Additionally, the broad band in the $3000\text{--}3700\text{ cm}^{-1}$ range represents the presence of moisture (Ali et al., 2015).

3.2. Chemical extractions

The results for single extraction procedures and sequential extractions of electrical industrial sludge are given in Table 2. The highest DTPA extractable metal was Cu (298.7 mg kg^{-1}), whereas the lowest extractable concentration was reported for Ni (1.8 mg kg^{-1}). The DTPA extractable Pb concentration was 2.3 mg kg^{-1} , which was much less compared to the concentration of extractable Cu (0.78%). The DTPA extractable concentration expresses the amount of metal that is bioavailable for plant uptake (Li et al., 2014). Meanwhile, the toxicity characteristic leaching

procedure (EPA: TCLP) helps determine the mobility of hazardous waste, both in organic and inorganic forms. Lead was not detected in the TCLP solution (Table 2). Although the TCLP extraction yielded concentrations of 1.2 and 0.1 mg L^{-1} for Cu and Ni, respectively, neither was considered a RCRA-8, hazardous metal by the US EPA (1992). However, the leaching of Cu and Ni, and their bioaccumulation in biota may pose a risk to human and ecosystem health (Brewer, 2010; Cui et al., 2010; Brocato and Costa, 2017).

In the sequential extraction, the total concentration of Cu from extraction (i) to (v) was $11,384.4\text{ mg kg}^{-1}$, while the total concentrations of Pb and Ni were 1257.8 mg kg^{-1} and 43.8 mg kg^{-1} , respectively. Therefore, the content of Cu in electrical industrial sludge is nine times higher than that of Pb and 260 times higher than that of Ni. The maximum concentration of Cu (7401.0 mg kg^{-1}), which is 65% of the total concentration, was found in the carbonate-bound fraction. Generally, the release rate of a particular metal under acidic conditions is directly influenced by the fraction that is associated with it (Wang et al., 2015). The carbonate-bound fraction is greatly influenced by variation in the pH, and the metal bound to it can be easily extracted by solid-state dissolution (Yang et al., 2019). The study of Han and Banin (1995) found that all the carbonates in calcareous soil with 10–20% of carbonates can be dissolved with a NaOAc-HOAc solution at pH 5.5. Therefore, the total release of metals bound to carbonate fraction can be expected, even with weak acids while the utilization of a strong acid will only increase the rate of dissolution. Thus, the high Cu content found in the carbonate fraction reflects the suitability of acid leaching for Cu extraction compared to the use of other leaching techniques. In contrast, the concentration of Pb was comparatively less (10.2 mg kg^{-1}) in the carbonate-bound fraction, while the greatest Pb concentration (800.6 mg kg^{-1}) was reported in the residual/silicate fraction. In the residual fraction, metals are captured in crystalline assemblages and release into the environment under natural conditions is uncommon. Generally, ordered silicates including, sheet, chain and network silicates, are less susceptible to dissolution with acids due the high strength of the Si—O bond (Terry, 1983). The least amount of Cu was bound to the exchangeable fraction (24.5 mg kg^{-1}), while Pb was not detected in that phase. Nickel was primarily observed as bound to the Fe—Mn oxide and carbonate-bound fractions (20.2 and 18.3 mg kg^{-1} , respectively). Copper, Pb, and Ni occupied individual fractions in the order of: carbonates > Fe—Mn oxides > organic matter > residual > exchangeable for Cu, residual > organic matter > Fe—Mn oxides > carbonates for Pb, and Fe—Mn oxides > carbonates > residual/silicate for Ni.

Table 2
Heavy metals distribution among different fractions of electrical industrial sludge.

Extractions	Fractions	Amount released ^a		
		Pb	Cu	Ni
Single extractions				
0.005 DTPA	Extractable	2.3	298.7	1.8
TCLP extraction	Toxicity	0.0	1.2	0.1
Sequential extractions				
1 mol L ⁻¹ MgCl ₂ (pH 7.0)	Exchangeable	ND	24.5	ND
1 mol L ⁻¹ NaOAc (pH 5.0)	Carbonates	10.2	7401.0	18.3
0.04 mol L ⁻¹ NH ₂ OH·HCl in 25% (V/V) HOAc (90 °C)	Fe—Mn oxides	40.5	2939.1	20.2
0.02 mol L ⁻¹ HNO ₃ , 30% H ₂ O ₂ (85 °C), 3.2 mol L ⁻¹ NH ₄ OAc	Organic matter	406.5	738.7	ND
HF, HClO ₄ , HCl	Residual/silicate	800.6	281.2	5.2
Total concentration from (i) to (v)		1257.8	11,384.4	43.8

^a Released amount of metals from all the extractions are represented in mg kg^{-1} , except concentration for TCLP extraction which is in mg L^{-1} .

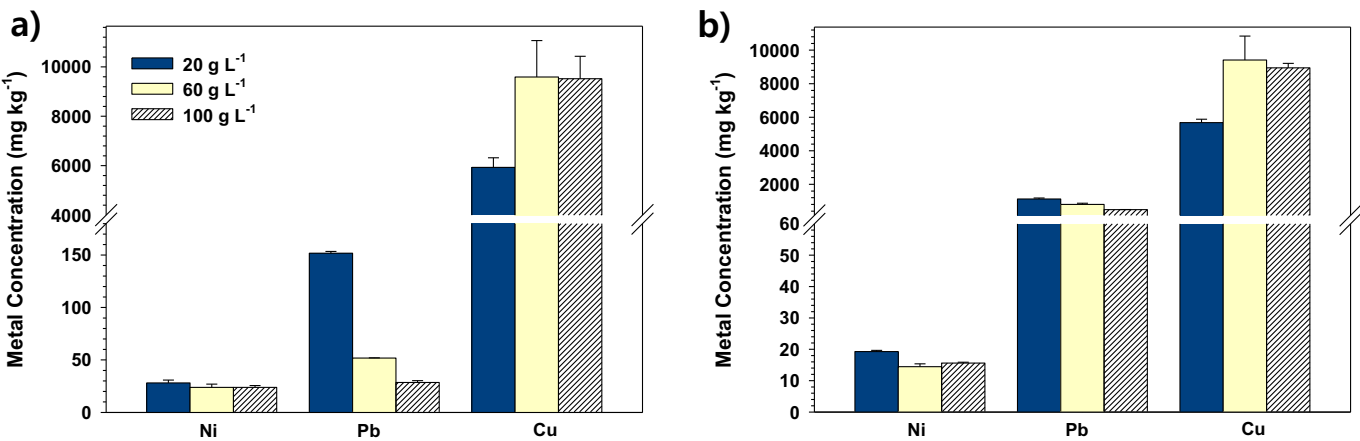


Fig. 3. Optimal solid:liquid (S/L) ratio for metal release from electrical industrial sludge with a) sulfuric and b) malic acid.

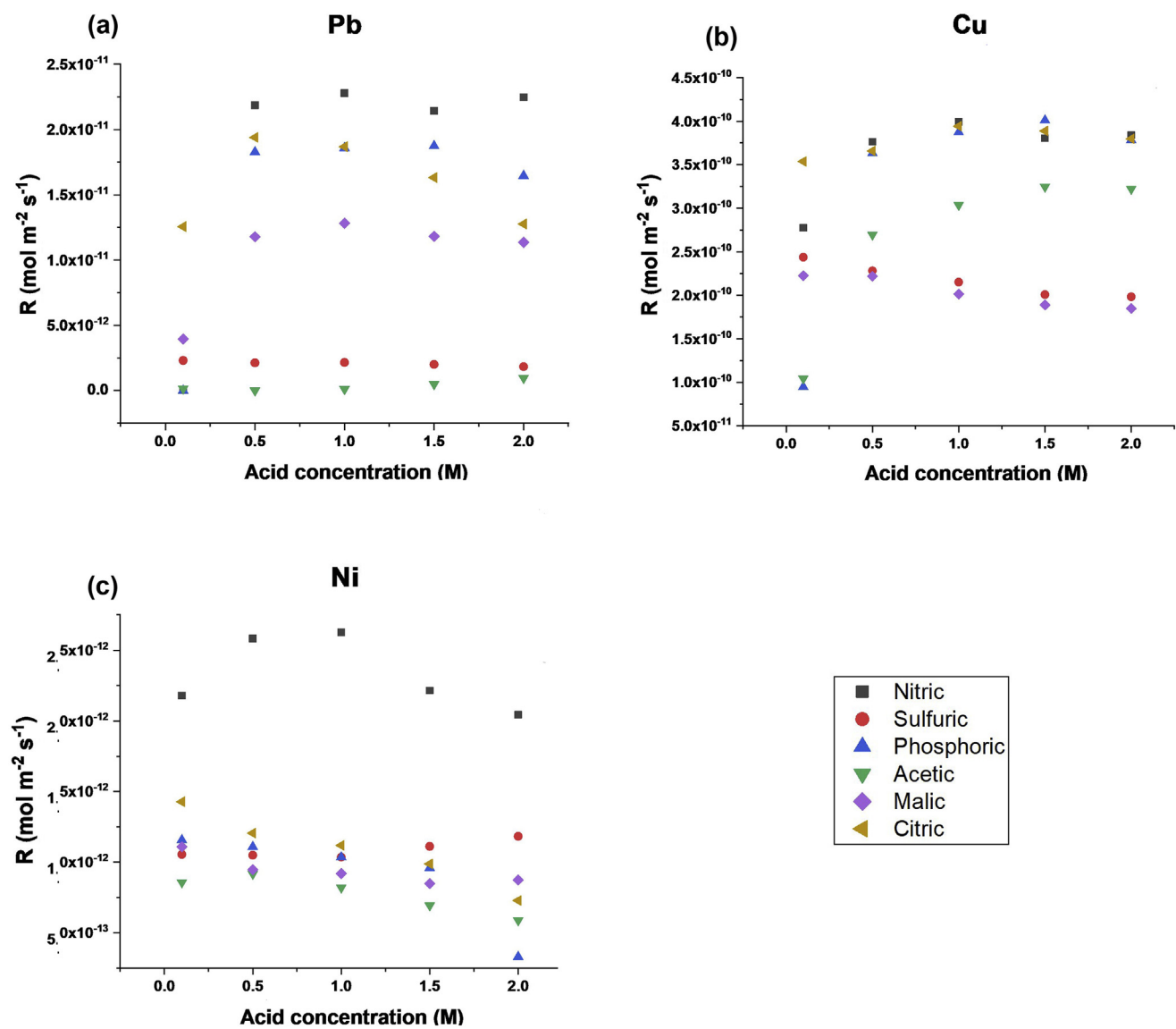


Fig. 4. Release rates for, a) Pb, b) Cu, and c) Ni by different acids under increasing concentrations.

3.3. Inorganic and organic acid extractions

3.3.1. Best solid to liquid ratio

As shown in Fig. 3, the maximum release of Cu was achieved with a S/L ratio of 60 g L⁻¹ for both sulfuric and malic acids (9592.19 and 9413.97 mg kg⁻¹, respectively). As opposed to the release of Cu, the release of Pb reached a maximum at the S/L ratio of 20 g L⁻¹. At that S/L ratio, sulfuric acid was responsible for the release of 151.82 mg kg⁻¹ of Pb while malic acid facilitated the release of 1122.61 mg kg⁻¹ of Pb. Similarly, the release of Ni was highest at a S/L ratio of 20 g L⁻¹ for both acids (28.13 and 19.28 mg kg⁻¹ for sulfuric and malic acid, respectively).

However, the maximum release of Cu by both sulfuric and malic acids was achieved at a S/L ratio of 60 g L⁻¹, while the maximum release of Pb and Ni was observed at 20 g L⁻¹. Moreover, the handling of electrical industrial sludge at high S/L ratios was difficult due to the gluey consistency of the sludge which clogged the filter papers. Therefore, 20 g L⁻¹ was considered as the optimal S/L ratio for the majority of heavy metals and it was used to carry out further experiments.

3.3.2. Release rate

The Fig. 4 shows the effect of the concentration of each acid on the release rates of Pb, Cu, and Ni. Nitric acid was responsible for the maximum release of Pb and Ni. The release of Pb exceeded a rate of 2.0×10^{-11} mol m⁻² s⁻¹ at nitric acid concentrations above 0.5 mol L⁻¹. Similarly, the highest release rate of Ni was governed by nitric acid. All five concentrations of nitric acid, ranging from 0.1 to 2.0 mol L⁻¹, yielded release of Ni above the rate of 2.0×10^{-12} mol m⁻² s⁻¹. The release rates of Cu from electrical industrial sludge by nitric, phosphoric, and citric acids were shown to be comparatively similar at concentrations above 0.5 mol L⁻¹.

Nitric, phosphoric, and citric acids led to considerably higher metal release rates than the other three acids at the concentration of 1.0 mol L⁻¹ (Fig. 5). However, nitric acid at 1.0 mol L⁻¹ concentration yielded the highest release rates for all three metals examined. The cumulative metal release rate from nitric acid was 4.25×10^{-10} mol m⁻² s⁻¹, and the rates for individual metals, Pb, Cu, and Ni were 2.28×10^{-11} ,

3.99×10^{-10} , and 2.63×10^{-12} mol m⁻² s⁻¹, respectively. The sum of the release rates of metals from electrical industrial sludge by 1.0 mol L⁻¹ acid increased in the order of: malic < sulfuric < acetic < phosphoric < citric < nitric.

3.3.3. Assessment of the proton- and ligand-promoted release of metals

It is useful to employ an enhancement factor to compare the rate of dissolution of elements by different acids. Previous studies have shown that metal release from soils and minerals in the presence of organic and inorganic acids is governed by both proton- and ligand-promoted mechanisms (Rajapaksha et al., 2012; Hamer et al., 2003). Both protons and ligands are capable of releasing metals by desorbing them from different fractions of the sludge. Ion exchange is the main proton-promoted mechanism for metal release. Moreover, high concentrations of protons from strong acids can dissolve the matrix associated with metals, resulting in metal release. On the other hand, ligands from inorganic acids comprise of various functional groups which have the capacity to make complexes with metals and facilitate metal release (Neale et al., 1997). Therefore, the total rate of metal release (R_T) is equal to the sum of the rates for proton-promoted release (R_H) and ligand-promoted release (R_L) (Welch and Ullman, 1996).

$$R_T = R_H + R_L \quad (3)$$

Eq. (2) was used to calculate log R_T for the release of each metal by both organic and inorganic acids at pH 1. To do so, the pH of each organic and inorganic acid used under each concentration was calculated by solution H⁺ concentration. The values obtained for R_T at these concentrations of acids were converted to a log scale and plotted against the calculated pH value of each acid at that particular concentration (Fig. 6). Linear fitting was done for resulting curves and rate constant (log K_T) and reaction order (n_T) in Eq. (2) were calculated using the intercept (log K_T) and slope (n_T) of the fitted curves. No ligand was integrated into nitric acid, thus, it was assumed that R_T from nitric acid was only generated from proton-promoted mechanisms (R_H); R_L was calculated using Eq. (3). All the values obtained for log K_T , n_T , R_T , and R_L are presented in Table 3.

At pH 1, the highest rate for Pb release is driven by malic acid (3.90×10^{-11} mol m⁻² s⁻¹). Similarly, malic acid poses the highest

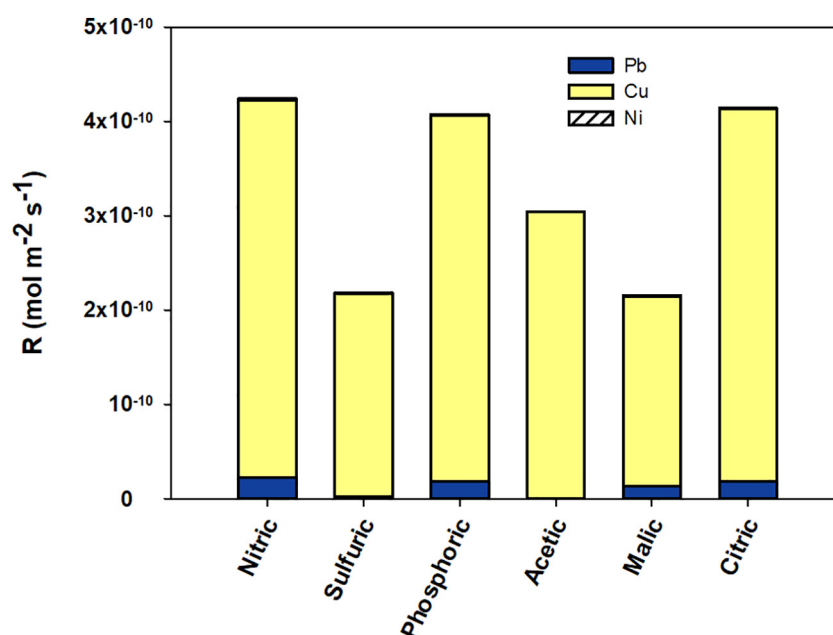


Fig. 5. Cumulative release rates for Pb, Cu, and Ni from electrical industrial sludge in the presence of inorganic and organic acid solutions at 1.0 mol L⁻¹ concentration.

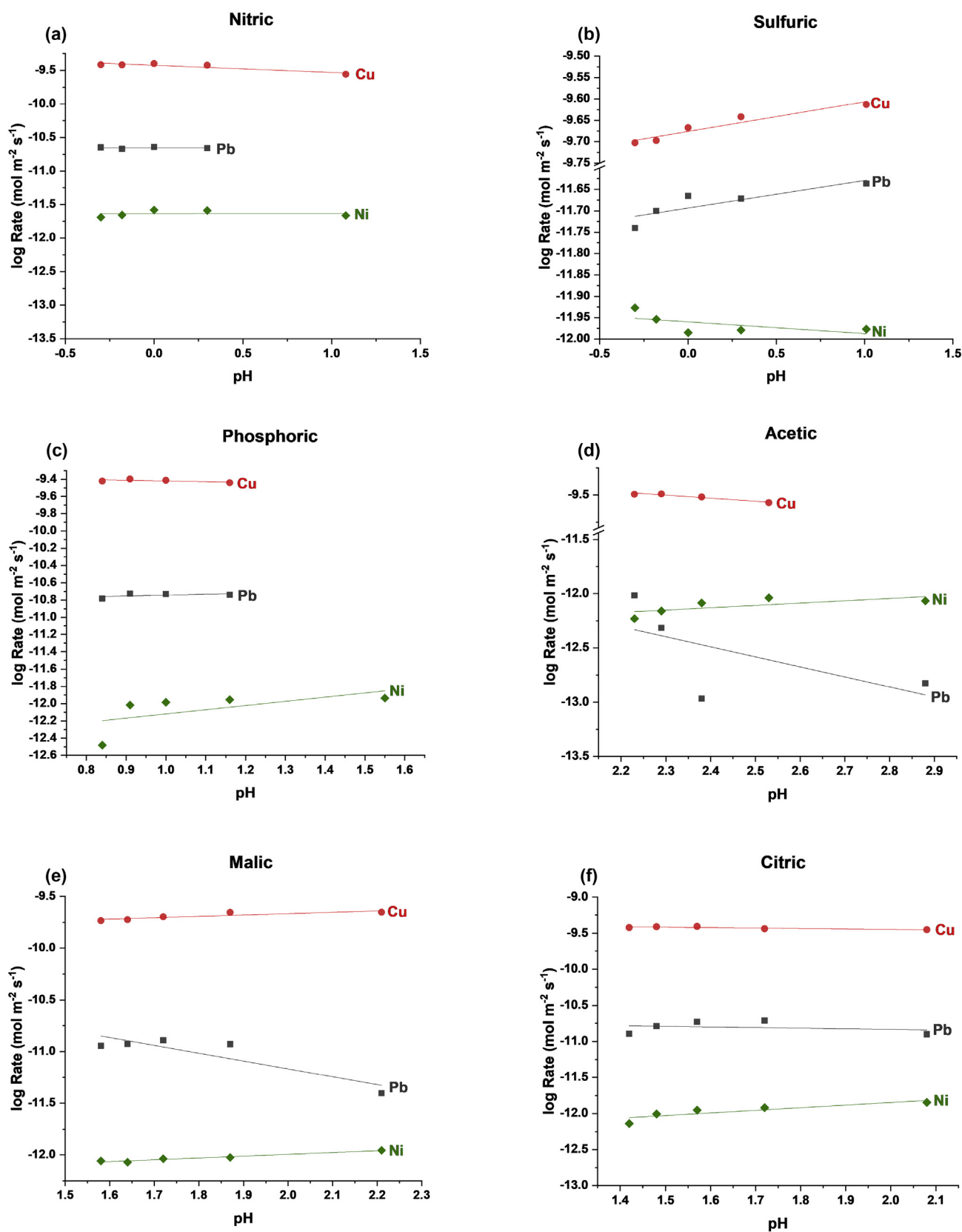


Fig. 6. Log rates of metal released from electrical industrial sludge by different acids (i.e., a) nitric, b) sulfuric, c) phosphoric, d) acetic, e) malic and f) citric) under different pH values.

R_L and R_T/R_H for Pb release. The presence of a high R_T/R_H ratio reveals that the release of Pb by malic acid is driven by ligand-promoted mechanisms rather than proton-promoted mechanisms. Malic acid

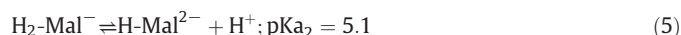
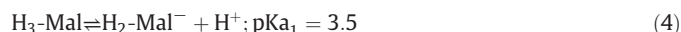
is known to increase dissolving efficiencies of divalent metal ions by chelating them and forming surface complexes (Seo and Kim, 2016; McKenzie et al., 1987). Malic acid has the ability to make

Table 3

Rate constant (K_T), reaction order (n_T), total rate of dissolution (R_T), ligand-promoted dissolution (R_L), and R_T/R_H ratio for Pb, Cu, and Ni released from electrical industrial sludge in the presence of different inorganic and organic acids.

Acid	$\log K_T$	n_T	R_T $\text{mol m}^{-2} \text{s}^{-1} \times 10^{-11}$	R_L	R_T/R_H
Release of Pb					
Nitric acid	-10.66	-0.01	2.18	0.00	1.00
Sulfuric acid	-11.69	0.06	0.23	-1.95	0.11
Phosphoric acid	-10.84	0.10	1.81	-0.37	0.83
Acetic acid	-10.27	-0.92	0.64	-1.55	0.29
Malic acid	-9.65	-0.76	3.90	1.71	1.79
Citric acid	-10.67	-0.08	1.78	-0.40	0.82
Release of Cu					
Nitric acid	-9.42	-0.11	29.48	0.00	1.00
Sulfuric acid	-9.68	0.07	24.74	-4.74	0.84
Phosphoric acid	-9.34	-0.08	38.07	8.59	1.29
Acetic acid	-8.86	-0.28	72.62	43.14	2.46
Malic acid	-9.93	0.13	15.96	-13.52	0.54
Citric acid	-9.32	-0.06	41.36	11.88	1.40
Release of Ni					
Nitric acid	-11.64	0.00	0.23	0.00	1.00
Sulfuric acid	-11.96	-0.03	0.10	-0.13	0.44
Phosphoric acid	-12.61	0.49	0.08	-0.16	0.32
Acetic acid	-12.64	0.21	0.04	-0.20	0.16
Malic acid	-12.34	0.17	0.07	-0.17	0.29
Citric acid	-12.57	0.36	0.06	-0.17	0.27

divalent metal-Mal complexes by acting as a chelator (Seo and Kim, 2016). In this study, the Pb-Mal complex was formed in the presence of Pb^{2+} . The two complexes are produced from the chelating reaction of Pb with malic acid, as Pb-HMal and $\text{Pb}(\text{H}_2\text{Mal})_2$. Moreover, each of the malic acid molecules can release two H^+ ions by a two-step process, as mentioned in Eqs. (4) and (5) (Li et al., 2010), enhancing the further release of Pb by proton-related mechanisms.



However, at pH 1, the lowest rate of Pb release was observed at $0.23 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$, of the reaction with sulfuric acid. Lead is mainly associated with residual/silicate bound fraction (Table 2) and sulfuric acid has a limited reaction with Pb containing silicates due to the solubility limits of sulfates of Pb (Terry, 1983).

Conversely, acetic acid produced the greatest rate of release of Cu ($72.62 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$) at pH 1. The calculated enhancement factor indicates that Cu release is facilitated by both ligand- and proton-promoted mechanisms ($R_L = 43.14 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$ and $R_T/R_H = 2.46$). Ionization of acetic acid releases H^+ (Eq. (6)), facilitating the release of Cu from sludge through proton-promoted mechanisms.



Moreover, acetic acid contains ligands that enhance the release rate of Cu, in a similar manner as in malic acid (Eq. (7)).



The concentration and activity of ligands are proportional to the release rate of metals (Rajapaksha et al., 2012). However, in this study, the release rates of Pb and Cu were promoted in different ways by the ligands from acetic, malic, and citric acids. Therefore, the nature of the ligand played a major role in the release of Pb and Cu from sludge. Moreover, chelating agents such as EDTA (Ethylenediamine tetraacetic

acid), DTPA (diethylenetriamine pentaacetic acid) and NTA (nitriloacetic acid) have been shown to have better performance in the removal of heavy metals from waste materials by making strong metal-ligand complexes (Zhang et al., 2015a). Among them, EDTA is the most widely used chelating agent and studies of Zhang et al. (2015b) and Zhang et al. (2016) have shown the high affinity of EDTA for Cu^{2+} in the removal of Cu from anammox granules. However, NTA has been reported as class II carcinogen while DTPA has been identified as a toxicant with potential carcinogenic activity (Zou et al., 2009). Although, EDTA has no known carcinogenic effects, it can induce cytotoxicity and weak genotoxicity. Moreover, EDTA has been reported to cause reproductive and developmental anomalies in animals after oral exposure (Lanigan and Yamarik, 2002). However, organic acids such as acetic and citric acids are considered as non-toxic and renewable compounds which can be easily biodegraded (Halpern et al., 2014; Chamorro et al., 2001). Therefore, the use of organic acids to chelate metals in sludge can be considered a feasible and effective technique when considering environment and human health risks. Moreover, unlike other chelating agents, further enhancement of metal removal can be expected by proton-related mechanisms resulting from the use of organic acids.

Unlike Pb and Cu, nitric acid facilitated the highest rate of release for Ni, at the rate of $0.23 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$. In contrast to the release of the other two metals studied, the release of Ni was not attributed to ligand-promoted mechanisms. As an inorganic acid, the nitric acid molecule does not contain chelating groups that assist ligand-promoted mechanisms in the release of Ni. In an aqueous solution, the complete ionization of nitric acid takes place, releasing H^+ ions as shown in Eq. (8). This results in ion exchange, a proton-promoted mechanism, releasing Ni from electrical industrial sludge.



4. Conclusions

This study demonstrates that electrical industrial sludge is mainly composed of Cu and Pb as heavy metals, and Ni is also present in small concentrations. Copper is predominantly found in the carbonate-bound fractions, emphasizing the feasibility of the acid leaching technique for recovering Cu from electrical industrial sludge. Lead, on the other hand, is mainly confined to the residual fraction, while Ni is primarily bound to the Fe—Mn oxide-bound fraction. The optimal S/L ratio for maximum release of Cu is 60 g L^{-1} for both sulfuric and malic acids. In contrast, 20 g L^{-1} resulted in the greatest release of Pb and Ni by sulfuric and malic acids. Maximum cumulative rates of release for Pb, Cu, and Ni at 1.0 mol L^{-1} acid concentration were facilitated by nitric acid and it is the optimum leaching solution for separation of all three examined metals from the sludge. At pH 1, the highest rate of release for Pb was with malic acid, while acetic acid was responsible for the highest release observed for Cu. The high rate of metal release by organic acids is attributed to the ligand-promoted mechanisms, which enhance the release of metal ions from the sludge forming complexes. In contrast to Pb and Cu, the rate of release for Ni was highest with nitric acid at pH 1, indicating proton-promoted mechanisms, mainly ion exchange. Therefore, knowledge of the release mechanism of heavy metals from waste materials is useful for determining the best acid type and concentration for efficient and effective recovery of metals. Further studies targeting different types of industrial sludge with dissimilar characteristics are necessary to reveal the exact mechanisms of metal release by acids.

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