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Comparative efficacy of electrokinetic and static leaching for selective metal recovery and nutrient release from porphyry cu tailings

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ABSTRACT

This study presents the first systematic comparison of electrokinetic (EK)-assisted and static leaching (SL) for the selective extraction of Cu from porphyry Cu tailings, while also assessing the potential biotoxicity and nutrient release within treated residues. Twelve lixiviants were tested, comprising: inorganic acids, organic acids, chloride solutions and deep eutectic solvents (DES). EK consistently enhanced metal leaching due to the additional mass transfer under a superimposed voltage gradient. Citric acid (0.5 M) proved most effective, achieving 60.8% Cu recovery with EK (2 V/cm) over 22 days, compared to 41.9% with SL. EK also markedly improved DES performance; $CaCl_2$:ethylene glycol achieved a 25-fold increase in Cu recovery (17.6% vs. 0.7% for SL), demonstrating that EK can substantially mitigate mass-transfer constraints in such viscous solvents. Principal Component Analysis showed greater variability under EK, indicating lixiviant-specific amplification of leaching efficacy. Whilst EK-assisted leaching increased the concentration of actually bioavailable toxic metals within treated residues, suggesting short-term ecological risks if such metals are not effectively captured, it simultaneously increased the bioavailability of plant-available nutrients: Fe, K, Mg and P, whilst also substantially decreasing the total potentially bioavailable concentration for all metals. Overall, these findings show that EK-assisted leaching, particularly when combined with citric acid, offers a potentially transformative approach for target metal recovery from porphyry Cu tailings whilst also lowering their total potential long-term ecological impact and enhancing nutrient availability.

1. Introduction

Metal mining is essential to ensure a sufficient supply of metals to support modern society and facilitate the green energy transition [1,2]. Despite this necessity it can also generate substantial social and environmental impacts, particularly due to the production of vast quantities of mine tailings [3], the residual solids left after ore processing.

Tailings constitute the largest waste stream worldwide, estimated at 13 billion tonnes annually [4], and are typically stored in tailings storage facilities (TSFs), which pose substantial environmental impacts, including dust emissions, leaching of toxic metals and the sudden release of material due to structural failure [5]. Whilst this can present a substantial long-term liability, they also offer a valuable secondary metal resource. This presents a major global opportunity to reduce primary resource consumption [6].

However, there are several persistent challenges associated with

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conventional recovery of metals from tailings via physical excavation and ex situ treatment [7]. These include the high energy costs for transportation, the substantial storage space required for material handling and to store post-treated residues, and the need for expensive mineral beneficiation facilities [8]. Instead, the recovery of target metals from mine tailings whilst it remains in situ (to simultaneously rehabilitate and recover metals of economic value), via the injection and circulation of a suitable lixiviant, known as in situ leaching (ISL), is a highly promising emerging area of interest [8–11]. Several major technical and economic challenges remain, which has limited its adoption. Specifically, tailings often exhibit low hydraulic conductivity, prevalent preferential flow and anisotropic hydrogeological behaviour, making it difficult to ensure effective lixiviant exposure to the target minerals and capture of the pregnant leachate.

To overcome this, there has been growing interest recently in the potential integration of electrokinetics with ISL (EK-ISL). This novel approach comprises the application of an imposed voltage gradient over a target location, which when combined with the injection of a suitable lixiviant, facilitates the in situ leaching and recovery of leached ions, via electromigration and electroosmosis, at recipient electrodes [12]. Therefore, whilst conventional ISL can only transport a lixiviant along an imposed hydraulic gradient, EK-driven ISL facilitated via a direct electric force which is less susceptible to prevailing hydrogeology, enabling enhanced movement of ions and fluids through materials of low hydraulic conductivity and even across preferential flow paths.

To date EK-ISL has received some interest for contaminated land treatment [13], primary ore mining [12,14–16], and industrial waste valorisation [17–19]. However, its application for the treatment of mine tailings remains largely unexplored and limited to only a few studies [20–23]. Whilst such work has provided some detailed insight into the EK-ISL process, to date this has only been undertaken for a relatively limited number of lixiviants and across a relatively restricted EK parameter range (voltage gradient, electrode spacing, etc.). Fundamental knowledge gaps, therefore, persist particularly regarding how EK interacts with lixiviants of differing chemistry and the mineral substrates on which they react, as well as the potential biotoxicity of treated residues. Critically, no studies to date have systematically compared electrokinetically assisted leaching of mine tailings across multiple lixiviant chemistries under identical conditions, while simultaneously linking metal recovery performance with the post-treatment environmental behaviour of the residues. This integrated understanding is essential for assessing the overall viability of EK leaching processes, which, in order to be successful, must have a dual objective of recovering economically valuable metals and rehabilitating the tailings material.

This study provides a broad mechanistic understanding of how EK influences the leaching behaviour and bioavailability of porphyry Cu tailings, which are one of the most abundant and problematic waste streams worldwide [24,25]. To achieve this, we investigated EK performance with lixiviants spanning the major chemical classes: inorganic acids, organic acids, chloride solutions, and deep eutectic solvents (DES). Whilst some of these lixiviant-EK systems have been tested individually [22,23], to the best of our knowledge, no study to date has systematically compared their relative behaviour. To extend these findings, we also evaluated EK-assisted leaching alongside conventional static leaching (SL) to elucidate the mechanisms driving differences in metal recovery kinetics, lixiviant efficiency, and post-treatment metal bioavailability. The work, therefore, has a dual aim: (1) to provide fundamental mechanistic insights into the selective recovery of target metals from mine tailings, and (2) to assess how EK treatment influences the bioavailability of residual tailings. By integrating electrokinetic transport, lixiviant chemistry, and environmental risk indicators within a single experimental framework, this study demonstrated the potential of EK-based tailings treatment as both a combined strategy for metal recovery and environmental rehabilitation.

2. Methodology

2.1. Porphyry cu tailings sample collection

The porphyry Cu tailings used in this study were sourced from TSF1 at the Philex Padcal Mine (Benguet, Philippines, 16.283894°N, 120.65525°E). TSF1 is a valley-infilling TSF deposited between 1971 and 1981 and contains approximately 85 Mt. of material [8]. A bulk sample of approximately 5 t was excavated from beneath the surface weathered zone (0.5 m), air-dried, manually homogenised and then sieved to a particle size less than 2 mm. Representative subsamples were then collected for use herein using coning and quartering.

2.2. Leaching experiments

A conventional three-compartment high-density polyethylene (HDPE) reactor (2 cm thickness) [26] was used for both EK and SL experiments (Fig. 1). Compartments I and III had identical inner dimensions (L = 5 cm, W = 10 cm and H = 10 cm) and housed the lixiviants. Compartment II (L = 2.5 cm, W = 10 cm and H = 10 cm), contained the tailings sample. Compartment I and III were separated from compartment II by 0.45 μm polytetrafluoroethylene (PTFE) membrane (MPTL270045, Microlab Scientific Co., Ltd., China) and cation exchange membrane (CAT, N4110, Mianyang Prochema Commercial Co., Ltd., China), respectively. For the EK experiments platinum-coated titanium mesh electrodes (10 cm × 9 cm × 0.1 cm) were positioned 2.5 cm from the membranes and connected to a DC power supply (Farnell, MP710503, UK).

Two leaching approaches (SL with and without EK superimposed), were each conducted using twelve lixiviants: inorganic acids (nitric, sulfuric and hydrochloric), organic acids (citric, acetic, malonic), chlorides (sodium chloride, ferric chloride), and DES (Table 1 and Table S1). Each lixiviant had a concentration of 0.5 M, except ferric chloride where 0.16 M was used because it equates to 0.5 M chloride, and DES were undiluted to maintain their non-aqueous composition.

For each leaching test, the tailings sample (200 g) was loaded into compartment II, gently tamped using a HDPE panel to ensure a flat

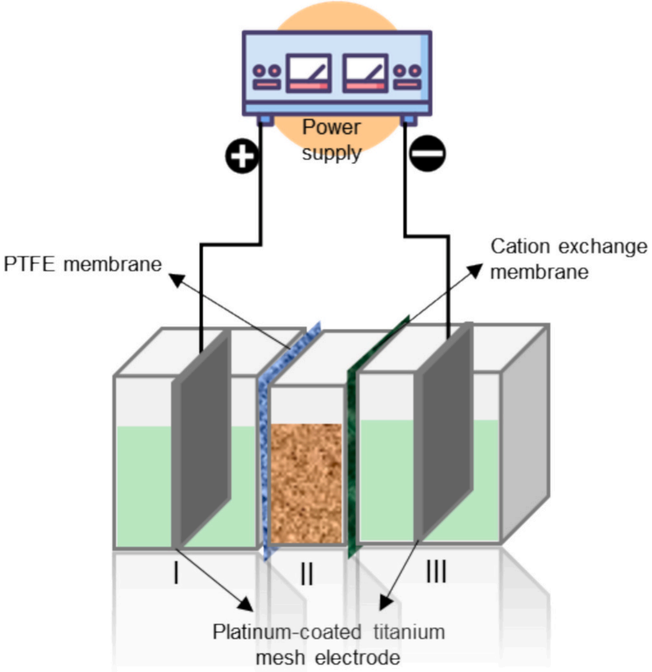

Fig. 1. Experimental setup for all EK leaching experiments (SL experiments were the same except the DC power supply was not connected).

Table 1
Conditions applied in the EK and SL (no voltage gradient) experiments.

Studied Lixiviant	Concentration(M)	EK experiment			SL experiment	
		No.	Voltage gradient (V/cm)	Duration (d)	No.	Duration (d)
MilliQ-water	–	EK1	2	7	SL1	7
Sulfuric acid	0.5	EK2	2	7	SL2	7
Nitric acid	0.5	EK3	2	7	SL3	7
Acetic acid	0.5	EK4	2	7	SL4	7
Citric acid	0.5	EK5	2	7	SL5	7
Malonic acid	0.5	EK6	2	7	SL6	7
Sodium chloride	0.5	EK7	2	7	SL7	7
Hydrochloric acid	0.5	EK8	2	7	SL8	7
Ferric chloride	0.16	EK9	2	7	SL9	7
Betaine/ Glacial acetic acid (1:4)	Molar ratio	EK10	2	7	SL10	7
Betaine/ Glacial acetic acid/ Phosphoric acid (1:4:1 wt%)	Molar ratio	EK11	2	7	SL11	7
$CaCl_2$/ Ethylene glycol (1:1)	Molar ratio	EK12	2	7	SL12	7
Citric acid	0.5	EK13	2	22	SL13	22
Ferric chloride	0.16	EK14	2	22	SL14	22

surface and a bulk density of 1.6 g/cm^3 (consistent with the field-measured bulk density of the tailings) and then fully saturated with each lixiviant (40 mL). Lixiviant was also added to compartments I and III until the liquid level equilibrated with the tailings surface in compartment II (total lixiviant volume used was 500 mL). The SL and EK experiments were identical except that a DC voltage gradient, fixed at 2 V/cm between the two electrodes, was applied for the latter. Daily resupply of Milli-Q water (18.2 MΩ·cm) was performed to Compartments I and III to compensate for EK driven hydrolysis and evaporation and to maintain fluid levels with the tailings surface in compartment II.

Two timeframes were applied for the SL and EK experiments. A 7-day duration was used for the initial screening of 12 lixiviants to identify those that reacted most rapidly and efficiently with the tailings. Subsequently, a 22-day duration was employed for the highest performing lixiviants (experiments 13 and 14) to better understand their leaching behaviour and to evaluate changes in residual biotoxicological risks over time (Table 1). The 22-day timeframe was chosen based on preliminary observations that, under the applied voltage in EK experiments, the current flow decreased to near-zero, indicating completion of the EK-driven metal recovery. Similarly, for the SL systems, during this period the electrical conductivity in compartments I and II reached steady-state values, indicating the cessation of leaching had occurred. At the end of each 7 or 22 day experiment, a liquid sample was collected from compartments I and III and then filtered using a 0.45 μm PTFE filter and prepared for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Agilent 5110) analysis (to determine the leaching efficiency of Al, Cu, Ca, Fe, Mn, K, Mg, P, S, V and Zn from the tailings). The treated Cu tailings from SL1–12 and EK1–12 (Table 1) were oven-dried at 30 °C and homogenised for analytical characterisation (Section 2.3). The treated tailings from EK13–14 and SL13–14 were first evenly divided into near-anode, middle and near-cathode sections before being dried and homogenised for analysis. The electrodes and membranes at the end of the experiments were immersed in 5 M and 1 M HNO_3, respectively, to dissolve all precipitated metals prior to analysis. All chemicals used were analytical grade.

2.3. Characterisation and analysis

Total concentrations of notable elements (Al, Cu, Fe, Mn, Ca, K, Mg, Na, P and S) in untreated and treated tailings were determined via ICP-OES after four-acid digestion (hydrofluoric, hydrochloric, nitric and perchloric acids). Metal availability and chemical fraction was assessed using the Bureau of Reference (BCR) sequential extraction method [27] (Table S2). The saturated moisture content of tailings was determined gravimetrically by gradually adding water to a known mass of dry tailings until saturation, then calculating the ratio of water mass to dry tailings mass. The crystalline structure of the untreated tailings was analysed using X-ray diffraction (XRD, Bruker D6 Phaser, Benchtop), while quantitative mineralogical composition was determined via Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN 4300). Bioavailable metal concentrations within the as-received tailings, EK-treated and SL-treated tailings were determined according to ISO 21268-2:2019 (hereafter denoted "actually bioavailable", using the 0.001 M $CaCl_2$ method) and ISO 17586:2016 (hereafter denoted "potentially bioavailable", using the 0.43 M HNO_3 method). Accordingly, the term "potential biotoxicity" is used throughout this manuscript to describe bioavailability-based proxy indicators of possible biological effects, rather than directly measured ecological toxicity. For the actually bioavailable concentration test, the pH and redox potential of the resulting eluent were measured using a multi-parameter probe (HI-991301, Hanna Instruments) [28]. The actual bioavailability represents the aqueous phase metal fractions, namely those that are in pore water, including dissolved, free and complexed ions, and thus constitute the fraction which is most readily available for uptake by plants and other organisms. The potential bioavailable represents the maximum concentration which may be released from the tailings into the tailings pore water under environmental conditions. This includes elements which are bound to cation exchange sites and those within acid soluble salts. To simulate ongoing environmental leaching, or the controlled washing of the treated tailings to rehabilitate the material, three successive 0.001 M $CaCl_2$ leaching cycles on treated tailings were performed. All procedures and measurements were performed in triplicate. The calculations for metal recovery rate, electrical energy consumption and bioavailable concentrations are shown in supplementary information.

3. Results and discussion

3.1. Characteristics of tailings sample

The total concentration of Al, Cu, Fe, Mn, V, Ca, K, Mg, P, and S) and geochemical composition of the tailings are displayed in Table 2 and Fig. 2. Notably, Al (79,000 mg/kg), Cu (1290 mg/kg), and Ti (4330 mg/kg) substantially exceeded levels typically reported in urban areas, natural sediments, and mining-impacted sediments [29,30]. BCR sequential extraction measurements (Fig. 2a) revealed Ti as predominantly within the residual fraction, indicating minimal environmental mobility, whereas Cu has the highest non-residual proportions (20% exchangeable, 12% reducible, 28% oxidisable), followed by Mn (10% exchangeable and 10% reducible). Zn showed smaller but notable labile fractions (5% exchangeable and 7% reducible). V, Fe, and Al were 97–99% residual, with minor contributions to the mobile fractions. The non-residual proportions of metals could pose potential ecotoxicological risks to the surrounding environment but also present opportunities for metal (especially Cu) recovery. In addition, essential nutrient elements (K, Na, P and S) surpassed concentrations typically recorded for agricultural soils [30], offering a potential role in supporting rehabilitation of the tailings provided they are not present at phytotoxic levels. XRD analysis (Fig. 2b) did not detect any crystalline Cu mineral phase, with quartz and aluminosilicates being the most dominant phases. This result was corroborated with the QEMSCAN analysis (Fig. 2c and d) which showed that the tailings are predominantly composed of plagioclase

Table 2
Characteristics of the tailings sample.

Parameter		Minimum value	Maximum value	Mean value	SD
pH_{CaCl2}		6.40	6.56	6.51	0.04
Electrical conductivity (mS/cm)		2.43	2.59	2.55	0.12
E_h (mV)		37.2	45.1	39.3	1.79
Saturated moisture (%)		18.3	19.4	18.8	0.57
Concentration	Al	77,800	81,900	79,000	1340
	Cu	1160	1470	1290	113
(mg/kg)	Ca	22,300	25,100	23,300	947
	Fe	75,100	81,500	78,300	2030
	Mn	812	939	862	46.2
	Ti	4090	4620	4330	216
	K	7620	8880	8200	433
	Mg	26,400	29,800	27,900	1310
	Na	27,800	28,700	28,100	278
	P	324	495	416	63.3
	S	615	2740	1100	659
	V	307	348	333	22.1
	Zn	63.7	71.6	68.1	3.07

(40.6 wt%), a feldspar mineral group spanning the compositional range from albite ($NaAlSi_3O_8$) to anorthite ($CaAl_2Si_2O_8$), and quartz (21.4 wt %). A minor concentration of chalcopyrite (0.3 wt%) was detected.

3.2. Metal leaching behaviour under electrokinetic and static leaching

Fig. 3 shows the recovery efficiencies of major metals (Al, Cu, Fe, Mn, Mg and K) from the tailings sample after 7 days of either SL or EK treatment. A substantial difference was observed, with the EK treatment consistently achieving higher metal recovery. EK treatment using Milli-Q water and sodium chloride both resulted in only a minor improvement: Cu recovery increased by 1.2% (0.01% in SL to 1.2% in EK) and 0.8% (1.7% in SL to 2.5% in EK) respectively. Given they are circumneutral pH, this slight improvement is attributed to anode-driven acidification (Anode reaction:$2H_2O - 4e^- = 4H^+ + O_2$) which can promote dissolution of acid-soluble minerals, such as carbonates.

In contrast, treatments with 0.5 M sulfuric acid, nitric acid or hydrochloric acid under EK resulted in moderate improvements in Cu recovery, increasing by 16.7% (21.9% in SL to 38.6 in EK), 14.2% (16.7% in SL to 30.9% in EK), and 8.1% (23.0% in SL to 31.1% in EK), respectively. While a similar minor contribution from EK-driven anodic acidification of the tailings, but also this substantial enhancement is attributed to EK-enhanced mass transfer mechanisms – particularly electromigration and electroosmotic flow, which remove surface passivation and facilitate the movement of metal ions away from mineral surfaces during the leaching process.

Despite their weaker acidity compared to mineral acids, EK treatments using 0.5 M citric acid and malonic acid yielded even greater improvements in Cu recovery: 24% (22.4 in SL to 46.4% in EK) and 22.6% (23.1% in SL to 45.7% in EK), respectively. Such behaviour was also recorded for other metals, notably Al, Fe and Mn. These findings align with previous studies that have reported EK-driven enhancements in metal leaching [31–33], however, the specific mechanisms remain unclear.

When EK was applied, Cu recovery followed the order: ferric chloride (0.16 M, 50%) > citric acid (0.5 M, 46.5%) > malonic acid (0.5 M, 45.7%) > sulfuric acid (0.5 M, 38.6%). In contrast, under SL conditions, the order was: malonic acid (0.5 M, 23.1%) > hydrochloric acid (0.5 M, 22.9%) > citric acid (0.5 M, 22.4%) > sulfuric acid (0.5 M, 21.8%). These results highlight the substantial, yet variable, enhancement of metal leaching for each lixiviant under EK.

Ferric chloride (0.16 M) is well documented as being susceptible to surface passivation of chalcopyrite under SL conditions, due to the formation of sulphur-containing layers on mineral surfaces (Eq. 4) [34], which may explain the substantially lower Cu recovery (10.7%) when EK was not applied. In contrast, when EK is superimposed passivating by-products, such as polysulfides, are actively transported away from the mineral surface via electromigration and electroosmotic flow.

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S \tag{4}$$

All three DES formulations tested were largely ineffective for Cu recovery under SL conditions, with 3.7%, 3.5% and 0.72% exhibited by betaine/acetic acid, betaine/acetic acid/phosphoric acid and $CaCl_2$/ethylene glycol, respectively. This low recovery is attributed to their relatively weak acidity (moderate pKa) and relatively low oxidising ability, as well as their high viscosity, which is likely to have inhibited the diffusion of reactants (e.g., H^+ ions) into the tailings and restricted the transport of leached Cu ions from the tailings into the effluent chambers [35,36]. Yet, when EK was applied, Cu recovery improved to 8.7%, 6.8% and 17.6% by betaine/acetic acid, betaine/acetic acid/phosphoric acid and $CaCl_2$/ethylene glycol, respectively, highlighting the strong capacity of EK to enhance mass transfer within such viscous lixiviants. This is also in alignment with previous studies which have shown that electrooxidation of minerals in DES can lead to the faster dissolution and recovery of metals from ores [37–39]. In these cases, it was the electrochemistry of the anion (S^{2-} and S_2^{2-}) which enables the solubilisation of the metal.

Principal component analysis (PCA) was conducted quantify the differential impact each lixiviant has on metal recovery (Al, Cu, Mn, Fe, Mg and K) under both EK and SL conditions (Fig. 4). The first two principal components collectively explained 94.7% of the total variance in metal recovery rates, with PC1 accounting for 85.1%. This dominant variance along PC1 reflects the pronounced difference in recovery efficacy between EK and SL treatments. Strong positive associations of Cu, Mn and Fe with PC1 corresponded to markedly higher recovery when EK was applied, highlighting the overriding influence of treatment method over lixiviant-specific performance. The close clustering of Cu, Mn and Fe along the positive PC1 axis, suggests similar recovery behaviour under EK. The larger spread of the EK treatment cluster in the PCA indicates greater variability in metal (Al, Cu, Mn, Fe, Mg and K) recovery, likely due to the dynamic mass transfer processes facilitated by EK – including electromigration and electroosmosis – which enhance ion mobility and promote continuous leaching. Notably, Mn recovery was strongly associated with EK3 and EK8, while Cu, Fe, and Al recovery were more closely linked to EK2, EK5, and EK6.

Overall, these results highlight that each lixiviant exhibits distinct behaviour in mobilising specific metals, depending on its chemistry and ability to react with host mineral phases, effects that are, in turn, differentially amplified under EK conditions.

3.3. Potential biotoxicity and nutrient release in treated tailings

Fig. 5a and b show the leached elements within the untreated and EK or SL treated tailings samples due to their exposure to 0.001 M $CaCl_2$ (ISO 21268-1:2019), which is a proxy for their 'actually bioavailable' fraction under natural conditions. This fraction is typically considered to encompass elements already in pore water, including dissolved, free and complexed ions, and those within solid phase minerals which are highly susceptible to leaching, thus constituting the fraction which is most readily available for biological uptake by plants and organisms.

The untreated tailings had very low 'actually bioavailable' concentrations of Al (0.075 mg/kg), Cu (0.057 mg/kg) and 0 mg/kg for Fe and Mn (below detection limit). Following EK treatment, however, this reached up to 1080 mg/kg of Al (using citric acid), 1400 mg/kg of Fe (using citric acid), 437 mg/kg of Cu (using ferric chloride), 92.9 mg/kg of Mn (using ferric chloride) in the treated tailings. In comparison, the SL treatment led to maximum concentrations of 707 mg/kg of Al (using malonic acid), 1040 mg/kg of Fe (using citric acid), 374 mg/kg of Cu (using ferric chloride), 51.1 mg/kg for Mn (using ferric chloride). The

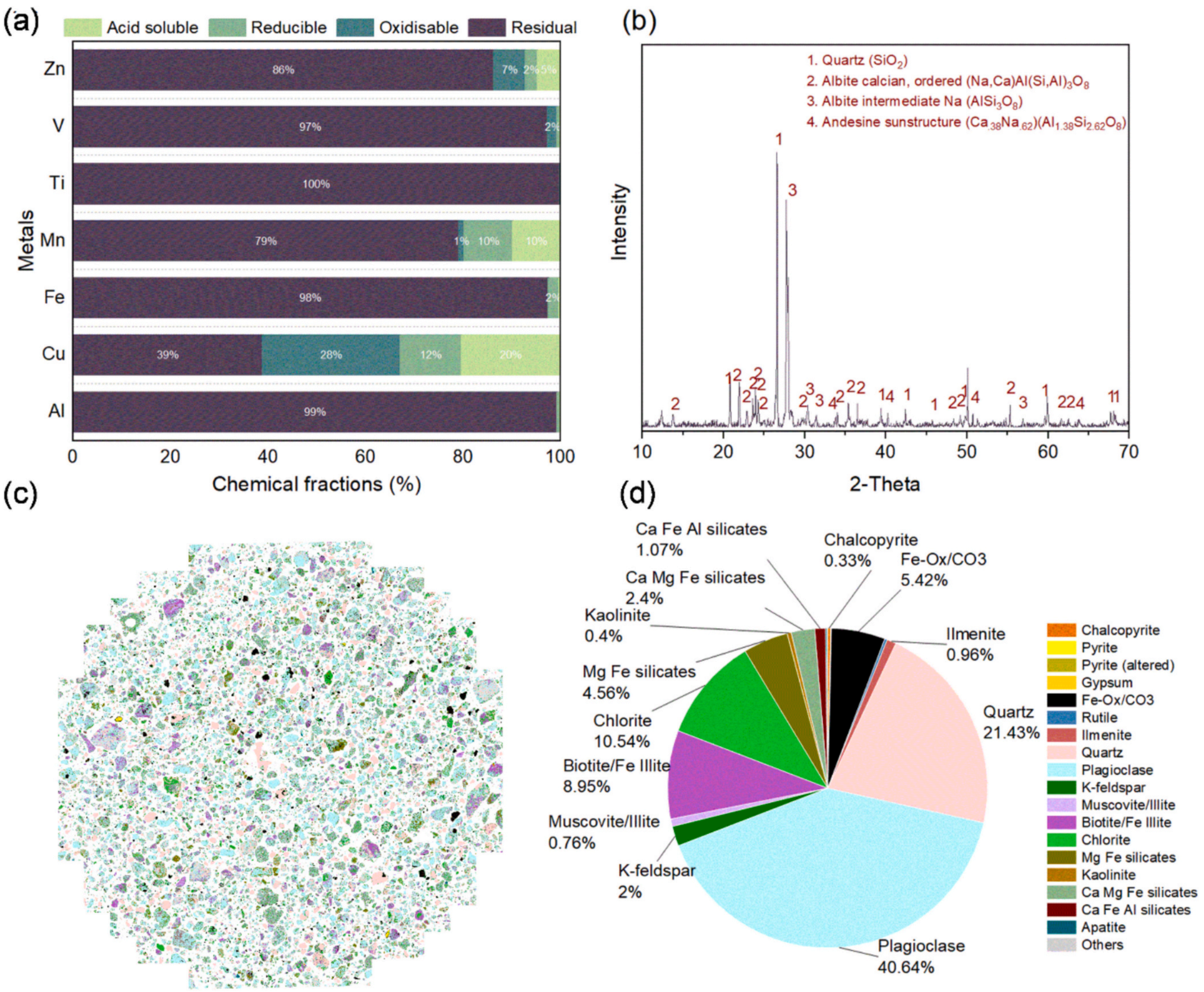

Fig. 2. Geochemical and mineralogical characterisation of the tailings sample: (a) Chemical fraction of metals determined using BCR sequential extraction; (b) crystalline mineral phases identified using XRD; (c) mineral physical distribution measured using QEMSCAN (measurement area diameter: 27 mm^2); and (d) mineral mass (%) distribution measured using QEMSCAN.

bioavailable concentrations of nutrient elements such as Ca, Mg, K, and P increased after the 7-day EK or SL treatment. Bioavailable P was not detected in the untreated tailings but increased to 65.5 mg/kg following EK treatment and 68.7 mg/kg following SL treatment, both using citric acid as lixiviant. These results indicate that lixiviant selection plays a substantial role in determining the level of residual bioavailable metals, particularly under EK conditions. For chloride based lixiviants (ferric chloride, sodium chloride) and inorganic acids (sulfuric acid, nitric acid, hydrochloric acid), EK consistently produced higher 'actually bioavailable' Cu and Mn in the treated tailings compared to SL. For instance, EK with ferric chloride yielded actually bioavailable Cu of 437.5 mg/kg and Mn of 92.9 mg/kg, compared to 373.7 mg/kg Cu and Mn of 51.1 mg/kg for SL. Conversely, organic acids (acetic acid, citric acid and malonic acid) resulted in lower 'actually bioavailable' Cu and Mn in EK-treated residues than in those treated with SL. For example, citric acid under EK conditions resulted in 157 mg/kg Cu and 16.8 mg/kg Mn, compared to 231.3 mg/kg and 29.9 mg/kg under SL. This suggests that EK treatment using organic acids not only leached metals to solution, but it also leaves a lower proportion of actually bioavailable Cu and Mn in the treated tailings, thereby lowering their potential biotoxicological risk.

The actually bioavailable element concentrations of treated tailings after being exposed to 0.001 M $CaCl_2$ multiple times are displayed in Fig. S1 and 6a – to simulate their potential longer-term environmental leaching behaviour. It can be observed that Al, Cu, Fe and Mn exhibit a substantially lower concentration (0–5 mg/kg) within the third 0.001 M $CaCl_2$ exposure. This indicates that the actually bioavailable metals in the treated tailings were from labile pools mobilized by EK or SL, which were quickly depleted. This means these residual metals are readily removed through natural processes (e.g., rainfall-driven leaching or runoff) and/or will likely be amenable to be extracted using an environmentally benign solvent, making their environmental risk likely to be minor and short-term. In contrast, several nutrient elements such as Ca, K and Mg retained notable residual concentrations after the third leaching cycle (Fig. 6a). This may be due to their association with moderately insoluble phases (e.g., adsorbed ions, secondary minerals) that enable gradual nutrient release.

Fig. 7 shows that both EK and SL treatments typically resulted in a substantial decrease in pH. However, successive $CaCl_2$ leaching gradually increased pH, suggesting that such small quantities of residual lixiviant can be readily buffered by natural rainfall (or mild rinsing with benign electrolytes) to restore the pH of the tailings to circumneutral (pH 5–8) which is conducive for plant growth and revegetation.

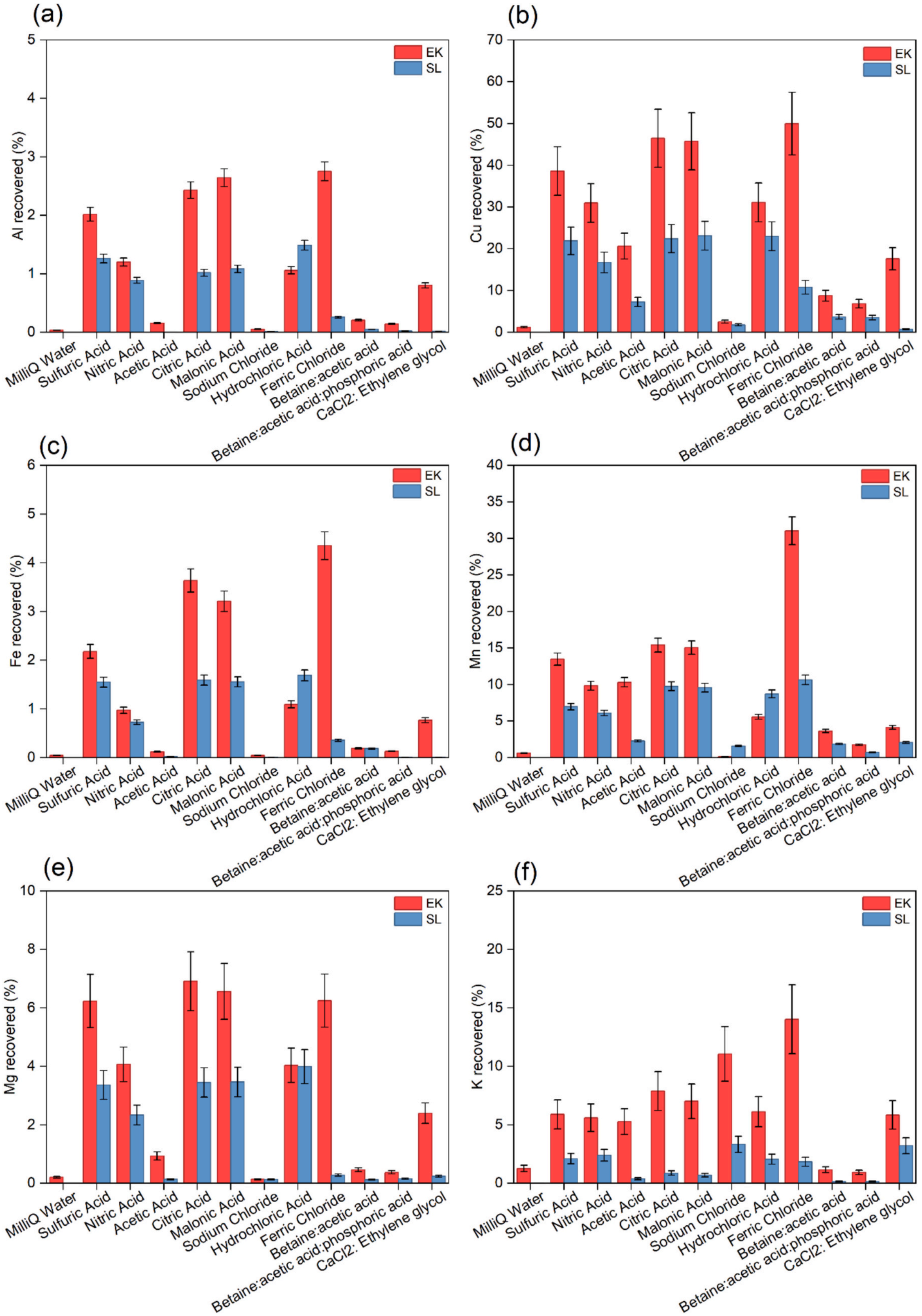

Fig. 3. Recovery efficiency (%) from tailings as a function of lixiviants after 7-day electrokinetic and static leaching treatment. Fig. 3 (a-f) represents recovery of Al, Cu, Fe, Mn, Mg and K.

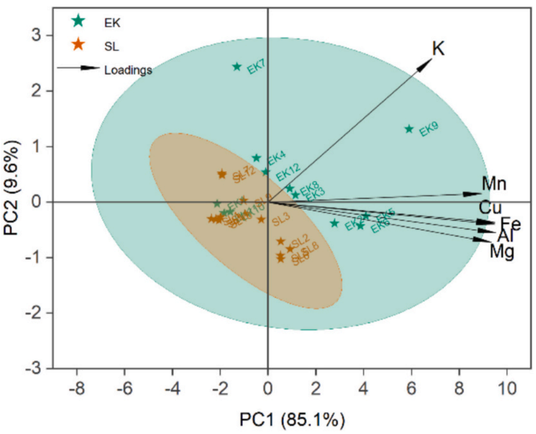

Fig. 4. Principal component analysis for 6 variables (recovery rate of K, Mn, Cu, Fe, Al and Mg, %) after 7-day electrokinetic and static leaching treatment using twelve lixiviants.

To assess the impact of EK and SL on the concentration of 'potentially bioavailable' elements within residues, the HNO_3 method (ISO 17586:2016) was applied. This represents the maximum concentration which can be released from the tailings into the pore water under mildly acidic conditions. This includes elements which are bound to cation exchange sites but also those within acid soluble salts. As illustrated in Fig. 5c and d, the untreated tailings contained high concentrations of potentially bioavailable metals: 680 mg/kg Cu, 3560 mg/kg Al, 3430 mg/kg Fe, 188 mg/kg Mn, 11.7 mg/kg V, and 10.6 mg/kg Zn. The EK and SL treatments significantly lowered these concentrations, with the degree of reduction dependent on the lixiviant and method (EK or SL) applied. For instance, EK with citric acid led to lower potentially bioavailable Cu (183 mg/kg) and Mn (36.1 mg/kg) compared to SL with citric acid (334 mg/kg Cu and 61.7 mg/kg Mn), while EK with ferric chloride resulted in 665 mg/kg Cu and 128 mg/kg Mn, compared to SL-treated tailings with 612 mg/kg Cu and 90.5 mg/kg Mn.

To assess their biotoxicological risk, metal concentrations in the tailings before and after treatment were compared to soil screening values (SSV) derived by the England and Wales Environment Agency

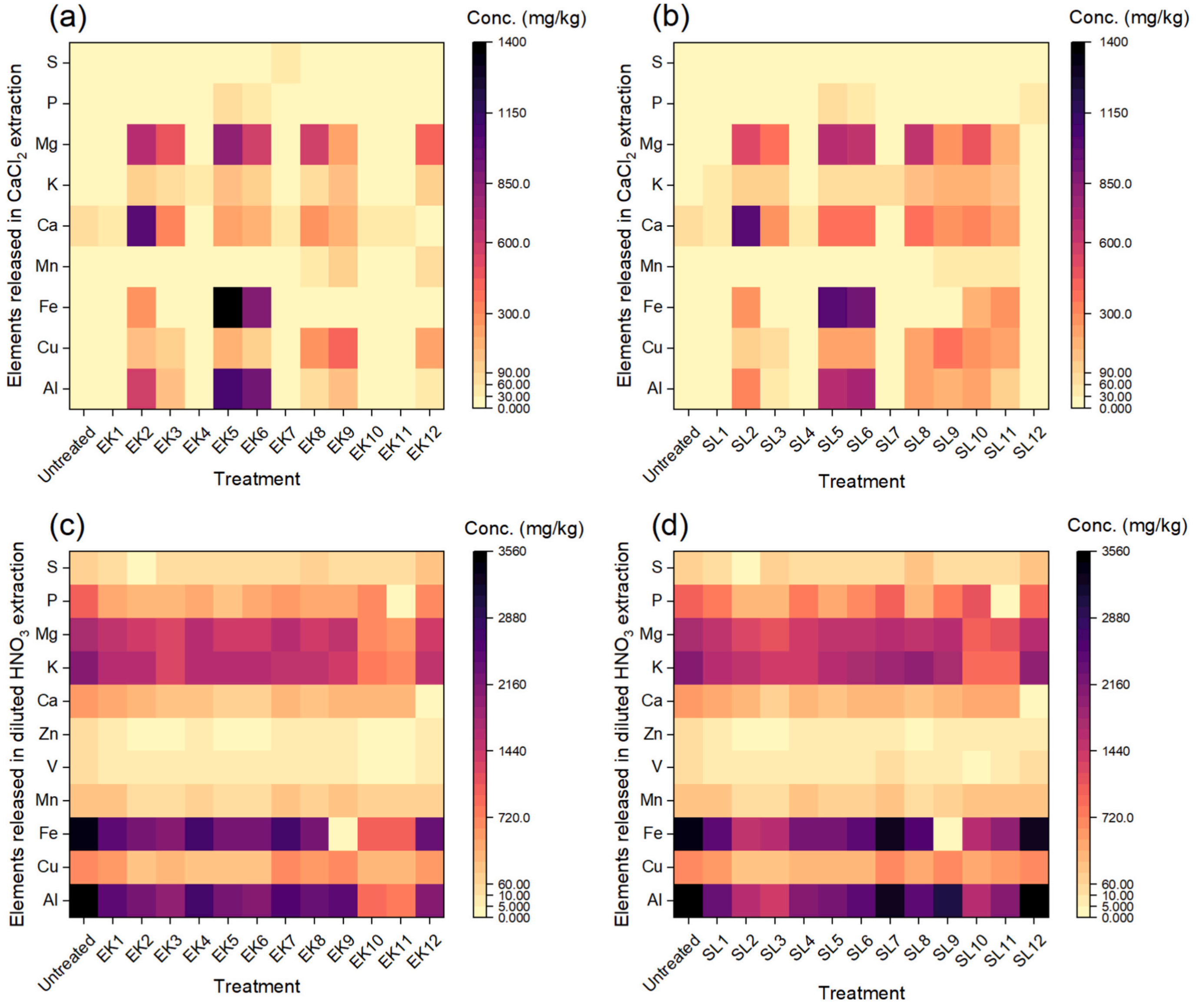

Fig. 5. Heatmap of released elements from treated tailings after exposure to 0.001 M $CaCl_2$ or 0.43 M HNO_3, to simulate their potential to undergo rainfall-driven leaching and their potentially bioavailable fraction respectively. (a) EK-treated tailings with $CaCl_2$ eluent, (b) SL-treated tailings with $CaCl_2$ eluent, (c) EK-treated tailings with 0.43 M HNO_3 eluent, and (d) SL-treated tailings with 0.43 M HNO_3 eluent.

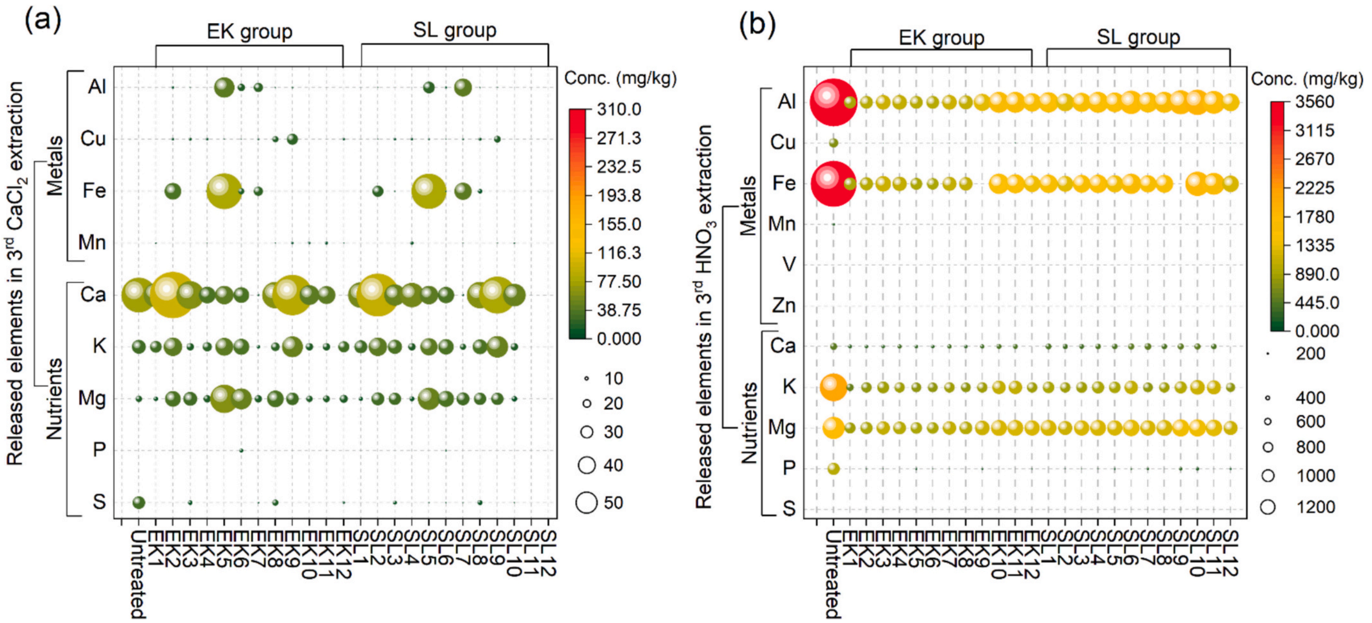

Fig. 6. Matrix bubble of bioavailable substances in tailings treated using electrokinetic and static leaching, measured after (a) third exposure to 0.001 M $CaCl_2$, (b) third exposure to 0.43 M HNO_3.

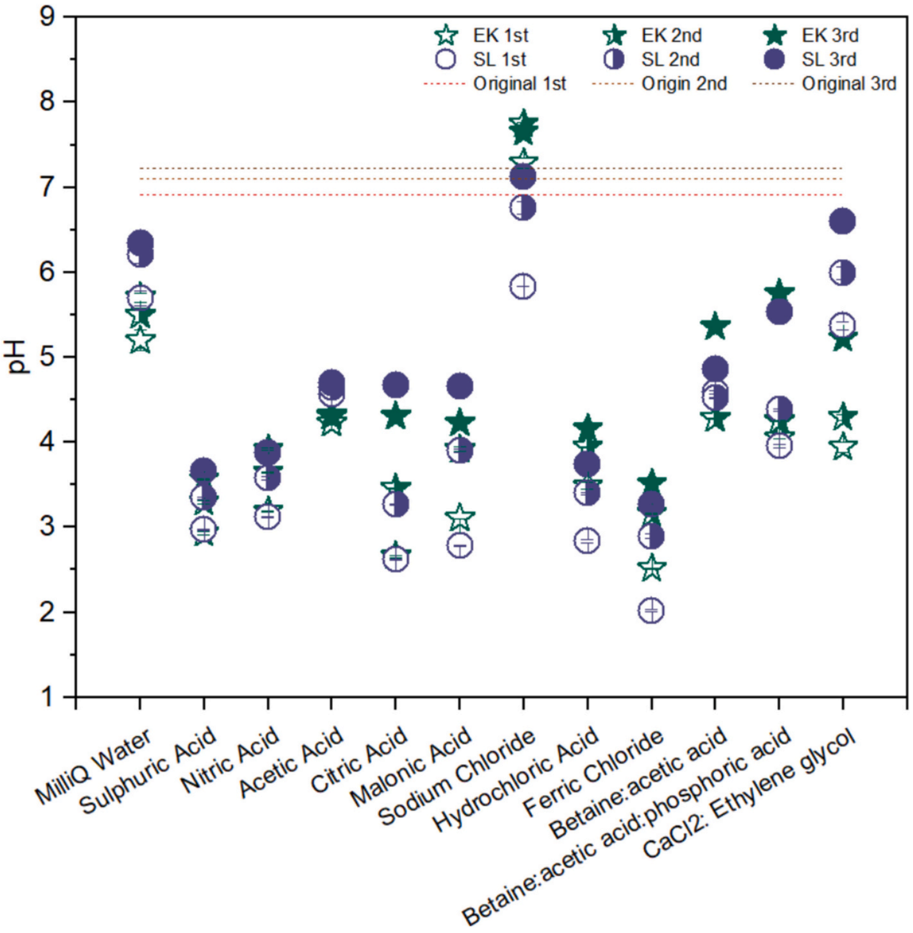

Fig. 7. pH changes of the tailings after 7-day electrokinetic and static leaching treatment, followed by three washing cycles with 0.001 M $CaCl_2$ solution.

(EA) [40]. Vanadium (V) exceeded the threshold concentration (2 mg/kg) suggested in the ecotoxicological risk assessment report [40], persisting after three extractions in both recovery methods (Fig. 6b). This indicates a long-term potential biotoxicity from V. Although Zn was released, its concentration in both EK and SL treatments was below the respective EA threshold (35.6 mg/kg), suggesting a relatively low biotoxicological risk. Despite substantial initial release of potentially bioavailable Cu (EK: 665 mg/kg; SL: 612 mg/kg) in first 0.43 M HNO_3 leaching, the Cu concentration declined below its toxicity threshold (35.1 mg/kg) after three successive leaching (Fig. 6b). Al, Fe, and Mn exhibited similar behaviour (indicating that the biotoxicological risks they pose may be short-lived).

Overall, both EK and SL treatments effectively reduced the concentrations of potentially bioavailable toxic metals compared to untreated tailings. Notably, EK with 0.5 M citric acid demonstrated the highest efficiency in decreasing toxic metals, thereby significantly mitigating long-term environmental risks.

3.4. *Metal recovery under long-term electrokinetic and static leaching*

Citric acid (0.5 M) and ferric chloride (0.16 M) were selected for extended (22-day) EK and SL experiments because they exhibited the greatest Cu recovery performance in the 7-day EK experiments. The extended treatments show a marked increase in metal (Al, Cu, Fe, Mn, Mg and K) recovery when using citric acid under both EK and SL conditions (Fig. 8), compared to 7-day treatment (Fig. 3). Notably, recovery under EK increased to 11.5% for Al (from 2.4%), 60.8% for Cu (from 46.5%), and 26.3% for Mn (from 15.4%). Under SL, recovery increased to 4.3% for Al (from 1.0%), 41.9% for Cu (from 22.4%), and 14.1% for Mn (from 9.8%).

In contrast, the 22-day SL treatment with ferric chloride did not yield further increase in Al, Cu, or Mn recovery. This was likely due to surface passivation during the prolonged SL process [34]. Although EK enhances metal transport through mechanisms, such as electromigration and electroosmosis, its long-term efficiency is hindered by cathode passivation and Fe^{3+} loss [41]. These factors collectively reduce the mobility and recovery of Cu, Al, and Mn over time, despite the initial strong solubilising capacity of ferric chloride. Future studies may consider optimizing electrode materials such as graphite felt or dimensionally stable anodes, to mitigate cathodic passivation. Electrolyte regulation strategies including Fe^{3+} replenishment and local pH control near the cathode, may help sustain favourable redox conditions and prevent iron precipitation. In addition, the incorporation of chelating agents or surfactants could suppress secondary precipitation and promoted sustained metal mobility, thereby enhancing the long-term stability and efficiency of EK-assisted leaching systems.

3.5. *Potential biotoxicity and nutrients in long-term treated tailings*

Following 22 days treatment, the lowest potentially bioavailable Cu (42.8 mg/kg) and V (8.65 mg/kg) in tailings still exceeded SSV (35.1 mg/kg of Cu, 2.0 mg/kg of V), still posing potential ecotoxicological risks and requiring further management. However, the 22-day EK treatment substantially reduced immediate and long-term biotoxicological risks compared to the 7-day treatment (Fig. 9). For actual bioavailability, 22-day EK treatment reduced Cu by 86.0% in citric acid systems (from 157 to 22.0 mg/kg) and 83.1% in ferric chloride systems (from 438 to 73.8 mg/kg), significantly outperforming SL treatment. For potential bioavailability, 22-day citric acid-based EK achieved a reduction of 77.1% (183 mg/kg to 42.8 mg/kg), substantially exceeding SL (49.2% reduction), while ferric chloride-based EK reduced Cu by 49.7% (665 mg/kg to 335 mg/kg), outperforming SL of 23.8% reduction.

Nutrient analysis revealed that the 22-day EK and SL treatments mobilized substantial quantities of actually bioavailable Ca, Fe, K, Mg, and P (Fig. S2). Notably, citric acid-based EK treatment led to higher actually bioavailable (plant-available) macronutrients (Fe, K, Mg, P) than SL, increasing Fe from 0 mg/kg to 2270 mg/kg, K from 29.9 mg/kg to 327 mg/kg, and Mg from 13.3 mg/kg to 930 mg/kg, and P from 0 mg/kg to 80.9 mg/kg relative to untreated tailings. These results suggest that EK treatment using citric acid acts to selectively target Cu recovery, while maintaining key nutrients needed for plant growth.

3.6. *Energy consumption and techno-economic considerations*

Across all lixiviants, EK consistently exhibited higher Cu recovery than SL, at the expense of additional electrical energy input. This is a key factor influencing the feasibility, economic viability, and sustainability of EK-based metal recovery, particularly for on-site and large-scale applications. Table 3 presents the electrical energy consumption during the 7-day EK treatment applied to 200 g of tailings. The energy demand of EK systems is controlled by multiple interacting parameters, including ionic mobility, electrolyte conductivity, solid–liquid interfacial properties, and lixiviant chemistry [42]. Lixiviant with higher leaching strength and ionic strength promote dissolution of both target and non-target ions, increasing the number of charge carriers in the system and thus the electrical current required to sustain electromigration[43]. Consequently, higher metal recovery is often accompanied by increased energy consumption.

To evaluate the economic impact of EK enhancement, the ratio of additional electrical energy consumption to the net increase in recovered metals (Cu and Al) relative to SL was calculated (Table 3). Based on the electricity cost (2023 electricity prices reported by the Department for Energy Security & Net Zero) with the average Cu trading price in 2023 from the London Metal Exchange, the additional value of metals

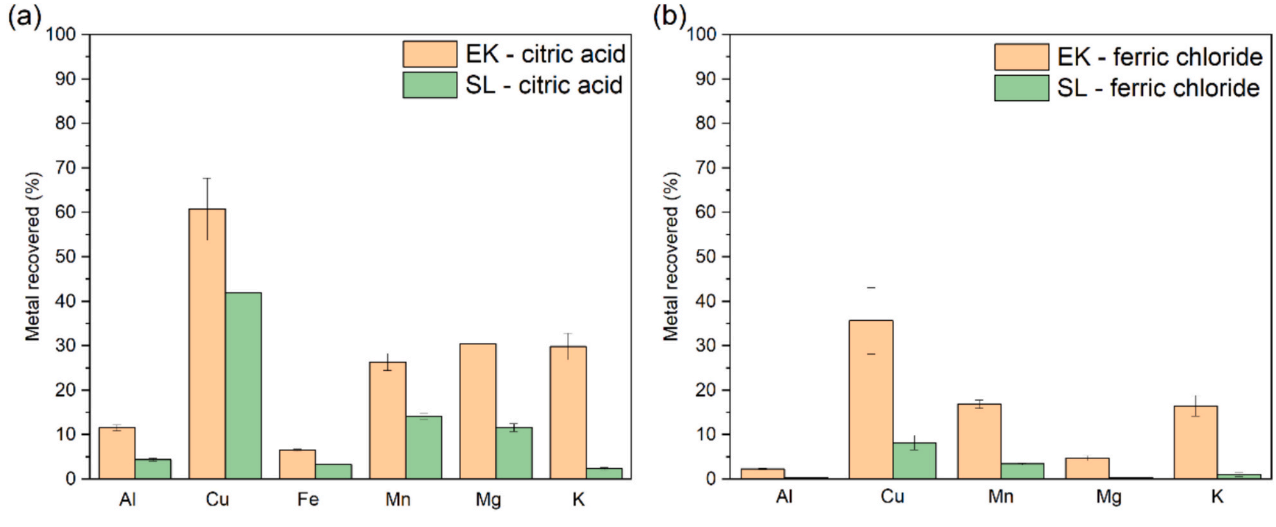

Fig. 8. Metal recovery after 22-day electrokinetic and static leaching treatment using (a) citric acid and (b) ferric chloride.

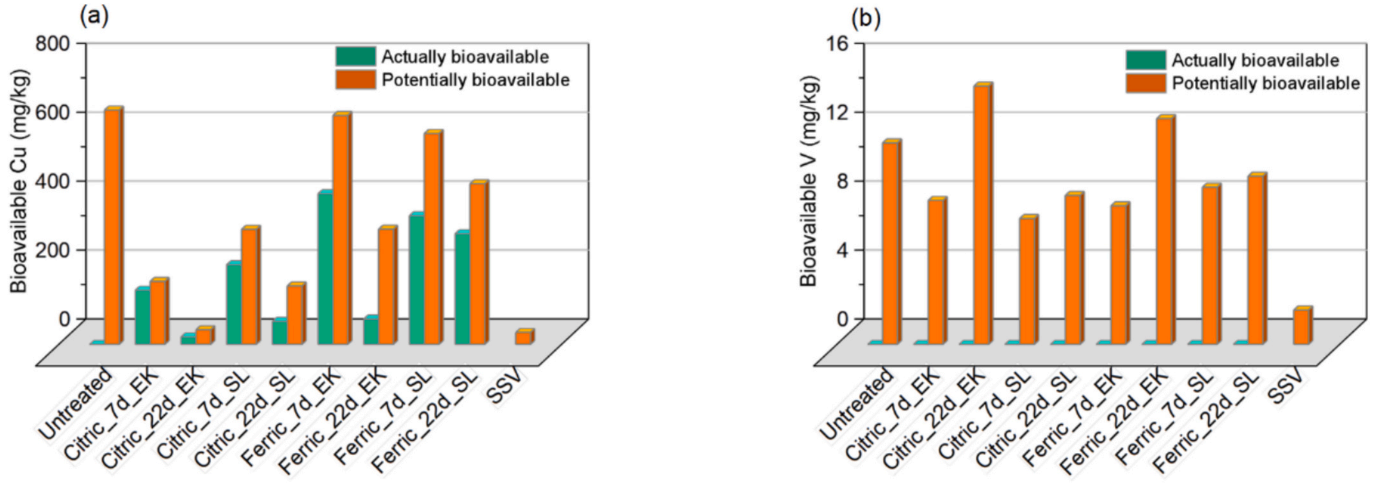

Fig. 9. Bioavailable Cu and V from untreated, 7-day and 22-day treated tailings upon exposure to 0.001 M CaCl2 (actually bioavailable fraction) and 0.43 M HNO_3 (potentially bioavailable fraction).

Table 3
Energy consumption of the 7-day EK recovery of Cu from tailings using different lixiviant.

Lixiviant	Energy consumption (Wh)		Metal recovery (mg)				Net recovery by EK (mg)		Energy consumption per net recovery (Wh/mg)	
	EK	SL	EK		SL					
			Cu	Al	Cu	Al	Cu	Al	Cu	Al
MilliQ Water	0	0	3.50	6.30	0	0	3.50	6.30	0	0
Sulfuric acid	31	0	111	328	62.9	206	48.1	123	0.64	0.25
Nitric acid	24	0	89.0	196	48.0	145	41.0	51.0	0.59	0.48
Acetic acid	2.7	0	59.3	25.5	20.9	0.50	38.4	25.1	0.070	0.11
Citric acid	30	0	134	396	64.4	166	69.2	230	0.43	0.13
Malonic acid	40	0	132	430	66.5	177	65.0	254	0.61	0.16
Sodium chloride	17	0	7.3	8.40	5.10	2.00	2.20	6.40	7.7	2.7
Hydrochloric acid	10	0	89.4	173	66.2	242	23.2	69.6	0.44	0.15
Ferric chloride	6.7	0	144	448	30.9	41.9	113	406	0.060	0.020
Betain:Glacial acetic acid	9.4	0	25.2	33.7	10.6	8.20	14.6	25.5	0.64	0.37
Betain: Glacial acetic acid: 1 wt% phosphoric acid	11	0	19.7	23.1	10.1	3.80	9.60	19.3	1.1	0.57
Calcium chloride: Ethylene glycol	73	0	50.7	131	2.10	2.80	48.6	128	1.5	0.57

recovered by EK did not fully compensate for the corresponding electricity cost under the experimental conditions. However, this comparison does not capture the full value of EK, including the improved process controllability, selective metal mobilization, and potential reduction of post-treatment environmental risks.

For practical application, organic acids such as citric acid demonstrated superior metal recovery under EK but are more expensive than strong inorganic acids or simple salts. However, it is important to note that lixiviant cost alone does not fully represent the overall economic and environmental performance of the process. Given organic acids are more biodegradable and associated with lower risk of secondary environmental contamination. These benefits can lower downstream environmental management and remediation costs, potentially offset their potentially higher procurement price when evaluated from a life-cycle or sustainability perspective. Therefore, the overall cost–benefit balance between organic and inorganic solvents should be carefully weighed using more comprehensive data, including chemical consumption, recyclability, environmental risk reduction, and long-term remediation outcomes. Electrode durability and system design are also critical for field applications. While no significant electrode degradation was observed during the short laboratory experiments, prolonged EK operation, particularly under acidic conditions, may lead to electrode corrosion, passivation, or fouling, potentially increasing maintenance and replacement costs. Optimization of electrode materials, spacing, current density, and treatment duration, together with renewable energy integration and lixiviant recycling, is therefore essential to improve the economic and environmental viability of EK-assisted tailings treatment at scale.

4. Conclusions and perspectives

This study provides clear evidence that EK leaching consistently enhances metal recovery from porphyry Cu tailings compared to SL, regardless of lixiviant chemistry. The most effective approach was a combination of EK and 0.5 M citric acid, which achieved 60.8% Cu recovery over 22 days.

Greatest EK-driven amplification of lixiviant performance was recorded for the deep eutectic solvent (DES): $CaCl_2$: ethylene glycol, where a 25-fold increase in Cu recovery was achieved. This is attributed to additional mass transfer for solvent leaching when under a superimposed voltage gradient, which accelerates ion transport and can remove passivation layers, overcoming key kinetic limitations.

In addition to high metal yields, treatment of the tailings using EK with 0.5 M citric acid liberated several macronutrients (Fe, K, Mg, P) needed for revegetation, which highlights its utility as an effective yet potentially environmentally compatible lixiviant.

Parallel metal bioavailability in residues from the EK + 0.5 M citric acid treatment showed that the potentially bioavailable Cu and Mn were reduced to negligible levels (0–5 mg/kg) within three washing cycles while potentially bioavailable Cu decreased by 93.7% - from 680 mg/kg (untreated) to 42.8 mg/kg (22-day EK treatment). These results demonstrate that biotoxic metals can be effectively removed from tailings, either by extraction at the cathode or flushing with non-hazardous solvents, thereby significantly reducing potential biotoxicity.

Overall, the dual capability of EK, which maximizes metal yield while producing a tailings residue which is conducive for long-term ecological restoration, positions it as a highly promising in situ technology for combined metal recovery and site rehabilitation.

Future research should focus on optimizing EK parameters such as voltage gradient and electrode design for field scalability, conducting additional microbial activity assay and phytotoxicity assays to confirm revegetation potential, and undertaking a comprehensive techno-economic analysis. Besides, future studies should incorporate detailed mineralogical and spectroscopic techniques (e.g., XPS, FTIR, SEM) to elucidate the specific mechanisms governing mineral-lixiviant interactions and to deepen the mechanistic understanding of the most effective recovery systems.

CRediT authorship contribution statement

Yujie Yan: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Gawen R. T. Jenkin:** Writing – review & editing, Funding acquisition, Conceptualization. **Andrew P. Abbott:** Writing – review & editing. **Alexandria Tanciongco:** Writing – review & editing. **Carlo A. Arcilla:** Writing – review & editing, Funding acquisition. **Cris Reven L. Gibaga:** Writing – review & editing. **Daniel J. Smith:** Writing – review & editing. **Djoan Kate Tungpalan:** Writing – review & editing, Funding acquisition. **Jonathan E. Chambers:** Writing – review & editing, Funding acquisition. **John Henry C. Gervasio:** Writing – review & editing. **James Symons:** Writing – review & editing. **Justine Perry T. Domingo:** Writing – review & editing. **Laura Newsome:** Writing – review & editing. **Mark Tibbett:** Writing – review & editing, Funding acquisition. **Michael J. Whelan:** Writing – review & editing. **Rico Neil M. Quierrez:** Writing – review & editing. **Rich Crane:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Rich Crane reports financial support was provided by UK Research and Innovation Natural Environment Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2026.174859.

Data availability

Data will be made available on request.

References

[1] R. Herrington, Mining our green future, Nat. Rev. Mater. 2021 6:6 6 (2021) 456–458. doi:https://doi.org/10.1038/s41578-021-00325-9.

[2] P.H.M. Kinnunen, A.H. Kaksonen, Towards circular economy in mining: opportunities and bottlenecks for tailings valorization, J. Clean. Prod. 228 (2019) 153–160, https://doi.org/10.1016/J.JCLEPRO.2019.04.171.

[3] K.A. Hudson-Edwards, D. Kemp, L.A. Torres-Cruz, M.G. Macklin, P.A. Brewer, J. R. Owen, D.M. Franks, E. Marquis, C.J. Thomas, Tailings storage facilities, failures and disaster risk, Nat. Rev. Earth Environ. 2024 (2024) 1–19, https://doi.org/10.1038/s43017-024-00576-4.

[4] O.A. Marín, A. Kraslawski, L.A. Cisternas, Estimating processing cost for the recovery of valuable elements from mine tailings using dimensional analysis, Miner. Eng. 184 (2022) 107629, https://doi.org/10.1016/J.MINENG.2022.107629.

[5] P.N. Owens, E.L. Petticrew, S.J. Albers, T.D. French, B. Granger, B. Laval, J. Lindgren, R. Sussbauer, S. Vagle, Annual pulses of copper-enriched sediment in a north American river downstream of a large lake following the catastrophic failure of a mine tailings storage facility, Sci. Total Environ. 856 (2023) 158927, https://doi.org/10.1016/J.SCITOTENV.2022.158927.

[6] É. Lèbre, G. Corder, A. Golev, The role of the mining industry in a circular economy: a framework for resource Management at the Mine Site Level, J. Ind. Ecol. 21 (2017) 662–672, https://doi.org/10.1111/JIEC.12596.

[7] M. Seredkin, A. Zabolotsky, G. Jeffress, In situ recovery, an alternative to conventional methods of mining: exploration, resource estimation, environmental issues, project evaluation and economics, Ore Geol. Rev. 79 (2016) 500–514, https://doi.org/10.1016/j.oregeorev.2016.06.016.

[8] G. Jenkin, C. Arcilla, A. Abbott, L. Bateson, A. Bautista VII, J. Chambers, M.C. Devanadera, S. Duddigan, E. Fernando, J.H. Gervasio, C. Gibaga, J.E. Lazaro, T. Menor, J. Naden, L. Newsome, Y. Pan, R. Quierrez, M. Quimado, J. Samaniego, V. Selvaraj, D. Smith, R. Swift, J. Symons, A. Tanciongco, M. Tibbett, D.K. Tungpalan, M. Whelan, Y. Yan, Recent developments in the science and technology of in situ solvent leaching of tailings for reprocessing, rehabilitation and closure, Proceedings of the International Conference on Mine Closure (2024) 29–44. doi:10.36487/ACG_REPO/2415_0.03.

[9] L. Sinclair, J. Thompson, In situ leaching of copper: challenges and future prospects, Hydrometallurgy 157 (2015) 306–324, https://doi.org/10.1016/J.HYDROMET.2015.08.022.

[10] G.R.T. Jenkin, A.Z.M. Al-Bassam, R.C. Harris, A.P. Abbott, D.J. Smith, D. A. Holwell, R.J. Chapman, C.J. Stanley, The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals, Miner. Eng. 87 (2016) 18–24, https://doi.org/10.1016/J.MINENG.2015.09.026.

[11] H.M. Lizama, In-situ leaching of copper from spent heaps, Hydrometallurgy 215 (2023) 105997, https://doi.org/10.1016/J.HYDROMET.2022.105997.

[12] E. Martens, H. Prommer, R. Sprocati, J. Sun, X. Dai, R. Crane, J. Jamieson, P. O. Tong, M. Rolle, A. Fourie, Toward a more sustainable mining future with electrokinetic in situ leaching, Sci. Adv. 7 (2021) 9971, https://doi.org/10.1126/SCIADV.ABF9971/SUPPL_FILE/ABF9971_SM.PDF.

[13] Z. Sun, M. Zhao, L. Chen, Z. Gong, J. Hu, D. Ma, Electrokinetic remediation for the removal of heavy metals in soil: limitations, solutions and prospection, Sci. Total Environ. 903 (2023) 165970, https://doi.org/10.1016/J.SCITOTENV.2023.165970.

[14] E. Martens, H. Prommer, X. Dai, J. Sun, P. Breuer, A. Fourie, Electrokinetic in situ leaching of gold from intact ore, Hydrometallurgy 178 (2018) 124–136, https://doi.org/10.1016/J.HYDROMET.2018.04.003.

[15] G. Wang, J. Zhu, X. Liang, B. Ling, J. Xu, Y. Yang, S. Kang, W. Tan, Y. Xu, X. Zou, L. Ran, J. Wei, H. He, Industrial-scale sustainable rare earth mining enabled by electrokinetics, Nat. Sustainability 2025 8:2 8 (2025) 182–189. doi:https://doi.org/10.1038/s41893-024-01501-9.

[16] G. Wang, X. Liang, B. Ling, J. Xu, L. Ran, J. Wei, R. Zhu, J. Zhu, H. He, Recovery of rare earth elements from weathering crust soils using electrokinetic mining technology☆, J. Rare Earths (2024) https://doi.org/10.1016/J.JRE.2024.06.007.

[17] H.L. Medina-Díaz, F.J. López-Bellido, J. Alonso-Azcárate, F.J. Fernández-Morales, L. Rodríguez, Can rare earth elements be recovered from abandoned mine tailings by means of electrokinetic-assisted phytoextraction? Environ. Sci. Pollut. Res. 31 (2024) 26747–26759, https://doi.org/10.1007/S11356-024-32759-3/FIGURES/4.

[18] J. Chen, J. Liu, M. Hu, J. Liu, Y. Yu, Y. Zhou, N. Bao, X. Han, X. Zhao, F. Guo, Potential and characteristics of heavy metals electrokinetic removal from the copper-zinc mine tailings: study on the simulated and actual tailings, Chem. Eng. J. 496 (2024) 154245, https://doi.org/10.1016/J.CEJ.2024.154245.

[19] F. Wu, C. Jin, R. Xie, G. Qu, B. Chen, J. Qin, X. Liu, H. Li, L. Kuang, Extraction and transformation of elements in phosphogypsum by electrokinetics, J. Clean. Prod. 385 (2023) 135688, https://doi.org/10.1016/J.JCLEPRO.2022.135688.

[20] D.M. Zhou, C.F. Deng, A.N. Alshawabkeh, L. Cang, Effects of catholyte conditioning on electrokinetic extraction of copper from mine tailings, Environ. Int. 31 (2005) 885–890, https://doi.org/10.1016/J.ENVINT.2005.05.040.

[21] A. Rojo, H.K. Hansen, L.M. Ottosen, Electrodialytic remediation of copper mine tailings: comparing different operational conditions, Miner. Eng. 19 (2006) 500–504, https://doi.org/10.1016/J.MINENG.2005.08.016.

[22] J. Almeida, R. Craveiro, P. Faria, A.S. Silva, E.P. Mateus, S. Barreiros, A. Paiva, A. B. Ribeiro, Electrodialytic removal of tungsten and arsenic from secondary mine resources — deep eutectic solvents enhancement, Sci. Total Environ. 710 (2020) 136364, https://doi.org/10.1016/J.SCITOTENV.2019.136364.

[23] G. Asadollahfardi, M.S. Sarmadi, M. Rezaee, A. Khodadadi-Darban, M. Yazdani, J. M. Paz-Garcia, Comparison of different extracting agents for the recovery of Pb and Zn through electrokinetic remediation of mine tailings, J. Environ. Manag. 279 (2021) 111728, https://doi.org/10.1016/J.JENVMAN.2020.111728.

[24] ICMM - Tailings Reduction Roadmap, (n.d.). https://www.icmm.com/tailings-reduction-roadmap (accessed March 24, 2025).

[25] K. Ibebunjo, Y. El Ouardi, J.K. Bediako, A. Iurchenkova, E. Repo, Selective recovery of copper from copper tailings and wastewater using chelating resins with bis-picolylamine functional groups, Heliyon 10 (2024) e27766, https://doi.org/10.1016/J.HELIYON.2024.E27766.

[26] Y. Yan, F. Xue, F. Muhammad, L. Yu, F. Xu, B. Jiao, Y. Shiau, D. Li, Application of iron-loaded activated carbon electrodes for electrokinetic remediation of chromium-contaminated soil in a three-dimensional electrode system, Sci. Rep. 8 (2018), https://doi.org/10.1038/s41598-018-24138-z.

[27] H. Muntau, P. Quevauviller, B. Griepink, Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities, Int. J. Environ. Anal. Chem. 51 (1993) 135–151, https://doi.org/10.1080/03067319308027619.

[28] ISO 21268-1:2019 - Soil quality — Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil-like materials — Part 1: Batch test using a liquid to solid ratio of 2 l/kg dry matter, (n.d.). https://www.iso.org/standard/68250.html (accessed April 24, 2025).

[29] D.B. Senoro, C.E.F. Monjardin, E.G. Fetalvero, Z.E.C. Benjamin, A.F.B. Gorospe, K. L.M. de Jesus, M.L.G. Ical, J.P. Wong, Quantitative assessment and spatial analysis of metals and metalloids in soil using the geo-accumulation index in the capital town of Romblon Province, Philippines, Toxics 2022, Vol. 10, Page 633 10 (2022) 633. doi:https://doi.org/10.3390/TOXICS10110633.

[30] J.P.T. Domingo, B.T. Ngwenya, M. Attal, C.P.C. David, S.M. Mudd, Geochemical fingerprinting to determine sediment source contribution and improve contamination assessment in mining-impacted floodplains in the Philippines, Appl. Geochem. 159 (2023) 105808, https://doi.org/10.1016/J.APGEOCHEM.2023.105808.

[31] I. Acosta Hernández, M. Muñoz Morales, F.J. Fernández Morales, L. Rodríguez Romero, J. Villaseñor Camacho, Removal of heavy metals from mine tailings by in-situ bioleaching coupled to electrokinetics, Environ. Res. 238 (2023) 117183, https://doi.org/10.1016/J.ENVRES.2023.117183.

[32] J. Valenzuela-Elgueta, Y.P. Jimenez, A.V. Delgado, S. Ahualli, Electrokinetics and stability of silica/clay mixtures at high copper concentration. Implications in the mining of copper, Miner. Eng. 134 (2019) 193–201, https://doi.org/10.1016/J.MINENG.2019.02.001.

[33] C. Cameselle, S. Gouveia, A. Cabo, Enhanced electrokinetic remediation for the removal of heavy metals from contaminated soils, Appl. Sci. 2021, Vol. 11, Page 1799 11 (2021) 1799. doi:https://doi.org/10.3390/app11041799.

[34] M. Al-Harahsheh, S. Kingman, A. Al-Harahsheh, Ferric chloride leaching of chalcopyrite: synergetic effect of CuCl2, Hydrometallurgy 91 (2008) 89–97, https://doi.org/10.1016/J.HYDROMET.2007.11.011.

[35] K. Binnemans, P.T. Jones, Ionic liquids and deep-eutectic solvents in extractive metallurgy: mismatch between academic research and industrial applicability, J. Sustain. Metall. 2023 9:2 9 (2023) 423–438. doi:https://doi.org/10.1007/S40831-023-00681-6.

[36] M.I. Martín, I. García-Díaz, F.A. López, Properties and perspective of using deep eutectic solvents for hydrometallurgy metal recovery, Miner. Eng. 203 (2023) 108306, https://doi.org/10.1016/J.MINENG.2023.108306.

[37] A.P. Abbott, F. Bevan, M. Baeuerle, R.C. Harris, G.R.T. Jenkin, Paint casting: a facile method of studying mineral electrochemistry, Electrochem. Commun. 76 (2017), https://doi.org/10.1016/j.elecom.2017.01.002.

[38] J.M. Hartley, A.Z.M. Al-Bassam, R.C. Harris, G. Frisch, G.R.T. Jenkin, A.P. Abbott, Investigating the dissolution of iron sulfide and arsenide minerals in deep eutectic solvents, Hydrometallurgy 198 (2020), https://doi.org/10.1016/j.hydromet.2020.105511.

[39] A.P. Abbott, A.Z.M. Al-Bassam, A. Goddard, R.C. Harris, G.R.T. Jenkin, F.J. Nisbet, M. Wieland, Dissolution of pyrite and other Fe-S-as minerals using deep eutectic solvents, Green Chem. 19 (2017), https://doi.org/10.1039/c7gc00334j.

[40] Derivation and use of soil screening values for assessing ecological risks, (n.d.). http://www.gov.uk/government/publications (accessed June 3, 2025).

[41] R. Winand, Chloride hydrometallurgy, Hydrometallurgy 27 (1991), https://doi.org/10.1016/0304-386X(91)90055-Q.

[42] Y. Yan, G.M. Kirkelund, Graphite particles as third electrodes to enhance metal removal and energy saving in a stationary electrodialytic soil system, Electrochim. Acta 407 (2022) 139896, https://doi.org/10.1016/j.electacta.2022.139896.