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Review

Using electrode electrolytes to enhance electrokinetic removal of heavy metals from electroplating sludge

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ABSTRACT

An enhanced EK (electrokinetic) process for the removal of heavy metals from an electroplating sludge was performed by adding electrolytes in electrode chambers. The EK experiments were conducted under a constant cell potential (32 V) for 5 days using tap water (TW) and aqueous solution containing sodium dodecylsulfate (SDS) and citric acid (CA) as electrolytes. The results indicated the removal efficiency of heavy metals using TW and aqueous solution containing SDS and CA as electrolytes were 20–51%, 26–65% and 34–69%, respectively, the highest metal removal performance was found using CA as electrolyte. And the removal efficiency of the five metals from sludge in all the EK experiments was Cr > Zn > Ni > Cu > Pb. And sequential extraction analysis revealed that the binding forms of heavy metals with sludge highly depended on the electrolytes, changed from the most difficult extraction type (residual form) to the easier extraction types (soluble, exchangeable, sorbed, sulfate and carbonate forms) after electrokinetic process.

1. Introduction

In the last decades, large amounts of polluted wastes associated with industrial, mining, agricultural, and chemical activities have been produced [1]. Electroplating sludge is a heavy metals-bearing byproduct that comes from the electroplating industry's activities. Some of it consists of multiple metals such as Cu, Ni, Zn, Cr, and Pb, etc. all together in a complicated liquid solid mixture. It is a discharged residue after chemical precipitation of heavy metals from acidic or alkaline solutions as well as rinse waters generated by the electroplating processes [2]. The sludge is categorized as hazardous waste. If disposed improperly, these metals may: (1) cause serious environmental damages polluting surface and ground water, and soil; (2) be transferred into human body via the food chain [3]. In China alone, every year more than 100,000 tons of valuable heavy metals in the form of electroplating sludge is wasted [4]. The U.S. Environmental Protection Agency estimated that about 1.3 million wet tons of electroplating sludge was generated a year in the states [5]. In order to have both sound environment protection and sustainable development that highly emphasizes resources reuse, it is of great importance to maximize the recovery and recycling of heavy metals economically from electroplating sludge. Over the past decades, many techniques have been developed for the removal and recovery of heavy metals. They include leaching-solvent extraction [6], electrolysis [7], ion exchange [8], membrane separation [9] and microbiological methods [10], etc.

The toxicity of metals in the environment is dependent on its chemical species. These species differ by their bioavailabilities and mobility, which have a significant impact on the removal efficiency of heavy metal [11]. The forms of heavy metals can be determined with the selective sequential extraction analysis, which consists of several extraction steps based on using of different chemical reagents and conditions [12–14]. The identification of metal forms in sludge generally include soluble, exchangeable, adsorbed, bound to organics and sulfides, bound to carbonate and residual components [15]. If heavy metals will be in less binding form such as soluble, exchangeable and adsorbed forms, they can be easily removed from sludge. Therefore, it is possible to enhance EK technology by using the electrode electrolytes to transfer heavy metals in the forms with higher mobility.

The electrokinetic process has been demonstrated to successfully and cost-effectively remove inorganic contaminants from soil in many bench scale and field scale studies [16–18]. However few studies have analyzed metals removal from sewage sludge by electrokinetic processes [19,20]. This process involves the application of an electrical field across a porous medium (sludge) to induce the movement of an electrolyte solution and the transport of soluble contaminants toward the electrodes. As the electrokinetic process starts, the movement of H^+ ions generated from the electrolysis of water at the anode advances through the sludge mass toward the cathode, this, in turn, causes contaminants to be desorbed and/or dissociated, and results in the initiation of electromigration,

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i.e., the transport of ions and polar molecules under the influence of the applied electric field. On the other hand, the hydroxide ions generated at the cathode by the reduction of water cause the precipitation of the existing metals, preventing their transport and reducing the treatment efficiency [21]. The applied electrical potential gradient also leads to a process known as electroosmosis. Electromigration and electroosmosis, and electrophoresis are the most important mechanisms acting during the electrokinetic removal of metals from soils [22].

To enhance the remediation efficiency of electrokinetic process, some researchers have conducted different applications such as conditioning the catholyte pH, adding chemical reagents to improve metal solubility, using ion-selective membranes to exclude OH^- migration from the cathode chamber into the soil, and using an electrolyte circulation to control electrolyte pH [23–25]. Electrolytes included acid solutions such as citric acid, acetic acid, oxalic acid, nitric acid, or complexing substances like ethylenediamine tetraacetic acid (EDTA), sodium dodecyl sulfate (SDS) and humic acid are added [26,27].

Citric acid was used to improve the removal of metals from soil because of being readily available, relatively inexpensive, and environmentally benign [28]. Yang et al. [29] proved that citric acid is effective in removing several metals as Pb, Zn, Cu and Mn from a contaminated soil. Citric acid was also used to improve the electroosmotic flow in the kaolinite sample towards the cathode [30]. Surfactants have been mostly used as additives in phase separation processes for the remediation of organic compound contaminated soils because its asymmetric structure enhances their aqueous solubility and mobility [31]. Moreover, it was determined that surfactants can enhance the desorption of heavy metals from soil and sludge [21,32], an effect largely due to the hydrogen bonding and electrostatic forces between the surfactants and metals. Using humic acid, a molecule with surfactant characteristics, Sawada et al. [33] were able to enhance the amount of $Cu(OH)_2$ removed from soils three fold which might result from the alteration of soil surface properties by humic acid. These results were just displayed an overview point of surfactant application in electrokinetic removal of heavy metals. However, few investigations studied in depth the electrokinetic removal of metals by surfactant in soil, not even to say in sludge.

The purpose of this study is to investigate the feasibility of two types of electrolytes (sodium dodecyl sulfate (SDS) and citric acid (CA)) enhanced electrokinetic removal of heavy metals (Cu, Zn, Cr, Ni and Pb) from electroplating sludge. The objectives are: (1) to explore the effect of pH, current and electrical conductivity, both of which are important in EK process, on the removal efficiency of metals from electroplating sludge; (2) to compare the removal efficiency of metals from electroplating sludge enhanced by two different types of electrolytes so as to provide guidance for the optimum selection of electrolytes to enhance the EK remediation efficiency; (3) to investigate the electrokinetic remediation mechanism in the presence of electrolytes.

2. Materials and methods

2.1. Sludge sample

The electroplating sludge sample was collected from an electroplate factory, which was stored in 5 L plastic barrels at 4 °C prior to analysis and experiments. The basic properties of the sample are summarized in Table 1.

Table 1
Characteristics of initial sludge.

Characteristics	Values
Moisture content (%)	70.32
Organics (%)	53.51
pH	8.22
Electrical conductivity (mS/cm)	1.51
Cu (mg/kg)	3911
Pb (mg/kg)	639.11
Zn (mg/kg)	112453.71
Cr (mg/kg)	70735.00
Ni (mg/kg)	4924.67

2.2. Electrolytes

SDS and CA were selected as the electrolytes in this study. The concentrations of SDS and CA were 0.024 and 1.0 M for EK experiments, respectively, which was calculated as three times of critical micelle concentration of SDS and 0.35 times of equivalents of metals involved in the initial sludge. The SDS is an anionic surfactant which contain a hydrophobic portion with little affinity with the bulk medium and a hydrophilic group that is attracted to the bulk medium [34]. Since SDS is biodegradable by soil and the degree of its adsorption on the soil is very low, it is friendly used for subsurface remediation [21]. Citric acid is a weak acid, which would acidify the sludge, making the heavy metals easy to desorb from sludge and it can form complexes with metallic ions [35]. The other electrolyte used was tap water, which mainly consists of $SO_4{}^{2-}$, Cl^- and $NO_3{}^-$ anions as well as Ca^{2+}, Mg^{2+}, K^+ and Na^+ cations. The electrolytes properties are summarized in Table 2.

2.3. Selective sequential extraction

The selective sequential extraction (SSE) method, used to determine the binding forms of heavy metals with sludge before and after EK treatment, was adapted from Oake et al. [12]. The chemical reagents used as extractants for heavy metals in SSE are listed in Table 3. The sludge samples were oven-dried at 105 °C and ground into powder with the diameter of size particles smaller than 0.15 mm. Approximately 1 g of powdered sludge was placed in a 100 ml bottle and chemical reagents were added in different ratios under agitation at 35 rpm. Samples were centrifuged after each step at 3000 rpm for 20 min. The supernatant was transferred to a volumetric flask and deionized water was added to adjust the final volume to 100 ml. The solution was filtered by middle-velocity quantitative filter paper. Subsequently, the following five fractions of heavy metals in the filtered solution were analyzed by atomic adsorption spectrometry (Perkin-Elmer Analyzer-100): (1) soluble, (2) exchangeable, (3) sorbed, (4) organic or sulfide and (5) carbonate. The fraction of heavy metals left in sewage sludge after selective sequential extraction was named “residual fraction”.

2.4. Electrokinetic experiments

Both the anode and cathode chambers (Fig. 1) were 3 cm in length and 8 cm in diameter. The reaction cylinder had a diameter of 8 cm and a length of 30 cm. Five orifices were drilled evenly on the top of the reaction cylinder to monitor current distribution during the experimentation. Two pieces of fiberglass filter paper (0.45 μm, 80 mm) were used to separate treated sludge and electrodes. Graphite electrodes with a diameter of 8 mm and a length of 20 cm were installed at each side of the sludge zone and right behind the filters. The electrolytes were placed into both anode and cathode reservoirs using a peristaltic pump (BT01-100) to maintain constant level and was replenished in the anode reservoir every half day. Three EK experiments were repeated two times under a constant cell potential (32 V) for 5 days with tap water, aqueous solution containing SDS and CA as electrolytes. About 1.05 kg of electroplating sludge was used in each EK experiment. The electric current was monitored every day with multimeter (MASTECH

Table 2
Characteristics of electrolytes: SDS, citric acid and tap water.

Characteristics	Sodium dodecyl sulfate (SDS)	Citric acid	Tap water
Charge	Anionic surfactant	Neutral	Neutral
Formula	$C_{12}H_{25}SO_4Na$	$C_6H_8O_7{\cdot}H_2O$	H_2O
Molecular weight (g/mol)	288	210	18
Cmc (mmol/L)	8.0		
pH	7.70	2.45	7.79
Water solubility	10% in water	Complete miscible	Complete soluble

Table 3
Sequential selective extraction procedure.

Steps	Fractions	Reagent added to sludge in ratio (v/w of dry matter)	Duration of extraction (h)
1	Soluble	Deionized water, 20:1	2
2	Exchangeable	1 M KNO_3, 50:1	16
3	Adsorbed	0.5 M KF, 80:1	16
4	Bound to organics or sulfides	0.1 M $Na_4P_2O_7$, 80:1	16
5	Bound to carbonate	0.1 M Na_4EDTA, 80:1	16

my60, China) during the experiment periods. After EK treatment, the sludge specimen was removed from the cell and sectioned equally into five segments. Sludge pH and electrical conductivity were measured in 1:10 (dry sludge:water) suspensions using pH meter (pHS-3C, China) and conductivity meter (DDS-11A, China), respectively. The total concentration of metals was determined with an atomic adsorption spectrometry (Perkin-Elmer analyzer-100, USA) and the content of the six fractions of the five tested metals in 1.0 of normalized distance from the anode to cathode along the sludge specimen was determined with selective sequential extraction (SSE) method adapted from Oake et al. [12]. All determinations were performed with triplicates.

3. Results and discussion

3.1. pH, current and electrical conductivity

The generation of H^+ and OH^- under an applied electric field will result in the movement of acid and basic fronts in electrokinetic cells, changing the sludge pH significantly during the electrokinetic process [36]. As shown in Fig. 2, the acid front generated at the anode reservoir flushed across the sludge specimen, lowering the sludge pH value from 8.22 to 5.66–7.41 in the anode area for all experiments. Near the cathode side, where the pH was 11.23 and 11.28 for the EK-TW and EK-SDS experiments, respectively, the migration of OH^- to the anode made the sludge pH hardly decrease even if H^+ ions being continuously swept into this region. However, the sludge pH near the cathode side decreased to 6.58 in the EK-CA experiments which may due to the buffering capacity of CA and CA is a good pH conditioner to extract metals from sludge and inhibit precipitation of metal hydroxide [37,38].

The electric current across soil cell is highly related to the concentration of mobile ions in soil cell [16]. The mobile ions might include two kinds of species: (1) H^+ and OH^- generated by water electrolysis; and (2) the species extracted from the original soil specimen due to mobilization mechanism such as ion exchange, desorption, dissolution, etc. [39]. As showed in Fig. 2, the current decreased drastically from 140–160 to 30–50 mA during the experiments. This effect may be due to: (1) clogging of complexing compounds in the soil pore or (2) a decrease in free metal ions moved from the sludge region to the electrode region during the electrokinetic process.

It was reported that a medium EC value is related to the surface charges of mineral particles and ion concentrations in the medium [40]. As shown in Fig. 2, electrical conductivity increases with distance from the anode in all the EK experiments, and the electrical conductivity in EK-SDS and EK-CA experiments is higher than that in EK-TW experiment, which is because electrolytes (SDS and CA) could activate the heavy metals, and make free metal ions and H^+ ions increase with distance from the anode in sludge. The electrical conductivity of sludge near the cathode in all electrokinetic experiments increased drastically, indicating that the place near the cathode has the highest concentration of positively charged metal chelating ions. This might largely be due to the accumulation of metal chelating ions near the cathode as a result of excessive movement of positive metal chelating ions to the cathode region [41].

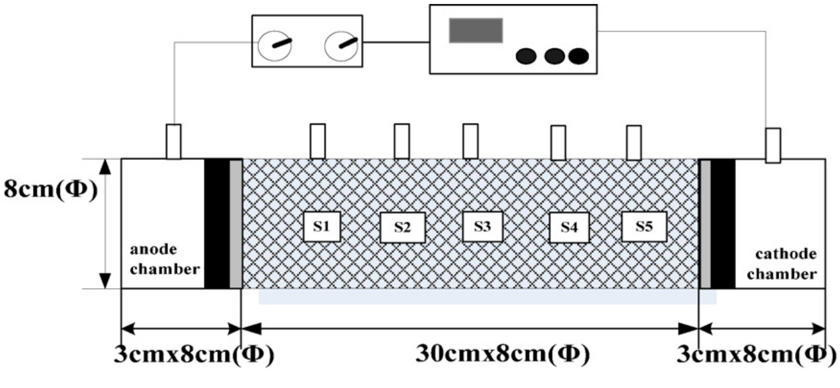

Fig. 1. Schematic diagram of experimental reactor for the electrokinetic treatment.

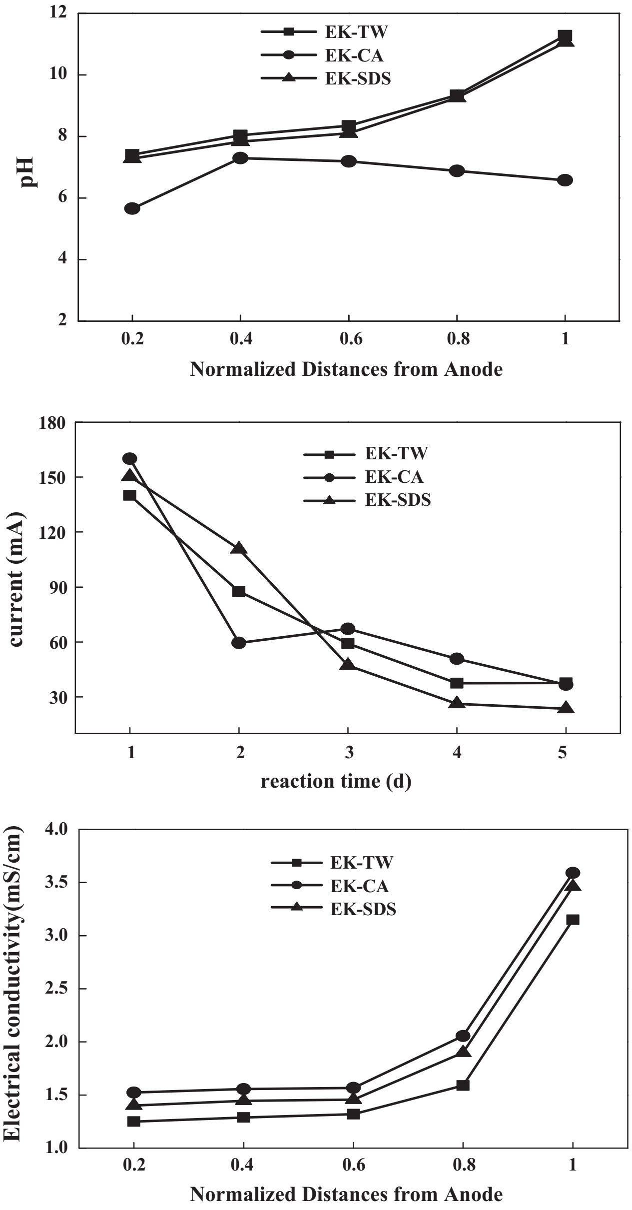

Fig. 2. pH, current and electrical conductivity in sludge in the electrokinetic experiments.

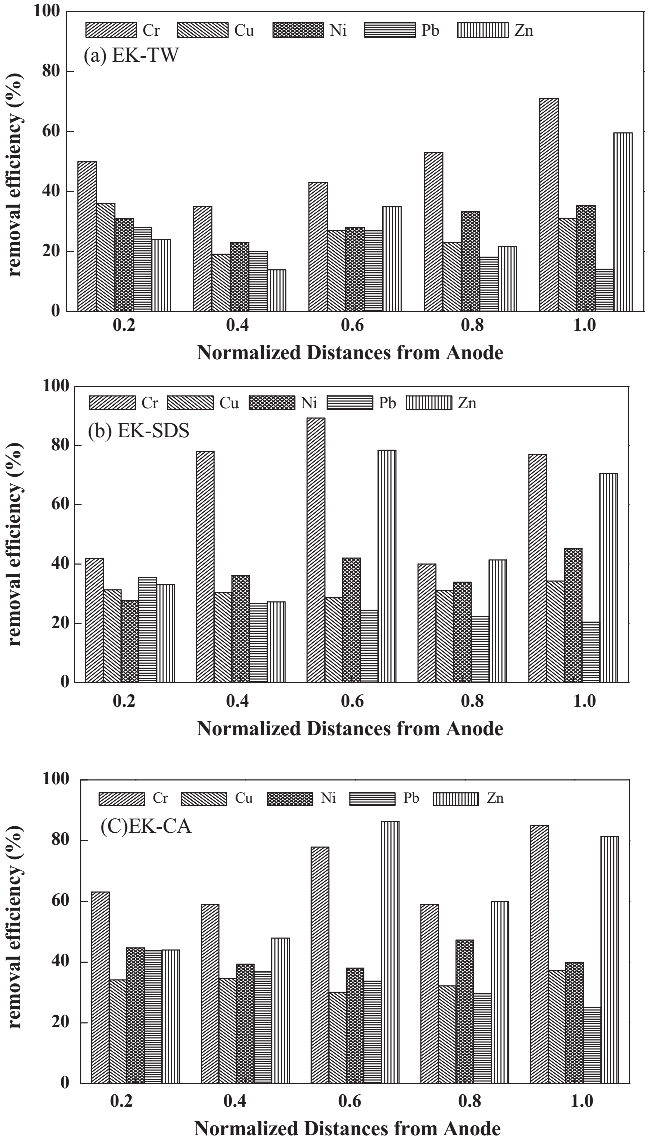

Fig. 3. Removal efficiency of heavy metals in (a) EK-tap water experiment, (b) EK-SDS experiment, and (c) EK-citric acid experiment.

3.2. Heavy metals removal efficiency

The removal efficiency of metals were 20–51%, 26–65% and 34–69% for EK-TW, EK-SDS and EK-CA experiments, respectively (Table 4). Total metals of 1.30 mol, 1.89 mol and 2.20 mol were removed after 5 days from EK-TW, EK-SDS and EK-CA treatment respectively in the sludge zone. As seen in Fig. 2, in EK-CA experiment, a lower sludge pH was found throughout the electrokinetic cell. Such a phenomenon neutralized the alkaline environment, reduced the electro-deposition of metals and obtained ligand forming stable complexes with metals, furthermore, the presence of citric acid in the soil could increase the electroosmotic flow favoring metal removal [29,30,42]. Therefore, CA is recommended as a good electrolyte to enhance electrokinetic removal heavy metals from sludge [30,43].

As shown in Table 4, the removal efficiency of the five tested metals from sludge was Cr > Zn > Ni > Cu > Pb. Additionally, the metal removal efficiency of the five metals in EK-CA was greater

Table 4
Results of electrokinetic experiments.

Experiment[a]	Electrolyte[b]	Total power consumption (kWh/t)	Metal removal efficiency (%)				
			Zn	Cu	Pb	Ni	Cr
EK-TW	Tap water	4057.42	29	28	20	30	51
EK-SDS	SDS (0.024 mol/L)	2842.50	50	31	26	37	65
EK-CA	Citric acid (1.0 mol/L)	2342.23	64	34	34	42	69

[a] All EK experiments were operated under a constant potential gradient of 32 V for 5 days.
[b] Concentration of SDS = cmc of SDS × 3.0; Concentration of citric acid = equivalents of metals involved × 0.35.

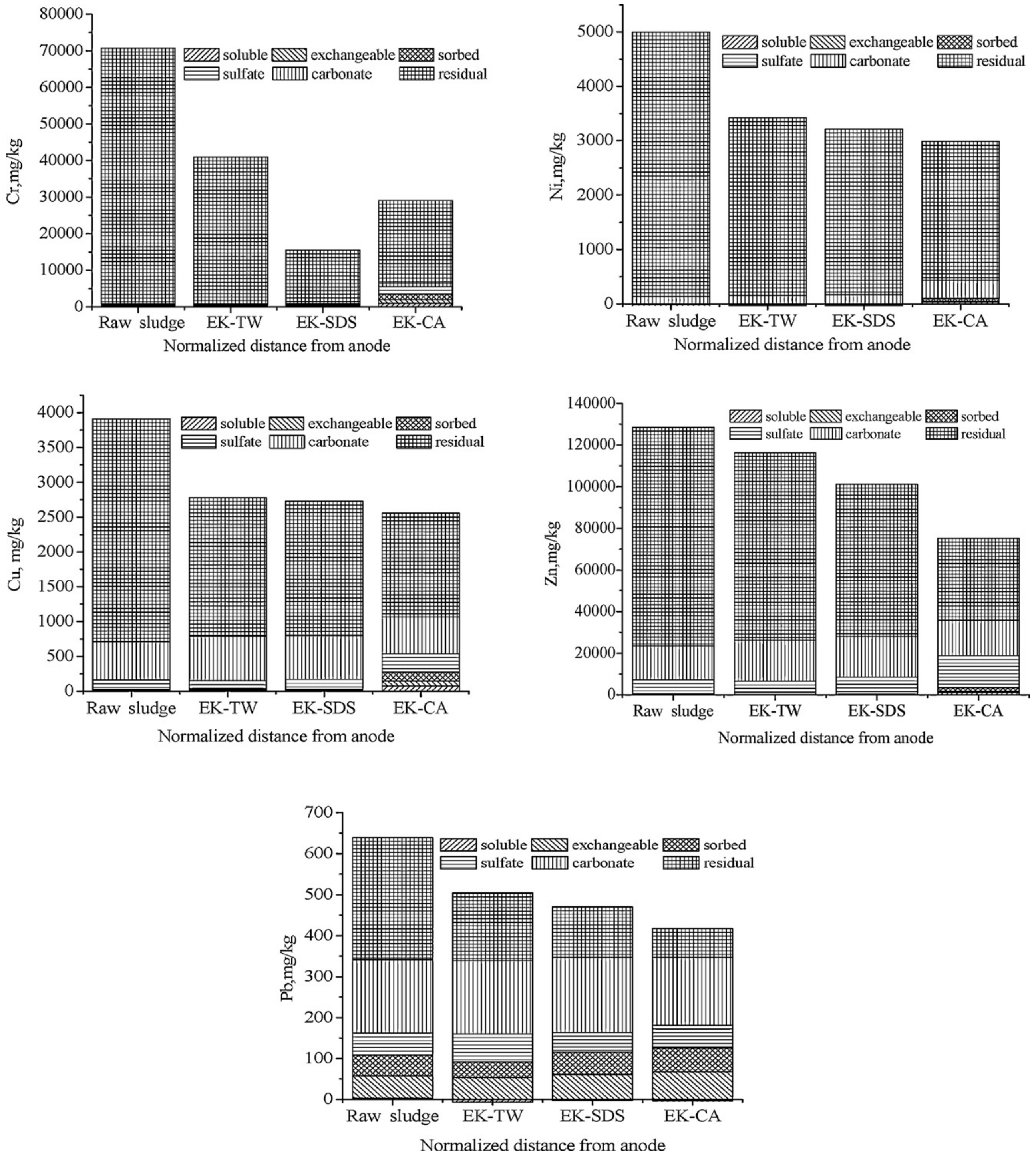

Fig. 4. Binding forms content of heavy metals in the sludge after the electrokinetic experiments.

than that in EK-SDS, possibly due to the easier formation of citric-metal complex ions in the lower pH [43], And SDS which could increase the solubility and mobility of heavy metals did not take effect during electrokinetic remediation, because it could not migrate to the sludge specimen when SDS was used as electrolytes in the electrode compartment [21].

The removal efficiency of metals along the sludge cell is shown in Fig. 3. It was previously expected that a higher potential would shift the metal concentration front toward the cathode area. As such, an accumulated phenomenon would occur in a lower potential experiment. The lowest removal efficiency of metals was 0.4 of normalized distance from the anode to cathode along the sludge specimen in EK-TW experiment. This suggested the potential was not sufficiently high to carry all the metals out. However, such accumulation phenomenon can be reduced by the addition of electrolytes. As Murillo-Rivera et al. [44] state that the metals removal can be controlled using a specific electric current density (depending on soil conductivity and texture), and the convenient electrolytes (type and concentration), since both variables define physical and chemical driving forces throughout the soil. As shown in the EK-SDS and EK-CA experiments and with the exception of Cr and Zn, the other metals concentrations were evenly distributed along the sludge cell. Due to the binding characteristics of SDS with metals and the buffering capacity of CA, more metals were removed from the sludge in EK-SDS and EK-CA experiments when compared to EK-TW experiment.

3.3. The binding forms content of metals

As shown in the Fig. 4, among all the investigated metals, the highest proportion of the residual fraction were found for Cr and Ni, respectively, in sludge both before and after the electrokinetic process. Among all the EK experiments, the residual fraction of the five tested metals decreased, and the degressive level was EK-CA > EK-SDS > EK-TW except for Cr, while the sulfate fraction of Cu and Zn increased steadily as order as EK-CA > EK-SDS > EK-TW. And the carbonate fraction of Cr and Ni increased with the same order while that of the other three metals had no remarkable change. Cu and Zn in sulfate form increased 3 and 4 times, respectively, of the raw sludge and their sorbed forms increased 11 and 12 times, respectively, of the raw sludge after EK-CA treatment. The residual form of Pb decreased while its exchangeable and sorbed forms increased after the three EK treatments. As shown in Fig. 4, the removal priority of the investigated metals from sludge by electrokinetic process was Pb > Zn > Cu > Ni > Cr. This might be largely related to the ion mobility of metals in the sludge.

The highest proportion fraction was performed as residual form and the other five fractions was determined very few in raw sludge for all the studied heavy metals (Fig. 4). This suggests heavy metals are difficult to extract from raw sludge. After EK-TW treatment, Pb, Cu and Zn in the residual form decreased while the carbonate and sulfate forms of all five measured metals increased in comparison to raw sludge. Furthermore, Ni, Cu, Zn and Pb in sorbed forms decreased while Cr, Cu, Zn and Pb in the soluble and exchangeable forms increased. After EK-SDS treatment, the residual fractions decreased while the carbonate fractions increased for all the tested metals in comparison to the raw sludge. Specifically, the levels of Cr and Ni in carbonate forms were 5.3 and 1.9 times greater than that in raw sludge, respectively. Additionally, Pb, Cu, Zn and Cr in sorbed, exchangeble and sulfate forms increased. A phenomenon similarly observed in EK-CA treatment, the residual forms for all the five studied metals were remarkably decreased while carbonate forms were increased, with Cr and Ni in the carbonate form being 9.9 and 3.9 times higher compared to that of raw sludge, respectively. Additionally, the fractions of all the studied metals, especially Cr and Cu in sorbed, exchangeble and sulfate forms, also significantly increased. This indicated that the binding types of metals with sludge changed from the most difficult extraction type (residual fraction) to the easier extraction types (exchangeable, sorbed, sulfate and carbonate fractions) by electrokinetic process. Further proper technologies based on the electrokinetic process to remove metals more effectively could result in this treated sludge being more beneficial for sludge utilization afterwards. Before being reused, the risk of heavy metals in the mobile forms to the environment should be further investigated. In addition, as shown in Fig. 4, the binding forms of heavy metals in sludge after electrokinetic process mainly relate to the electrolytes applied.

4. Conclusions

With the experimental results of heavy metal removal from electroplating sludge by the three EK experiments, the important conclusions have been summarized as follows.

The removal efficiency of metals was in the range of 20–51%, 26–65% and 34–69% for EK-TW, EK-SDS and EK-CA, respectively. The best performance was found in EK-CA. And the removal efficiency of the five investigated metals from sludge by electrokinetic process was Cr > Zn > Ni > Cu > Pb. Furthermore, when using SDS and CA as electrolytes, the accumulation phenomenon of metals in sludge would decrease.

Sequential extraction analysis revealed that the binding forms of heavy metals with sludge highly depended on the electrolytes, changed from the residual form to the soluble, exchangeable, sorbed, sulfate and carbonate forms after electrokinetic process.

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