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Evaluation of Electrokinetic Technique for Industrial Waste Decontamination

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Abstract: Several industrial activities produce large amounts of metal-polluted sludge, disposal of which could pose serious environmental and ecological problems because of the usual high content of mobile metals. In this work, an electrokinetic technique was used to reduce the high metal content of two industrial wastes: sludges from mining (SM) and from the iron-steel (SIS) industry. Initially, a physical-chemical characterization of the sludge was carried out and different extraction assays were tested. Due to the particular characteristics of each of the sludges, in terms of acid buffering capacity or electrical conductivity, different operational conditions were necessary to enhance the electrokinetic treatment.

The results established that for metal remediation of wastes with low acid buffering capacity, such as SM sludge, pH control in the cathode chamber could be an alternative to enhance the electrokinetic technique. The best metal removal results (around 66% Mn) were obtained when sulphuric acid was used to control the pH. Then, to remediate sludges with high acid buffering capacity, such as SIS sludge, pH control in electrode chambers was an inefficient technique and the addition of complexing agents was the best alternative for the electrokinetic process. The extraction assays established that EDTA and citric acid were adequate enhancement agents. However, in the electrokinetic experiments, the use of EDTA as enhancement agent gave the best remediation values with Pb removal of 75%.

The results obtained in the present work demonstrate that the electrokinetic technique could be enhanced by the selection of an adequate strategy that depends on the physical-chemical characteristics of the sludges to treat.

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Keywords: Enhanced electrokinetic, iron-steel industry, mining, sludge

INTRODUCTION

In the last decades, large amounts of polluted wastes associated with industrial, mining, agricultural, and chemical activities have been produced. Among them, the iron-steel industry and mining activities stand out as metal-waste producers.

The iron-steel industry covers the manufacture of steel in basic shapes and forms. In the steel processing units a high quantity of hazardous sludge is generated, disposal of which could pose serious environmental and ecological problems due to the high content of mobile heavy metals (1).

The main environmental impacts of mining activities are vegetation destruction, soil destruction, and mineral oxidation. Acid mine drainage is associated with this last impact which occurs at many mine sites when exposed to residual sulphide minerals contained in waste rock and tailings or exposed in rock cuts and underground workings react with air and water. Their acidity can promote the solubilization of metal pollutants such as Mg, Fe, Cu, Zn, Ni, Co, and As which appear in non-compliant concentrations in water bodies downstream of the mining activities (2). Acid mine drainage must be treated, hence, mining sites usually have wastewater plants. In these places, several agents are used to precipitate metals. Thus, the sludge generated from a wastewater plant contains a high concentration of contaminating metals.

Therefore, in both industries the sludges should be treated prior to disposal, to immobilize and/or extract the soluble metallic constituents. In the last years, several methods such as soil washing, phytoremediation, electrokinetic, and stabilization techniques have been studied as effective alternatives to conventional solidification/stabilization and disposal options (3).

Among them, the electrokinetic technique is receiving more and more attention, because it is a new treatment, technically innovative, and more cost effective than conventional methods. Electrokinetic extraction involves the movement of charged particles suspended in a soil solution, initiated by an electric gradient (4). Electromigration, electroosmosis, and electrophoresis are the main mechanisms responsible for the electrokinetic removal of metals from soils by neutral or charged chemical reagents (5). During electrokinetic treatment, hydrogen ions (H^+) are generated at the anode due to water electrolysis, and migrate into the bulk of the soil. A low pH develops through the soil causing desorption of metal pollutants from the soil solid phases (6). However, the basic front generated in the cathode increases the pH nearest this chamber, reducing the efficacy of the treatment.

Although the electrokinetic technique uses the electrical current to extract metals, usually this treatment is enhanced by using several experimental set-ups and additives such as membranes, complexing agents, or pH control in the electrode chamber (7–9). In addition, the electrokinetic technique has been demonstrated to be successful and cost-effective in removing a wide variety of heavy metals in many bench- and field-scale studies (10–13). However, much work remains to be done on this topic.

In this work, the reduction of metal contents using the electrokinetic treatment of two sludges from mining activities and the iron-steel industry was studied. Kim et al. (14) found that during the electrokinetic technique removal efficiencies of metals were significantly dependent on their speciation in the sludge matrices. Accordingly, metals must be in solution to be extracted using an electric field, thus, metal speciation in the sludge is a property that directly affects the viability of the electrokinetic treatment. This speciation depends on sludge characteristics, such as pH, mineralogy, organic matter content, texture, and the pollution source (15). Consequently, for effective treatment the source of the metal pollutants and the sludge characteristics must be known. Therefore, initially the physical-chemical properties of the sludge were characterized and appropriate electrokinetic treatments were designed as a function of the sludge characteristics.

MATERIALS AND METHODS

Sludge Samples

Sludge samples, SM and SIS, were collected from mining and iron-steel industry, respectively, both sites located in Galicia (northwest Spain). For all experiments, the samples were sieved and the fraction containing particles of sizes lower than 2 mm was selected.

Analytical Methods

Metal Concentration

The protocols used for the chemical extraction and analysis of metals were performed in accordance with EPA Methods 3010 and 3050. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used to analyze metals. Duplicate measures were carried out with an experimental error lower than 3%.

Sludge pH

It was measured adding 1 M KCl solution to dry sludge in a ratio 2.5 ml · g^{-1}. After 1 h contact time, pH was measured using a pH meter (Sentron model 1001).

Sludge Electrical Conductivity

Sludge electrical conductivity was measured as described by Nystrom (16). In this procedure distilled water was added at a ratio of 2.5 ml · g^{-1} 1 dry sludge and the suspension agitated for 30 minutes. After a repose period (20 min.), conductivity was measured using a conductivimeter (Crison Basic 30).

Sludge Acid Buffering Capacity

Buffering capacity is defined as the ability of sludge to resist changes in pH. The assays were performed using the procedure described by Reddy et al. (17). Acid buffering capacity of the sludge was assayed by titration. A suspension of sludge sample in water (6.7% w/v) was stirred for 30 minutes and the pH was analyzed. Successive 1 ml additions of concentrated HCl were made every 30 minutes and pH was measured thereafter. This procedure was repeated until the pH value was constant. The results obtained were plotted as pH versus HCl added (ml). The results were elucidated in qualitative form, comparing the profiles corresponding to sludge sample with those of kaolin, which is commonly known to have low acid buffering capacity.

Extraction Assays

In several cases, complexing agents were added to increase metal solubility. Therefore, extraction assays were carried out to determine which extraction agent was more adequate. These experiments were performed in 250 ml Erlenmeyer flasks containing 5 g of sludge mixed with 100 ml of 0.1 M complexing agent solution such as ethylenediaminetetraacetic acid (EDTA), citric and oxalic acid. The Erlenmeyer flasks were kept on an orbital shaker (Thermo Electron Corporation, model 420) at 300 rpm and 30°C. Samples were taken after 72 hours and the metal concentration was assayed. The experiments were performed twice, within an experimental error margin below 3%.

Electrokinetic Cell

The experiments were performed in a cylindrical glass cell containing a sample compartment (18). Graphite electrodes, supplied by Carbone Lorraine, were selected due to their inertia. The two electrode chambers were placed at each end of the sample compartment isolated from each other by filter paper and porous stones. Three auxiliary electrodes allowed measuring the electric field distribution throughout the sample. Electrode chambers were filled with processing fluid and recirculation of liquid was achieved using pumps in both compartments to avoid concentration gradients. In some experiments the pH in the electrode chamber was controlled by using a pH controller (Consort, R735).

Methodology

The experimental procedure was based on that established in previous papers (19) in which kaolin was used as soil sample. Thus, a constant potential difference of 30 V ($3\,\mathrm{V\cdot cm^{-1}}$) was applied during treatment in all experiments. Readings of the voltage drop, current intensity, and the pH in the electrode compartments were taken periodically. Every 15 days electrode fluids were renovated and graphite electrodes were changed. Upon completion of each experiment, samples were taken from the cathode and the anode solutions and from the sludge for chemical analyses. The sludge sample was divided into five sections (S1–S5, namely from anode to cathode) and each one was analyzed for pH and metal concentrations.

RESULTS AND DISCUSSION

In this work, the viability of metal remediation of industrial sludges by electrokinetic technique was assessed. Initially, a detailed study of the sludge characteristics was necessary to test different strategies to improve the efficacy of the electrokinetic treatment. Some factors, such as sludge origin, pH, metal content, conductivity, and buffering capacity, were analyzed.

Sludge Characterization

SM Sludge Origin

As mentioned in the Introduction section, the main problem of the mining-electrical complex is that the acid mine drainage must be treated in a wastewater plant. In this site, to precipitate metals several agents such as carbonates and/or hydroxides are used. Consequently, the sludge generated contains a high concentration of contaminating metals that must be reduced prior to release into the environment.

In this study a sludge, named SM, obtained from a mining-electrical complex in Galicia (NW Spain) was used. The analytical measures reveal that this sludge possesses a slightly acid pH and the highest metal concentrations correspond to Fe, Al, Mg, and Mn (Table 1).

SIS Sludge Origin

The iron-steel industry produces steel from ferric scrap metals. During the manufacturing process sludge with high metal contents is generated and its disposal could pose serious environmental and ecological problems. Sludge supplied by an iron-steel industry, located in Galicia (NW Spain), was considered a representative sample for this kind of industry. Table 1 shows the main metals and their concentrations determined in the sludge characterization. The presence of Pb and Zn is due to their use in the founding process as alloy agent and steel protector, respectively.

Physical and Chemical Characteristics of Sludges

Sludge pH. Metal speciation is strongly pH-dependent, thus, the initial pH is an important aspect to determine the solubilization ability of the metal present in the sludges. As shown in Table 1, SM sludge has a slightly acid pH, around 6.8. Thus, Mn and Mg will be kept as carbonates; however, the high pK values of the main polluting metals, Fe

Table 1. Metal composition and properties of sludge from mining (SM) and from iron-steel industry (SIS)

	SM	SIS
Fe ($mg \cdot Kgds^{-1}$)	41,147.09	–
Al ($mg \cdot Kgds^{-1}$)	12,046.61	–
Mg ($mg \cdot Kgds^{-1}$)	2,575.33	–
Mn ($mg \cdot Kgds^{-1}$)	792.42	–
Pb ($mg \cdot Kgds^{-1}$)	–	215,632.18
Zn ($mg \cdot Kgds^{-1}$)	–	44,189.09
pH	6.80	9.22
Moisture (%)	27.8	30.0
Electrical Conductivity ($mS \cdot cm^{-1}$)	1.383	2.890

and Al, allow these species to be present in the sludge as hydroxides with high stability in a wide range of pHs (Table 2). In contrast, SIS sludge has a slightly basic pH, thus, the main contaminating metals, Zn and Pb, are retained in the sludge as hydroxides.

Sludge Electrical Conductivity. This parameter gives an indication as to how the electrical current will pass through the sludge. If the electrical conductivity is high, the sludge has low electrical resistance and the electrical current travels easily through the sludge. The opposite occurs when the electrical conductivity is low. In this study, both sludges SM and SIS have high conductivity (Table 1), three- and seven-fold the kaolin value ($0.42\,\mathrm{mS \cdot cm^{-1}}$), respectively. Consequently, in these sludges the low electrical resistance favors the electrokinetic treatment.

Sludge Acid Buffering Capacity. This factor is defined as the ability of sludge to resist changes in pH. In Fig. 1 the acid buffering capacity of kaolin versus sludges is plotted. Similar profiles were obtained for kaolin and SM sludge. The SM acid buffering capacity was neutralized after addition of 1 ml of concentrated HCl. This shows that the pH of the SM sludge can be easily diminished. Subsequently, the acid front generated during the electrokinetic treatment could be able to reduce the

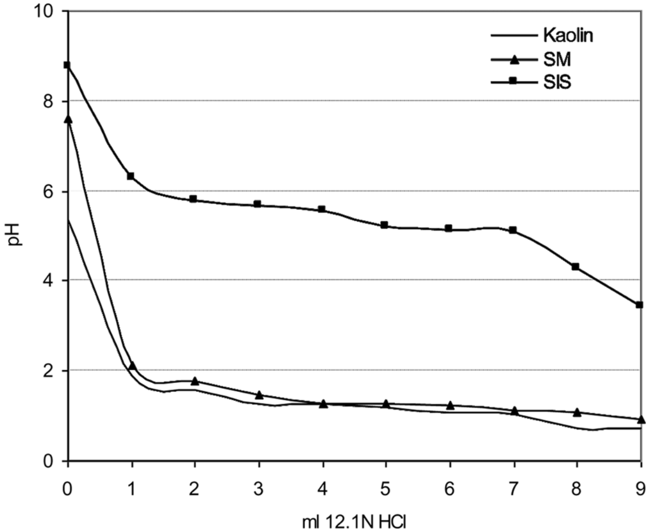

Figure 1. Buffering capacity of kaolin and sludges: from mining (SM) and from iron-steel industry (SIS).

sludge pH and therefore metals could be extracted from the sludge. Therefore, for this kind of sludges, pH control of the process could be a viable alternative. As shown in Fig. 1, the SIS pH was difficult to change and only after addition of 7 ml of concentrated HCl was the pH drastically reduced. This parameter has a great influence on the remediation process, given desorption of metal pollutants from the sludge is favored at low pH. For this reason, in sludges with high acid buffering capacity addition of enhancing agents such as complexing agents is necessary to keep the metals in solution.

SM Electrokinetic Treatment

After SM sludge characterization, enhanced electrokinetic treatment using pH control in the cathode chamber was proposed. Under these operational conditions, the basic front generated in the cathode chamber is neutralized. Therefore, the acid environment permits the pollutants to stay in the interstitial solution and then they could be transported towards the electrode chamber by action of the electric field.

Several neutralizing agents can be used to depolarize the cathode reaction; however, these agents must have some requirements. Depolarizing agents cannot originate secondary reactions on the surface of the electrodes, they must be economical, and they should not form metal-polluted insoluble compounds (20). Based on previous papers (21,22), two acids, sulphuric and citric, were chosen. Citric acid is an organic acid, which would acidify the soil, making metal desorption from soil easier and it can form mononuclear, binuclear, or polynuclear and bi-, tri-, and multidentate complexes with metal ions (23). Furthermore, Yuan and Chiang (5) found that citric acid was a good pH conditioner

Table 2. Main carbonates and hydroxides of the sludges metals, pKs and pH stability (37)

Metals	Reactions	pKs	pHs
Fe(III)	$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$	37	~2–14
Al(III)	$Al(OH)_3 \leftrightarrow Al^{3+} + 3OH^-$	33.5	~3.5–12.5
Mg(II)	$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$	11.1	~9.5–14
	$MgCO_3 \leftrightarrow Mg^{2+} + CO_2^{-3}$	5	
Mn(II)	$Mn(OH)_2 \leftrightarrow Mn^{2+} + OH^-$	12.7	~8.5–14
	$MnCO_3 \leftrightarrow Mn^{2+} + CO_2^{-3}$	9.3	
Zn(III)	$Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$	14.8	~7.5–11.5
Pb(II)	$Pb(OH)_2 \leftrightarrow Pb^{2+} + 2OH^-$	14.4	~7.8–12.4

Table 3. Operational conditions of experiments

Experiment	Duration (d)	Field ($V \cdot cm^{-1}$)	Process fluid	Control pH place (Value)	Depolarizing agent
SM0	15	3	Water	–	–
SM1	22.71	3	Water	Cathode (6)	0.1 M Sulphuric acid
SM2	51.93	3	Water	Cathode (6)	0.1 M Citric acid
SIS0	15	3	Water	–	
SIS1	36.79	3	0.1 M Citric acid	–	–
SIS2	82.83	3	0.1 M EDTA	Anode (7)	0.1 M NaOH

to inhibit precipitation of metal hydroxide and consequently when this compound was present the dissolution reaction becomes dominant in the electrokinetic system. Then, sulphuric acid is a mineral acid that is abundant in mining countries and that seems to be a good additive for mine tailings during the electrokinetic remediation (24).

In this study, an economical perspective was considered to choose the pH control value. In our previous studies using a sample model, low pH in the system increased the electric consumption and therefore the cost of the treatment (25). Considering preliminary studies, a slightly acid value (pH 6) was selected to control the pH in the cathode chamber. The experimental conditions carried out in the electrokinetic treatments of this sludge are shown in Table 3.

pH Control with Sulphuric Acid Experiment (SM1)

Figure 2 shows the normalized concentration of polluting metals in the sludge after SM1 treatment. In the control experiment (SM0) no changes in metal distribution were detected. However, when pH control was applied the electrokinetic process was successfully undertaken and different metallic behaviors were found, classified into two groups:

1. metals that migrated towards the cathode chamber but that accumulated in sections S3–S5 and
2. metals that migrated towards the cathode chamber but that did not accumulate in either section.

Fe and Al were the most plentiful pollutants and their concentration decreased in sections S1 and S2 and in sections S3–S5 their concentration was slightly decreased. This behavior could be attributed to pH distribution. Sections S1 and S2 had low pH and this fact provoked the highest

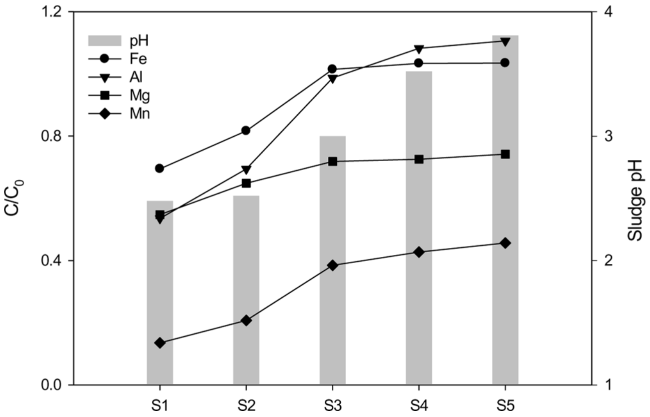

Figure 2. Metal and pH distribution after experiment SM1.

elimination. Removal percentages of Fe and Al were 8.3% and 11.8%, respectively. Although these values were relatively low, in the cathode chamber higher amounts of these metals were found.

The second group of metals had large removal levels in all sludge sections. Among them, Mn showed the best removal degree. 66% of the initial Mn in the sludge sample was collected in the cathode chamber. Mg removal was lower than that of Mn, only 32.6%, this value obtained given Mg is more abundant than Mn. Mg concentration was almost three-fold higher than that of Mn. The highest removal values were reached in sections S1 and S2.

pH Control with Citric Acid Experiment (SM2)

To ascertain the influence of the depolarizing agent on metal removal, a treatment using citric acid was applied (SM2). Citric acid is a weak acid that is environmentally friendly; addition of citric acid to the cathode chamber had two purposes: to neutralize the alkaline environment and to obtain ligand forming stable complexes with metals. Furthermore, some researches have demonstrated that the presence of citric acid in the soil increased the electroosmotic flow favoring metal removal (26,27).

As shown in Fig. 3, Fe and Al removal was low, similar to that obtained in the experiment SM1. Metal recovery in the cathode chamber was 7.9% and 0.23% of the initial Fe and Al amount, respectively. The concentration of these metals decreased in the first section of the sludge and accumulated in subsequent sections, especially where the pH jump occurred (S2–S4).

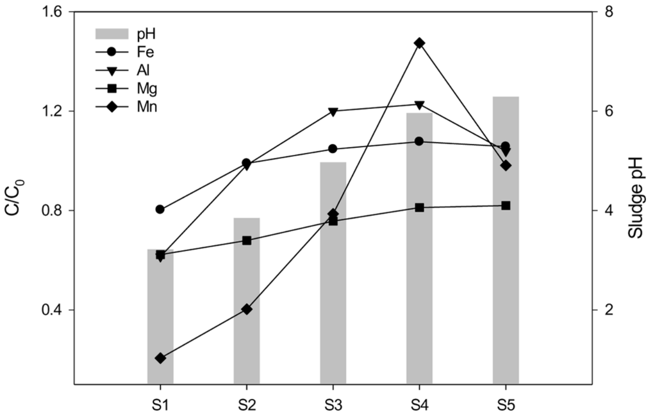

Figure 3. Metal and pH distribution after experiment SM2.

Mn presented an accumulation profile different than shown in experiment SM1. Although treatment time was more than two-fold higher, the removal percentage reached was only 33%. However, Mg was transported through the sludge to the cathode chamber and around 31% of Mg was removed. In addition, no metals were detected in the anode chamber, demonstrating that negative complexes were not formed by the action of the citrate ion. Although Yuan and Weng (28) reported that the presence of citric acid decreases the sludge pH and metals could be extracted efficiently from sludge, in this case, sludge acidification in SM2 was low, the pH ranging from 3.2 to 6.3. However, when sulphuric acid was added this range was from 2.5 to 3.8 (Fig. 2 and 3) and the highest reduction in metal contents was achieved. The results are in accordance with those of Al-Shahrani and Roberts (21) who found that inorganic acid, such as nitric or sulphuric, gave higher removal rates and more uniform pH distribution than citric acid.

Furthermore, no electroosmotic flow in these electrokinetic experiments was detected, possibly attributed to the reduction in zeta potential as a result of sludge acidification that was ascertained by Wang et al. (29).

In this kind of sludge, pH control using sulphuric acid is a suitable strategy to follow when the aim is to enhance the electrokinetic treatment.

SIS Extraction Assays

The physical and chemical characteristics of SIS, especially its high buffering capacity, indicated that to enhance the electrokinetic technique the use of complexing agents could be a possible alternative. It is known that complexing agents increase the solubility of metal species, forming soluble complexes in a wide range of pHs (30). Thus, metals could migrate through the matrix under the electric field without retention and in some cases favoring electroosmotic flow (31). In the selection of complexing agents several considerations must be taken into account: metallic complex originated must be stable in a wide pH interval, the ratio between the complexing agent and metal should be 1:1, complexing agents and their complexes must not be adsorbed to the soil particles and the price of complexing agents must be reasonable (32).

Series of extraction assays were elucidated to determine the best complexing agent for metal removal in SIS. Based on our previous researches (33), citric acid, EDTA and oxalic acid were analyzed as complexing agents. Moreover, in the literature several papers have reported the use of these agents for the solubilization of Pb and Zn. Del Mundo-Dacera and Babel (34) carried out a lab-scale study on the efficiency of citric acid and oxalic acid in the extraction of Cr, Cu, Pb, Ni, and Zn from anaerobically digested sludge. At pH 3, citric acid seemed to be highly effective in extracting Pb (at 100%) at 1 day leaching time, although higher removals were also attained for Ni (70%) and Zn (80%) at only 2 hours leaching time. Polettini et al. (35) performed several washing treatments using the four chelating agents EDTA, nitrilotriacetic acid (NTA), citric acid and S,S-isomer of the ethylenediaminedisuccinic acid ([S,S]-EDDS) aiming at the remediation of metal-contaminated sediment. The use of an EDTA solution at pH 5 gave the best results for Zn and Pb extraction.

In this study, the metal extraction capacity from the SIS sludge was evaluated at two pH values, 4 and 7. When oxalic acid was used negligible metal extraction was detected. Although operating at pH 4 in the presence of citric acid metal removal was around 30% for Pb and 45% for Zn, the highest total metal removal efficiency obtained when EDTA was used at pH 7 (Fig. 4).

SIS Sludge Electrokinetic Treatment

The extraction assays demonstrated that EDTA and citric acid could increase the free metal in solution. For this reason, the selection of both complexing agents as strategy to enhance the electrokinetic process was assessed. Recently, these solutions were proposed by several researchers. Thus, Yuan and Weng (28) evaluated different extracting agents in the electrokinetic treatment of industrial wastewater sludge polluted with Cr, Cu, Fe, Ni, Pb, and Zn. They found that citric acid reached the highest removal values, around 43–78% depending on the nature of the metal.

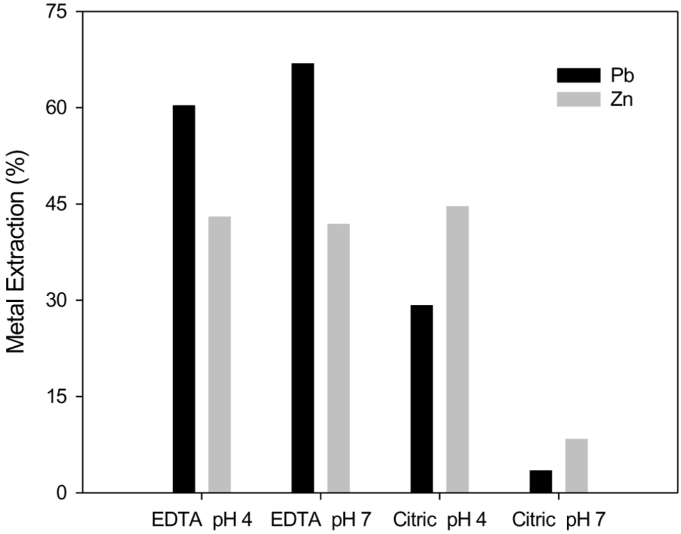

Figure 4. Extraction assays using 0.1 M citric acid and 0.1 M EDTA, at pH 4 and 7.

Then, Amrate et al. (36) demonstrated that EDTA was an adequate complexing agent to treat a soil contaminated with Pb.

From the results of the extractions assayed and of these previous reports, several experiments were carried out to evaluate the influence of EDTA and citric acid on the electrokinetic treatment of this kind of sludge (Table 3).

Initially, a control electrokinetic treatment (SIS0) was performed. No removal was achieved after treatment.

Citric Acid Experiment (SIS1)

An electrokinetic experiment (SIS1) using citric acid as processing fluid in both electrode chambers was carried out. pH control in the cathode chamber was proposed to avoid the negative effect of the basic front. The presence of citric acid in the cathode chamber permitted to keep this site under acid conditions (pH 2) during the treatment time without pH control.

Figure 5 shows the distribution of Zn and Pb, in the sludge sample, at the end of the experiment, as well as the pH profile. In this experiment, neither Zn nor Pb was detected in the anode chamber. However, in section S1, the percentage of removal reached a level of more than 60%

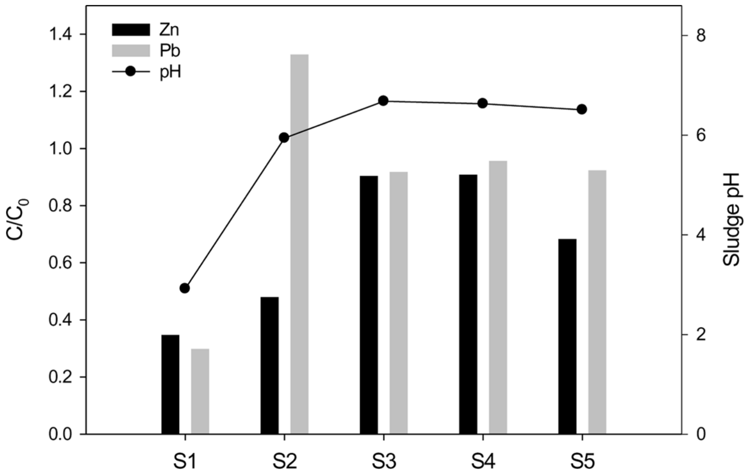

Figure 5. Metal and pH distribution after experiment SIS1.

for both metals; however, this removal decreased in the second section, especially for Pb removal. There was a clear relationship between metal accumulation and pH profile (Fig. 5) as a consequence of the pH jump observed between S1 and S2. In this treatment slight metal migration towards the cathode was reached which was favored for the electroosmotic flow generated with an average value more than $6\,\mathrm{mL \cdot d^{-1}}$. At the end of the treatment, about 26% of Zn and 6% of Pb were extracted from the sludge. These results disagree with those reported by Yuan and Weng (28) when citric acid was used as an enhancing agent, a removal of around 60% was reached for both metals (Pb and Zn). Although the metal recovery percentage obtained in SIS1 was low, especially for Pb, a significant amount of metal was extracted due to the high concentrations of these pollutants in the sludge.

EDTA Experiment (SIS2)

A third electrokinetic experiment (SIS2) using a complexing agent was carried out with EDTA instead of citric acid (Table 3). EDTA is not soluble at very acid pH (below 3.5) so, in this experiment, the pH was controlled in the anode chamber at a value of 7.

Initially, the electric field was adjusted to 30 V ($3\,\mathrm{V \cdot cm^{-1}}$); however, the highest current intensity registered in the system forced to limit the current intensity at a value of 50 mA to avoid electric heating. The increase in the electrical current and the basic pH inside the sludge

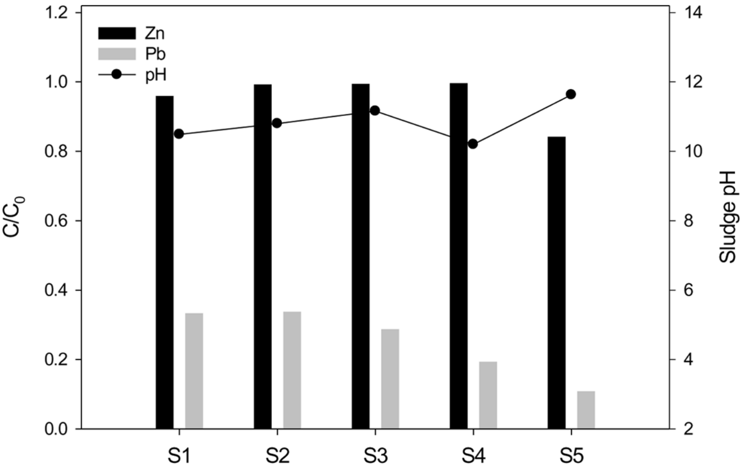

Figure 6. Metal and pH distribution after experiment SIS2.

enhanced the electroosmotic flow, reaching an average value of $15.3\,\mathrm{ml \cdot d^{-1}}$. This value is higher than that of the electroosmotic flow registered in the previous experiment. After the electrokinetic treatment, around 4% of Zn and 75% of Pb reached the anode chamber. No metals were detected in the cathode chamber.

As seen in Fig. 6, Pb removal was high in sections S1 and S2, the profile confirming its transportation towards the anode chamber. Sludge pH was kept under basic conditions, favoring metal complexation. Under these operational conditions, Pb seems to form a negative complex with EDTA. This was verified during the treatment as the apparition of different colors in the anode chamber, which is typical of complex formation. In contrast, only section S5 showed a clear reduction of Zn content. Metal recovery could be influenced by metallic compound origin and how the metal is linked to the sludge. In the case of Zn, EDTA was not able to extract the metal under the conditions assayed. These results are in accordance with the extraction assays where Zn removal was lower than that of Pb (Fig. 4).

CONCLUSIONS

The results obtained in this work demonstrate that the unenhanced electrokinetic technique is inadequate to reduce the metal content of polluted sludges. However, addition of several agents could increase the efficiency of this technique. Moreover, it was ascertained that acid buffering capacity was a key variable to determine the more appropriate strategy to follow to enhance the electrokinetic treatment. Sludges with low acid buffering capacity can be easily acidified and pH control in the cathode chamber is the best enhancing method for the electrokinetic treatment. Then, for sludges with high acid buffering capacity, the electrokinetic technique using complexing agents was proposed.

pH control in the cathode chamber was selected as an alternative approach used to enhance the electrokinetic technique of SM sludge. In this sludge, each metallic species showed different behaviors when the electric field was applied. However, all metals studied tended to mobilize and migrate towards the cathode chamber. The elimination rate changed as a result of metal concentration, metal compound origin, and depolarizing agent. Metal removal largely depended on the sludge pH value. The highest removal value was achieved in the sections where the pH value was sufficiently acid. Metals were dissolved at acid pH and migrated towards the cathode side, where they accumulated. The highest metal reduction was obtained using sulphuric acid as depolarizing agent, showing a reduction of about 66% for Mn content in the sludge.

In contrast, addition of complexing agents to sludge SIS was considered an adequate enhancement technique. The electrokinetic experiments showed that the best agent to treat this sludge was EDTA. Nearly 75% of Pb was extracted from the sludge.

The results obtained in the present study reveal that the enhanced electrokinetic technique can be used to reduce the metal content of mining and iron-steel processing sludges.

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REFERENCES

1. Rachana, M.; Rubina, C. (2006) Leaching behavior and immobilization of heavy metals in solidified/stabilized products. *J. Hazard. Mater.*, *137* (1): 207.
2. Volke Sepúlveda, T.; Velasco Trejo, J.A.; de la Rosa Pérez, D.A. (2005) *Suelos Contaminados por Metales y Metaloides: Muestreo y Alternativas para su Remediación*; Instituto Nacional de Ecología (INE-Semarnat) Press: Mexico.

3. Dermont, G.; Bergeron, M.; Mercier, G.; Richer-Laflèche, M. (2008) Metal-Contaminated soils: Remediation practices and treatment technologies. *Pract. Period. Hazard. Toxic Radioactive Waste. Manag.*, *12* (3): 188.
4. Lestan, D.; Luo, C.-L.; Li, X.-D. (2008) The use of chelating agents in the remediation of metal-contaminated soils: A review. *Environ. Pollut.*, *153* (1): 3.
5. Yuan, C.; Chiang, T.-S. (2008) Enhancement of electrokinetic remediation of arsenic spiked soil by chemical reagents. *J. Hazard. Mater.*, *152*: 309.
6. Acar, Y.B.; Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation. *Environ. Sci. Technol.*, *27* (13): 638.
7. Puppala, S.K.; Alshawabkeh, A.N.; Acar, Y.B.; Gale, R.J.; Bricka, M. (1997) Enhanced electrokinetic remediation of high sorption capacity soil. *J. Hazard. Mater.*, *55* (1–3): 203.
8. Zhou, D.M.; Deng, C.F.; Cang, L. (2004) Electrokinetic remediation of a Cu contaminated red soil by conditioning catholyte pH with different enhancing chemical reagents. *Chemosphere*, *56* (3): 265.
9. Reddy, K.R.; Chinthamreddy, S. (2003) Effects of initial form of chromium on electrokinetic remediation in clays. *Adv. Environ. Res.*, *7* (2): 353.
10. Lageman, R.; Pool, W.; Seffinga, G. (1989) Electro-reclamation: Theory and practice. *Chem. Ind. (london)*, *18*: 585.
11. Acar, Y.B.; Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation. *Environ. Sci. Technol.*, *27*: 2638.
12. Kim, S.O.; Kim, K.W. (2001) Monitoring of electrokinetic removal of heavy metals in tailing-soils using sequential extraction analysis. *J. Hazard. Mater.*, *85*: 195.
13. Altin, A.; Degirmenci, M. (2005) Lead(II) removal from natural soils by enhanced electrokinetic remediation. *Sci. Total Environ.*, *337*: 1.
14. Kim, S.O.; Moon, S.H.; Kim, K.W.; Yun, S.T. (2002) Pilot scale study on the ex situ electrokinetic removal of heavy metals from municipal wastewater sludges. *Water Research*, *36*: 4765.
15. Cala, V.; Kunimine, Y. (2003) Distribución de plomo en suelos contaminados en el entorno de una planta de reciclaje de baterías ácidas. *Rev. Intern. Contam. Ambient*, *19* (3): 109.
16. Nystrom, G.M. (2001) Investigations of Soil Solution During Enhanced Electrodialytic Soil Remediation. Denmark Technical University BYG-DTU R009.
17. Reddy, K.R.; Donahue, M.; Saichek, R.E.; Sasaoka, R. (1999) Preliminary assessment of electrokinetic remediation of soil and sludge contaminated with mixed waste. *J. Air Waste Manage. Assoc.*, *49* (7): 823.
18. Ricart, M.T.; Hansen, H.K.; Cameselle, C.; Lema, J.M. (2004) Electrochemical treatment of a polluted sludge: Different methods and conditions for manganese removal. *Sep. Sci. Technol.*, *39* (15): 3679.
19. Pazos, M.; Gouveia, S.; Sanromán, M.A.; Cameselle, C. (2008) Electromigration of Mn, Fe, Cu and Zn with citric acid in contaminated clay. *J. Environ. Sci. Health, Part A*, *43* (8): 823.

20. Yeung, A.T.; Hsu, C.N.; Menon, R.M. (1997) Physicochemical soil-contaminant interactions during electrokinetic extraction. *J. Hazard. Mater.*, *55* (1–3): 221.
21. Al-Shahrani, S.S.; Roberts, E.P.L. (2005) Electrokinetic removal of caesium from kaolin. *J. Hazard. Mater.*, *122*: 91.
22. Chang, P.-W.; Tan, Y.-C.; Wang, I.-S. (2008) On-farm remediation and fertility enhancement of cadmium-contaminated silt loam by electrokinetic treatment process in Taiwan. *Irrig. Drain.*, *57*: 187.
23. Bassi, R.; Prasher, S.O.; Simpson, B.K. (2000) Extraction of metals from a contaminated sandy soil using citric acid. *Environ. Prog.*, *19*: 275.
24. Hansen, H.K.; Rojo, A.; Ottosen, L.M. (2007) Electrokinetic remediation of copper mine tailings. Implementing bipolar electrodes. *Electrochim. Acta*, *52*: 3355.
25. Pazos, M. (2007) PhD. Aplicación de Técnicas Electrocinéticas en el Tratamiento de Suelos Contaminados. Deparment of Chemical Engineering University of Vigo.
26. Eykholt, G.R.; Daniel, D.E. (1994) Impact of system chemistry on electro-osmosis in contaminated soil. *J. Geotech. Eng.*, *120* (5): 797.
27. Yang, G.C.C.; Lin, S.-L. (1998) Removal of lead from a silt loam soil by electrokinetic remediation. *J. Hazard. Mater.*, *58* (1–3): 285.
28. Yuan, C.; Weng, C.H. (2006) Electrokinetic enhancement removal of heavy metals from industrial wastewater sludge. *Chemosphere*, *65* (1): 88.
29. Wang, J.Y.; Zhang, D.S.; Stabnikova, O.; Tay, J.H. (2005) Evaluation of electrokinetic removal of heavy metals from sewage sludge. *J. Hazard. Mater.*, *124* (1–3): 139.
30. Peters, R.W. (1999) Chelant extraction of heavy metals from contaminated soils. *J. Hazard. Mater.*, *66* (1–2): 151.
31. Zhou, D.M.; Zorn, R.; Kurt, C. (2003) Electrochemical remediation of copper contaminated kaolinite by conditioning anolyte and catholyte pH simultaneously. *J Environ. Sci.-China*, *15* (3): 396.
32. Peters, R.W.; Shem, L. (1992) Use of chelating agents for remediation of heavy metal contaminated soil. *ACS Symposium Series Environ. Rem.*, *509*: 70.
33. García Nogueira, M.; Pazos, M.; Sanromán, M.A.; Cameselle, C. (2007) Improving on electrokinetic remediation by adittion of complexing agents. *Electrochim. Acta*, *52*: 3349.
34. Del Mundo-Dacera, D.; Babel, S. (2006) Use of citric acid for heavy metals extraction from contaminated sewage sludge for land application. *Water Sci. Technol.*, *54* (9): 129.
35. Polettini, A.; Pomi, R.; Rolle, E. (2007) The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment. *Chemosphere*, *66* (5): 866.
36. Amrate, S.; Akretche, D.E.; Innocent, C.; Seta, P. (2005) Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction. *Sci. Total Environ.*, *349* (1–3): 56.
37. Burriel Martí, F.; Lucena Conde, F.; Arribas Jimeno, S.; Hernández Méndez, J. (1989) *Química Analítica Cualitativa*; Paraninfo Press: Spain.