



## Effect of EDTA as washing solution on removing of heavy metals from sewage sludge by electrokinetic

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### ABSTRACT

This paper presents the effect of ethylene diamine tetraacetic acid (EDTA) as a washing solution on the electrokinetic process for removal of Cr, Pb and Zn from sewage sludge. The sequential chemical extraction scheme according to the guidelines of BCR (Community Bureau of Reference) was applied to the sludge samples to evaluate the effect of EDTA on metal fractionation during electrokinetic processes. The highest removals of the heavy metals were 34% for Cr, 27% for Pb and 20% for Zn with 0.1N EDTA. The removal priority of the metals by electrokinetic process was found to be Cr > Pb > Zn. According to the results of BCR analysis, addition of EDTA did not create the inter-transformation of Cr, Pb and Zn although the metal concentration decreased.

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### 1. Introduction

Sewage sludge which contains toxic elements such as heavy metals is commonly utilized as a fertilizer around the world due to its high valuable nutrients and organic matter, improving the physical, chemical and biological properties of soil. Heavy metals cause soil and groundwater contamination in the case of continual application. The risk from heavy metals can be solved by limiting the amounts of sludge applied to soil. A significant way for overcoming the problem is to remove the heavy metals from sludge. Hence, several methods such as chemical extraction, bioleaching, super critical fluid extraction and electrokinetic have been used by many researchers [1–3]. On the other hand, the determination of the total concentration of heavy metals does not give the knowledge on the potential environmental impact, metal solubility, mobility, bioavailability and leaching rates. Sequential extraction method should be applied to the sludge in order to obtain these data [4,5]. It is known very well that heavy metals easily move in the cases of soluble, exchangeable and adsorbed forms, but cannot easily mobilize with organic ligands [6].

Electrokinetic technology requires a low-level DC potential gradient or an electric current. Low-level current varies physico-chemical and hydrological properties of soil due to many reactions. The reactions may include electrolysis of water, mineral decom-

position, precipitation of salt hydrolysis, oxidation, reduction, and physical–chemical sorption [7]. Among these mechanisms, the electrolysis of water is the main reaction that changes the pH values through a soil level during electrokinetic process, causing the pH decrease to 2 near anode and pH increase to 11 near to cathode. When the electric potential is applied to the soil mass, the cations such as heavy metals present in the soil move toward to the cathode and the anions move to the anode due to ionic migration. However, high pH near the cathode is a main obstacle to solubilize and migrate of heavy metals. It is well known that they adsorb to soil particles or precipitate as hydroxides in the high pH zone and those ions desorb, solubilize and migrate in the low pH zone. In order to improve the effectiveness of the process in terms of removing heavy metals from sludge, 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<sup>−</sup> migration from cathode chamber into the soil, and using an electrolyte circulation to control electrolyte pH [7–9]. Among the used chemical reagents, ethylene diamine tetraacetic acid (EDTA) has been commonly added to the catholyte [10–12] and soil system [13–16] due to its strong chelating ability for different heavy metals, which is a negligible effect on soil properties as compared with flushing agents such as acids.

Many researchers have generally focused on the using EDTA as washing solution to improve the performance of electrokinetically metal extraction from contaminated soils [14–18]. Virkutyete et al. [13] evaluated the changes in the copper fractionation after complexation with EDTA of artificially copper contaminated anaerobic

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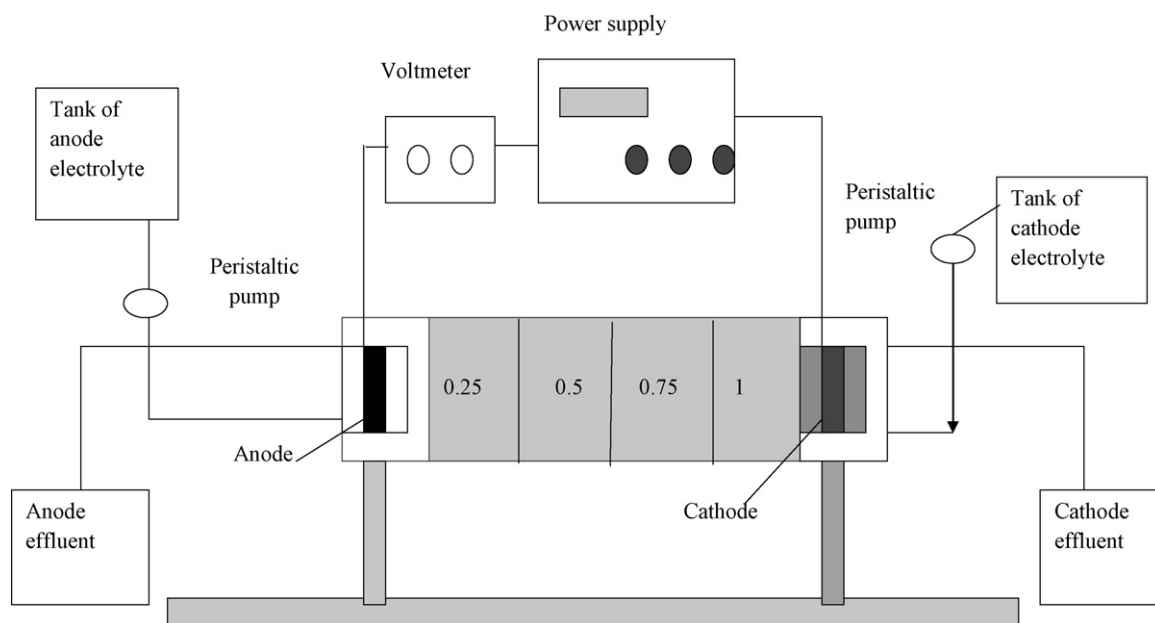


Fig. 1. The schematic diagram of electrokinetic system.

granular sludge [13]. Hence, there is not enough knowledge about the effect of EDTA as washing solution on heavy metal extraction by electrokinetic from sewage sludge and on the changes in the form of heavy metals. Therefore, in this study the aim was to examine the removal of Cr, Pb and Zn present in sewage sludge obtained from treatment plant and to determine the impact on the chemical forms of heavy metals during the electrokinetic process, using EDTA as a washing solution at different concentrations.

## 2. Materials and methods

### 2.1. Sewage sludge

Sewage sludge used in the experiments was sludge cake stabilized by means of mechanic dewatering unit following anaerobic digestion in municipal wastewater treatment plant located in the province of Kayseri, Turkey. The treatment plant treats both industrial and domestic wastewaters corresponding to 800,000 population equivalent, and is operated as an extended aeration system.

### 2.2. Electrokinetic system

The experimental equipment included in three main parts; sludge cell, electrode compartments and electrolyte reservoirs, as seen in Fig. 1. The sludge cell was a cylindrical fiberglass with a length of 15 cm and inner diameter of 5.5 cm and was filled with dried sewage sludge. Four orifices were drilled on the sludge cell to collect the sludge samples and to measure the voltage differences through the cell. The electrode compartments had a diameter of 5.5 cm and a length of 5 cm and each of them were open at the top to vent the electrolysis gases. Inert graphite disc electrodes with diameter of 5 cm were placed at both cathode and anode compartments. In order to avoid sludge particles from passing into the electrode compartments, two sheets of filter paper separated the sludge cell and the electrode compartments. Two tanks with a volume of 9 L were used as electrolyte reservoirs and other two tanks with 20 L were used as effluent reservoirs. Electrolyte solutions were pumped at 0.5 mL/min flow rate to the anode and cathode compartments using by two peristaltic pumps. A DC power supply was applied to

maintain a constant current of 20 mA, corresponding to a current density of  $0.84 \text{ mA/cm}^2$ . The changes of the voltage were monitored by Konstar KS803 multimeter.

### 2.3. Experimental approach

To evaluate the influence of EDTA usage as a washing solution on the removal and chemical forms of heavy metals, EDTA was added to sludge at three different concentrations such as 0.1, 0.05 and 0.01N EDTA solution. It was prepared at desired concentration and added into sewage sludge at the ratio of 3 g:1 mL (the sludge weight: the volume of solution). Sewage sludge prepared in each experiment was oven dried at  $103^\circ\text{C}$  for 24 h. The electrical current was applied to the sludge cell as soon as the sewage sludge was ground to achieve homogeneity and compacted in the sludge cell. The current was stopped only while the samples were collected from the system. Distilled water was used as an anode electrolyte as distilled water adjusted pH to 2 by adding 5N  $\text{H}_2\text{SO}_4$  was used to be cathode electrolyte and both of them were replenished daily. During the experiments, the overall voltage changes across the sludge cell were measured daily while the pH, conductivity, total metal contents, and metal fractions of sludge samples were analyzed once every other day. Sludge pH and electrical conductivity (EC) were measured in 1/10 (dry sludge/water) suspensions using a pH (Orion SA-120) and conductivity meter (Jenway) [19]. Experimental conditions used in the study were presented in Table 1.

### 2.4. Chemical and analytical methods

All chemical used in the experiments were analytical grade. EDTA solutions were prepared with disodium salt dihydrate. Total heavy metal concentration was determined by AAS (Model UNICAM 929) after digestion of the samples with microwave system (Milestone Ethos D.) 7 mL  $\text{HNO}_3$  (65%, w/w), 2 mL HF (40%, w/w) and 1 mL  $\text{HClO}_4$  (60 w/w) were added as soon as 0.25 g dry sludge (<150 mesh) was weighed in a PTFE digestion vessel. The digestion vessel was placed in the chamber of the microwave system. After digestion, the sample solution was allowed to air-cool and then diluted with deionized water to 50 mL.

**Table 1**  
Experimental conditions.

Parameter	Conditions
Analyzed heavy metals	Cr, Pb and Zn
Applied Current	20 mA
Current Density	0.84 mA/cm <sup>2</sup>
Amount of treated sewage sludge	About 0.55 kg (dry matter)
Sludge pH	6.13
Sludge conductivity (mS/cm)	1.48
Sludge water content (%)	70
Sludge organic matter content (%)	65.2
Duration (day)	8
Anode electrolyte solution	Deionized water
Cathode electrolyte solution	Deionized water at pH of 2
Washing solution	0.1 N EDTA
	0.05 N EDTA
	0.01 N EDTA

The sequential extraction was performed using the three-step procedure recommended by the modified BCR [20]. The method details are summarized in Table 2. Briefly,

- Step 1: A total of 20 mL of acetic acid was added to 0.5 g dry sludge and shaken overnight. The mixture was centrifuged to separate the extract from the residue.
- Step 2: A total of 20 mL hydroxylammonium chloride, adjusted with nitric acid to the pH given in Table 2, was added to the residue from Step 1 and the extraction performed as explained above.
- Step 3: The residue from Step 2 was treated twice with 8.8 mol/L hydrogen peroxide, evaporated to near dryness, then 25 mL of ammonium acetate, adjusted to pH 2 with nitric acid, was added and the extraction was performed as explained above.
- Step 4: The material remaining at the end of the BCR procedure was digested with microwave assistance as described above.

In step 2, an increased concentration of NH<sub>2</sub>OH.HCl and lower pH were applied as recommended by Mossop and Davidson [20] to improve reproducibility due to a more efficient dissolution of the reducible fraction of the sludge. These extractions are related to exchangeable (Step 1), reducible (bound to iron and manganese oxides, Step 2), oxidizable (Step 3) and residual fraction (Step 4) as reported by Alonso Alvarez et al. [4].

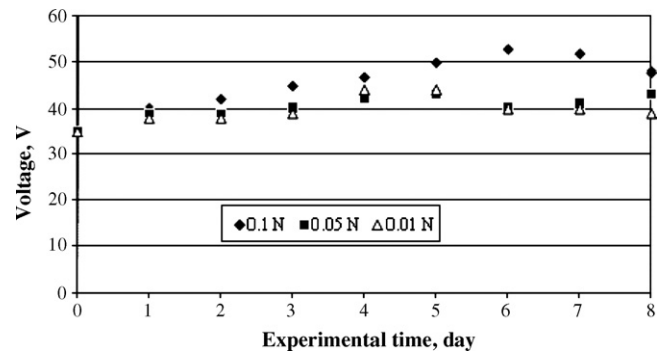
### 3. Results and discussion

#### 3.1. Effect of EDTA on voltage variation

The current variations and trends can explain the resistance, power consumption and transportation phenomena of existing species in the solid system [21]. Moreover, it is stated that addition of washing solution with ionic charge carriers such as EDTA produces an increasing current [17,22]. Higher voltages took place with a washing solution of 0.1N EDTA as compared with other concentrations of EDTA (Fig. 2). However, the voltage trends were similar in all of the experiments. It was shown that first voltage gradually increased and then decreased after 6 days of operation. In the initial stage, the dissolution and desorption mechanisms were dominant

**Table 2**  
Sequential extraction procedures.

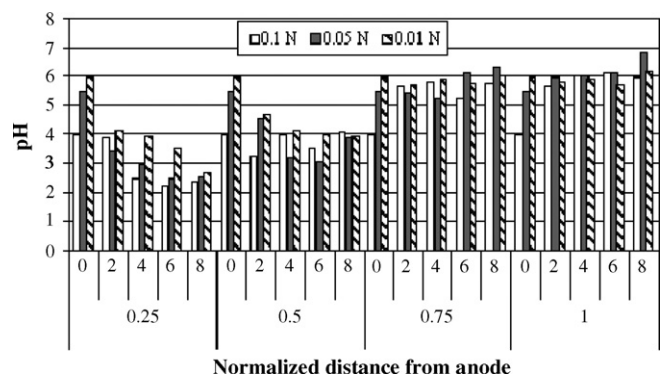
Step	Fraction	Target phases	Modified BCR
1	Exchangeable, water and acid soluble	Soluble species, carbonates, cation exchange sites	0.11 mol/L acetic acid
2	Reducible	Iron and manganese oxyhydroxides	0.5 mol/L hydroxylammonium chloride at pH 1.5
3	Oxidizable	Organic matter and sulphides	Hydrogen peroxide followed by 1.0 mol/L ammonium acetate at pH 2
4	Residual		7 mL HNO <sub>3</sub> + 2 mL HF + 1 mL HClO <sub>4</sub>

**Fig. 2.** Voltage variation during electrokinetic process.

in the sludge system, and this led to an increasing resistance and voltage within the sludge cell. However, in the later stages of the treatment, the migration of hydrogen ions and the desorbed species became of minor significance, and the voltage decreased. Additionally, this might result from clogging of sludge pores by metal oxides precipitation.

#### 3.2. Effect of EDTA on pH of sewage sludge

Electrokinetic processes caused pH decrease through sludge cell because the hydrogen ions from EDTA neutralized a fraction of OH<sup>-</sup> ions generated in cathode cell. The pH drop was very clear with applying 0.1N EDTA as washing solution (Fig. 3). The pH values of sludge were higher than 4 at the beginning of the experiments. Electrolysis reactions in anode and cathode cells influenced the whole sludge cell and the sludge pH near the anode decreased from 4 to about 2.3 and increased to approximately 6 near the cathode. It was thought that the catholyte amount in this study was not enough to decrease the pH, especially near cathode. The high pH near the cathode may result in two different circumstances. First, in the presence of the EDTA as a washing agent, the high pH value promotes a metal complex with EDTA. Second, when the metals migrate toward to cathode under electric field, they tend to be precipitated in the high pH zone. Further comments about relationship between met-

**Fig. 3.** pH values during electrokinetic process (the number of 0.25, 0.5, 0.75 and 1 represent the ratio of distance from anode to the length of soil cell, the remains (0–8) represent the operating time of electrokinetic process).

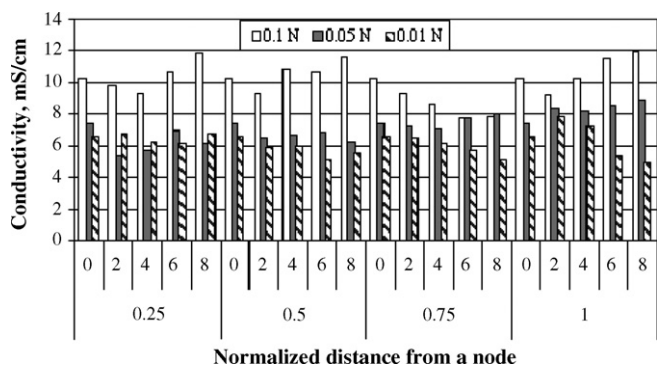


Fig. 4. The conductivity variation during electrokinetic process.

als removal and pH values across whole sludge cell were detailed in the Section 3.4.

### 3.3. Effect of EDTA on conductivity of sewage sludge

Although there was no a remarkable change in conductivities of sludge samples obtained from the addition of EDTA at three different concentrations, the lowest conductivities were shown with application of 0.01N EDTA in the whole sludge cell during electrokinetic process (Fig. 4). Since lower conductivity causes a decrease in ion movement formed by electromigration, the remediation process would take a great deal of time [14]. Especially in the experiment series with 0.01N EDTA, the lower conductivities near cathode were due to both the higher initial sludge pH and the lower initial conductivity as compared with other EDTA concentrations. On the other hand, the conductivity values decreased significantly at 0.75 section of sludge cell when 0.1N EDTA was applied to sludge. The pH junction zone where the protons (produced at the anode) and hydroxide ions (produced at the cathode) meet resulted in the metal accumulation during the electrokinetic process, which means a decrease in the sludge conductivity. Kimura et al. [16] stated that the accumulation of Cu ions and Cu-EDTA complexes formed at pH junction zone. Gidararakos and Giannis [18] also observed that Zn ions accumulated in the middle of the soil cell when EDTA was used as washing and purging solution.

### 3.4. Contents and fractionations of Cr, Pb and Zn in sludge cell

Fig. 5 indicates Cr fractions of sludge from anode to cathode during electrokinetic process. Initially the oxidizable and residual fractions of Cr were 483 and 475 mg/kg in sludge, respectively. Many researchers reported that Cr was mainly in residual forms in sewage sludge [23–25]. No changes were found in Cr fractions in all the experiments, but addition of EDTA led to a decrease in all fractions in the whole sludge cell. Furthermore, the highest Cr removal was obtained at the concentration of 0.1N EDTA. On the other hand, in the case of additions of 0.05 and 0.01N EDTA, Cr concentrations near cathode increased due to high pH (6.8) at this section and metal precipitation occurred as hydroxyls. The increase in Cr mobility could be expected due to low pH near the anode section even though the initial Cr fractions were in the immobility forms such as residual and oxidizable. Since Cr ions forming a complex with EDTA near the cathode are anionic which migrates to anode by electromigration, Cr-EDTA complexes entering to the acidic section could be dissociate from each other. Hence, Cr concentrations near anode were determined to be higher relatively than other sections.

Many researchers reported that Pb in sewage sludge is generally available in the residual and oxidizable fractions [6,9,21–23]. We also determined that Pb in sludge was available to be 304 mg/kg in residual and 255 mg/kg in reducible fractions, and EDTA addition

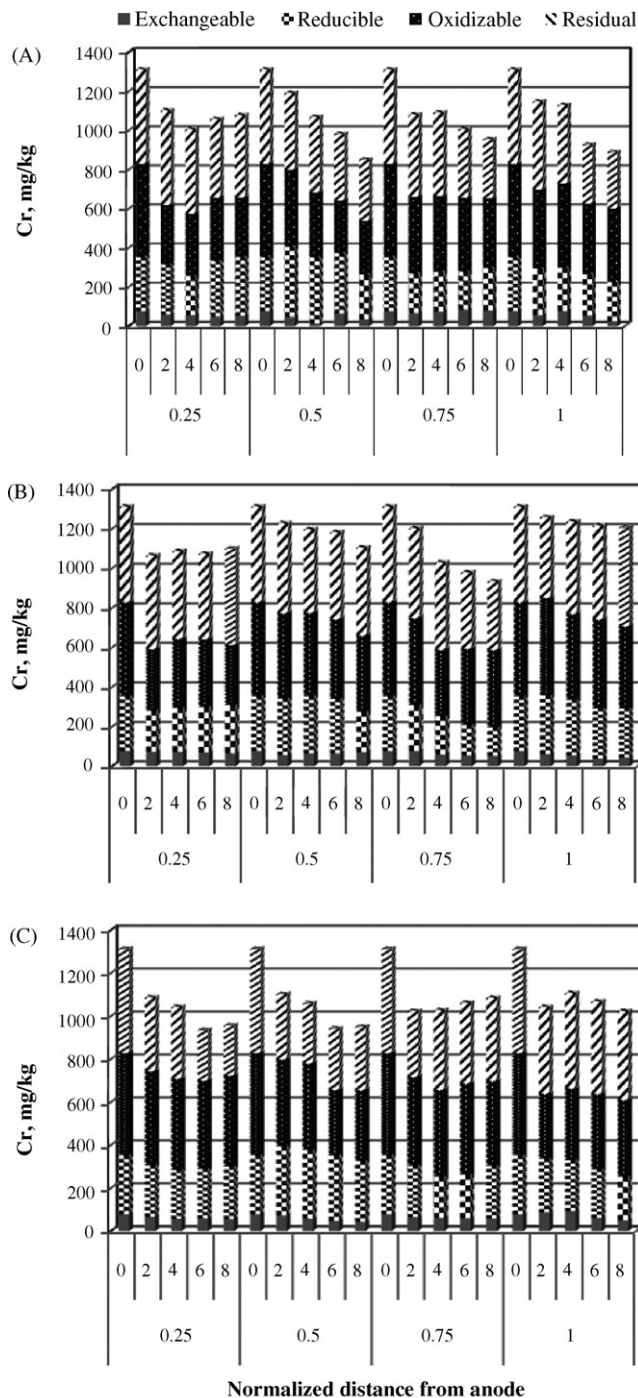


Fig. 5. Cr fractions in sludge cell during electrokinetic process, (a) 0.1N EDTA, (b) 0.05N EDTA and (c) 0.01N EDTA.

did not cause a significant change in fractions (Fig. 6). The reducible fraction, which is high mobility, decreased to 94 mg/kg near the anode (Section 0.25) with addition of 0.1N EDTA, which means a movement toward to cathode. Although EDTA is an efficient chelating agent since it forms stable complexes with most of metals over a broad pH range [26], the concentration of the enhancement agent such as EDTA must be carefully determined from laboratory investigations [27]. Moreover, Barona et al. [28] reported that EDTA might strongly produce the complexes with a variety of metals. Probably, using 0.05 and mainly 0.01N EDTA as washing solution was insufficient to form a significant complex with metals in sewage sludge.

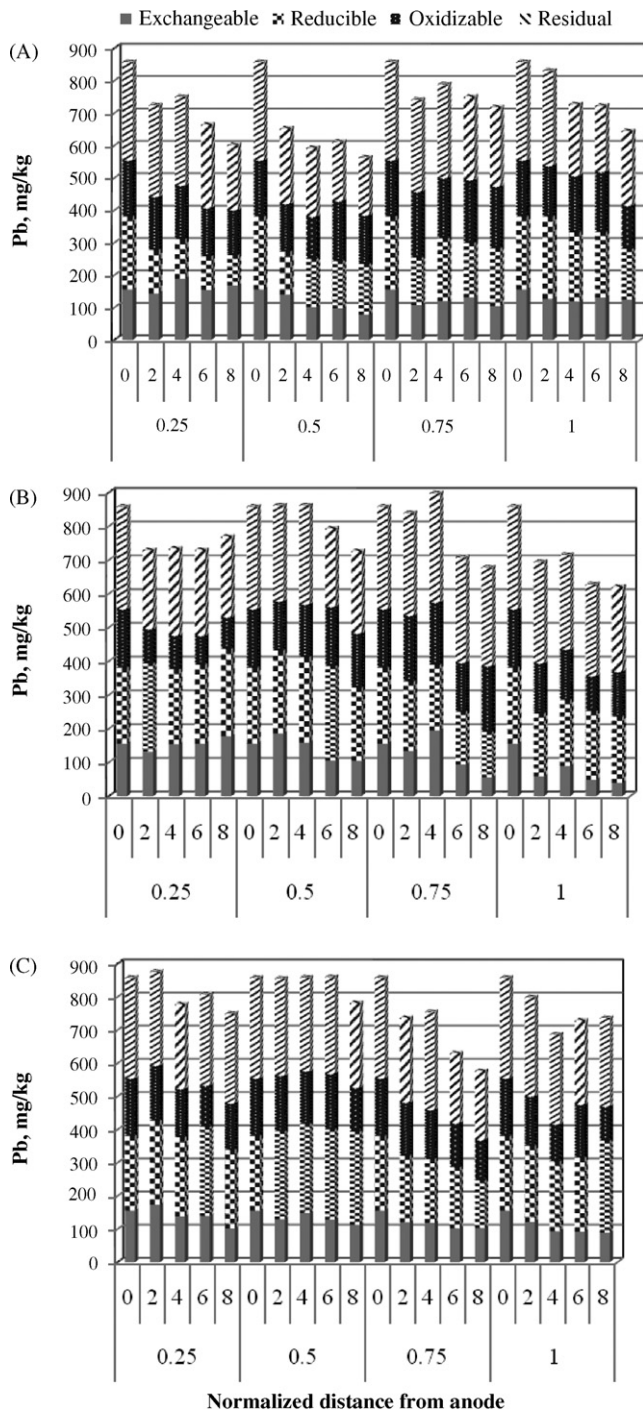


Fig. 6. Pb fractions in sludge cell during electrokinetic process, (a) 0.1N EDTA, (b) 0.05N EDTA and (c) 0.01N EDTA.

Results showed that Zn was partitioned in the sludge as follows: 1855 mg/kg exchangeable, 2012 mg/kg reducible, 2211 mg/kg oxidizable and 1647 mg/kg residual fraction (Fig. 7). No changes in Zn fractions occurred by adding EDTA as a washing solution to sludge. Wong et al. [10] stated that EDTA had also ability to dissolve the precipitated metal. We determined that 0.01N EDTA was insufficient to mobilize the precipitated metal since the total metal concentrations were high particularly near cathode.

Tables 3–5 present the results on the sum of the four fractions, total amount obtained after the sequential extraction scheme proposed by the BCR, the total contents determined after microwave digestion, and the percentages of the each metal recovered. Recov-

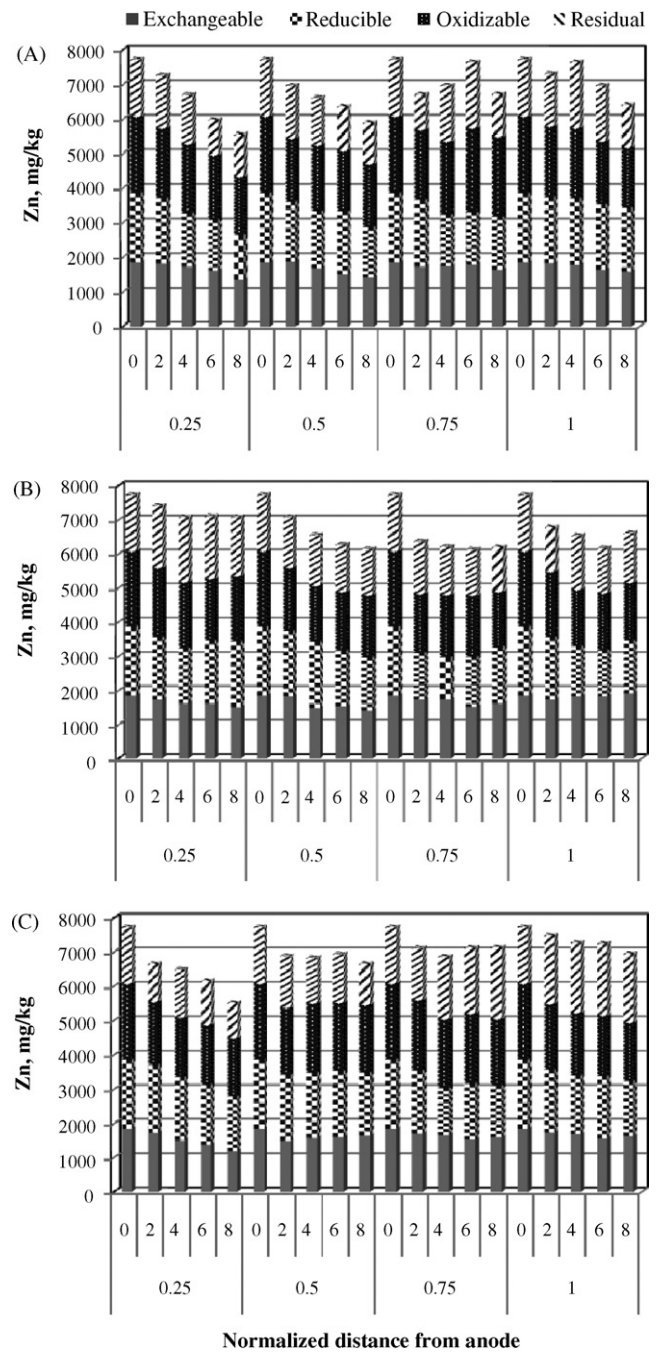


Fig. 7. Zn fractions in sludge cell during electrokinetic process, (a) 0.1N EDTA, (b) 0.05N EDTA and (c) 0.01N EDTA.

eries of Cr, Pb and Zn varied in the ranges of 93–126%, 87–110%, 96–118%, respectively. Hence, the sum of four fractions is reasonably similar to the total metal contents. The results are comparable with the findings in various studies in which the same extraction scheme was applied [5,29,30].

### 3.5. Effect of EDTA on removals of Cr, Pb and Zn

Before the applying the electrical current to the sewage sludge, the total concentrations of Cr, Pb and Zn were determined to be 1347 mg/kg, 890 mg/kg and 7680 mg/kg (dry sludge), respectively. Also these values were presented in first line of Tables 3–5. The removals of Cr, Pb and Zn by using electrokinetic process were evaluated with the mass balance calculation. The removal percentages

**Table 3**  
Cr concentrations in total and the sum of four fraction and the percentages of metal recovered for the different concentration EDTA.

EDTA, N		0.1			0.05			0.01		
From anode to cathode	Time (day)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)
0.25	0	1312	1347	97	1312	1347	97	1312	1347	97
	2	1103	1055	105	1065	968	110	1086	1129	96
	4	1006	1044	96	1086	955	114	1041	1047	99
	6	1059	1137	93	1074	952	113	935	937	100
	8	1078	983	110	1099	965	114	956	954	100
0.5	2	1191	991	120	1228	989	124	1101	998	110
	4	1069	1055	101	1196	983	122	1058	956	111
	6	982	973	101	1182	1003	118	942	993	95
	8	851	752	113	1104	994	111	950	938	101
0.75	2	1081	953	113	1202	1120	107	1022	945	108
	4	1092	869	126	1028	1005	102	1026	1046	98
	6	1006	888	113	978	967	101	1061	1045	102
	8	955	891	107	933	903	103	1084	1011	107
1	2	1148	1047	110	1258	1095	115	1041	995	105
	4	1130	1057	107	1237	1143	108	1107	1046	106
	6	927	940	99	1217	1190	102	1067	1013	105
	8	889	903	98	1205	1115	108	1022	990	103

**Table 4**  
Pb concentrations in total and the sum of four fraction and the percentages of metal recovered for the different concentration EDTA.

EDTA, N		0.1			0.05			0.01		
From anode to cathode	Time (day)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)
0.25	0	858	890	96	858	890	96	858	890	96
	2	724	703	103	729	755	97	876	837	105
	4	750	712	105	734	763	96	778	728	107
	6	664	678	98	730	712	103	808	736	110
	8	601	645	93	769	752	102	750	712	105
0.5	2	652	678	96	862	882	98	856	867	99
	4	592	665	89	862	880	98	859	822	105
	6	611	684	89	793	757	105	860	855	101
	8	563	584	96	726	743	98	782	754	104
0.75	2	741	717	103	839	845	99	737	742	99
	4	789	745	106	898	882	102	755	754	100
	6	750	722	104	708	761	93	630	689	91
	8	718	737	97	678	692	98	577	583	99
1	2	831	801	104	694	684	101	799	802	100
	4	727	745	98	715	702	102	687	792	87
	6	722	720	100	628	665	94	729	783	93
	8	644	672	96	620	632	98	737	754	98

**Table 5**  
Zn concentrations in total and the sum of four fraction and the percentages of metal recovered for the different concentration EDTA.

EDTA, N		0.1			0.05			0.01		
From anode to cathode	Time (day)	Total (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)	Total BCR (mg/kg)	Total concentration (mg/kg)	Recovered (%)
0.25	0	7725	7680	101	7725	7680	101	7725	7680	101
	2	7264	7352	99	7411	7325	101	6656	6553	102
	4	6704	6817	98	7082	6888	103	6494	6584	99
	6	5985	6027	99	7106	6921	103	6161	6023	102
	8	5561	5892	94	7088	6923	102	5515	4930	112
0.5	2	6971	7014	99	7084	6892	103	6890	6721	103
	4	6627	6782	98	6554	6533	100	6837	6728	102
	6	6370	6627	96	6272	6349	99	6949	6829	102
	8	5903	6017	98	6137	5849	105	6653	6221	107
0.75	2	6712	6827	98	6371	5914	108	7114	6849	104
	4	6974	6827	102	6210	5920	105	6872	6712	102
	6	7659	7566	101	6127	5891	104	7126	7013	102
	8	6725	6241	108	6197	5704	109	7135	7322	97
1	2	7311	7019	104	6779	5757	118	7498	7434	101
	4	7662	7524	102	6542	6413	102	7279	7493	97
	6	6977	7012	100	6166	6028	102	7254	7050	103
	8	6415	6627	97	6609	6492	102	6959	6820	102

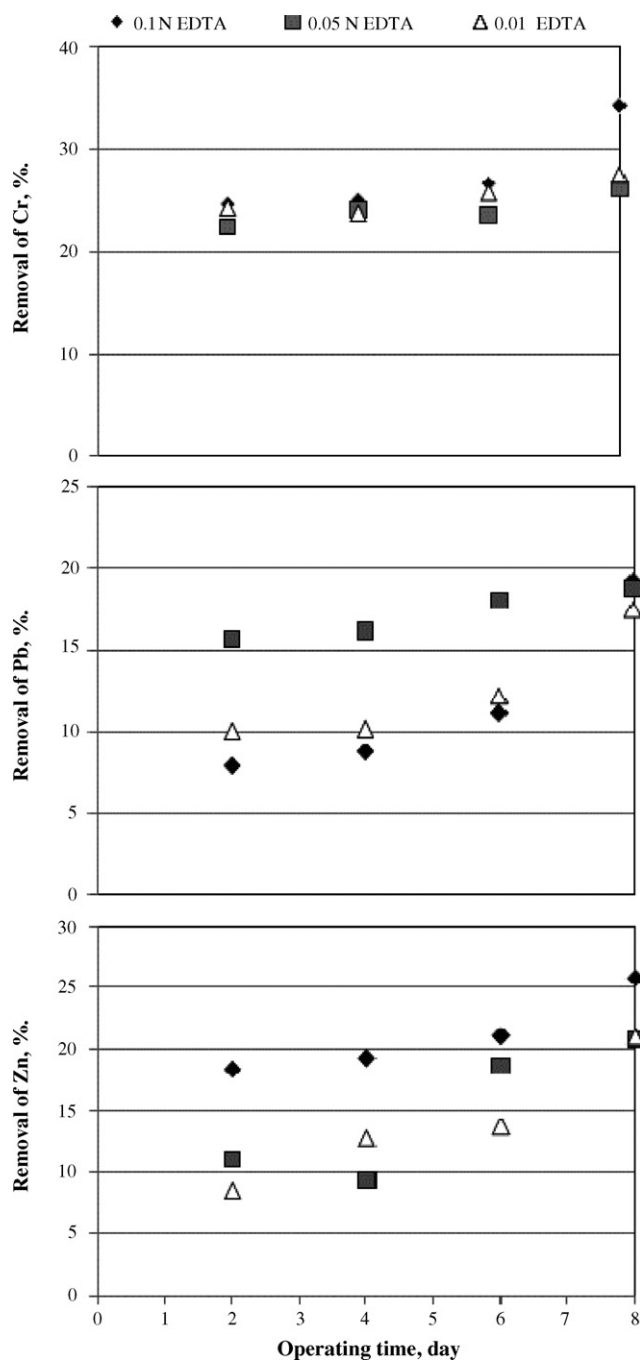


Fig. 8. The removal ratios of Cr, Pb and Zn.

of Cr were 34%, 26% and 27% for concentrations of 0.1, 0.05 and 0.01N EDTA, respectively (Fig. 8a–c). The results showed that 0.05 and 0.01N EDTA have nearly same effect on Cr removal from sewage sludge. Application of EDTA to sludge as a washing solution in electrokinetic process did not significantly accomplish Cr removal from sewage sludge. In application of 0.1N EDTA, the removal percentage was found to be 26% as it decreased to 20% at 0.05 and 0.01N EDTA (Fig. 8b). It was shown that the proportion of Pb in the dissolved phase increased with an increase in EDTA concentration. Yeung et al. [31] reported that the addition of EDTA reduced the proportion of lead in the dissolved phase when the pH was lower than approximately 4.5. Additionally, Wong et al. [10] stated that the metal was available as the doubly negatively charged chelate at pHs above 4 for Pb and 5 for Zn. In this study, since the pH changed between 2

and 4 mainly near the anode, EDTA might have not formed strong water-soluble chelates with Pb. Hence, Pb might have remained as a cation and migrated toward to cathode. Since this possibility was not assayed, controlling the pH near the anode section or conditioning the anode was not performed in this study.

Zn was initially found to be more abundant as 7680 mg/kg in the sewage sludge, and the removal of Zn did not unfortunately exceed 20%. Probably, the EDTA concentrations became insufficient to complex with Zn because more EDTA than the concentration of 0.1N was needed. Wong et al. [10] reported that the Zn is present as the doubly negatively charged chelate when the pH is about for 5. In all the experiments, the pH values near anode and at the section of 0.5 were observed to be less than 5.

#### 4. Conclusions

This study showed that the EDTA did not affect the fractions of Cr, Pb and Zn but there was a little decrease in total concentration of metals studied during electrokinetic process. Metal–EDTA complexes entering to the acidic section dissociated since metal ions forming a complex with EDTA near the cathode migrated to anode by electromigration. At studied dosages, EDTA was not able to improve metal removal from sewage sludge during electrokinetic process. This study demonstrates that the usage of EDTA as only washing solution in electrokinetic process is not enough for a satisfactory metal removal from sewage sludge since dosages more than 0.1N EDTA are not applicable in a large scale facility.

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