Electroremediation of Cu-Contaminated Soil

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Abstract-This study investigated the removal efficiency of electrokinetic remediation of copper-contaminated soil at different combinations of enhancement reagents used as anolyte and catholyte. Sodium hydroxide (at 0.1, 0.5, and 1.0 M concentrations) and distilled water were used as anolyte, while lactic acid (at 0.01, 0.1, and 0.5 M concentrations), ammonium citrate (also at 0.01, 0.1, and 0.5 M concentrations) and distilled water were used as catholyte. A continuous voltage application (1.0 VDC/cm) was employed for 240 hours for each experiment. The copper content of the catholyte was determined at the end of the 240-hour period. Optimization was carried out with a Response Surface Methodology - Optimal Design, including F test, and multiple comparison method, to determine which pair of anolyte-catholyte was the most significant for the removal efficiency. "1.0 M NaOH" was found to be the most significant anolyte while it was established that lactic acid was the most significant type of catholyte to be used for the most successful electrokinetic experiments. Concentrations of lactic acid should be at the range of 0.1 M to 0.5 M to achieve maximum percent removal values.

Keywords—Electrokinetic remediation, copper contamination, heavy metal contamination, soil remediation

I. INTRODUCTION

THE prevention of heavy metal pollution in soils is crucial for the reason that remediation of contaminated soils is complicated and expensive. However, once these metals contaminate the environment, they will remain undegraded [20]. Unlike organic substances, metals do not degrade easily except for mercury and selenium which are transformed and volatilized by microorganisms. This is the reason why metals are very much difficult to eliminate from the environment [22].

During the past decades, several solutions for efficient heavy metal removal from soils were investigated by experts. One emerging technology is electrokinetic remediation. Electroremediation, electrorestoration, electroreclamation, electrochemical decontamination, or electromigration are the other terms that may be referred to the said technology. This method is able to remove heavy metals from low permeability contaminated soils under the influence of an applied direct current [3], [4], [15], [19], [24].

Electrokinetics essentially involves installing a pair of electrodes into the subsurface to border the contaminated region [18]. After the electrodes are in place, a low electrical potential will be applied across the anode (positively charged electrode) and the cathode (negatively charged electrode) [21].

As a result of the electrical gradient produced, different physico-chemical reactions and transport of contaminants occur due to various mechanisms that happen within the soil [25].

In general, contaminants should be in soluble form to effect significant migration [11]. If they are not soluble, they need to be desorbed, dissolved, and/or solubilized into the pore solution before these can be adequately transported from the soil to the electrode reservoirs [12].

Various methods have been suggested for the control and improvement of contaminant removal in electrokinetic remediation [10]. To provide uniform conditions between electrodes, the simple periodic reversal of electrode polarity can be used. This method helps in avoiding excessive buildup of chemicals and other complications within the soil [7], [8].

The type of contaminant present and soil conditions are needed for choosing the right enhancement reagent to be used. For unsaturated soils, the addition of water at the anode is necessary to replace the water lost at the cathode [16]. Desorption and transport of metal ions to the cathode can be enhanced by flushing the soil with an acid [2]. Naturally occurring weak acids may be used because they are less harmful than strong acids. Strong acids may destroy the soil and in the case of hydrochloric acid, chlorine may be formed at the anode. Solutions containing non-toxic ions can also be used to flush the soil [13], [17].

When the soil contains ample amounts of soluble metal compounds, (e.g. carbonates, phosphates, hydroxides, and sulfides), difficulties may arise during the electrokinetic remediation process [1], [12]. To avoid these complications, enhancement solutions are thereby greatly needed.

In this study, electrokinetic experiments were conducted to recover the copper from a copper-contaminated soil taken from an area beside a former mine tailings site of an abandoned copper mine at Marinduque province. Specifically, the study undertaken investigated the removal efficiency of electrokinetic remediation of copper-contaminated soil by different combinations of enhancement reagents used as anolyte and catholyte. Sodium hydroxide (at 0.1, 0.5, and 1.0 M concentrations) and distilled water were used as anolyte, while lactic acid (at 0.01, 0.1, and 0.5 M concentrations), ammonium citrate (also at 0.01, 0.1, and 0.5 Μ concentrations), and distilled water were employed as catholyte. These comprised the twenty-eight (28) experiments conducted in his study. The electrokinetic setup adapted was similar to that of [6].

This study focuses solely on the copper removal from a Cucontaminated soil by electrokinetic process. This study will not cover the effect of multiple heavy metal contaminants in the removal of copper. A comprehensive discussion on the

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geochemical processes involved in the electrokinetic removal of copper from soil is also beyond the scope of this study.

II. MATERIALS AND METHODS

Samples of polluted soil were taken according to the Standard Operating Procedures described by the U.S. EPA Environmental Response Team [23], from an area beside a former mine tailings site of an abandoned copper mine at Marinduque province. Soils were sampled at a 10 m x 10 m grid (or a total of 100 sampling points), on a depth of 1 m. The samples taken from each sampling point were mixed thoroughly to obtain a homogenous sample representative of the entire sampling intervals. Samples averaged about 100 L to represent the large area of the site.

The soil sample was air-dried, ground to remove large clumps, mixed thoroughly, and then stored in a large plastic container at room temperature. The homogenized sample was then characterized for electrical conductivity, organic carbon, organic matter, cation exchange capacity, available phosphorous, copper, zinc, and iron concentrations, texture, water holding capacity, and field capacity (Table 1).

TABLE I SOIL PROPERTIES

Parameter	Content	Parameter	Content
Cu (mg/kg)	234.43	Field capacity (1/3 bar)	19.44
Zn (mg/kg)	4.43	pН	3.20
Fe (mg/kg)	3.91	Electrical Conductivity (mmhos/cm)	1.43
Sand (%)	43.60	Organic carbon (%)	0.27
Silt (%)	34.80	Organic matter (%)	0.46
Clay (%)	21.60	Cation Exchange Capacity (cmol(+)/kg)	12.70
Water Holding Capacity(%)	43.30	Available P (mg/kg)	18.40

The setup used by [6] was modified to suit the requirements of the bench-scale electrokinetic reactor that was utilized in this study. The reactor for this study (Fig. 1) was comprised of a specimen cell, an anode and a cathode compartment, overflow containers, a DC power supply, and a multimeter.

The reactor was made of plexiglass. The thickness of the plexiglass was 15 mm. The dimensions of the specimen cell were 20 cm \times 5 cm \times 10 cm. Each electrode compartment had dimensions of 5 cm \times 5 cm \times 10 cm. Top side of the reactor was open to the atmosphere to allow the escape of the gases produced during the electrolysis process. At the left and right sides of the cell, there was an opening with dimensions 8 cm x 3 cm. Filter paper was used to hinder the soil sample in the cell from going to the electrode compartments. Two cylindrical graphite electrodes with a diameter of 1.5875 cm and 12 cm length were placed next to the filter paper at both electrode compartments to serve as anode and cathode.

The overflow containers were attached to the compartments by rubber tubing. The multimeter was used to measure the voltage and current across the reactor. An AC-DC converter with specifications [Input: 100-240V \sim 1.5A, 50-60 Hz, Output: 100 VDC (max), 350 mA], was used to supply the power requirement in the reactor.



Fig. 1 Electrokinetic diagram: a - setup, b - dimensions, c - actual setup

Approximately 1223.6 g of soil was used for each test. As soon as the sample was prepared for the treatment process, it was then uniformly packed and compacted into the specimen vessel using a handheld spatula. The anolyte and catholyte solutions were then allowed to flow into the anode and cathode compartments respectively, until the level of the soil in the specimen vessel was reached, and the desired requirement of 20 V DC was applied for 10 days for each experiment.

After each experiment, the copper concentration at the catholyte was measured, and the percentage of copper removal from the soil was represented by this equation:

% Cu removal =
$$\frac{\text{mass of Cu in the catholyte}}{\text{initial mass of Cu in the soil}} \times 100\%$$
 (1)

A design of experiments software [5], using Response Surface Methodology – Optimal Design, and an F test with multiple comparison method using [9], were used to establish which pair of anolyte and catholyte was the most significant for electrokinetic remediation of Cu-contaminated soil.

The variables "Anolyte" and "Catholyte" were considered as discrete numerical factors while "Percent removal" was considered to be the response value, to serve as inputs to the Design-Expert[®] and IBM[®] SPSS[®] Statistics softwares. "Anolyte" had four levels coded 1 to 4, to represent the four different types of anolyte used in the experiment. Consequently, "Catholyte" had seven levels coded 1 to 7, to 0.5 M lactic acid

represent the seven different types of catholyte used. The response values for percent removal were coded (R) (Appendix, Table 6).

III. RESULTS AND DISCUSSION

Percent removals of Cu based from the results of the experiments (Appendix, Table 5) were used to determine which variables had the highest levels of significance on the electrokinetic remediation process. Using IBM[®] SPSS[®] Statistics software, an ANOVA was performed to identify significant differences between variables. This was followed by a Tukey test, a type of a post hoc test, in order to find out specifically the significant differences between levels of that same significant variable. To determine the overall significance of the said variables on percent removal, solutions were carried out through numerical optimizations of the model through the Design-Expert[®] software.

Percent removal signifies the amount of copper in the catholyte after each experiment, in mg, divided by the initial mg of Cu in the soil. Thus, the higher percent removal values correspond to the most successful experiments. The anolyte-catholyte pair of 1.0 M NaOH and 0.5 M lactic acid was considered the most successful, with a 76.23% removal value, while when distilled water was used as anolyte and catholyte, the percent removal value was only 10.46% (Fig. 2).



Fig. 2 Percent removal values vs. anolyte-catholyte type

The performed ANOVA through the IBM[®] SPSS[®] Statistics software showed that all variables (the model, Anolyte, and Catholyte), with their significance level values at $\approx 0.000 < 0.05$, presented significant differences among them.

The variables "Anolyte" and "Catholyte" were then considered for the Tukey test, to determine significant differences among their own levels.

All levels of "Anolyte" presented significant differences among them in terms of percent removal (as denoted by the significance value of $\approx 0.000 < 0.05$ for all levels).

Homogenous subsets were then used for "Anolyte" and "Catholyte" levels to group levels that were homogenous based from their observed means (the percent removal) and therefore do not have significant difference among them (Table II and III).

TABLE II Homogenous Subset for Anolyte					
	HOMOGENOUS SUBSET FOR ANOLYTE Subset				
Anolyte	Ν	1	2	3	4
Water.a	7	24.24			
0.1 M NaOH	7		40.96		
0.5 M NaOH	7			52.96	
1.0 M NaOH	7				64.41
	Homoge	TABLI NOUS SUBSE	E III T FOR CATHO	LYTE	
		Subset			
Catholyte	N	N 1	2	3	4
Water.c	4	33.2800			
0.01 M am. citrate	4		39.4975		
0.1 M am. citrate	4		41.7450		
0.5 M am. citrate	4			47.4700	
0.01 M lactic acid	4			47.6150	
0.1 M lactic acid	4			52.5325	52.5325

Based from the subsets presented for "Anolyte" and "Catholyte" levels, it can be said therefore that 1.0 M NaOH used as anolyte, and lactic acid concentrations of 0.1 and 0.5 M were the most successful anolyte-catholyte pairs that provided the highest percent removal values for the electrokinetic experiments.

57.3925

An ANOVA was again carried out through the Design-Expert[®] software. The results correspond with the results from the IBM[®] SPSS[®] Statistics software – that the model, the "Anolyte" and "Catholyte" were all significant terms, with their significance values at < 0.05.

Numerical optimization was then carried out on the model to find factor settings to meet the defined goals – in this case, it was to find out which anolyte-catholyte best suit to achieve the highest percent removal.

The criteria for "Anolyte" and "Catholyte" ranges were set based from their respective number of levels, 1 to 4 for "Anolyte" and 1 to 7 for "Catholyte". The goal for the percent removal was set to "maximize".

Model solutions were then generated as to which level of factors represent the maximum values for percent removal with highest desirability (Table IV). This value of desirability represents the operating conditions that will provide the "most desirable" response. The closer the value of desirability to 1, the more successful the anolyte-catholyte pair was to attain the maximum percent removal values based on the model.

The solutions generated shows that the "most desirable" anolyte to be used was 1.0 M NaOH (coded 4 in the table) as it occupied the top five solutions generated.

As for the choice of the best catholyte, it was still not that clear which specifically, among the different concentrations used for lactic acid, was the "most desirable" to attain

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maximum percent removal, although it was obvious enough that lactic acid provided significant values higher than those of ammonium citrate and water. This was in accordance with the results from the Tukey test for "Catholyte" that there was no significant difference between 0.5 M (coded 4) and 0.1 M lactic acid (coded 3), and between 0.1 M (coded 3) and 0.01 M (coded 2) lactic acid.

TABLE IV NUMERICAL OPTIMIZATION OF DESIGNED MODEL

Rank Anoly	Anolyte	Catholyte	Percent	Desirability	
	Anolyte	Catholyte	removal		
1	4	3	73.1453	0.9531	
2	4	4	69.2137	0.8933	
3	4	2	69.162	0.8925	
4	4	7	65.0884	0.8306	
5	4	5	62.8832	0.7970	
6	3	3	61.0679	0.7694	
7	4	6	59.6695	0.7482	
8	3	4	57.7974	0.7197	
9	3	2	56.4053	0.6985	
10	3	7	55.5456	0.6855	
11	3	5	52.1097	0.6332	
12	4	1	51.748	0.6277	
13	3	6	49.5205	0.5938	
14	2	3	49.1705	0.5885	
15	2	4	45.834	0.5378	
16	2	2	44.5557	0.5183	
17	2	7	43.2743	0.4988	
18	2	5	40.0619	0.4500	
19	3	1	38.2937	0.4231	
20	2	6	37.37	0.4091	
21	1	3	33.286	0.3470	
22	1	2	29.4461	0.2886	
23	1	4	29.1563	0.2842	
24	2	1	26.4736	0.2434	
25	1	7	24.1072	0.2074	
26	1	5	22.5727	0.1840	
27	1	6	19.051	0.1305	
28	1	1	12 1207	0.0251	



The generated solutions by the model were plotted in Figure 4, with values of desirability (represented by the white dots) against the type of anolyte and catholyte used. The flagged dot represents 1.0 M NaOH as anolyte and 0.1 M Lactic acid as catholyte (coordinate A4, B3) as having the highest desirability value of 0.953.

Using water as both anolyte and catholyte did not show good result for Cu removal (only 10.47%). Because no external ions were added in the electrolytes, metal hydroxide precipitates developed near the cathode, and the percent removal was of low level (Zhou et al., 2004).

Meanwhile, when NaOH was used as anolyte instead of water, the percent removal values were significantly higher. The application of NaOH in the soil resulted to higher electrical conductivity and thus increased Cu removal values (Zhou et al., 2004).

The flow of process fluid (the enhancement solutions) across the electrodes helps in desorbing the Cu from the soil and the dissolution of hydroxides (Acar et al., 1995). As when lactic acid was used in the catholyte, the low pH caused by the acid kept Cu dissolved and the OH⁻ formed at the cathode were neutralized (Zhou et al., 2005), therefore making the transport of Cu toward the cathode (Virkutyte et al., 2002), which resulted to much higher percent removal values (up to 76.23%).

Percent removal was lower when ammonium citrate was used in the catholyte (as compared to when lactic acid was used), as further optimizations were needed when using this kind of enhancement solutions (Ottosen et al., 2005). Ammonium citrate forms complexes with the Cu in the soil, thus transport to the cathode was possible through the electroosmotic flow, but the percent removal values from the experiments (15-65%) showed that the complexes formed were prevented to some extent to be transported to the cathode.

IV. CONCLUSION

1.0 M NaOH was considered the most significant "Anolyte" for the electrokinetic remediation of Cu-contaminated soil. It can be concluded that using NaOH as an enhancement reagent instead of water as anolyte greatly improves the electrokinetic process for better percent removals.

Even though there was no significant difference between the different concentrations used for lactic acid, it was clear that percent removal values were significantly higher for lactic acid, as compared to those of ammonium citrate and distilled water. Therefore, among the three types of catholyte used, lactic acid was the best to use as an enhancement reagent, followed by ammonium citrate, and then water.

From the results of this study, it can be concluded that to attain maximum percent removal values, the concentration of lactic acid to be used as catholyte must be at the range of 0.1 M to 0.5 M; however, further experiments are necessary to find out if higher concentrations of lactic acid can result to significantly higher percent removal values.

APPENDIX

Experiment	Anolyte	Catholyte	% removal
1	Distilled water	Distilled water	10.47
2	Distilled water	0.01 M Lactic acid	28.52
3	Distilled water	0.1 M Lactic acid	33.55
4	Distilled water	0.5 M Lactic acid	38.91
5	Distilled water	0.01 M Ammonium citrate	15.36
6	Distilled water	0.1 M Ammonium citrate	18.36
7	Distilled water	0.5 M Ammonium citrate	24.57
8	0.1 M NaOH	Distilled water	31.79
9	0.1 M NaOH	0.01 M Lactic acid	39.62
10	0.1 M NaOH	0.1 M Lactic acid	44.35
11	0.1 M NaOH	0.5 M Lactic acid	50.56
12	0.1 M NaOH	0.01 M Ammonium citrate	37.27
13	0.1 M NaOH	0.1 M Ammonium citrate	38.84
14	0.1 M NaOH	0.5 M Ammonium citrate	44.31
15	0.5 M NaOH	Distilled water	39.22
16	0.5 M NaOH	0.01 M Lactic acid	54.48
17	0.5 M NaOH	0.1 M Lactic acid	60.74
18	0.5 M NaOH	0.5 M Lactic acid	63.87
19	0.5 M NaOH	0.01 M Ammonium citrate	46.68
20	0.5 M NaOH	0.1 M Ammonium citrate	49.54
21	0.5 M NaOH	0.5 M Ammonium citrate	56.21
22	1.0 M NaOH	Distilled water	51.64
23	1.0 M NaOH	0.01 M Lactic acid	67.84
24	1.0 M NaOH	0.1 M Lactic acid	71.49
25	1.0 M NaOH	0.5 M Lactic acid	76.23
26	1.0 M NaOH	0.01 M Ammonium citrate	58.68
27	1.0 M NaOH	0.1 M Ammonium citrate	60.24
28	1.0 M NaOH	0.5 M Ammonium citrate	64.79

TABLE VI

DEFINITION OF VARIABLES		
Code	Variable	
Α	Anolyte	
1	Distilled water	
2	0.1 M NaOH	
3	0.5 M NaOH	
4	1.0 M NaOH	
В	Catholyte	
1	Distilled water	
2	0.01 M lactic acid	
3	0.1 M lactic acid	
4	0.5 M lactic acid	
5	0.01 M ammonium citrate	
6	0.1 M ammonium citrate	
7	0.5 M ammonium citrate	
R (response)	Percent removal	

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