

Recycling of chelating agents after extraction of heavy metals contaminated in soil

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(Manuscript received on August 20, 2001)

Heavy metals such as Cu, Ni, Cd, and Pb were chemically extract from the contaminated soils using the chelating agents, EDTA and DTPA. These chemical extraction have been focused on its applicability to a wide range of soils. Results of extractive efficiency for heavy metal follow the order : Cu-EDTA \geq Ni-EDTA > Pb-EDTA > Cd-EDTA > Cu-DTPA > Pb-DTPA. This result is coincided with order of conditional formation constants(K_f) of metal-chelate agent. The second study involved the recovery of the metals and EDTA from complex solutions by an electromembrane process. The overall processes of regeneration, recovery, and reuse were evaluated. The electrochemical studies showed that copper could be chosen as an electrode to plate Cd, Cu, and Pb. At least 95 % of EDTA and associated Cu or Pb could be recovered by the electromembrane process. Recovery of Cd by electrodeposition was not possible with the copper electrode. The percent EDTA recovery is equal to the percentage of metal electroplated from the chelates.

Key words : Chelating agent, Heavy metals, Electromembrane process, Recovery, Electrodeposition

1. Introduction

Heavy metal contaminated soil at uncontrolled waste sites has been a problem of major concern in recent years. There are four main paths of exposure to human resulting from soils contaminated by toxic heavy metals. These are (a) direct ingestion by eating soil or unwashed produce, (b) consumption of plants accumulated by levels of metal, grown in contaminated soil, (c) drinking of contaminated ground water supplies, and (d) drinking of contaminated surface water. Because heavy metals are toxic to humans and highly retained in soils, if it is likely to exposure for a longer time. To reduce the risk, contaminated soil should be cleaned.

Several methods have been proposed for the remediation of heavy metal contaminated soils¹⁻³. These methods are based on two principles: immobilization of metal or removal of the metals from the soil matrix⁴. The chelating agents, ethylenediamine tetraacetic acid(EDTA)⁵ and dimethyl

triamine pentaacetic acid(DTPA)⁶ have been added to soil to form complexes with heavy metal such as cadmium, copper, zinc, lead, and nickel. These complexes are more strongly retained by clay than the metal cations alone⁴.

The metal chelation⁷ is a common extraction method, based on the solubilization. Removing toxic heavy metals from the soil matrix by adding EDTA or DTPA is quite efficient. Peters and Shem⁸ reported that lead could be removed from spiked soil with efficiencies ranging from 54 to 68 %. Extractions using the organic chelating agents mentioned above are promising one for a remediation of soil that can support plant growth and is suitable for other uses. The metal complexed in liquid stream can be separated by electrolysis. This technology can separate and remove metals for reuse or recycle more efficiently than conventional technologies.

The goal of this work is to find a suitable chemical extractants applicable to the soil-bound metals that can potentially be available to soil

organisms. The second purpose of this research is investigate the feasibility of batch electromembrane process for the regeneration of the metal from the EDTA-copper or -lead complex. This provides a separation of metal that can be removed or recycled and reclaimed EDTA or DTPA streams can be used for treating additional contaminated soil. This recycle may offset the high cost of EDTA that has precluded its use in the remediation of metal contaminated sites.

In this paper, the effects of the chelating agent concentration on metals extraction and comparisons of extract to total recoverable metals and of recycle EDTA or DTPA after remediation of metal-contaminated site have been discussed. This technology can potentially be applied to solids and slurries such as ash, sludges, and contaminated solids.

2. Experimentals

2.1. Material and Methods

In this study, three experiments were conducted: soil extraction, metal removal, and the recovery of organic chelating agents. In the batch experiment of soil extraction experiment, the effects of EDTA or DTPA concentration were investigated. The second experiment was designed to recover heavy metals from the solution including EDTA or DTPA. Figure 1 shows the procedure for soil clean-up process.

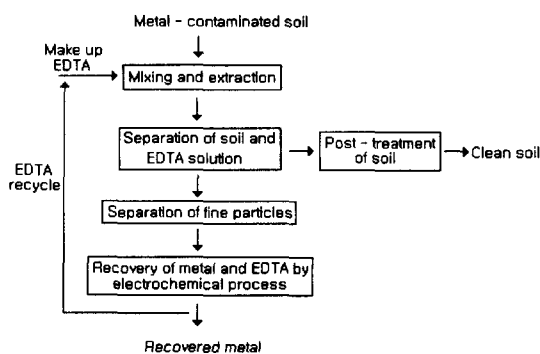


Fig. 1. Flow sheet for soil clean-up by extraction process.

2.2. Soil Collection

Five soils were collected from around the

Gwang-Ju and Jun-nam areas. Some soils were agricultural settings, others were mildly contaminated with certain metals, and others were not considered contaminated at all.

Before sampling, glass, twigs, and debris in the top most litter layer was cleaned. The soil surface was removed. And then top 15~18 cm of soil at a particular site was sampled with a clean stainless tool. The amount of soil samples collected was 100 to 150 kg. The soils were then placed in plastic containers and shipped to Chosun University in Gwang-ju metropolitan city.

2.3. Soil Processing

Soils were unpacked and spread out as thinly as possible in 20 L plastic box. The plastic box was covered with aluminum foil, and the soils were air-dried. After air-dry, soils were lightly crushed in a large ceramic mortar and pestle. The crushed soil was sieved with a 2.0 mm polyethylene sieve. All fractions of the soil were weighed. The soil remaining on 2.0 mm sieve was discarded. The soil passing through the 2.0 mm sieve was thoroughly homogenized and subsampled with a plastic spade. Approximately 1.0 kg of each soil was subsampled for soil testing. Approximately 500 g of the soil was placed in plastic bags. The remaining subsample was placed in plastic containers for extraction testing and metal analysis. These subsamples were thoroughly homogenized to increase analytical precision.

2.4. Spiked soils, Soil extractions and Digestions

Soil parameters tested by the UDSTL methods⁹⁾ are : pH, buffered pH, organic matter(OM), sand, silt, clay, cation exchange capacity(CEC), and total/crystalline/amorphous oxides of Fe, Mn, and Al.

Five soils were selected to spike with metal salts of Cd, Cu, Ni, Pb, and Zn. All extractions were carried out with an orbital shaker at 100 rpm for 24hours time period. All samples were centrifuged at 4000 rpm for 20 minutes and filtered with 0.45 μ m cellulose membrane filters(Fisher Scientific, Fairlawn, NJ). The further extraction was tested by DTPA and EDTA solution

Initial work on the EDTA or DTPA extraction

methodology consisted of testing the variation of metal extraction as a function of EDTA or DTPA concentration. Five soils were extracted with Na_2EDTA (ACS grade Fisher chemical Co.) or DTPA (Reagent grade, Aldrich Chemical Co) concentrations of 0.005, 0.01, 0.05, 0.1, and 0.25 M for EDTA and of 0.002, 0.005, 0.01, and 0.05 M for DTPA. Each of the five soils was extracted in triplicate at each EDTA or DTPA concentration. The samples were then immediately analyzed for pH and refrigerated. The samples were then analyzed for metals by ICP (JY 70+, France). The original extraction methodology set forth by Lindsay and Norvell included 0.01 M CaCl_2 and 0.1 M triethanolamine (TEA)⁶⁾. The addition of 0.01 M CaCl_2 was meant to suppress dissolution of CaCO_3 in the soil and concurrent release of CaCO_3 occluded metals.

2.5. Analysis of total soil metal and soil extract metal

Metals extracted or recovered were analyzed by ICP emission spectrophotometer (Jovin-Ybon, JY-70 Plus) equipped with ultrasonic nebulizer (USN). The matrix of standard solutions were matched to the matrix of extracts as possible.

2.6. Electromembrane Process

Figure 2 shows the apparatus for electrolysis experiments. The rectangular unit was made of 0.65 cm (thickness) plexiglass. The electrode holding bar was made of 0.97 cm plexiglass. It was assembled by two independent identical chambers and an electrode holding bar. Both independent chambers had an inner mounting wall with a 5.08 cm by 6.35 cm cut-out and 1.64 cm flanges. Then six brass screws were inserted in order to attach a cation exchange membrane between the two chambers. It should be noted that the screw holes on the flange of chamber 1 were drilled, but the screw holes of chamber 2 were threaded. So, the two chambers could tightly be attached. The membrane was cut 12.9 cm by 12.9 cm square and glued into the inner mounting wall of two chambers with Dow Corning 100 % Silicone Rubber Sealant (Dow Corning Corp., Midland, MI) to prevent any leakage between two chambers. The outer wall of each chamber had a boss with

tapped hole for fixing the electrode holding bar that placed on the top of the cell to hold the electrodes.

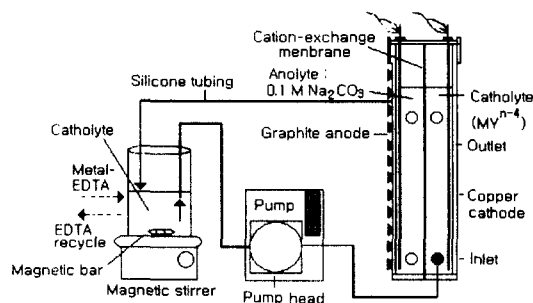


Fig. 2. Heavy metal removal and recovery system by EDTA-extraction.

Two electrodes were used in this electro-membrane process. The anode was a dimensionally stable anode (DSA) designed for evolving oxygen that was supplied by Electrosynthesis Company Inc. (ES2 ICI Metcote flag anode, East Amherst, NY). It was iridium oxide coated on titanium. The nickel electrode was also supplied by the same company mentioned above.

The Cd or Pb was removed from the nickel or copper cathode plate by dissolving the material with concentrated HCl solution. The HCl would also dissolve nickel or copper and would leave a fresh surface for the next experiment. Another alternative way would be to reverse of the nickel or copper electrode to an anode to remove the product.

The cation exchange membrane used in this study was Ionics Modacrylic fiber-backed cation transfer membrane (Ionics Incorporated, 61CZL386, Watertown, MA). It was a homogeneous film comprising cross-linked sulfonated copolymers of vinyl compounds on synthetic reinforcing fabrics. Physically it had a specific weight of 14 mg/cm^2 , a thickness of 0.6 mm, a burst strength of 8 kg/cm^2 , and a capacity of 2.7 meq/dry gram resin.

Each run was started by addition of 250 mL of 0.1 M sodium nitrate solution (anolyte) to anode chamber. In addition, 250 mL of 0.01 M Cd-EDTA or Pb-EDTA complex solution (catholyte) was placed in the cathod chamber. Then each electrode was placed in the cell by suspending it from an electrode holding bar approximately 2.60 cm from

the membrane surface. The electrodes were totally immersed in the solution. Complex solution was stirred by the Fisher Scientific Model 220T Thermix Stirrer. A test began when voltage was applied and current was set at proper amperage.

During electrolysis, samples were taken at regular time intervals from the cathode chamber. An appropriate portion of the solution was rapidly transferred into a graduate polystyrene tube by using micropipette to obtain required dilution with deionized distilled water. An aliquot of the solution in the tube was analyzed by ICP to determine the soluble metal concentration. The current efficiency of the system was calculated by equation (1) using the metal concentration remaining at each sampling time. The pH value of the catholyte was measured and electricity consumed were recorded at each sampling time and cumulated as a function of time.

$$\alpha = \frac{Q_{\text{product}}}{Q_{\text{consumed}}} \times 100 \quad (1)$$

Where Q_{product} is the coulombs required for recoverable product. Q_{consumed} is the coulombs consumed by the cell. Cathode washing was accomplished by placing the electrode in beaker of 10 % nitric acid. A steel wire brush was used to remove the plate metal. This procedure was repeated as necessary to remove all of the deposited metal. The electrode was then reconditioned using a belt driven industrial burnishing steel wire brush until a clean, shiny copper surface was obtained. The electrodes were then dipped in hydrochloric acid for approximately 2 hours. The anode was thoroughly washed with tap water after each experiment. It was stored in clean deionized distilled water during not in use.

3. Results and Discussion

Metals on soil may dissolve in soil solution by desorption and/or dissolution⁽¹⁰⁾. Desorption processes depend primarily on the characteristics of the soil, complexation of the desorbing metal, pH, ionic strength of solution, the type and species of possible exchanging ions in solution, and kinetic effect.

Research concerning metal behavior in soil systems has mainly used various chemical extraction methods in describing forms of metal

in soils. Beckett⁽¹¹⁾ described many of these methods. Many of the extractions dealt with metal deficiencies rather than metal contamination. Lindsay and Norvell⁽⁶⁾ used a DTPA as an extractant to assess levels of Zn, Fe, Mn, and Cu in soils. Mitchell et. al.⁽⁵⁾ used EDTA to extract Cu and assessed Cu status in agricultural soils.

Cu concentrations in Na_2EDTA extraction solutions of varying concentrations are shown in Figure 3. For the five soils tested, the Cu extracted reaches a maximum with the concentration of EDTA(0.05 M) originally suggested by Mitchell et al.⁽⁵⁾.

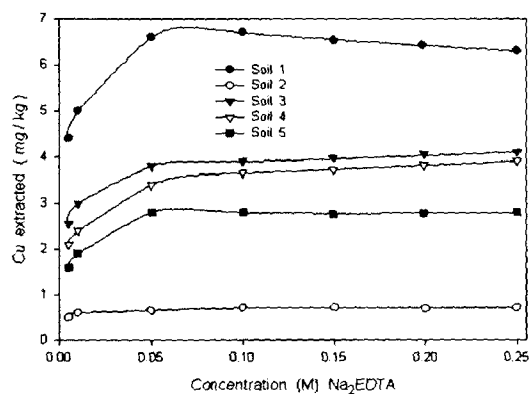


Fig. 3. Cu extracted in varying concentrations of Na_2EDTA .

Results for Cd are shown in Figure 4. Results for Zn, Pb, and Ni were almost similar; all metal concentrations reached a maximum with the 0.05 M EDTA concentration. Increasing of concentration of EDTA also increased the coloration of the soil extracts. The increased deep brown color in the higher concentrations of EDTA was attributed to the solubilization of soil organic matter by EDTA. EDTA has been employed to extract soil organic matter⁽¹²⁾. EDTA is a strong chelating agent and extracts much higher concentrations of Cu and Cd than the CaCl_2 extractions⁽⁶⁾.

Results for the extraction of Cu by DTPA are shown in Figures 5. Results for Cd, Zn, Pb, and Ni were almost similar.

Generally, metals extracted reached a maximum with the 0.1 M DTPA extraction solution. The extraction scheme of Lindsay and Norvell⁽⁶⁾ includes triethanolamine(TEA) as a buffer and

CaCl₂ to suppress the dissolution of CaCO₃ in the soils. The results did not differ from those shown

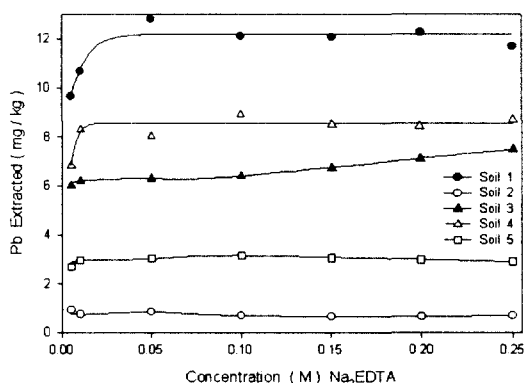


Fig. 4. Cd extracted in varying concentrations of Na₂EDTA.

in Figures 5. For this set of coastal, moderately acidic soils, dissolution of CaCO₃ and metals occluded by CaCO₃ was barely insignificant. TEA is important for maintaining the extract pH. Without the addition of TEA the extract pH tends governed by DTPA solution.

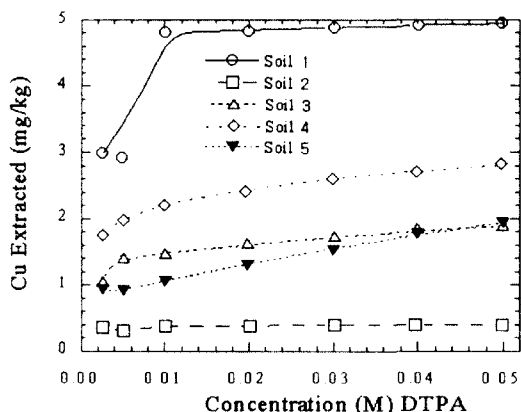


Fig. 5. Cu extracted in varying concentrations of DTPA.

As with the EDTA extractions, the color-intensity of the extractant was increased with increasing DTPA concentration. This is attributed to the solubilization of soil organic matter by DTPA. And all results indicate that the heavy metal(%) extracted by EDTA and DTPA were increased with decrease of clay(soil 2 ; 23 %, soil 5 ; 21 %, soil 3 ; 16 %, soil 4 ; 10 %, and soil

1 ; 6 %) in soils. Clay minerals contain a variety of surface which exhibit electrical charge properties having a strong influence on the sorption of ionic and polar species. The charge on the surface of the soil must be counterbalanced in the aqueous phase to maintain electroneutrality. As a result, electrical double layer exists at the clay/water interfaces. The clay minerals were tested in an original form, so, in the electrical double diffusive layer, Na, Ca, Mg, K, etc. elements were expected being in both the Stern layer and diffuse layer¹³. These result suggest that adsorption and desorption has been controlled by process of clay-metal and EDTA-metal or DTPA-metal in the solution.

When solution contains metal ions and chelating agent such as EDTA or DTPA ligand, it generally contains uncomplexed and complexed species. The affinity between uncomplexed free metal ion and its hydrous species may be drastically different from trace of complexed ions. It is essential to understand solution composition for the interpretation of metal-chelating agent formation behavior.

Therefore, the extracting efficiency of heavy metals which have been adsorbed by organic clay in soil is controlled by concentration or kinds of chelating agents.

Figure 6 and 7 compares metals extracted by five extractions 0.01 M CaCl₂, 0.1 M HCl, 0.05 M EDTA, 0.01 M DTPA, and H₂O(1.0 g soil : 0.8 mL H₂O) with total recoverable metals from soils 1-5. The data for the H₂O extraction was obtained from previous studies on these soils¹⁵. The extractability of Cu by EDTA and DTPA was well correlated with concentration of total recoverable copper. But the extractability of Cu by water and CaCl₂ solution was not correlated with concentration of total recoverable copper. 0.1 M HCl is strong enough to approach a pH of the extraction in the system. Thus, the Cu extracted by the 0.1 M HCl correlates significantly with total recoverable copper. Data for Zn, Cd, Pb, and Ni is similar to that for Cu shown in Figure 6. In many instances, the concentration of Cd and Pb extracted by the water and CaCl₂ solution were below the detection limit of the ICP.

The agent must mobilize the contaminant, which is chemically or physically attached to the soil particles. Basically, the extraction and recycle process consists of the following three steps : The

first, the contaminant adsorbed or attached to the soil particles or located between the particles are dissolved or dispersed in the exchanging agent

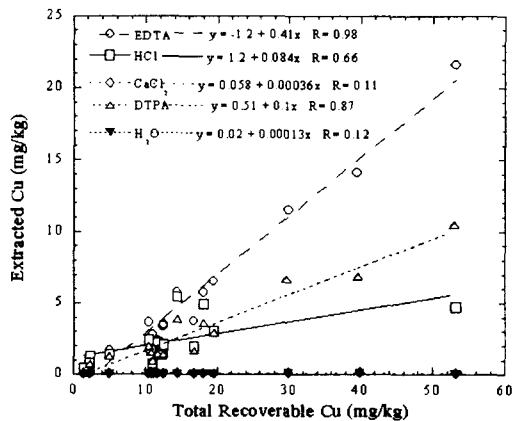


Fig. 6. Extractable Cu vs. total Recoverable Cu for soils.

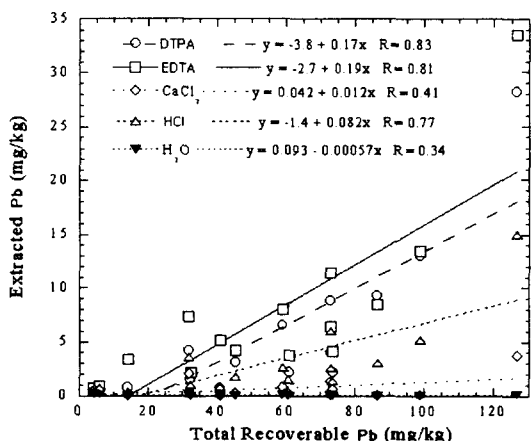


Fig. 7. Extractable Cd vs. total recoverable Cd for soils.

by mixing the extracting agent and the contaminated soil. In the second and final step, the separation of contaminated extracting agent and soil particles, and the cleaning and recycling of the extracting agent were conducted in this study, respectively.

Although the experiment demonstrated that the reclaimed EDTA can be reused for extraction of metal from soil, EDTA and metal recovery should be used to reduce another pollutants. Thus, electromembrane process can be advantageously employed. The recovery of metal(Cd, Cu, and Pb)

and their EDTA complex solutions were studied in an electromembrane cell. The current was supplied by power source that could produce up to one ampere(A). This one ampere current developed a current density at the membrane surface of approximately 25.8 mA/cm² which has less value than 30 mA/cm² in industrial electrolysis systems¹⁷⁾.

Figure 8 shows the percentage of Cd and Cu remaining in the catholyte as a function of electrolysis time when the nickel electrode has been used as a cathode for removal of the heavy metals at 0.1 A applied current in the electromembrane process.

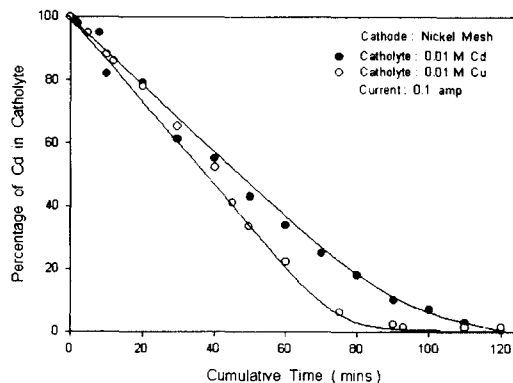


Fig. 8. The variation of cadmium and copper concentration as a function of electrolysis time when Nickel electrode has been used as a cathode.

Electrodeposition of cadmium was done at controlled current of 0.1 A. Within the first three minutes, Cd(OH)₂ precipitate was formed in the cathode chamber and pH was increased from 3 to 12. When the pH value was greater than 8, the catholyte was severely cloudy, and hydrogen evolution is responsible for carrying the current. The electrolysis time takes longer from the initial pH 2.9 to the final 11.49 than applying 1.0 A to the cell. But the catholyte is less cloudy than 1.0 A was applied, and the pH was greater than 8.0. The percentage of Cd removal was 90% and the current efficiency was 65.4 % at 0.1 A.

Electrodeposition of copper was done at 0.1 A as a controlled current. During the electrolysis, the pH changed slowly. The percentage of copper removal was 99.15 % and the current efficiency

is 49.42 %. Comparing the electrodeposition of Cd and Cu, within the 40 min as a function of electrolysis time, the percentage of Cd removal was similar to that of Cu; after 40 min, the electrodeposition of Cu was better.

Figure 9 shows the percentage of CuY^{2-} remaining in the catholyte as an electrolysis time when the nickel electrode has been used as a cathode for removal of the heavy metals at 0.75 A applied current in the electromembrane process.

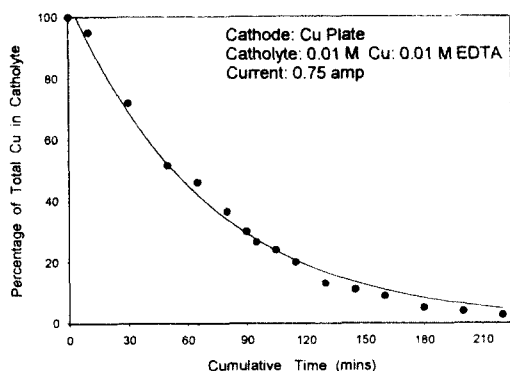


Fig. 9. The variation of copper concentration as a function of electrolysis time at Cu electrode in the presence of EDTA.

Electrodeposition of Cd from Cd-EDTA solutions was investigated at controlled current of 1.0 A. Although no electrodeposition of Cd was found, some observations can still be stated here. Due to the higher complex formation constant, the Ni-EDTA complex will form and replace the Cd-EDTA complex. Thus, the stoichiometric equivalent of Cd^{2+} ion will be released in the catholyte, as the pH increases, excess Cd^{2+} ion will form $\text{Cd}(\text{OH})_2$. After several tests, it was found that if the pH of catholyte was above pH 3, or if during the electrolysis the pH was adjusted with first removing the cathode, nickel will neither dissolve into the catholyte nor form $\text{Cd}(\text{OH})_2$. In these studies, the final catholyte was analyzed for Cd and Ni by ICP emission spectrophotometer. Dissolved nickel is less than 5 % of total cadmium in the catholyte. Most of cadmium is still remaining in the catholyte. Therefore, to prevent Ni dissolution from the cathode, the cathode should be taken out whenever the pH of the catholyte was adjusted.

Electrodeposition of Cu-EDTA solution was conducted at controlled current of 0.1 amp and 1 amp. No copper could be plated on the cathode at 0.1 amp. When 1.0 A current was applied, the dominant reduction on the cathode is due to proton formation. Therefore, the pH of catholyte quickly rise above 10. Copper is reduced gradually through the electrolysis time. The percentage of Cu removal is 97.27 % and the percentage of EDTA recovered is 94.99 % while the current efficiency is only 9.01 %.

1.0 A of current is applied to the cell for the electrodeposition of the Cd-EDTA complex. No $\text{Cd}(\text{OH})_2(\text{s})$ was observed during the electrolysis. But Cd was not coated or deposited on the copper electrode.

Cu can successfully be electrodeposited on the copper electrode from Cu-EDTA at current of 0.75 A or higher. Figure 10 indicates the percentage of total Cu remaining in the catholyte as a function time of electrolysis time. Most of the Cu is plated above pH 10. The percentage of Cu removal and EDTA recovered are 97.68 % and 99.26 %, respectively, while the current efficiency is only 3.2 %.

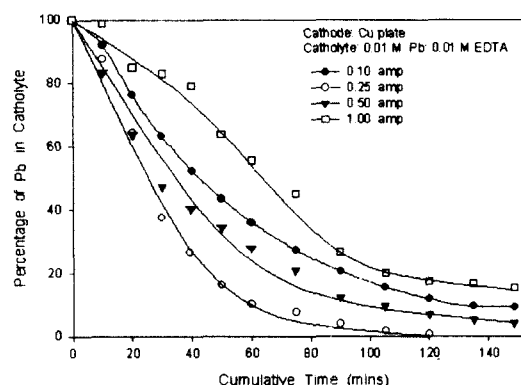


Fig. 10. The variation of lead concentration as a function of electrolysis time at Cu electrode in the presence of EDTA different applied current.

Table 1 shows the comparative results of Cu deposition from Cu-EDTA solution on nickel and copper electrodes. It should be noted that the percentage of free EDTA yield of the nickel cathode was smaller than that of the copper cathode. Due to the formation of Ni-EDTA complex, the crucial

achievement of this process was the electrolysis of Pb-EDTA solution for regeneration of EDTA. Figure 10 shows the percentage of Pb removal at various current supply as a function of electrolysis time. Comparing the percentage of Pb removal versus electrolysis time in the catholyte containing various concentration of Pb-EDTA, the Pb was less reduced in the presence of EDTA than in the absence of EDTA (Figure 12). Results of Pb-removal (Figure 10-11) were increased with increasing the applied current except the 0.1 A, and the removal efficiencies of Pb^{2+} in free Pb^{2+} solution was higher than that in PbY^{2-} solution at the same applied current. When a 0.1, 0.25, 0.5, or 1.0 A controlled current was applied to the cell, the current density at the copper electrode was 1.90, 4.74, 9.48, and 18.96 mA/cm^2 , respectively. Figure 12 shows the percentage of Pb removal versus electrolysis time at four various current densities.

These observations imply that for electrolysis time less than 60 min, the effectiveness of Pb removal was in the following order : 4.74 mA/cm^2 > 9.48 mA/cm^2 > 1.90 mA/cm^2 > 18.96 mA/cm^2 .

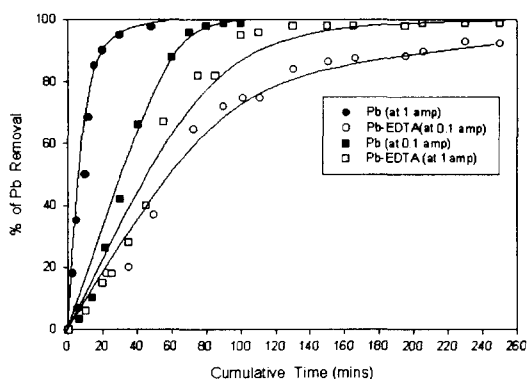


Fig. 11. The percentage of lead removal as a function of electrolysis at Cu electrode and different applied current for lead solution and lead-EDTA solution.

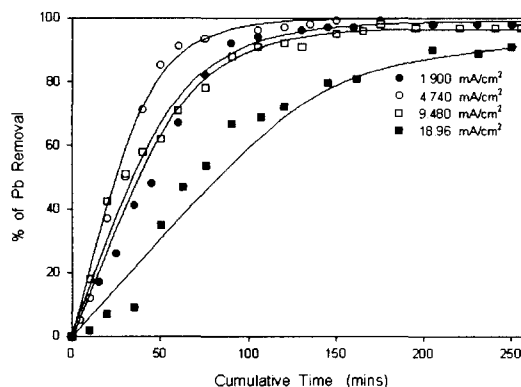


Fig. 12. The percentage of lead removal as a function of electrolysis time at various current densities and Cu electrode.

Moreover, the effectiveness of Pb removal after 60 minutes as a function of electrolysis time was 4.74 mA/cm^2 > 1.90 mA/cm^2 > 9.48 mA/cm^2 > 18.96 mA/cm^2 . This result also indicates that in general, removal-efficiency of the metal was increased with decreasing of the current density except the 1.90 mA/cm^2 . This result indicates that the efficiency having 4.740 mA/cm^2 exhibit the best improvement.

The generation of Pb and EDTA from Pb-EDTA solution was indicated in Table 2. The side reaction, hydrogen evolution, occurred to a significant extent at high current. In other words, a shorter electrolysis time is required to achieve a fixed percentage of Pb removal. In addition, the higher the current applied to the cell, the less the current efficiency. This phenomenon is probably due to secondary reaction of hydroxide ion production at higher current densities that consumed more energy.

From Table 2, it should be noted that the yield of free EDTA at 0.1 A was not consistent with the percentage of Pb removal, After 250 min of electrolysis time, the pH of catholyte was adjusted from 11.48 to 3.01. Then the electrolysis proceeded again and EDTA was recovered from final solution.

Table 1. Recovery Cu and EDTA from Cu-EDTA solution by electromembrane process on different cathodes

Cathode	Cu Conc. (ppm)	EDTA Conc. (M)	Initial pH	Current Applied (amp)	Reaction time (min)	Final pH	Final Cu Conc. (ppm)	Cu removal (%)	Free EDTA (%)	Current efficiency ζ
nickel	572.4	0.01	2.28	1.00	75	12.36	15.63	97.27	94.99	9.02
copper	437.0	0.01	3.27	0.75	221	12.78	10.16	97.68	99.26	3.12

The pH of anolyte was less than 2 during the whole electrolysis. Due to the low pH maintained in the anolyte for a long time, some amount of recovered EDTA is precipitated and attached onto the surface of the cation exchange membrane.

This explains why the percentage of recovered EDTA was unusually low in this test. Graven¹⁵⁾ noted that EDTA is almost insoluble in water up to a pH of approximately 3.5. This suggest that suitable substitute of anolyte should be used instead of sodium nitrate to prevent EDTA precipitation.

Allen et. al.¹⁶⁾ studied the effect of anolyte composition in the electromembrane process. Hydrochloric acid, sulfuric acid, and sodium carbonate solutions were used. They found that when hydrochloric or sulfuric acid was used, EDTA was partially deposited during the regeneration in the cathode chamber, primarily on the membrane surface, and then reduced the conductivity of membrane. This problem could be resolved using sodium carbonate instead of acid in the anode chamber.

Comparing the results in Tables 1 and 2 the recovery of Pb from the Pb-EDTA complex was less efficient than recovery of Cu from the Cu-EDTA complex. This is because the reduction potential of Pb is more negative than that of Cu for Pb recovery. The required electrolysis time was longer and the current efficiency was lower than those of Cu.

In this study, 75 grams of soil sample (soil-1) was extracted with 1500 mL of 0.05 M EDTA. The EDTA concentration remaining in the filtrate was analyzed to know whether EDTA combined with calcium or lead. The results show that the concentration is 3.602×10^{-2} M (with calcium) or 3.673×10^{-2} M (with lead).

Figure 12 shows the percentage of total lead remaining in the catholyte as a function of el

ectrolysis time. The percentage of Pb removal and EDTA recovered were 99.0 % and 91.74 % respectively while the current efficiency was 14.12 %. The percentage of Pb removal in this study was compared with that of the previous study¹⁶⁾. These data imply that only slightly less Pb was deposited with the soil extraction process than when pure Pb-EDTA was electrolyzed. However the current efficiency decreased from 21.50 % to 14.12 %.

This study has successfully proven that the electromembrane process is applicable to the regeneration of heavy metals and EDTA contents in the soil extract. According to the data calculation, regeneration of 1 kg of lead at current density of 1.0 mA/cm² would require approximately 3.26 kw/hour of electric energy.

4. Conclusions

The goal of this work was to find a suitable chemical extractants applicable to the soil-bound metals that can potentially be available to soil organisms. The second purpose of this research was investigate the feasibility of batch electromembrane process for the regeneration of the metal from the EDTA-copper or -lead complex.

All metal concentrations had the best extraction efficiency in the condition of 0.05 M-EDTA or DTPA concentration. The organic chelating agents extract much higher concentration of metals than the CaCl₂ or HCl extraction. This was attributed to the solubilization of soil organic matter by EDTA or DTPA. Therefore, the extracting efficiency of heavy metals which have been adsorbed by organic clay in soil was increased and controlled by concentration or selectivity of chelating agent for the metals.

Metals and EDTA from complex solutions were recovered by the way of an electromembrane

Table 2. Recovery Pb and EDTA from Pb-EDTA solutions by electromembrane process

Ca Final pH thode	Pb Conc. (ppm)	EDTA Conc. (M)	Initial pH	Current Applied (amp)	Reaction time (min)	Final pH	Final Pb (ppm)	Pb removal (%)	Free EDTA (%)	Current Efficiency (%)
copper	1786.2	0.01	2.12	0.10	250	11.48	34.20	98.10	71.16	21.50
copper	1946.6	0.01	2.17	0.25	250	12.16	27.82	98.57	91.96	18.40
copper	1707.7	0.01	2.20	0.50	250	12.50	141.11	91.74	90.79	9.76
copper	1746.0	0.01	2.14	1.00	90	12.20	470.22	73.07	74.16	5.20

process. The overall processes on the regeneration, recovery, and reuse were evaluated. The Cu metal electrode used as a cathode had smaller current efficiency than Ni electrode. And then the Cu electrode had much more removal efficiency than Ni electrode in the process of removal of heavy metals by electromembrane method.

The electrochemical process showed copper could be chosen as an electrode to plate Cd, Cu, and Pb. At least 90% of EDTA and associated Cu or Pb could be recovered by the electro-membrane process. The overall process could successfully separate the Pb-EDTA complex that resulted from the soil extraction with EDTA.

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