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Recovery of copper and chelating agents from sludge extracting solutions

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Abstract

Removal of extraction solution containing chelated copper from printed circuit board industry sludge by cementation on powdered iron was studied. This work applied the recovery and extraction of ethylene diamine tetraacetate (EDTA) and diethylene triamine pentaacetate (DTPA) as remediation agents and metal precipitated from printed circuit board sludge extracting solutions. The recovery of copper by cementation process using powdered iron was dependent on the Fe:Cu molar ratio. Results of the experiments showed that recovery efficiencies were typical of those of a Fe:Cu molar ratio as high as 8:1 for each sludge sample. The differences of recovery efficiencies may be due to competition for active sites on the surface of the powdered iron. Copper deposits on the surface almost always occur in the form of the copper metal that are well distributed, with purified copper powder being observed in characterization with scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The recycled extract containing EDTA or DTPA was used to chelate supplementary fresh copper-containing sludge. Extraction efficiencies of copper by using Fe-precipitated EDTA or DTPA from previous cementation were higher than sequential application of the Fe-EDTA or Fe-DTPA solution. Similar copper extraction efficiencies using both pristine and reused extract containing chelants validates the enduring chelating capability of EDTA and DTPA and suggests further opportunities to employ recycled chelant to reduce its usage. This work confirmed the feasibility of copper removal from sludge chelated wastewater by cementation and subsequent recycling of chelant extraction.

Keywords: Recovery; Chelated wastewater; Copper; Chelant; Printed circuited board sludge

1. Introduction

Rapid industrial development and greater use of chemical products have led to a progressive increase in cases of heavy metal sludge [1]. In Taiwan, as much as 4.1×10^5 metric tonnes of hazardous metallic sludge are produced from electronic and computer industries annually. From environmental and economic perspectives, the retrieval of metals from waste is important. Various treatment methods have been employed, e.g., pretreatment, physical separation, thermal processes, biological decontamination, stabilization/solidification and washing [2]. Washing as well as the extraction of metals by chelants have been some of the more effective treatment methods [3–5]. The most common chelant found in the literature is ethylene diamine tetraacetic acid (EDTA) [3–11]. Studies have established that EDTA and DTPA can effectively remove Cu, Zn, Pb, Hg and Cd from contaminated soil or incinerator fly ashes [3–5,7–14].

Many studies have used EDTA or DTPA for the extraction of heavy metals from contaminants. But EDTA and DTPA have the disadvantage that they are quite persistent in the environment due to their low biodegradability [1,11,14–16]. This may cause a rather high risk of metal leaching to the environment [16]. EDTA removes almost all natural and anthropogenic heavy metals, but its potential adverse health effects make its use difficult for treatment [17]. Additionally, to keep treatment costs low, it is necessary to achieve a cleanup so that the heavy metal can be recovered, and it should be possible to reuse the chelant for further extraction cycles. The electrochemical reduction process can remove metal ions from the synthetic solution and field samples and can deposit elemental metals on the cathodic plate to enable EDTA to be recovered for reuse from power plants [18,19]. But they are affected by several operating problems, e.g., membrane fouling and degradation [20]. Therefore, the cementation process is a promising technology for recovery of metal copper from copper-containing wastewater [21–26].

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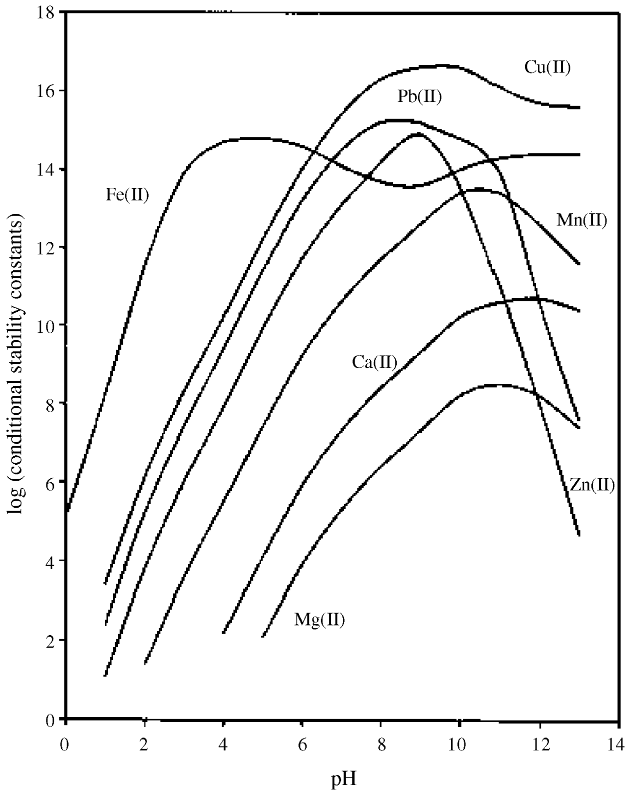

Fig. 1. Effect of pH on conditional stability constants of metal-EDTA complex at 20 °C with ionic strength of 0.1 M [20].

Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salts by another electropositive metal. Fig. 1 provides a comparison of conditional stability constants with pH for various metal-EDTA complexes. As shown in Fig. 1, it seems to be the most reasonable and simple method for recovery of copper by powdered iron (for low pH conditions) and results in a copper ion readily reduced on iron surface. Various studies have shown that the removal efficiency of highly concentrated heavy metal wastewater was high, regardless of heavy metal species [23–28].

EDTA and DTPA have ionic structures and dissolve better in more alkaline solutions. When acid is added to such solutions to reduce their pH value, dissolved EDTA and DTPA adopt a molecular structure which favors coagulation. EDTA and DTPA then precipitate by crystallization, and can be separated from heavy metals and are thus recovered. After solid/liquid separation, the supernatant can be recovered and reused again as chelants for soil extracting or flushing solutions [14,17,20,29–30]. Most studies on this pertain to equimolar solutions of metal and chelants [20,30]. These studies differ from the case of solutions extracted from contaminated soils, as the metal concentration is very low and the solutions are characterized by a large excess of EDTA. There is a need to develop a method for recovering the high concentration chelated copper wastewater that contains strong complex formation agents such as EDTA and DTPA.

The major objective of this research was to evaluate the process of copper precipitation and the recycling of chelants from printed circuit board sludge extracting solutions. The recovery efficiency of copper was studied by cementation on powdered iron. The recovered copper has been characterized using XRD and SEM. The effectiveness of recycling chelants for repeated use in the treatment of copper-containing sludge is also evaluated.

2. Materials and methods

2.1. Sludge characterization and preparation

The sludge materials used in this study were taken from two printed circuit board factories (sludges A and B) and a metal surface treatment plant (sludge C) in Taiwan. The sludges were dehydrated in an oven at 60 °C for 48 h, then pulverized and sieved to <2 mm, and stored in glass containers until analysis. All of the sludges in this study were oven-dried. Sludge properties are shown in Table 1. The total concentrations of heavy metals in the sludges were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon—JY24), following acid digestion [31]. The three sludges contained high Cu concentrations, especially sludge A. The molar sum of the heavy metals Pb, Cd, Cr, Cu, Zn and Ni was 4.55 mmol g^{-1} for sludge A, 1.94 mmol g^{-1} for sludge B and 1.78 mmol g^{-1} for sludge C. Mobility of metal in the samples was evaluated by using the sequential extraction scheme of BCR (the BCR method which was researched by the European scholars [32]). This scheme is a three-step sequential extraction procedure that was proposed to harmonize and validate the methods used for speciation studies in soils and sediments. It was designed based on acetic acid extraction (step 1), hydroxylamine hydrochloride extraction (step 2), and hydrogen peroxide oxidation and ammonium acetate extraction (step 3). These extractions are associated with the exchangeable, water and acid soluble phase (bound to carbonate, step 1), the reducible phase (bound to iron and manganese oxides, step 2), and the oxidizable phase (bound to organic matter, step 3). The results of BCR sequential extraction

Table 1
Sludge properties

Sludges	pH	Ca (g kg−1)	Fe (g kg−1)	Pb (mg kg−1)	Cd (mg kg−1)	Total Cr (mg kg−1)	Cu (g kg−1)	Zn (g kg−1)	Ni (g kg−1)	Sum of heavy metals (mol kg−1)	Leaching concentration (mg l−1)		
											Cu	Zn	Ni
A	9.15	84.5	3.2	<0.3[a]	<0.04	<0.04	282.7	2.8	3.5	4.55	484.2	9.5	42.8
B	6.54	59.8	160.6	100.0	<0.04	<0.04	120.9	0.8	1.2	1.94	2278.0	18.3	65.9
C	8.62	44.3	22.6	<0.3	<0.04	683.0	94.1	9.2	8.3	1.78	611.4	97.6	61.2

[a] Not applicable, all values below detection limits.

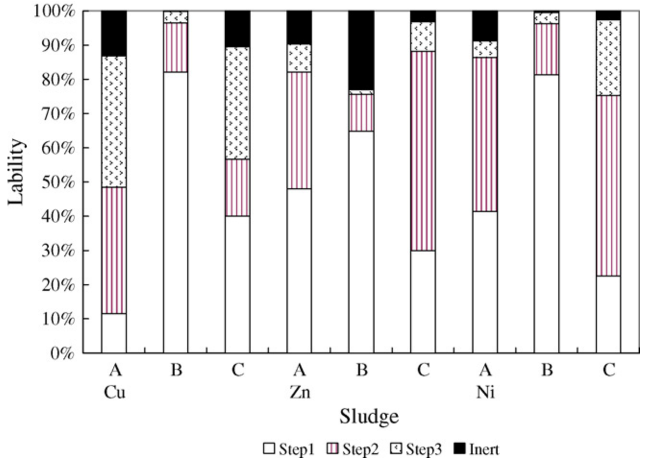

Fig. 2. Mobility of studied metals from initial sludge given as percentage of heavy metals concentration.

[32] of metals from the sludge are shown in Fig. 2. The sludge differed in the modes of metal retention within the sludge. In sludge A, Cu was mostly accumulated in step 2 (37% of all fractions) and step 3 (38%). On the other hand, for sludge B, Cu in step 1 accounted for 82% of the total amount obtained by summation of all fractions. In sludge C, Cu was mostly accumulated in step 1 (40%) and step 3 (33%).

Studies regarding the extraction of heavy metals from soil generally used a concentration of 0.005–0.1 M [4,20,30,33]. Therefore, the 0.1 M extraction solution was used to dispose of printed circuit board wastewater sludge. The pH of the extraction solution is adjusted to 7 by a 1 M NaOH or HNO_3 solution. Five grams of sludge were shaken with 100 ml 0.1 M EDTA or DTPA (liquid/solid ratio: 20/1) in a reciprocal shaker for 24 h to analyze the extraction efficiency of copper. The chelant:Cu molar ratio was 0.45 for sludge A, 1.05 for sludge B and 1.35 for sludge C. This is only 35% of the Cu content extracted from sludge A, but copper that was extracted from these sludge sources by chelating agents ranged in concentration from 0.72–0.81 mol Cu mol^{-1} EDTA to 0.57–0.80 mol Cu mol^{-1} DTPA. The samples were centrifuged as before, and the supernatant was filtered through a Whatman no. 42 filter. The total concentrations of metals in the extract were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon—JY24).

2.2. Metal precipitation by cementation processes

As shown in Fig. 1, ferric ions had a stronger affinity than cupric ions for EDTA, given a low pH (less than 5) in the sludge or solution. One molar nitric acid was added to lower the pH to 2.0, 3.0 and 4.0. Thereafter, powdered iron was used to break down the Cu-EDTA or Cu-DTPA complex and copper was recovered by the following reaction [22]:

$$\mathrm{Fe(0)} + \mathrm{Cu\text{-}EDTA} \rightarrow \mathrm{Fe(II)\text{-}EDTA} + \mathrm{Cu(s)} \tag{1}$$

$$\mathrm{Fe(0)} + \mathrm{Cu\text{-}DTPA} \rightarrow \mathrm{Fe(II)\text{-}DTPA} + \mathrm{Cu(s)} \tag{2}$$

The solutions containing chelated metals were shaken with powdered iron at Fe:Cu molar ratios of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 20.0 and 40.0 in a reciprocal shaker with a constant-temperature water bath for 6 h, then centrifuged, filtered and analyzed as above, to estimate the influence of the powdered iron concentration on the recovery of copper. The specific surface area of powdered iron was equal to 0.328 m^2/g and the particle sizes of powder iron were 100 μm. A PANalytical X'Pert Pro X-ray powder diffraction with Cu Kα radiation was used to analyze the crystallinity of recovered copper. A scanning electron microscope (SEM) was used for morphological observations of the recovered copper.

2.3. Recovery of chelant from extract

After the recovery of copper, the reuse of extracted solution took place in three phases:

1. One molar NaOH was added to the solution to bring its pH up to 13 and permit the formation of $Fe(OH)_3$ and $EDTA^{4-}$ [20] or $DTPA^{5-}$:

$$\mathrm{EDTA\text{-}Fe} + \mathrm{OH^-} \rightarrow \mathrm{EDTA^{4-}} + \mathrm{Fe(OH)_3(s)} \tag{3}$$

$$\mathrm{DTPA\text{-}Fe} + \mathrm{OH^-} \rightarrow \mathrm{DTPA^{5-}} + \mathrm{Fe(OH)_3(s)} \tag{4}$$

2. The supernatant liquid was filtered through a Whatman no. 42 filter and analyzed to determine the concentration of chelant and residual copper in the solution.
3. The concentrations of chelants were indirectly measured by a total organic carbon (TOC) furnace (O-I-Analytical, model 700). The average natural organic content in the extract solution that extracts the sludge using distilled water was less than 100 mg l^{-1} and may be considered negligible.

2.4. Extraction using recovered chelant

The chelant solution, after precipitating its Cu, may be used as an extraction solution again, provided the solution pH is adjusted to 7 by a 1 M HNO_3 solution. The copper extraction efficiencies using the recovered EDTA or DTPA solutions with Fe-removal were compared against the results of Fe-EDTA or Fe-DTPA solutions and fresh EDTA or DTPA solutions with a similar set of extraction experiments. The concentration of Fe-EDTA or Fe-DTPA was adjusted to the actually measured concentration after Fe-removal. To evaluate the reproducibility of the results, all experiments were measured in triplicate samples. The diagram of metal precipitation and recovery processes are described in Fig. 3.

3. Results and discussion

3.1. Sludge extraction

Table 2 shows the results of the sludge extraction. The extracting solutions had a high copper concentration, regardless the kind of sludge or type of chelant. The concentrations of Pb, Cd, Cr, Zn and Ni in solutions were relatively lower than copper. If no chelant was used, the concentration of copper in solution B was 1734.9 mg l^{-1}. From BCR sequential extraction of the

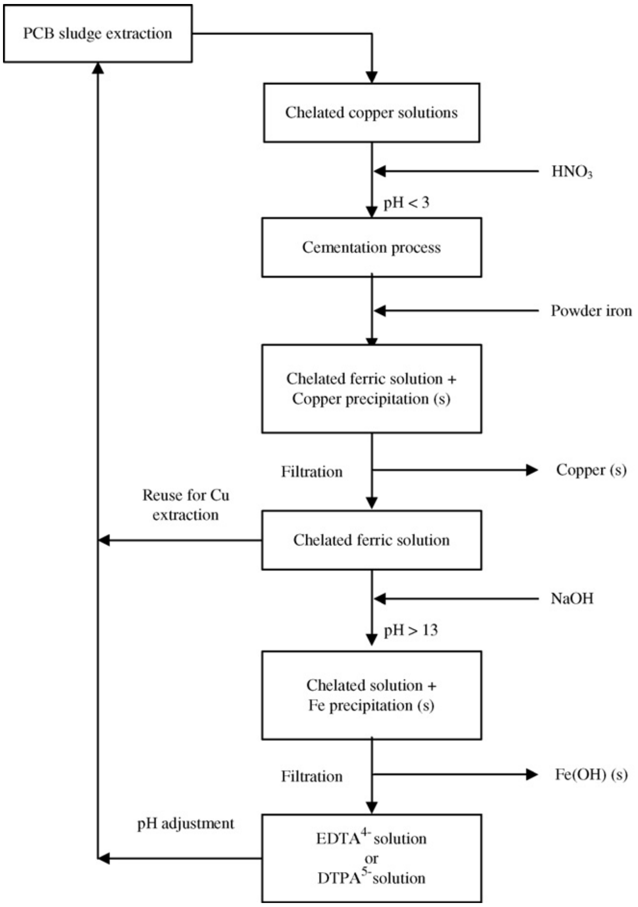

Fig. 3. Diagram of the metal precipitation and recovery process.

sludge, we found that Cu in step 1 for sludge B accounted for 82% of the total amount obtained by summation of all fractions. Therefore, the leachability of sludge B was superior to that of sludges A or C. Copper that was extracted by chelants from dry sludge ranged from 0.72–0.81 mol Cu mol^{-1} EDTA to 0.57–0.80 mol Cu mol^{-1} DTPA/g of sludge. DTPA was a strong effective chelant, similar to EDTA in the extraction of contaminant metals from printed circuit board sludge. Other studies performed under similar conditions have already shown that the extraction of heavy metals from soil or MSW (municipal solid waste) fly ash by EDTA or DTPA was highly efficient [5,11,14,20,30]. However, most of these studies used artificial contaminated soils and the concentrations of heavy metals in soil or MSW fly ash were lower than that of the printed circuit board sludge used in this study. In fact, heavy metal extraction from artificially prepared sludge using chelant tended to be much easier than extraction from actual wastewater sludge, even though artificial factitious sludge may promote consistency in the sludge samples.

Table 2
Percentages of heavy metals extracted from sludge at various chelants

Extracting solutions	Pb (%)	Cr (%)	Cd (%)	Cu (%)	Zn (%)	Ni (%)
EDTA						
A	NA[a]	NA	NA	35.0	53.4	49.6
B	89.6	NA	NA	85.2	67.5	96.2
C	NA	70.9	NA	97.9	97.4	98.1
DTPA						
A	NA	NA	NA	32.7	58.4	59.3
B	95.5	NA	NA	83.6	68.5	99.8
C	NA	60.6	NA	93.7	98.3	98.8
No chelant (pure water)						
A	NA	NA	NA	0.0	NA	NA
B	NA	NA	NA	28.7	30.5	93.0
C	NA	NA	NA	0.5	NA	0.1

[a] NA: not applicable, all values below detection limits.

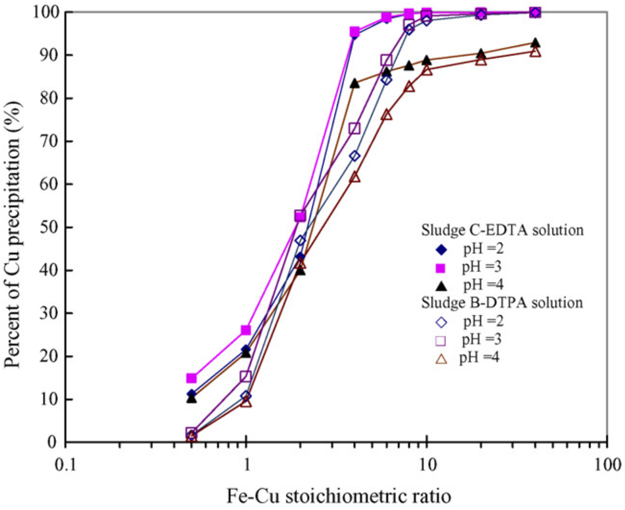

Fig. 4. Stoichiometric and pH effects on copper precipitation for the sludge C-EDTA solution and sludge B-DTPA solution (6-h cementation period).

3.2. Copper precipitation by cementation processes

Copper precipitation efficiencies for different Fe–Cu stoichiometric ratios and solution pH for sludge C-EDTA and sludge B-DTPA extracting solutions are presented in Fig. 4. Cementation time for these experiments was 6 h. The figure shows that the cementation with solution pH as low as 2 on a mass basis was similar to that of a solution pH of 3 for both extracting solutions. The cementation efficiencies were found to be dependent on the quantity of iron powder present. Considering the requirement that wastewater generated from the cementation process should be treated before disposal, reducing the mass of iron powder would reduce the treatment costs and provide additional savings with the application of chelant recovery technology. It is interesting to note that the cementation efficiency for sludge B-DTPA extracting solutions was gradual for higher Fe–Cu stoichiometric ratios, while for sludge C-EDTA extracting solutions, the change in cementation efficiencies seemed to be quite steep for a small change in higher Fe–Cu stoichiometric ratio. Figs. 5 and 6 show the results of copper, nickel and zinc precipitation from metal chelated wastewaters for Fe–Cu stoichiometric ratios between 0.5 and 40 over a 6-h cementation period with pH 2. The figure demonstrates that copper precipitation efficiency for each extracting solution was different and that copper precipitation was a function of the stoichiometric ratio of the applied Fe concentration to the total copper concentration

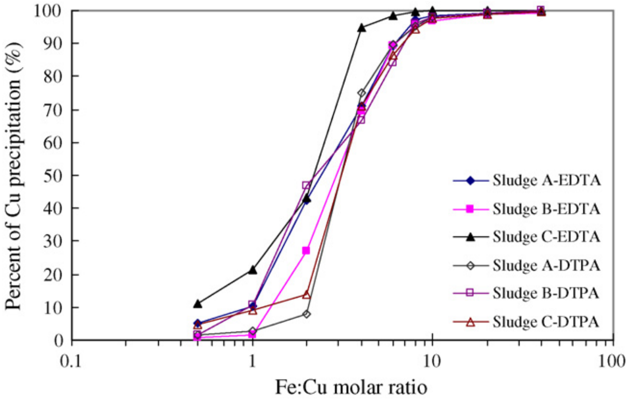

Fig. 5. Impact of iron:copper molar ratio on copper precipitation by cementation processes (20 ml of sludge extracting solution to iron) (6-h cementation period with pH 2).

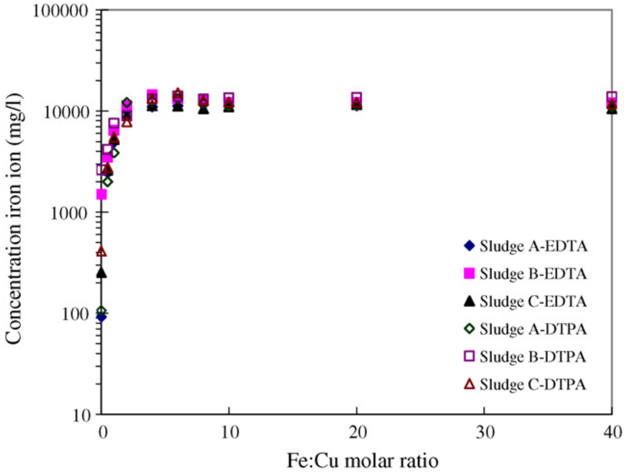

Fig. 7. Effect of iron concentrations on the cementation of copper ions in solutions of different Fe:Cu molar ratios (20 ml of sludge extracting solution to iron) (6-h cementation period with pH 2).

in the extracting solution. If a sufficiently large amount of Fe is applied, all the copper may be deposited from the extracting solution. The deposit of copper on the iron particle surface gradually coalesced as the cementation proceeded [22]. Fe undergoes oxidation more readily than Ni. However, since E^0_{cell} is small (+0.19 V), it is not sensible to electroplate Fe with Ni. A cementation process using iron powder for recovering chelated zincic wastewater was impossible because Zn has a greater tendency to undergo oxidation than does Fe ($E^0_{\text{cell}} = +0.32$ V). The deposit of zinc results from the coprecipitation on copper precipitated by cementation processes [34]. The higher Fe:Cu molar ratio was necessary as a result of the surface sites of iron already held by the deposit of copper. The iron concentrations under various experimental conditions are presented in Fig. 7. It is interesting to note that the effect of various concentrations of iron on the cementation of copper ion with Fe:Cu molar ratios as high as four seemed to be quite stable. The tendency of copper precipitation efficiency is similar.

Fig. 8 presents the results of XRD analysis of recovered copper from the chelated cupric wastewater with solution pH of 2 with Fe:Cu molar ratios of 2 and 6. It indicates that copper deposits on the surface almost entirely in the form of the copper molecules that are well matched with purified copper powder; no indications of any Cu–Fe alloy or metal oxides/hydroxides were found on the surface. However, the sample is not fully crystallized. The cementation process to recover copper during the tests using various Fe:Cu molar ratios was observed by SEM (Fig. 9). The SEM analysis shows that the cemented surface had fine, dense copper deposits of relatively uniform size with irregular iron surface possibly caused by the etching of iron.

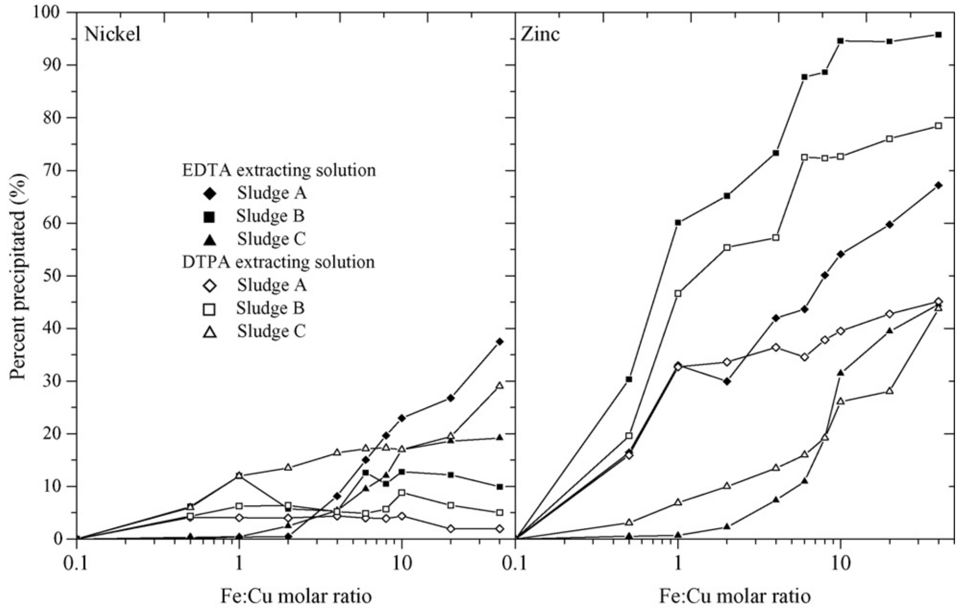

Fig. 6. Impact of iron:copper molar ratios on Ni and Zn precipitation by cementation processes (20 ml of sludge extracting solution to iron) (6-h cementation period with pH 2).

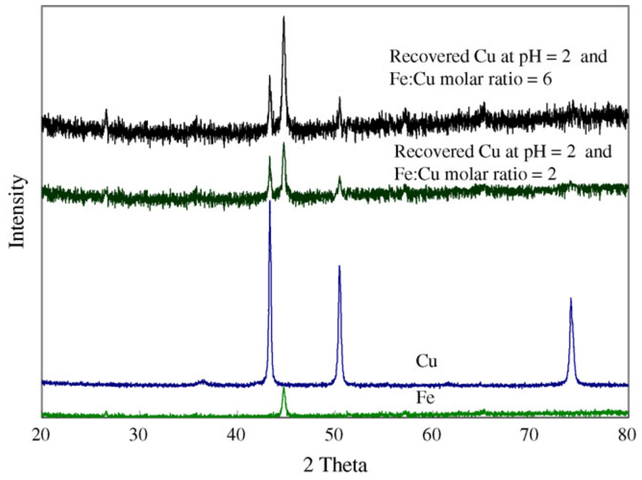

Fig. 8. X-ray powder diffraction patterns of copper prepared in different conditions for sludge A-EDTA extracting solution.

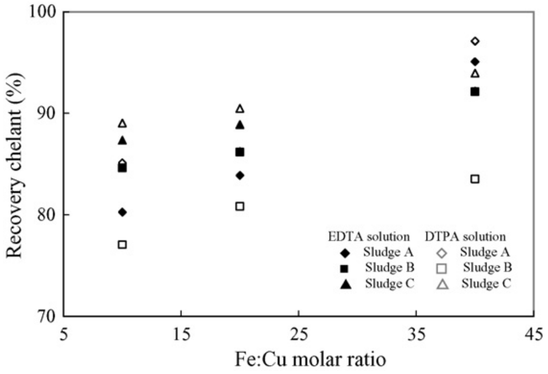

Fig. 10. Chelant recovery yield after Fe-precipitation treatment.

Besides this, ring-shaped copper was grown completely from the acicular copper after raising the Fe–Cu molar ratio to 10 (see Fig. 9). It is believed that ring-shaped copper was formed during the cementation process on iron powder. The high purity of fine powder and the controllability of particle shape and size are of importance for its practical use. It is noted that the Fe:Cu molar ratio plays an important role in determining the shape and size of the particles.

3.3. Extraction using recovery chelant

The recovery efficiency of chelant with Fe-precipitated chelated solution on the cementation of copper ion is shown in Fig. 10. As more powdered iron was used, a higher recovery efficiency of EDTA and DTPA was observed. The loss of chelant should result from the adsorption of chelant within sludge in the extractive process.

Fig. 11 shows the extraction efficiencies of copper from copper-contaminated sludge (sludge A) with the chelated wastewater treated by cementation on powdered iron to precipitate copper ions, followed by Fe(III) precipitation. The reclaimed Fe-precipitated EDTA showed much higher copper extraction efficiency than in sequential applications of Fe-EDTA solution. The extraction efficiency of sequential applications of 0.1 M EDTA dropped to approximately 45% of the extraction efficiency of fresh EDTA after the third application, while the extraction efficiency for reclaimed Fe-precipitated EDTA remained at about 57%. The extraction of heavy metals was associated with the exchangeable, water and acid soluble phase (bound to carbonate, step 1) which could be easily extracted from heavy metal contaminant [32]. The models showed lower accumulation of Cu in step 1 (11%) from the results of BCR sequential extraction of sludge A. The molar sum of the heavy

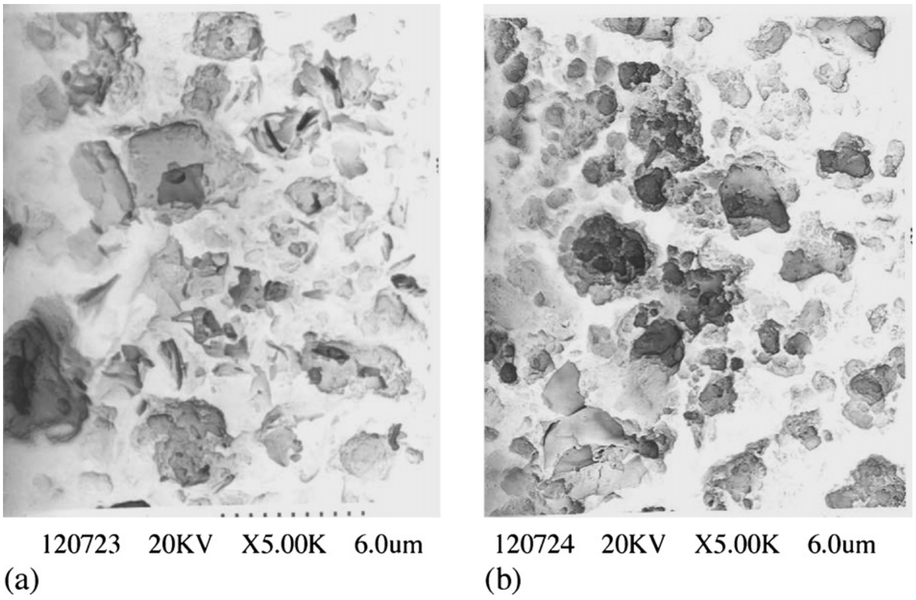

Fig. 9. Scanning electron microscopy analysis of copper prepared from sludge C-EDTA extracting solution by iron cementation (pH 2) at different Fe:Cu molar ratios (a) 4:1 and (b) 10:1.

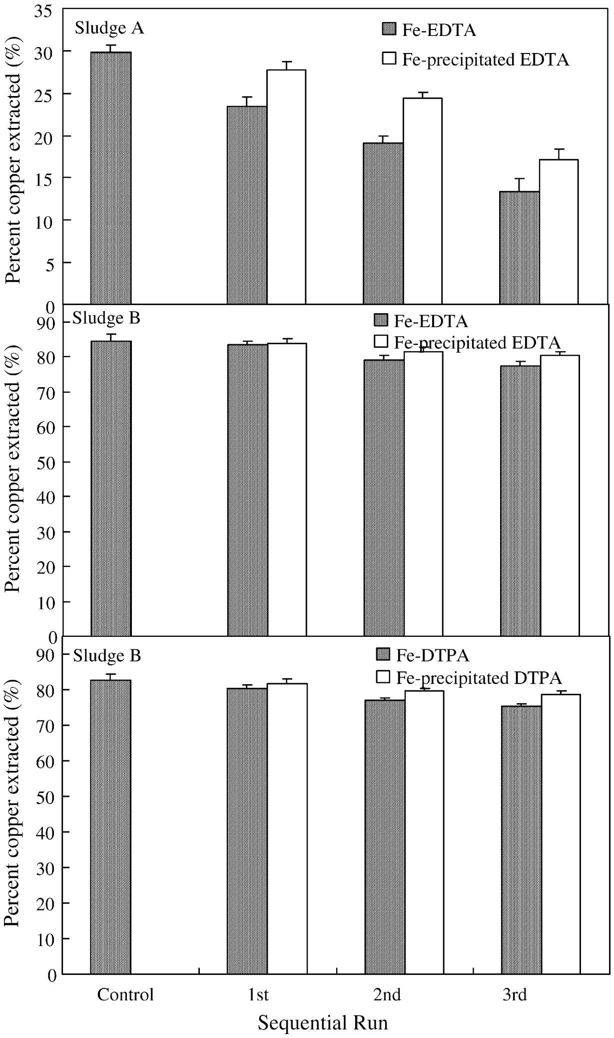

Fig. 11. Percent copper extracted from sludge with reclaimed chelated solution (S.D. for triplicates; without and with precipitated treatment at pH 7.0).

metals was higher in sludge A. Therefore, the copper extraction efficiency was as low as the precipitant for copper and iron.

Regarding sludge B, the extraction efficiencies of the recycled EDTA solution were about 91% to 100% of the extraction efficiencies of fresh EDTA solution, as shown in Fig. 11. Similar results were obtained using DTPA as the extracting solution (Fig. 11), although the extraction efficiencies were slightly lower than those using EDTA. The models showed high accumulation of Cu in step 1 (82%) from the results of BCR sequential extraction of sludge B. Therefore, the copper extraction efficiency was as high as 82% even after being reclaimed over three cycles. The reclaimed chelated solution may be as efficient as fresh chelant for extracting copper from printed circuit board sludge, even after the chelated solution has been reclaimed for a third time.

4. Conclusions

The experiments using chelated wastewater performed in this study examined copper removal, recycling of chelant, and extraction of hazardous heavy metals from sludge. The results of these experiments have led us to conclude the following:

1. The extracting solutions have a high copper concentration, regardless of the kind of sludge or chelants used.
2. Cementation on powdered iron was adopted to remove or recycle the heavy metals from wastewater that contained chelated metals. Powdered iron promoted the separation of copper from copper-containing wastewater.
3. Copper deposits on the surface of the iron occurred almost entirely in the form of copper molecules that are well matched with purified copper powder.
4. The recycling of Fe-precipitated EDTA or DTPA showed much higher copper extraction efficiency than the use of sequential applications of the Fe-EDTA or Fe-DTPA solutions.
5. The copper extraction efficiency for sludge A with recycled Fe-precipitated EDTA remained about 57%. However, the copper extraction efficiency for sludge B was as high as 82%, even after being reclaimed over three cycles. The models of metal retention within the sludge serve to determine the extraction efficiency of metal.
6. The processes using chelated copper from hazardous metallic sludge, successive powdered iron recovery of copper from extract, and resulting reuse of chelants, are proved according to this study and interrelated literatures [20,29]. As a result of the recovery of copper and the reuse of chelants, those processes used in this study will be economically feasible to treat hazardous metallic sludge.

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