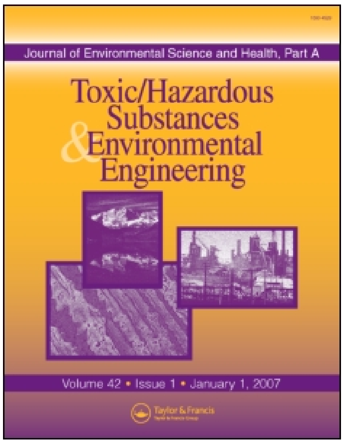

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Removal of Metals from Industrial Sludge by Extraction with Different Acids

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ABSTRACT

This study addresses the feasibility of removing Cu and Ni from sludges of printed circuit board (PCB) plants by acidic extraction. Citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid at various concentrations were experimentally examined to determine preferred conditions for removing Cu and Ni. Experimental results indicate that the removal ratios of Cu were 57% (citric acid), 79% (acetic acid), 81% (hydrochloric acid), 91% (nitric acid), and 92% (sulfuric acid), and that of Ni was 74% (citric acid), 70% (acetic acid), 75% (hydrochloric acid), 92% (nitric acid), and 93% (sulfuric acid), using 1 N extractants. The removal ratios obtained using sulfuric acid or nitric acid at a particular concentration were in the order Pb > Ni > Cu > Zn. The kinetic extraction results revealed that the extraction of Cu and Ni by nitric acid and sulfuric acid exhibited a lagphase after 60 min and the removal ratio was then around 90%. The kinetic results also revealed that the extraction rate constants of Cu and Ni increased with the concentration of the acid. The extraction rate

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constants of Cu and Ni followed the order sulfuric acid > nitric acid > acetic acid, and it also showed that Ni was more easily extracted than Cu from PCB sludge. The total percentages of Cu extracted by 1 N acetic acid, nitric acid, and sulfuric acid, determined in three replicate extractions were 78, 94, and 94%, and those of Ni were 89, 94, and 98%, respectively. The residue sludge, following three replicate extractions using 1 N acetic acid, nitric acid, and sulfuric acid, was further tested by toxicity characteristic leaching procedures (TCLP), and more than 15 mg/L of Cu was leached, exceeding the legal concentration in Taiwan. This observation reveals that the residue sludge following three replicate extractions by acids remained hazardous waste. Further treatment, such as solidification, must be performed before the sludge is disposed of.

Key Words: Metal removal; Copper; Nickel; Acid extraction; Industrial sludge.

INTRODUCTION

In 2002, about 750,000 t of heavy metal sludge was produced in Taiwan. The sludge is expensive to handle and no satisfactory solution exists for finally disposing of sludge with a high heavy metal content. Moreover, industrial sludge that contains heavy metals is classified as hazardous waste. Hence, the removal of heavy metals from sludge is very important.

The cost of disposing of sludge that contains toxic metals has been exponentially rising and the number of landfills that will receive such sludge in Taiwan has been declining. Strong economic reasons account for the need to consider the use of a removal system, as an instead. The extraction of heavy metals from industrial sludge before composting is therefore necessary step to increase the sustainability of the sludge treatment, but the efficiency of removal of the heavy metals depends on the heavy metal and the wastewater treatment plant.

Methods for recovering metals include pyrometallurgical and hydrometallurgical processes. Pyrometallurgical processes produce volatile oxides that pollute the environment. Hydrometallurgical processes are more environmentally friendly; consume less energy than the primary metal production, and are pyrometallurgical. Various hydrometallurgical methods that involve acids and solvents have been developed for recovering metals. Direct acid extraction is a highly effective means of removing the metal contents of sludge since a low pH destabilizes several inorganic constituents. Rabah[1] and Abdel Basir and Rabah[2] used both acidic and alkaline solutions to recover Zn, Cu, and Pb from brass melting slag, to which hydrogen peroxide had been added. The extraction using acids followed the order nitric acid > hydrochloric acid > sulfuric acid. Gbor et al.[3] achieved 77% Co and 35% Ni removal from nickel smelter slag that contained 0.13% Co and 0.29% Ni, by aqueous sulfur dioxide leaching. Sukla et al.[4] extracted over 80% Cu and 80% Co from slag by leaching with sulfuric acid. Sulfuric acid has been used to extract Ni and Co from nickel smelter slag.[5] Electric arc furnace dusts have been treated using sulfuric acid as an extractant to recover Zn and 80% Zn removal was achieved at low sulfuric acid concentrations and room temperature.[6] Copper smelter flue dust was also leached in the sulfuric acid and metal recovered following purification.[7,8] The use of sulfuric acid is beneficial because it has a low cost and the associated leach mixture is relatively easy to filter.[9,10] Wu et al.[11] compared the efficiencies of three types of extractant in removing heavy metals from sewage sludge, indicating that directly adding concentrated sulfuric acid resulted in a higher efficiency and a lower cost than the use of EDTA and NH_4HCO_3. Banza et al.[12] demonstrated that sulfuric acid under hydrogen peroxide at 70°C could effectively extract base metals from a copper smelter. Arslan and Arslan[13] recovered Cu, Co, and Zn from a copper smelter and extracted 88% Cu, 87% Co, and 93% Zn by roasting with sulfuric acid. Ahmed et al.[14] stated that over 70% Co, Fe, and Zn could be extracted from smelter slag using aqueous sulfur dioxide, and that the extraction was accelerated by increasing the concentration of sulfur dioxide and the temperature, and by reducing the slag loading and particle size.

Hydrochloric acid is also employed in the hydrometallurgical processing of wastes that contain Zn. Chlorinated water is used to dissolve Zn as its chloride.[15] Hydrometallurgical processes for recovering Zn from Zn ash and electric arc furnace dusts using sulfuric acid, hydrochloric acid, ammoniacal solution, and sodium hydroxide, have been described. Sulfuric acid and ammonia solutions have been found to be effective reagents for treating Zn ash and electric arc furnace dusts.[16] Yoshizaki and Tomida[17] found that heavy metals in sewage sludge can be easily removed by treating a sludge filter cake with phosphoric acid that contains hydrogen peroxide for 1 h at room temperature. Kazi and Cooper[18] recovered metals from industrial wood preservative sludge by sequential extraction and oxidation using sodium hypochlorite and phosphoric acid. Clevenger and Novak[19] evaluated the feasibility of acetylacetone (HAA), dithizone, sodium diethyldithiocarbamate (NaDDC), 8-hydroxyquinoline (8HQ), and thenoyltrifluoracetone (HTTA) for separating and recovering metals from electroplating wastes; they found that HAA and HTTA are both effective in cleanly extracting Cu. Petrochemical industry sludge can be leached using ammonia solution to recover copper, and the leaching efficiency increases with the concentration of the solid and the temperature.[20] Jenkins et al.[9] demonstrated that EDTA extracting Cd, Pb, and Cu very efficiently, but the cost of the chemical is high.

Numerous studies have focused on the removal of metals from slag, ash, sewage sludge, and industrial sludge using nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid, ammonia solution, EDTA, and other extractants. However, little information is available on the extractability of heavy metals in industrial sludge by different organic and inorganic acids at various concentrations. This investigation elucidates the feasibility of removing Cu and Ni from sludge of PCB plants through acidic extraction. Citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid at various concentrations were used experimentally to determine suitable conditions for separating Cu and Ni. Various extraction times were also examined to determine the removal rate constants of Cu and Ni, and the most economic extraction time. Finally, the sludge was tested following three replicate extractions by TCLP to determine whether it remained hazardous waste.

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MATERIALS AND METHODS

Properties of Sludge

Industrial sludge was obtained from a PCB plant in Tao-Yuan County, Taiwan. A 20 g sample of sludge was mixed with 20 mL deionized water for 5 min. The sample was centrifuged and filtered through a 0.45 μm membrane filter, and the acidity of the filtrate was measured using a pH meter.

The amount of heavy metals in the industrial sludge was determined after it was digested in aqua regia (a mixture of concentrated HCl and concentrated HNO_3). The suspension was cooled and filtered through a 0.45 μm membrane filter and the filtrate was analyzed for Cu, Ni, Pb, and Zn by inductively coupled plasma (ICP) spectrometry. The pH value and the heavy metals content were measured in three replicate tests.

Removal of Heavy Metals by Acidic Extraction

The sludge was oven-dried at 105°C until it reached a constant weight. It was then crushed until it could pass through a 9.5 mm screen. The main differences in the extraction tests were the extractants and their concentrations. Table 1 lists the conditions of extraction. Different extractants and concentrations of the extractant were adopted to compare efficiencies of metal removal.

The kinetics of extraction from industrial sludge were obtained using acetic acid, nitric acid, and sulfuric acid at 1 N; the extraction times were 5, 30, 60, 90, 120, 150, and 180 min. All other conditions were as stated in Table 1. Three replicate extractions were performed using each of acetic acid, nitric acid, and sulfuric acid in 1 N for 1 h; the other parameters were as in Table 1. Three samples of the extracted sludge were collected and dried. Each extracted sample of the sludge was tested by TCLP to measure the leaching of heavy metals after extraction, and to determine whether the sludge remained hazardous. After each extraction, all the suspensions were centrifuged and the supernatants were filtered through a 0.45 μm membrane

Table 1. Conditions for different extraction procedures.

Conditions	Extraction procedure
Sludge (g)	5
Diameter	< 9.5 mm
Solid/liquid ratio (S/L)	1/20
Extractant	Citric acid, acetic acid, hydrochloric acid, nitric acid, sulfuric acid
Concentration (N)	0.1, 0.5, 1.0, 1.5, 2.0
Time (h)	18
Mixing (rpm)	30

filter. The filtrate was acidified to pH < 2 before being analyzed for heavy metals. The concentration of each heavy metal concentrations was determined by inductively coupled plasma (ICP) spectrometry. The difference between the total heavy metals in PCB sludge and the heavy metals in the supernatant; the percentages of Cu and Ni extracted were obtained. The extraction rate constants of Cu and Ni at various concentrations were determined by,

$$\frac{dC}{dt} = -kC \tag{1}$$

where C is the percentage of residual heavy metal in PCB sludge and k is the extraction rate constant (min^{-1}) associated with the heavy metal.

RESULTS AND DISCUSSION

Properties of the Industrial Sludge

The moisture content of the industrial sludge was $61.6 \pm 0.4\%$. The industrial sludge was analyzed by ICP, which determined that the total amounts of metals Cu, Ni, Pb, and Zn in the sludge were 157.07, 1.45, 0.18, and 0.80 mg/g, respectively. Concentrations were expressed in terms of dry mass. A high Cu concentration rendered the industrial sludge hazardous. Given the high content of Cu and Ni in the sludge, Cu and Ni were selected as the target metals to be removed. The pH of the sludge was 6.54 ± 0.01. The doses of the chemicals used and process conducted in the wastewater treatment plant in the PCB plant affected the pH of the generated sludge. The efficiency of removal depends on the type of heavy metal and the pH of the sludge.

Extraction of Heavy Metals from Industrial Sludge

Citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid were used as extractants for removing Cu and Ni from PCB plant sludge; the concentrations of the extractant were between 0.1 and 2 N (Figs. 1 and 2). The results were expressed as the amount of heavy metals extracted as a percentage of the original content. A 20-fold increase in acid concentrations (0.1–2 N) approximately doubled the extraction of Cu and Ni after 18 h. About 1 N acid was required to extract large amounts of Cu and Ni. The dependence of Cu and Ni extraction on the strength of extractants was strong at low extractant concentrations. Figures 1 and 2 reveal that the ratios of extraction of Cu and Ni increase with the concentration of the acid. The mechanisms of the retention of heavy metals in sludge involve (i) adsorption to suspended solids and (ii) presence as hydroxide precipitates; the latter is the dominant mechanism. At low pH, heavy metals adsorbed into the solid phase are exchanged by high concentrations of protons and heavy metal hydroxides are dissolved. The metals are removed accordingly from the industrial sludge. Ahmed et al.,[14] Yoshizaki and Tomida,[17] and Kazi and Cooper[18] claimed that the higher concentration of acid leach the more content of heavy metals from slag and sludge.

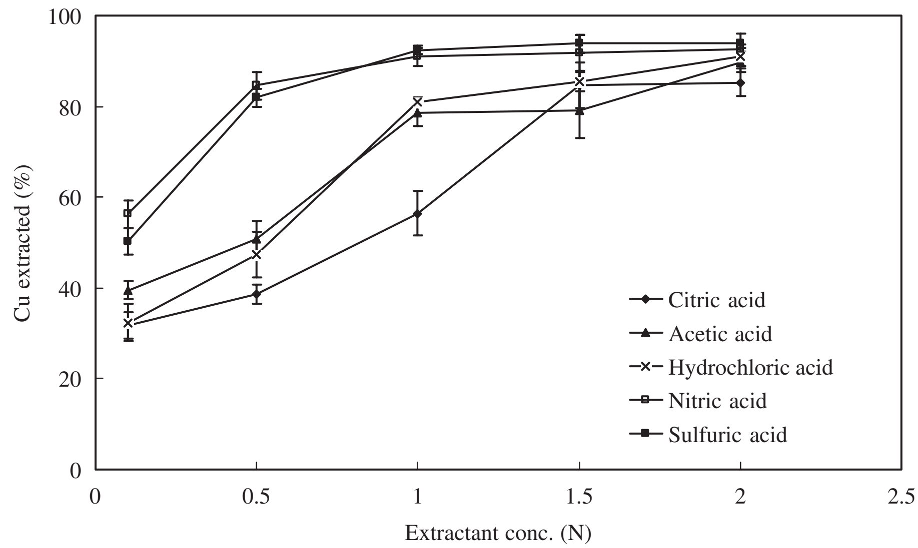

Figure 1. Cu extraction efficiency as a function of concentration of citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid.

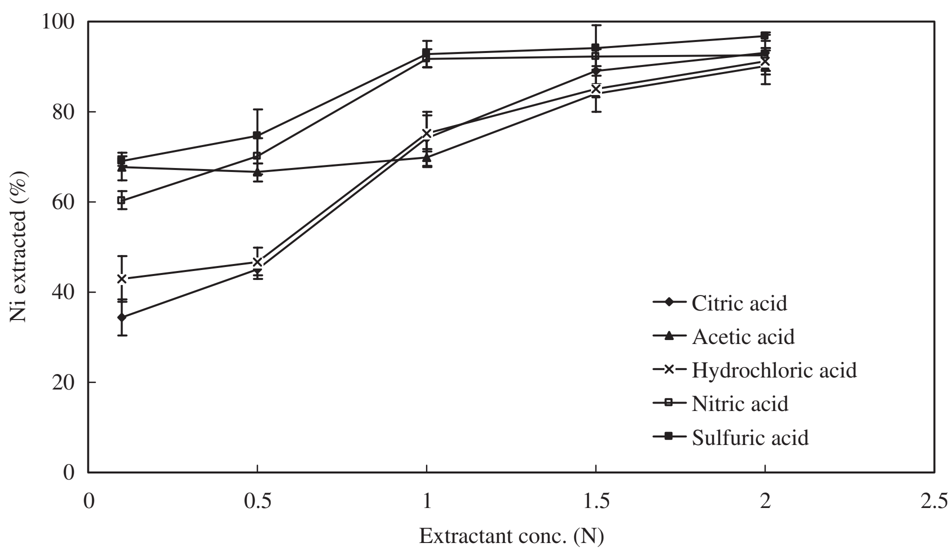

Figure 2. Ni extraction efficiency as a function of concentration of citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid.

Using 1 N extractant, the removal ratios of Cu were 57% (citric acid), 79% (acetic acid), 81% (hydrochloric acid), 91% (nitric acid), and 92% (sulfuric acid) (Fig. 1), and those of Ni were 74% (citric acid), 70% (acetic acid), 75% (hydrochloric acid), 92% (nitric acid), and 93% (sulfuric acid) (Fig. 2). Under the same conditions, the removal ratios of Pb were 68% (citric acid), 92% (acetic acid), 93% (hydrochloric acid), 94% (nitric acid), and 95% (sulfuric acid), and those of Zn were 48% (citric acid), 82% (acetic acid), 80% (hydrochloric acid), 86% (nitric acid), and 85% (sulfuric acid) (Figs. 3 and 4). The extraction by the different extractants followed the order sulfuric acid $\geqq$ nitric acid $>$ hydrochloric acid $>$ acetic acid $>$ ci- citric acid. Given the same concentration of sulfuric acid and nitric acid, the removal ratios followed the order Pb $>$ Ni $>$ Cu $>$ Zn. The strong inorganic acids (sulfuric acid, nitric acid, and hydrochloric acid) reacted with the metals in the sludge by proton exchange and dissolution of the formed heavy metal hydroxides. The organic acids (acetic acid and citric acid) react with metals by an additional mechanism—complexation of the metal ions with the organic acid anions. The organic acids react with metals in three reactions, but acetic acid and citric acid are weak acids. The results plotted in Figs. 1–4 imply that proton exchange and dissolution of heavy metal hydroxides were the most effective means of removing metals from sludge. Such extraction is almost entirely attributable to the action of protons. Several studies have addressed that the effectiveness of strong acids (sulfuric acid, nitric acid, and hydrochloric acid) in extracting metals from sludge and slag.[1,2,4–11,13,15,16]

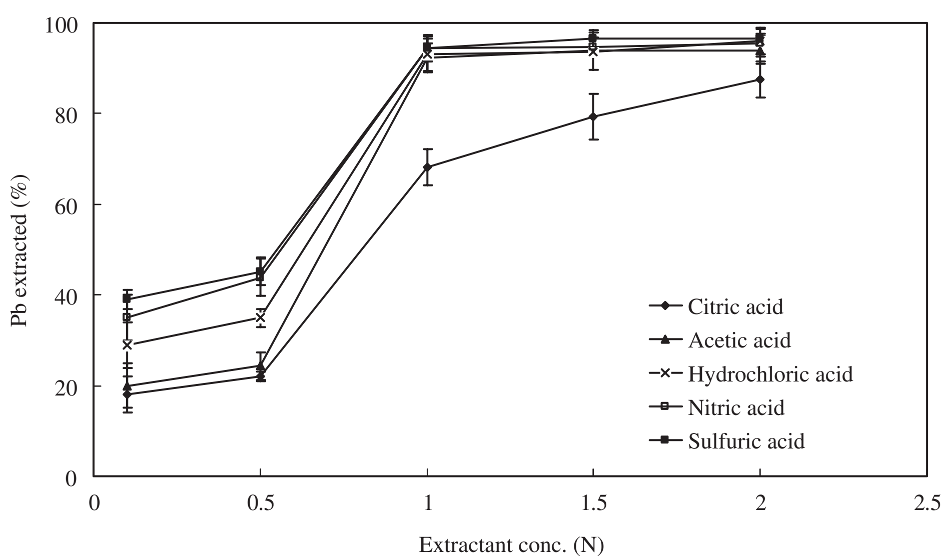

Figure 3. Pb extraction efficiency as a function of concentration of citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid.

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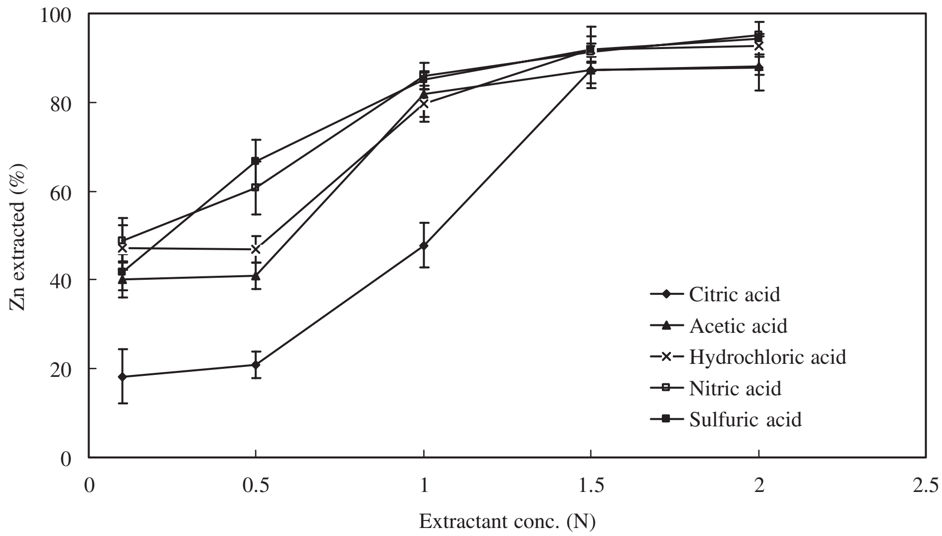

Figure 4. Zn extraction efficiency as a function of concentration of citric acid, acetic acid, hydrochloric acid, nitric acid, and sulfuric acid.

Kinetics of Removal of Metals by Acid Extraction

The kinetics of the Cu and Ni extraction process by acetic acid, nitric acid, and sulfuric acid at various concentrations (0.1 N, 0.5 N, and 1 N) are described. Figures 5 and 6 depict the kinetics of the extraction of Cu and Ni using 1 N extractants over 180 min. From 55 to 95% Cu and Ni was extracted using 1 N nitric acid and sulfuric acid, from 5 to 180 min. From 15 to 85% Cu and Ni was extracted using 1 N acetic acid from 5 to 180 min. Nitric acid and sulfuric acid extracted Cu and Ni from sludge much more rapidly than acetic acid. The extraction of Cu and Ni by nitric acid and sulfuric acid exhibited a lagphase after 60 min and the removal ratio was approximately 90%. In practical situations, a shorter extraction period can be obtained using smaller reactor, with lower associated capital and operating costs. Economically, nitric acid and sulfuric acid were better extractants than acetic acid, because of their high extraction ratio and high extraction rate, and an adaptive extraction time of approximately 60 min.

From 35 to 50% Cu and Ni was extracted using 0.1 N nitric acid and sulfuric acid, from 5 to 180 min (Figs. 7 and 8). From 10 to 40% Cu and Ni was extracted by 0.1 N acetic acid from 5 to 180 min (Figs. 7 and 8). From 40 to 70% Cu and Ni was extracted using 0.5 N nitric acid and sulfuric acid, and from 30 to 50% Cu and Ni was extracted using 0.5 N acetic acid from 5 to 180 min (Figs. 9 and 10). Table 2 presents the extraction rate constants of Cu and Ni obtained using various extractant concentrations. The kinetic results reveal that the extraction rate constants of Cu and Ni increased with the concentration of acid. The extraction rate constants of Cu and Ni followed the order sulfuric acid > nitric acid > acetic acid, and showed that Ni was more easily extracted than Cu from the PCB sludge. Less stronger binding heavy

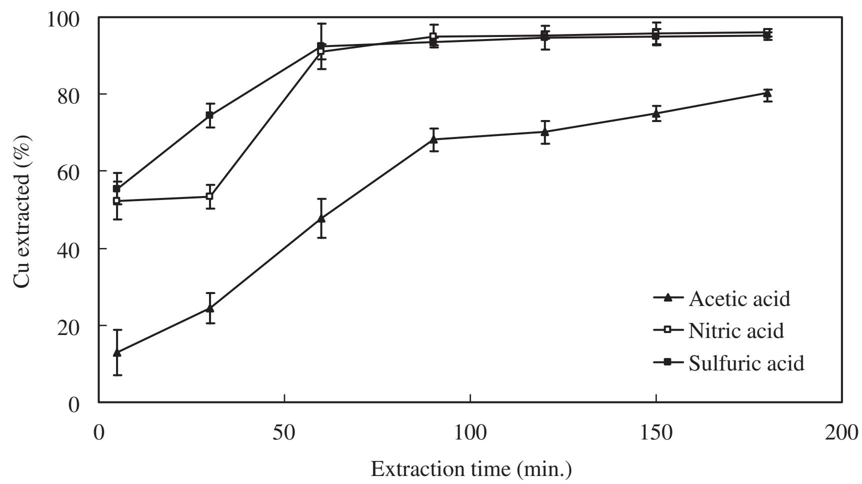

Figure 5. Kinetics of Cu extraction from industrial sludge using 1 N acetic acid, nitric acid, and sulfuric acid.

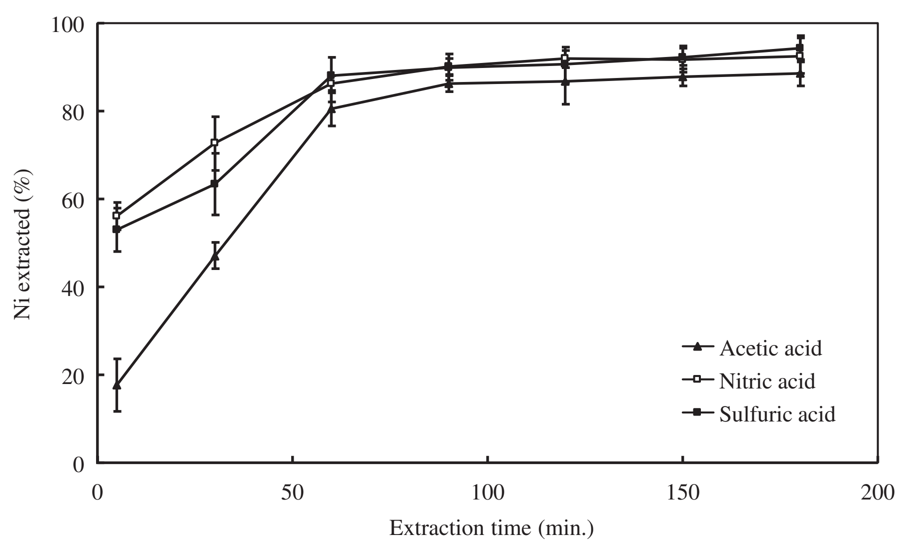

Figure 6. Kinetics of Ni extraction from industrial sludge using 1 N acetic acid, nitric acid, and sulfuric acid.

metal is extracted rapidly from the sludge while the stronger binding heavy metal takes a longer time to reach equilibrium. This finding implies that Cu forms a more strongly binding than Ni in the PCB sludge. The heavy metals are incorporated predominantly as hydroxides in sludge and acid extraction takes time because the hydroxides must diffuse from sludge into the bulk solution. Additionally, the rate of extraction depends on the accessibility of the metals to the extractants. Protons are

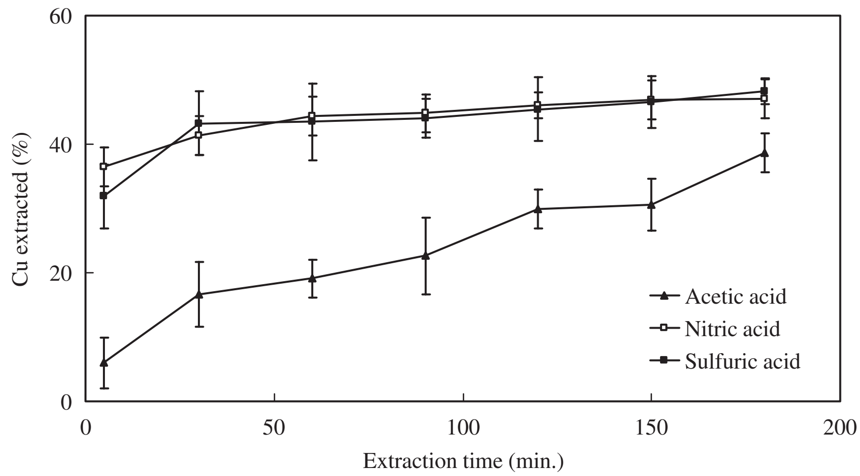

Figure 7. Kinetics of Cu extraction from industrial sludge using 0.1 N acetic acid, nitric acid, and sulfuric acid.

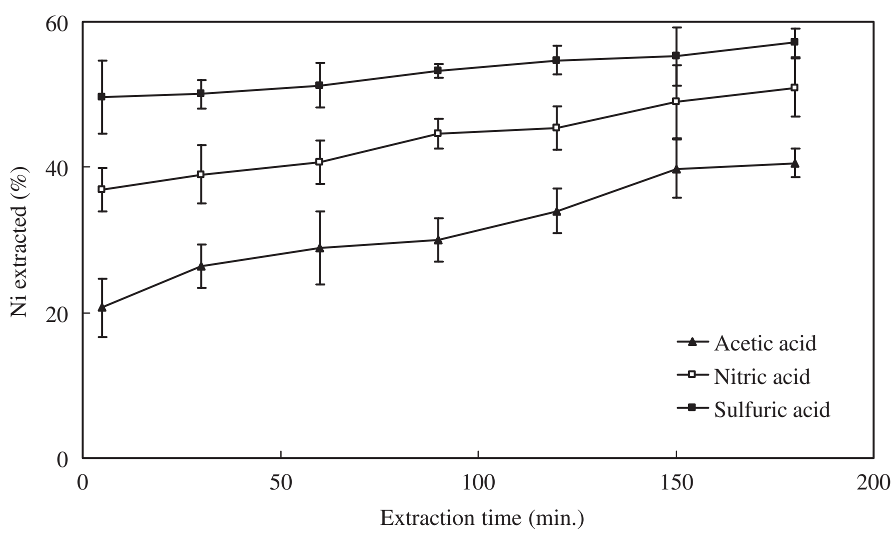

Figure 8. Kinetics of Ni extraction from industrial sludge using 0.1 N acetic acid, nitric acid, and sulfuric acid.

small ions and can easily penetrate the sludge and react with the hydroxides. Consequently, the strong acids (nitric acid and sulfuric acid) extracted heavy metals more quickly than the weak acid (acetic acid) at a particular concentration, because the strong acids were completely ionized. Heavy metals extracted by acetic acid not only exchange metal ions with protons but also complex with acetate. The larger acetate may not be able to enter the sludge, in which case metal ions can reach the

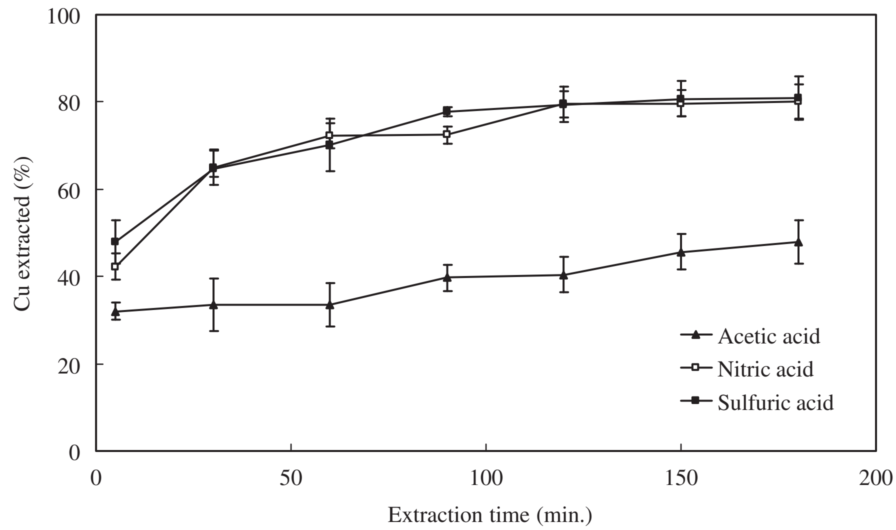

Figure 9. Kinetics of Cu extraction from industrial sludge using 0.5 N acetic acid, nitric acid, and sulfuric acid.

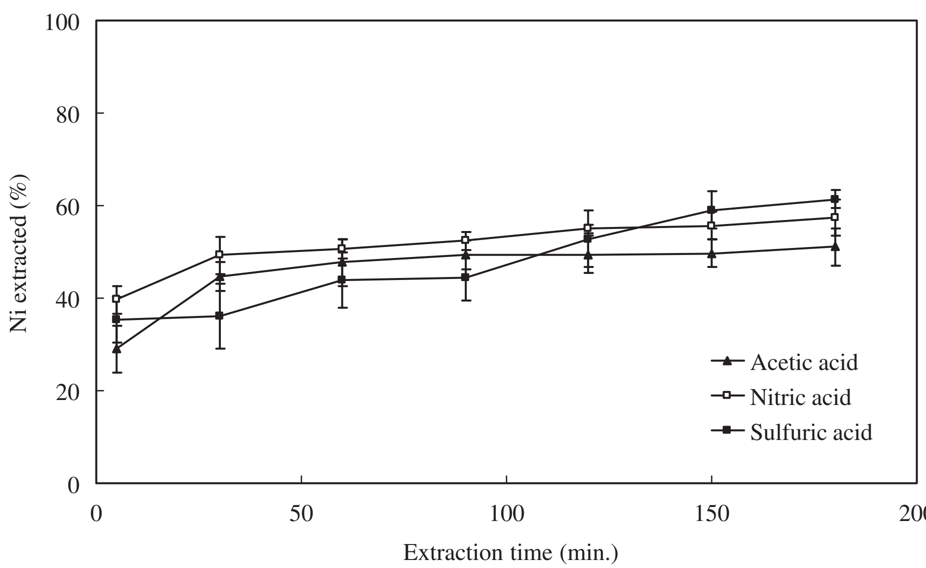

Figure 10. Kinetics of Ni extraction from industrial sludge using 0.5 N acetic acid, nitric acid, and sulfuric acid.

bulk solution only by diffusion. This process takes a long time because the driving force is small. The results of this work imply that the dissolution of hydroxide precipitates was faster than the diffusion of metal ions from the sludge to the bulk solution. This finding is verified by the observation that the extraction rate constants

Table 2. Extraction rate constants of Cu and Ni in various concentrations of acetic acid, nitric acid, and sulfuric acid.

Metal	Cu			Ni		
Conc. (N)	0.1	0.5	1.0	0.1	0.5	1.0
Acetic acid	0.0025	0.0034	0.0091	0.0028	0.0036	0.0124
Nitric acid	0.0032	0.0075	0.0179	0.0037	0.0042	0.0147
Sulfuric acid	0.0032	0.0091	0.0154	0.0043	0.0051	0.0158

Unit: min^{-1}.

increase with the concentration of acetic acid and the extraction time. Veeken and Hamelers[21] observed the same phenomena in the extraction of heavy metals from sewage sludge by citric acid.

Three Replicate Extractions

Figure 11 summarizes the results of three replicate extractions of Cu and Ni using 1 N acetic acid, nitric acid, and sulfuric acid for 1 h. The total percentages of Cu extracted by 1 N acetic acid, nitric acid, and sulfuric acid during three replicate extractions were 78, 94, and 94%, and those of Ni were 89, 94, and 98%, respectively. The removal percentage of the first extraction exceeded that of second and third extractions. The percentages of Ni extracted by acetic acid, nitric acid, and sulfuric acid in the third extractions were all zero, but those of Cu were 2, 1, and 4%. Comparing the total percentage of Cu extracted in three replicate extractions and the percentages of Cu extracted in the third extraction with those of Ni reveals that Ni is more easily extracted than Cu from PCB sludge by acids. This result was consistent with the extraction rate constants in the preceding section, which implied that Cu formed a stronger binding than Ni in PCB sludge.

The residual sludge following three replicate extractions by 1 N acetic acid, nitric acid, and sulfuric acid was further tested by TCLP to determine whether the extracted sludge remained hazardous waste. The concentrations of leached Cu all exceeded that allowed by Taiwanese law (15 mg/L). This outcome reveals that the residue sludge, even after three replicate extractions by acid, remained hazardous. Further treatment, such as by solidification, is required before the sludge can be disposed of.

Although the residue sludge after the extractions remains hazardous, the utilization of acid extraction effectively removes heavy metals and reduces environmental pollution by heavy metals contained in PCB sludge.

CONCLUSION

This investigation demonstrates that PCB plant sludge contains a high concentration of Cu (157.07 mg/g) and Ni (1.45 mg/g), which should be separated

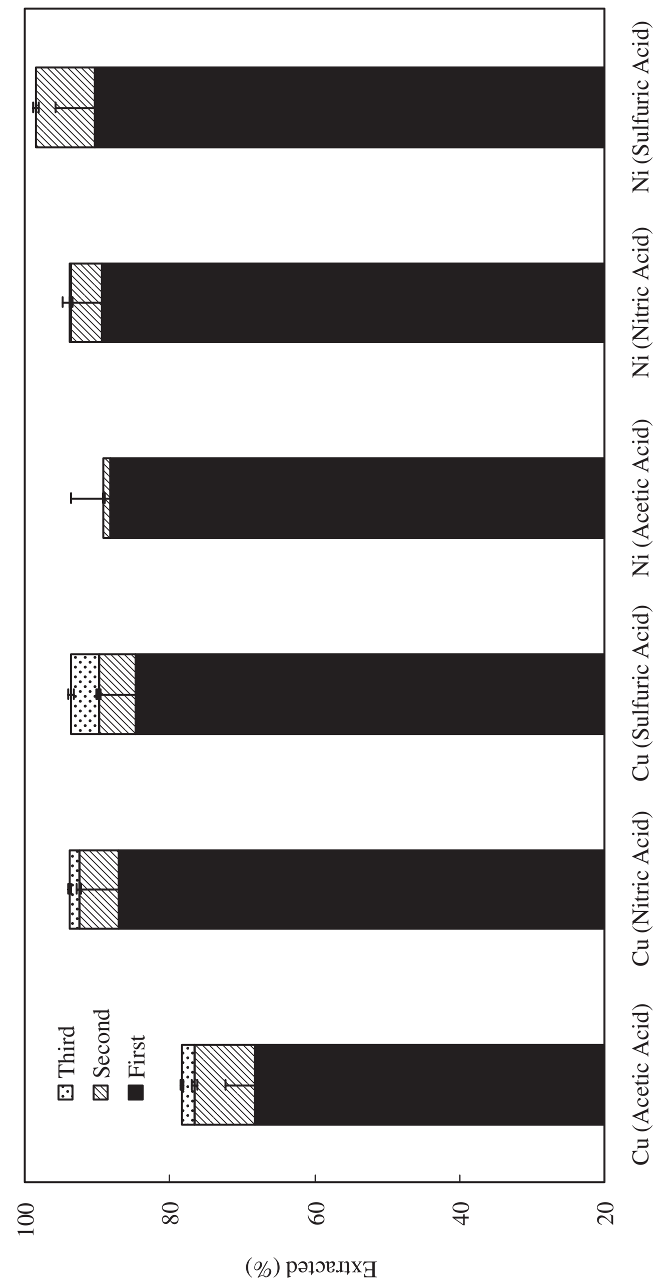

Figure 11. Proportion of Cu and Ni extracted in three replicate extractions using 1 N acetic acid, nitric acid, and sulfuric acid.

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and reused. The order of the effectiveness of extraction by different acidic extractants was sulfuric acid ⩾ nitric acid > hydrochloric acid > acetic acid > citric acid. The strong inorganic acids (sulfuric, nitric, and hydrochloric) react with metals in the sludge by proton exchange and the dissolution of heavy metal hydroxides. The extraction is almost wholly attributable to the action of the protons. From 55 to 95% Cu and Ni was extracted using 1 N nitric acid and sulfuric acid from 5 to 180 min and about 15–85% Cu and Ni was extracted using 1 N acetic acid from 5 to 180 min. Nitric acid and sulfuric acid extracted Cu and Ni from sludge much more rapidly than acetic acid. The kinetic results also indicated that the extraction rate constants of Cu and Ni increased with the acid concentrations and Cu formed a stronger binding than Ni in the PCB sludge. The extraction percentages of Cu and Ni by 1 N acetic acid, nitric acid, and sulfuric acid after three replicate extractions indicated that the removal percentage during the first extraction exceeded that in the second and third extractions, and that the residue sludge following three replicate extractions by acids remained hazardous. Although the residue of the extracted sludge requires further treatment before it is disposed of, this study provided a feasible acidic extraction procedure for eliminating and removing heavy metals from industrial sludge.

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