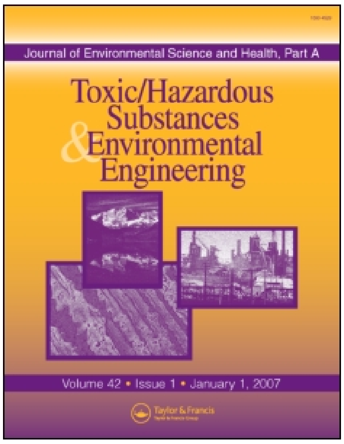

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In this study various leaching technologies were applied to extract heavy metals from sludge from the printed circuit board process. These methods included traditional acid extraction (TAE) and microwave assisted treatment (MAT). The target heavy metal was copper. Experiments were performed to determine the acid the leaching efficiency by changing operating conditions, including acid type and concentration, leaching time, microwave power, and solid to liquid ratio (S/L). The TAE method demonstrated that copper leaching from a sludge of fine particle sizes ($d < 150\ \mu m$) was 74% efficient at an S/L of 1/6, a leaching time of 18 hr, using nitric acid in the leaching solution. Then, when the microwave powers were 800 W and 400 W; the leaching time was 30 mins, and the coarse particle size ($d < 9.5$ mm) was by 1 N sulfuric acid, the copper leaching effects were 93% and 77%, respectively. The MAT procedure reduced the leaching time and improved the leaching efficiency above that obtained by TAE.

Key Words: Copper; Sludge; Traditional acid extraction (TAE); Microwave-assisted treatment (MAT).

INTRODUCTION

Industrial sludge that contains heavy metals is classified as hazardous waste. It is expensive to handle and no satisfactory means of finally disposing of sludge

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with high heavy metal content is available. Accordingly, the cost of disposing of sludge that contains toxic metals has been exponentially increasing, and the number of landfills that can receive such sludge in Taiwan has been falling. Heavy metals must therefore be leached from industrial sludge before composting to increase the sustainability of sludge treatment.

Various TAE methods that involve acids and solvents have been developed to recover metals. Acid extraction is a very effective means of leaching the metal contents of sludge because a low pH destabilizes numerous inorganic constituents. The effectiveness of the acids followed the order nitric acid > hydrochloric acid > sulfuric acid. Sukla et al.[1] leached over 80% Cu and 80% Co from slag using sulfuric acid. Sulfuric acid has been adopted to leach Ni and Co from nickel smelter slag[2] and copper smelter flue dust has been leached in sulfuric acid and metal was recovered following purification.[3,4] Wu et al.[5] compared the efficiencies of three extractants in removing heavy metals from sewage sludge. They found that directly adding concentrated sulfuric acid was more efficient and cheaper than using EDTA and NH_4HCO_3. Banza et al.[6] demonstrated that sulfuric acid under hydrogen peroxide at 70° could effectively leach base metals from a copper smelter. Arslan and Arslan[7] leached Cu, Co, and Zn from a copper smelter and leached 88% Cu, 87% Co, and 93% Zn by roasting with sulfuric acid.

Various TAEs can be modified using heat, but energy is transferred to the material through convection, conduction, and radiation from the surfaces of the material in a conventional thermal process. In contrast, microwave energy is delivered directly to materials via a molecular interaction with an electromagnetic field. This difference in the way energy is delivered offers various potential advantages.[8] Moreover, microwave heating offers various potential advantages in treating wastes. The important characteristics are, (i) significant considerable reduction in the volume of wastes; (ii) rapid heating; (iii) high temperature capacities, and (iv) treatment or immobilization of hazardous components to meet regulatory equirements for storage, transportation, or disposal.[9]

Industrial processes that form wet solid sludge that contains organic or inorganic toxic compounds are becoming increasingly restricted and costs associated with disposal are increasing. Most of such industrial sludge is currently disposed of at specialist waste landfills, which are not only expensive, but carry a risk of future environmental liability. Microwave treatment of hazardous industrial sludge and infectious wastes is attracting increasing interest.[10,11] Gan[11] revealed that during the initial drying process, the most microwave energy was) absorbed by water molecules, which have a high dielectric loss factor. The microwave-assisted mitigation and binding of free metal ions with polymeric molecules in the sedimentary solids may not be effective until the sediment solids are dry, but the exact sequence of the absorption of electromagnetic energy by the different molecular species in the wet sedimentary solids is not clear. However, microwave-induced pyrolysis may occur if the raw material is mixed with an effective receptor of microwave energy, such as carbon or certain metal oxides.[12–14]

Several 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, and other leachants. However, little information is available on the leachability of heavy metals in industrial sludge by microwave-assisted treatment. This work describes the feasibility of removing Cu from sludge from industrial plants using TAE and MAT methods. Various leaching times were also studied to determine the removal rate constant of Cu, and the most economic treatment time.

MATERIALS AND METHODS

Characteristics of Sludge

Industrial sludge was obtained from a PCB plant in Tao-Yuan County, Taiwan. The content of heavy metals in the industrial sludge was determined after it had been digested in aqua regia, which is 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 to identify Cu, Ni, Pb, and Zn by inductively coupled plasma (ICP) spectrometry. Additionally, 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.

Leaching of Copper by TAE and MAT

The sludge was oven-dried at 105°C until it reached a constant mass. It was then crushed until it could pass through a 9.5 mm or 150 μm screen. The kinetics of the leaching of the industrial sludge was determined using reaction times for TAE and MAT. A leached sample of the sludge was tested by TCLP to measure the leaching of heavy metals following treatment, when all of the suspensions were centrifuged; the supernatants were filtered through a 0.45 μm membrane filter and the concentrations of heavy metals were determined by inductively coupled plasma (ICP) spectrometry.

In MAT, the input power of the microwave equipment was set to 400~800 W and the microwave frequency used was 2450 MHz, corresponding to a wavelength of 12.2 cm and an energy of 1.02×10^{-5} eV. The temperature of the sample during microwave treatment was measured using an infrared optical pyrometer.

For comparison, two samples of the wet sewage sludge were treated in a conventional electric furnace. The pH value and the heavy metal content were measured in three replicate tests. The results of the proximate and ultimate analysis were presented as dry wt%.

RESULTS AND DISCUSSION

Characteristics of Raw Sludge

The pH of the industrial sludge was 9.0 ± 0.5 and the moisture content was $62.7 \pm 2.0\%$. The metal sludge was analyzed using ICP and the total proportions of metals Cu, Ni, Pb, and Zn in the dry-mass sludge were 106.3, 0.7, 2.3, and 1.8 mg/g, respectively. A high copper concentration rendered the industrial sludge hazardous. Given that copper was the heavy metal present in the greatest amount in the sludge, copper was the target metal to be removed. The efficiency of removal depended on the partitions of the heavy metal and the pH of the sludge.

Leaching Efficiency of TAE

Figure 1 plots the kinetics of extraction using 1N sulfuric and nitric acids using the TAE method. The results were presented as the amount of copper extracted as a percentage of the original amount present. Approximately 1N acid was required to extract large amounts of copper, and the extraction efficiencies of nitric acid and sulfuric acid were 81% and 76% at an extraction time of 48 h, respectively. At low pH, heavy metals adsorbed onto the solid phase are exchanged with high concentrations of protons; heavy metal hydroxides are dissolved, and the metals are accordingly removed. Numerous studies[15–17] have shown that higher concentrations of acid leaching correspond to the presence of more heavy metal in the slag and the sludge.

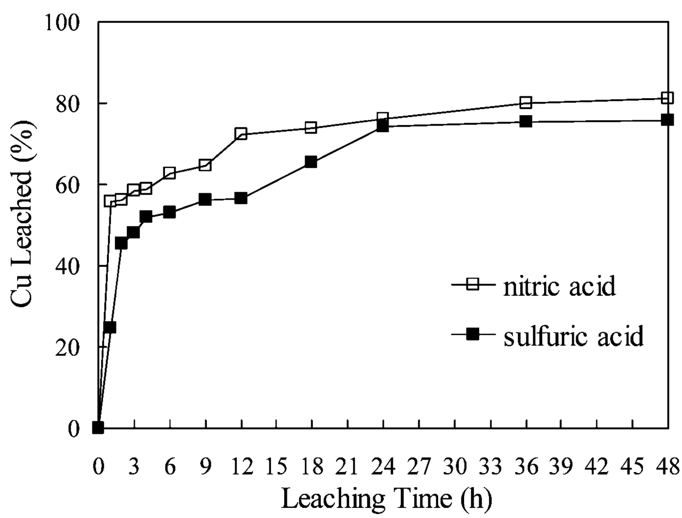


Figure 1: Cu leaching efficiency as a function of leaching time (acid conc.: 1N, sludge size: <150 μm, S/L: 1/6, 25°C).

The extraction of Cu by the TAE method exhibited a lag after 12 h. For a given extraction time, 12 h, the proportions of copper extracted using nitric acid and sulfuric acid were 72% and 56%, respectively. After 48 h, the corresponding values were 81% and 76%. The extraction rate constants k of Cu using the TAE method were determined by first-order kinetics, and the k values of nitric and sulfuric acid were 0.0179 and 0.0178 h^{-1}, respectively. A comparison of the k values associated with the use of sulfuric and nitric acids in TAE revealed that the k associated with nitric acid was similar to, but a little higher than, that associated with sulfuric acid. However, the experimental data demonstrate that copper can be leached from fine sludge particles ($d < 150\ \mu m$) using nitric acid and sulfuric acid after 48 h. The leaching copper of copper was weaker, indicating that the S/L ratio and acid concentration dominated TAE; the extraction rate increased as the S/L ratio fell. Li et al.[18] established that the extracted Ca concentrations at S/L ratios of 1/8 and 1/16 were 35.4 and 62.9 mg/g, respectively.

Leaching Efficiency of MAT

Based on the results of TAE, 1N sulfuric and nitric acid were employed in MAT tests. Figure 2 presents the extent of MAT nitric acid and sulfuric acid extraction at various microwave powers—400, 600, and 800 W—and two S/L ratios—1/6 and 1/20. The copper extraction efficiency increased rapidly over the first 5 min, reaching equilibrium about 10 to 20 minutes. After the first) 5 min, the proportions of copper extracted from the coarse sludge particles at 800 W-1/6 and 800 W-1/20, using 1N nitric acid, were 63% and 78%; at 30 min, the extraction rates were 93% and 96% (Table 1). Therefore, in Table 1, a lower S/L ratio corresponded to more efficient copper extraction at the first leaching time; however, the effect of the S/L ratio was insignificant at a leaching time of 30 min. Moreover, after the first 5 min, and an S/L ratio of 1/6, the percentages of copper extracted from the coarse sludge particles at 800, 600,

Table 1: Comparisons with size of sludge and microwave power of leaching copper during difference leaching time.

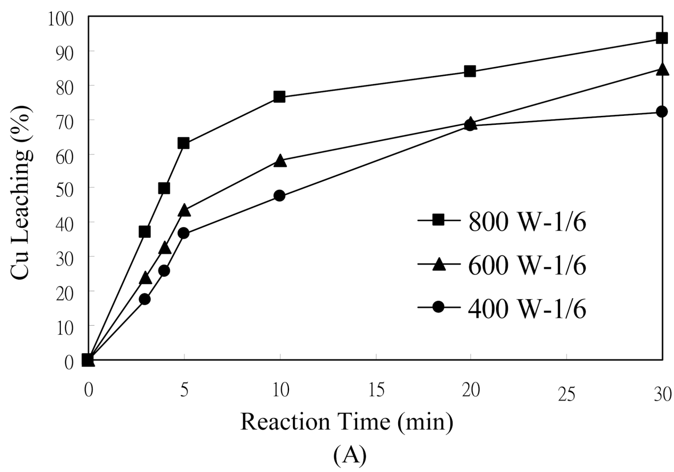
Microwave power	Leaching time (min)	Copper leaching (%) $d < 9.5$ mm	Copper leaching (%) $D < 150\ \mu m$
800 W	5	78	85
	10	81	93
	30	96	96
600 W	5	59	65
	10	73	74
	30	85	90
400 W	5	43	48
	10	57	63
	30	79	85

Leachant: nitric acid 1 N; S/L (solid to liquid ratio): 1/20.

Table 2: Comparisons with size of sludge and leachant of leaching copper during difference leaching time.

Leachant	Leaching time (min)	Copper leaching (%) at S/L: 1/20		Copper leaching (%) at S/L: 1/6	
		d < 9.5 mm	d < 150 μm	d < 9.5 mm	d < 150 μm
Nitric acid	5	78	85	63	74
	30	96	96	93	96
Sulfuric acid	5	73	74	92	48
	30	95	94	92	93

Microwave power: 800 W; S/L: solid to liquid ratio.



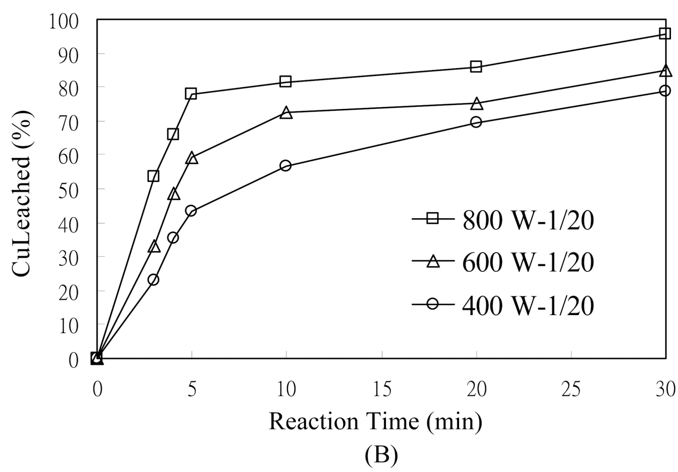
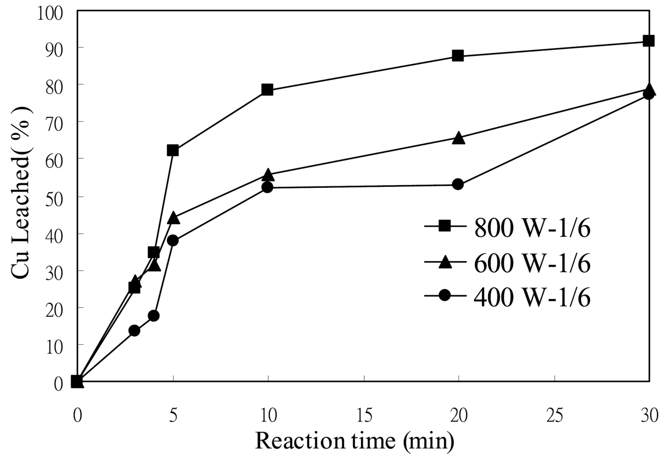
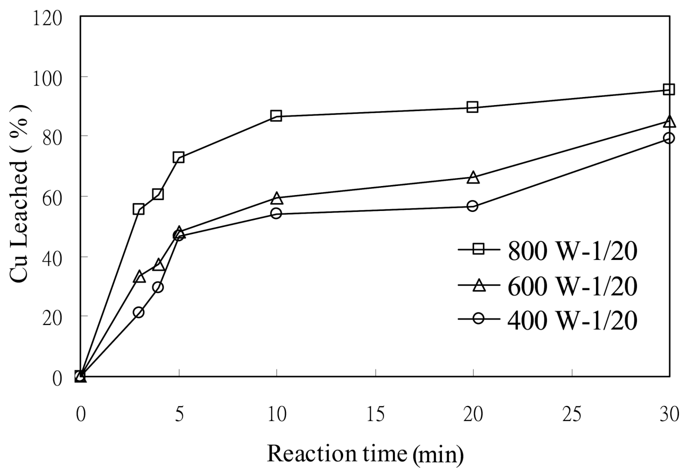


Figure 2: Coarse sludge of Cu leaching efficiency with reaction time using a acid/microwave (A) S/L: 1/6, nitric acid; (B) S/L: 1/20, nitric acid; (C) S/L: 1/6, sulfuric acid; (D) S/L: 1/20, sulfuric acid (leachant: 1N, sludge size: <9.5 mm, 160°C). *(Continued)*



(C)



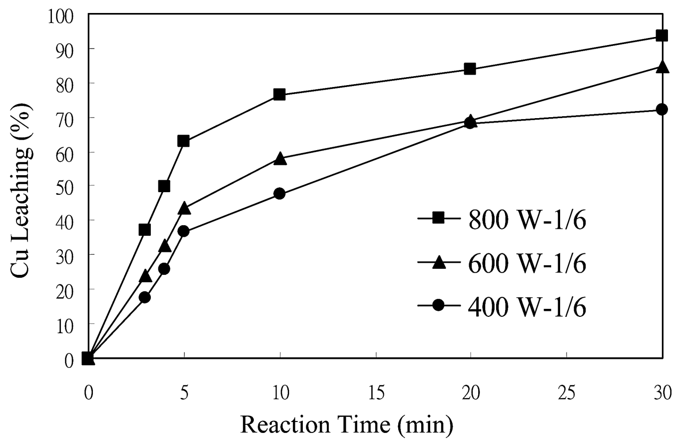
(D)

Figure 2: (Continued)

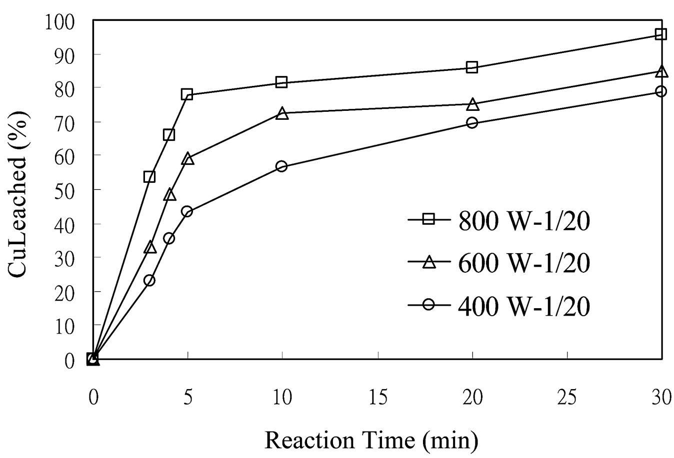
and 400 W using 1 N nitric acid were 63%, 44%, and 37%, respectively. At 30 min, the corresponding values were 93%, 85%, and 72%. These data revealed that a higher microwave power corresponded to more efficient copper leaching.

The experimental results in Figure 3, concerning fine sludge particles (d $< 150\ \mu$m) also indicated that a higher microwave power and lower S/L ratio corresponded to more efficient copper extraction. Furthermore, a comparison of Figures 2 and 3 and Table 2 reveal that the effect of the size of the sludge particles was insignificant. The Experimental results (Fig. 3) also demonstrated that the S/L ratio was the most important factor in removing copper from industrial sludge using MAT.

Figures 2(C) and (D) and 3(C) and (D) display MAT with sulfuric acid at various microwave powers, sludge particle sizes and S/L ratios. Table 2 presented similar results for sulfuric and nitric acids in MAT. In both cases, a higher microwave power and a lower S/L ratio corresponded to more efficient extraction of copper (Figs. 2 and 3). Xia and Pickles[19] found that the effect of the power level was significant. The dissolution rates increased with the microwave power and as the S/L ratio declined as determined in microwave leaching tests.[19] Standish et al.[20] reported that the particle size was an important, but not always consistent, factor in the heating of granular material. They noted that, during the microwave heating of granular alumina and magnetite, fine Al_2O_3

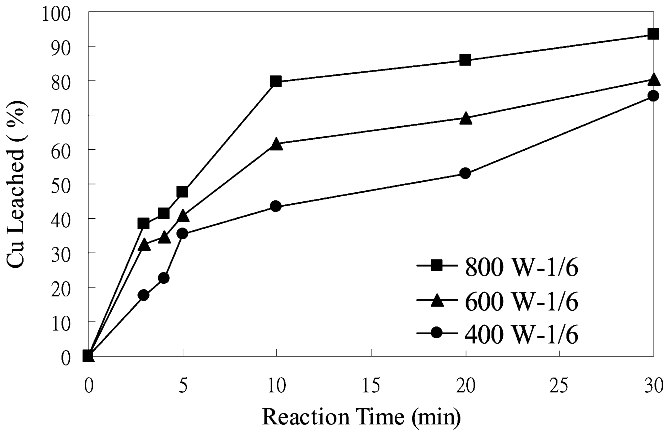


(A)



(B)

Figure 3: Fine sludge of Cu leaching efficiency with reaction time using a acid/microwave (A) S/L: 1/6, nitric acid; (B) S/L: 1/20, nitric acid; (C) S/L: 1/6, sulfuric acid; (D) S/L: 1/20, sulfuric acid (leachant: 1N, sludge size: <150 μm, 160°C) *(Continued)*.



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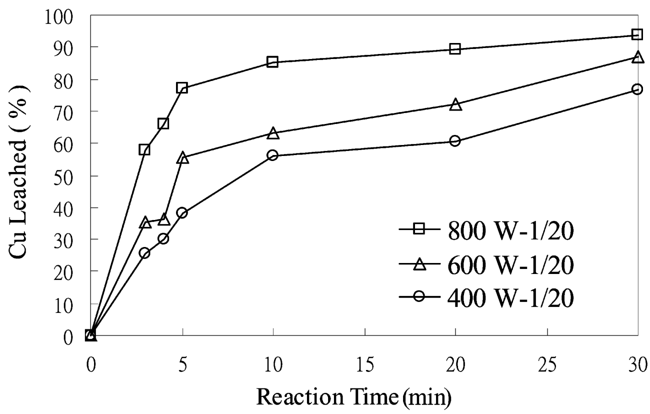

(D)

Figure 3: (Continued)

became hotter more rapidly than coarse Al_2O_3, whereas coarse $Fe3O_4$ became hotter more rapidly than fine $Fe3O_4$.

Comparison of TAE and MAT

At an S/L ratio of 1/6, 85% and 79% of copper was leached after 10 min of MAT-800W using nitric and sulfuric acid, respectively; however, 81% and 79% of copper was leached after 48 h of TAE using nitric and sulfuric acid, respectively (Table 3). The microwave energy reduced the leaching time and the effect in the fine sludge was more significant. Weian[21] also stated that microwave-assisted leaching promoted the dissolution of copper, which result was consistent with the results shown herein. MAT is more expensive than TAE; however, the efficiency of the removal of copper by MAT was 200 times greater (48 h: 10 min) than that of TAE.

Table 3: Comparisons with TAE and MAT of leaching efficiency.

	TAE		MAT (800 W)	
Leachant	**Leaching time (h)**	**Copper leaching (%)**	**Leaching time (min)**	**Copper leaching (%)**
Nitric Acid	48	81	10	85
Sulfuric Acid		76		79

TAE, Traditional acid extraction; MAT, Microwave-assisted treatment; d < 150 μm; S/L (solid to liquid ratio): 1/6.

Figures 2 and 3 plot the leaching efficiency and associated leaching times. The leaching efficiency began at zero during the period of heating, increasing abruptly to a maximum value. The rate of copper leaching reached a maximum during the first 5 min of the reaction; a higher microwave power and a lower S/L ratio corresponded to a higher rate. Above experimental findings reveal that the most important factors in MAT were the microwave power input followed by the S/L ratio. However, the size of the sludge particles did not markedly influence the extraction of copper.

In Table 4, extraction rate constants *k* of Cu using MAT and TAE methods were determined by first-order kinetics, and the k values of nitric and sulfuric acid were 1.79×10^{-2} and 1.7810^{-2} h^{-1}, respectively. Comparing the k values associated with MAT and TAE indicated that the k associated with nitric acid was similar to that associated with sulfuric acid. However, the k value associated with nitric acid slightly exceeded that associated with sulfuric acid in TAE; the values obtained using the MAT method were 2.40~4.57 h^{-1}. Additionally, the results revealed that the *k* values increased with the microwave power; those associated with MAT almost doubled as the microwave power was increased from 400 W to 800 W, and increased by a factor of 1.5 as the microwave power was increased from 400 W to 600 W. The *k* values associated with the MAT (800 W-1/6) and the TAE (1/6) are nearly 257 times higher, and 135 times higher, respectively, than those associated with MAT (400 W-1/6) and

Table 4: Comparisons with TAE and MAT using first-order reaction kinetics data.

	k (h^{-1})	R^2
TAE (nitric acid; S/L: 1/6)	1.79×10^{-2}	0.90
TAE (sulfuric acid; S/L: 1/6)	1.78×10^{-2}	0.87
MAT (800 W; S/L: 1/6)	4.57	0.96
MAT (800 W; S/L: 1/20)	4.36	0.90
MAT (600 W; S/L: 1/6)	3.24	0.97
MAT(600 W; S/L: 1/20)	2.80	0.87
MAT (400 W; S/L: 1/6)	2.40	0.94
MAT (400 W; S/L: 1/20)	2.68	0.96

TAE, Traditional acid extraction; MAT, Microwave assisted treatment; TAE: d < 150 μm; MAT: nitric acid; d < 9.5 mm; S/L: solid to liquid ratio.

TAE (1/6). MAT leached copper from industrial sludge more rapidly than did TAE.

CONCLUSION

This study compared TAE and MAT leaching procedures to extract Cu metals from sludge. At low pH, heavy metals adsorbed onto the solid phase are exchanged with high concentrations of protons. Heavy metal hydroxides are dissolved and the metals are thus removed from the industrial sludge. The efficiency of copper leaching from a sludge of fine particles ($d < 150\ \mu m$) using the TAE method was 74% at an S/L of 1/6, after a leaching time of 48 h. At microwave powers of 800 W and 400 W, the leaching time was 30 mins. When coarse particles ($d < 9.5$ mm) were treated with 1N nitric acid, the corresponding copper leaching rates were 96% and 79%. The respective values of fine particles ($d < 150\ \mu m$) were 96% and 85%.

In MAT, the copper extraction efficiency rose abruptly during the first 5 min to around 70%, reaching an equilibrium of around 95% after 10 to 30 min. Experimental results verified that the most important factors in MAT were the microwave power input followed by the S/L ratio. However, the size of the sludge particles did not significantly affect the leaching rate. A comparison between the k values associated with MAT and those associated with TAE almost.The leaching time associated with the MAT procedure was shorter than that associated with TAE, and the leaching efficiency was greater.

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