



A study on heavy metal extractability and subsequent recovery by electrolysis for a municipal incinerator fly ash

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Abstract

The extractability of heavy metals (Pb, Cd, Cr and Cu) from a municipal incinerator fly ash (designated MIFA S) using an acidic or basic extractant and their subsequent recovery by electrowinning using an electrolytic cell of the fluidized-bed type was investigated. The extractants studied were HCl, HNO₃, H₂SO₄, HOAc, NaOAc (pH = 8.15), and NaOAc (pH = 3) having 0.1 N in concentration. Of which, NaOAc (pH = 3) outperformed the others and was selected for further studies. A 2⁴⁻¹ fractional factorial experimental design was adopted using liquid-to-solid (L/S) ratio, extractant concentration, extraction time, and initial pH as the experimental factors. The results show that L/S and extraction time played an important role in Pb extraction while L/S ratio and extractant concentration were important for Cr extraction. However, no controlling parameter was determined for Cd extraction, but a lower extraction efficiency was obtained if an initial pH of greater than 5 was used. For the study of electrolytic recovery, the experiments were carried out based on a 2³⁻¹ fractional factorial design using current density, initial pH, and operating temperature as the experimental factors. It was determined that current density was important to electrolytic recovery of Pb and Cu, but with an opposite effect. The other two experimental factors were insignificant, 96.70% of Pb and 93.69% of Cu were recovered from the leachate of MIFA S when 0.4 A-h of electrical charge was applied. The results obtained suggest that the recovery of heavy metals from MIFA S by solvent extraction and electrolytic recovery is technically feasible. © 1998 Elsevier Science B.V.

Keywords: Municipal incinerator fly ash; Heavy metal; Extraction; Recovery; Electrolysis; Fractional factorial design; Effect analysis

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1. Introduction

It is widely accepted that municipal incinerator fly ash (MIFA) is hazardous due to its high leaching toxicity of heavy metals and high toxic equivalents of dioxin-like compounds [1–16]. In Taiwan, it was reported that some 8400 thousand metric tons of municipal solid waste (MSW) was generated in 1995 [17]. Of which, 79.24% was landfilled and 14.98% was incinerated. Currently, R.O.C. Environmental Protection Administration (EPA) has faced the problems that a majority of landfills will come to their ends of lives within a year or two and new landfill sites are difficult to obtain. Therefore, R.O.C. EPA has planned to construct 22 large-scale MSW incineration plants by the end of year 2000. (Presently, five MSW incineration plants are in continuous operation.) It was estimated that at least 1700 metric tons day⁻¹ of municipal incinerator ashes will be generated in the future [1]. Fifteen to twenty percent out of these ashes will be the MIFA fraction, which is potentially hazardous. A proper treatment and/or disposal of MIFA is needed.

Six treatment options has been identified by Wiles [16] for the treatment of municipal incinerator residues. Of which, solidification/stabilization, and vitrification of MIFA have been practiced on a commercial scale while chemical extraction was only investigated in the laboratory. In a study by Gong and Kirk [7], the leachability of various metals from MIFA was compared for different solvents, including H₂O, NaOH, HCl, H₂SO₄, HClO₄, HNO₃, and HAc. HCl was found to be the most effective in this regard. The experiments with HCl concentrations from 0 to 6 M showed that HCl concentration did not affect the leachability of most elements above 0.5 M HCl. For lead and copper, however, leachability increases up to 1 M HCl. Results of extraction studies of MIFA conducted by Kosson et al. [18] and by Legiec et al. [19] have indicated that acidified sodium chloride and sodium acetate solutions at pH 3 had the highest lead extraction capabilities. In the same investigations, results of kinetic studies and electrochemical recovery of lead were also briefly reported.

Traditionally, treatment technologies for heavy metals-containing solutions have three categories: (1) chemical methods (e.g. chemical precipitation), (2) physical methods (e.g. concentration by vaporization), and (3) electrochemical methods (e.g. electrodeposition) [20]. Generally, electrochemical reactions are the reduction/oxidation reactions occur at the interface of electrodes and the electrolyte. The driving force of the redox reactions comes from the potential difference between two electrodes. The molar changes of reactants and products follow the Faraday's law [21]. During the electrolysis, chemical reductions occur at the cathode while chemical oxidations occur at the anode. Thus, gases of hydrogen and oxygen are generated at the cathode and anode, respectively. In addition, metal is deposited on the cathode as well. The most commonly encountered problem in electrolysis is the removal or recovery of metals from a solution of low concentration. The following two options can be employed to solve this problem: (1) by increasing the specific surface areas of the electrodes and (2) by increasing the mass transport in the electrolytic cell [22]. In so doing, an increase of the limiting current will thus increase the efficiency and the rate of electrolysis.

Mechanisms of metal deposition on the cathode during the electrolysis can be found elsewhere [23]. However, the operating parameters that affect the electrolytic recovery

of metals will be briefly introduced here. They are: (1) current density, (2) temperature, (3) mixing, (4) pH, and (5) electrode spacing [20]. For a solution of low concentration, the rate of metal deposition increases with a high current density. Nevertheless, this practice generally will result in a lower current efficiency, a higher energy consumption, and a lower adhesion of the recovered metal. Particularly, when it is operated at a current density greater than the limiting current, powdered metal(s) of low adhesion will be obtained. Conversely, operated at a low current density will result in a better current efficiency, a lower energy consumption, and a denser recovered metal. But it needs a longer operating time to do the job. It is well known that an increase of the operating temperature will decrease the viscosity of solution, thereby resulting in an enhance of diffusion and migration of metal ions from the bulk solution to the cathode. This will also be accompanied by an increase of the limiting current density and a decrease of energy consumption during the electrolysis. Generally, the employment of mixing during the electrolysis will decrease the thickness of the diffuse layer, thereby increasing the coefficient of mass transport and the limiting current density. For pH, it will affect the properties of the electrolyte such as the solubility of metal salts, complexation of metal ions, etc. By decreasing the electrode spacing, it will increase the mixing efficiency and decrease the energy consumption. But a short circuit must be avoided by not contacting the anode and the cathode as a result of the metal deposition.

The design of an electrolytic cell also plays an important role in the metal recovery process. The plate-in-tank cell, plate cell, rotating cylinder electrode cell, and Chemelec Cell have been used for this purpose [22,24]. By using the Chemelec Cell, porous electrodes and a current density of 3 mA/cm², Tyson [25] was able to recover 99% of cadmium from an electroplating rinsewater having a cadmium concentration of 200 mg/l. For an extract (containing copper of 1000 mg/l and cadmium of 100 mg/l) from a hydrometallurgical process, Boyanov et al. [26] was able to decrease the concentrations of copper and cadmium to 1–5 mg/l by using the Chemelec Cell, porous electrodes, a current density of 60 A/m², and an operating time of 8 h. In addition, using a fluidized-bed electrolytic cell with a nonconductive bed medium offers the following advantages: (1) increasing mass transport rate, (2) better environment for nucleation and crystal growth of metal. Therefore, it is suitable for metal recovery from solutions [24–30] and quality improvement of electrodeposited metals [31,32].

The objectives of this work were to study the extraction characteristics of heavy metals in a MIFA specimen by various solvents and to determine the feasibility of recovering heavy metals in the extracts by using a fluidized-bed electrolytic cell.

2. Experimental

2.1. Materials

This study is based on a MIFA specimen obtained from a modern waste-to-energy (WTE) plant in northern Taiwan. This WTE plant has two incinerators of 450 m t/day each in capacity and it employs cyclones, spray dry scrubber, and fabric filters as air

pollution control devices. The MIFA specimen studied (designated MIFA S in this work) are the larger size fraction of particulates collected by cyclones. Therefore, its appearance and characteristics are very different from the 'reaction products', which consists of primarily calcium chloride, unreacted lime and diatomaceous earth. HCl, HNO₃, H₂SO₄, HOAc, NaOAc (pH = 8.15), and NaOAc (pH = 3) were selected as the extractants in this work based on the results of previous studies [7,18,19]. Nitrates of lead, copper, cadmium, zinc, and chromium were used for preparing the stock solutions of various electrolytes. All chemicals used are reagent grade. Water used is ASTM Type I deionized water.

For the analysis of cyclic voltammetry, platinum sheets (used as the counter electrode and working electrode) were made in Taiwan with a purity of 99.99%.

During the electrolytic recovery of metal, metal sheets (5 cm × 5 cm; 99.95% in purity) of the same material were used as the cathode (i.e. working electrode). Copper sheets were obtained from Nilaco in Japan. Sheets of lead and zinc were obtained from Goodfellow, England. Cadmium sheets were obtained from Johnson Matthey, USA. Sheets of stainless steel (No. 316), used as the anode, was manufactured in Taiwan. Nonconductive glass beads of 2 mm and 0.5 mm in diameter (made in Taiwan) were used as the fluid distributor and bed medium, respectively in the electrolytic cell of the fluidized-bed type.

2.2. Experimental design

The fractional factorial design introduced by Box et al. [33] was employed in this work. For this design approach, the interactions among the experimental factors and some confounding relations are taken into account by using the proper defining relations. In so doing, experimental results obtained from the fractional factorial design will be in good agreement with those obtained by the full factorial design. It is worth pointing out that only a few experiments have to be carried out for the former while a good number of experiments have to be conducted for the latter. Usually, the effect analysis is conducted for the results obtained from the fractional factorial design to determine which factor has the main effect. This can be further presented by using the normal probability plot and the normal probability plot of residuals developed by Daniel [34].

In this work, 2⁴⁻¹ fractional factorial design was used for the extractability study while 2³⁻¹ fractional factorial design was used for the electrowinning study. The experimental factors selected for the former study are liquid-to-solid (L/S) ratio, extractant concentration, extraction time, and initial pH. On the other hand, the experimental factors selected for the latter study are current density, initial pH, and operating temperature. Details of the fractional factorial designs are shown in Tables 1 and 2.

2.3. Apparatus

In this work, the cyclic voltammetry of the leachate of MIFA S specimen was carried out using a potentiostat manufactured by EG&G, USA, Model 253. The experimental

Table 1

The experimental factors used in 2^{4-1} fractional factorial design for the extractability study of heavy metals from a municipal incinerator fly ash (MIFA S)

Experimental factor	Symbol	Level		
		–	+	
Liquid-to-solid ratio	<i>A</i>	20	40	
Extractant concentration (M)	<i>B</i>	0.25	0.50	
Extraction time (min)	<i>C</i>	60	90	
Initial pH	<i>D</i>	1	3	
Experimental run no.	Experimental factor			
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
1	–	–	–	–
2	+	–	–	+
3	–	+	–	+
4	+	+	–	–
5	–	–	+	+
6	+	–	+	–
7	–	+	+	–
8	+	+	+	+

Note: the defining relations are $D = ABC$ and $I = ABCD$.

set up consists of a power supply, a potentiostat, an analysis micro-cell, a working electrode (Pt), a counter electrode (Pt), and a reference electrode (Ag/AgCl).

The schematic diagram of the experimental set up including the electrolytic cell is shown in Fig. 1. Based on the design of the experimental equipment used by Lopez-Cacicedo [24] and Lin [20], an electrolytic cell of the fluidized-bed type was constructed in our laboratory. The electrolytic cell was made of acrylic resin. The bed medium was

Table 2

The experimental factors used in 2^{3-1} fractional factorial design for the electrolytic recovery of heavy metals from the leachate of a municipal incinerator fly ash (MIFA S)

Experimental factor	Symbol	Level	
		–	+
Current density (mA/cm ²)	<i>E</i>	0.25	0.50
Initial pH	<i>F</i>	2	4
Operating temp. (°C)	<i>G</i>	27	40
Experimental run no.	Experimental factor		
	<i>E</i>	<i>F</i>	<i>G</i>
1	–	–	+
2	–	+	–
3	+	–	–
4	+	+	+

Note: the defining relations are $G = EF$ and $I = EFG$.

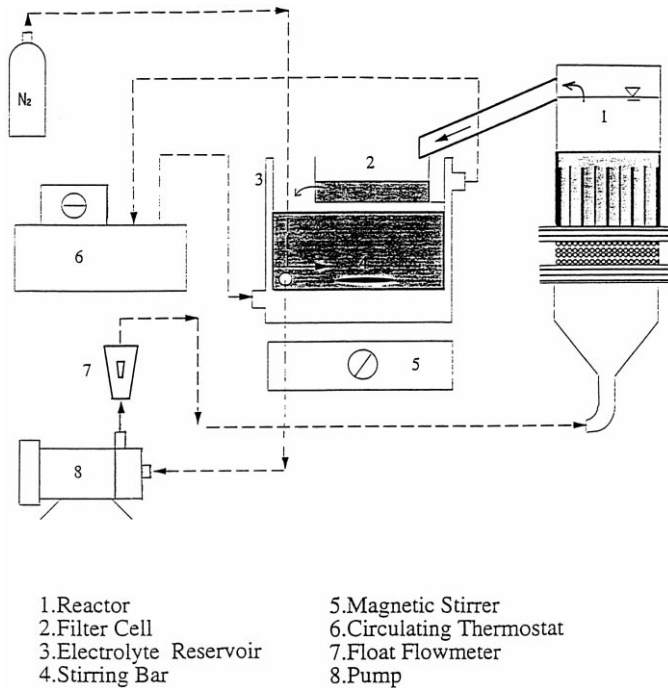


Fig. 1. The schematic diagram of the electrolytic cell (reactor) and the related experimental setup.

nonconductive glass beads of 0.5 mm in diameter. In the electrolytic cell, five sheets of stainless steel and four sheets of the metal of interest were installed alternately as electrode pairs with an electrode spacing of 0.6 cm. One side of the working electrode was coated with resin to avoid this side of electrode material in contact with the electrolyte. In each test, the counter electrode used the same material as the working electrode in order to maintain the concentration of metal ions in the electrolyte. (Here, the electrolyte was the leachate of MIFA S specimen.) Ag/AgCl electrode was the reference electrode used throughout this study. In this investigation, a batch circulating system was employed (see Fig. 1). The electrolyte was introduced into the electrolytic cell from the bottom by a pump. Its flowrate was controlled by a float flowmeter. After passing through the cell, the electrolyte entered the electrolyte reservoir. The electrolyte reservoir has double walls. The electrolyte in the reservoir was constantly agitated by a magnetic stirrer and purged with nitrogen gas 30 min before and during the experiment. Water in between the two walls was circulated to and back from a water bath in which a constant temperature of water was adjusted and controlled.

2.4. Methods

MIFA S specimen was first characterized using various standard methods adopted by Republic of China and United States [35,36]. The determined properties included the moisture content, pH and total contents and TCLP leaching toxicity of heavy metals. In

addition, the particle size distribution was determined by a Coulter LS100 Particle Size Analyzer; and loss on ignition, by ASTM C 311-90 [37].

The extracts (or 'the leachates'; these two terms were used interchangeably in this text) obtained from the extractability study were acid-digested and analyzed for the concentrations of various metals by flame absorption spectroscopy. Then the extraction efficiency for each metal was calculated.

For the analysis of cyclic voltammetry, the metal-containing solution was the leachate of MIFA S specimen obtained from the optimal extraction condition determined by the extractability study. In this test, 15 ml of the leachate of MIFA S specimen was placed in the analysis micro-cell, then purged with nitrogen gas 10 min before and during the test. The cyclic voltammetry was conducted at a sweep rate of 50 mV/s. The sweep range was set between -1200 mV to 500 mV. The sweep pattern was expressed as electric current vs. electric potential.

For the electrolytic recovery of metals, each batch 2.2 l of the leachate of MIFA S specimen was placed in the electrolyte reservoir. The flowrate of the electrolyte pumped into the electrolytic cell was maintained at 6580 ml/min. During the experiment, the degree of fluidization maintained at about 250% and the voidage of the fluidized-bed was in the neighborhood of 0.75. By varying other experimental parameters, the electrolysis was carried out for each current density selected. Five milliliters of the electrolyte was sampled at an interval of 0.05 A h in this study for Pb and Cu. The sample was diluted, if necessary, and acid-digested before the analysis of metal concentration by flame atomic absorption spectroscopy. After the experiments, the removal efficiency of the metal, current density, and energy consumption were calculated. The formula for the above calculation can be found elsewhere [38].

3. Results and discussion

3.1. Characteristics of the municipal incinerator fly ash

Characterization results of MIFA S specimen studied in this work are shown as follows: (1) moisture content (%): 0.20; (2) pH in 0.01 M CaCl_2 : 10.69; pH in H_2O : 10.11; (3) total contents of heavy metals (mg/kg): lead, 4450 ± 26 ; cadmium, 189.0 ± 0.2 ; chromium, 195.8 ± 4.3 ; zinc, $11\,558 \pm 117$; and copper, 1532 ± 9 ; (4) TCLP leaching toxicity (mg/l): lead, 2.45 ± 0.25 ; cadmium, 7.50 ± 0.55 ; chromium, 0.23 ± 0.04 ; zinc, 256.6 ± 59.7 ; and copper, 0.23 ± 0.02 ; (5) particle size (μm): mean, 22.86; and median, 25.73; (6) loss on ignition (%): 5.53. From the TCLP leaching toxicity of heavy metals shown above, the leached cadmium concentration of MIFA S specimen is greater than the current R.O.C. EPA regulatory threshold (i.e. 1 mg/l). Therefore, MIFA S specimen studied in this work was identified as a hazardous waste. In this study, an attempt was made to extract and recover heavy metals from the leachate of MIFA S specimen by electrolysis rather than using solidification/stabilization processes.

Table 3

The concentrations of Pb, Cd, and Cr leached from a municipal incinerator fly ash (MIFA S) subjected to various extractants of 0.1 N and different extraction time

Heavy metal	Extraction time (min)	Leached concentration (mg/kg)					
		HCl	HNO ₃	H ₂ SO ₄	HOAc	NaOAc (pH = 8.15)	NaOAc (pH = 3)
Pb	10	44.50	31.15	22.25	102.35	13.35	106.80
	60	26.70	22.25	22.25	44.50	8.90	57.85
	180	22.25	13.35	22.25	26.70	13.35	35.60
Cd	10	132.87	126.44	121.91	123.80	1.32	164.43
	60	136.46	110.94	109.81	124.17	0.76	154.60
	180	130.60	61.99	109.43	113.78	1.32	144.59
Cr	10	9.59	9.79	9.59	2.35	13.71	13.31
	60	9.79	12.14	3.13	6.46	13.90	8.22
	180	10.38	9.59	8.62	17.04	18.60	8.81

Table 4

The extraction efficiencies of Pb, Cd, and Cr based on the experimental conditions indicated in Table 1

Experimental run no.	Extraction efficiency (%)		
	Pb	Cd	Cr
1	31.44	89.31	25.63
2	43.72	88.89	38.08
3	35.51	91.22	30.88
4	47.83	92.91	47.09
5	24.20	90.16	21.68
6	35.98	91.85	41.72
7	22.59	91.01	32.41
8	44.54	91.64	46.88

Table 5

The effect analysis for the extraction efficiencies of Pb, Cd, and Cr based on the results indicated in Table 4

Item of effect	Estimate of effect		
	Pb	Cd	Cr
Average	35.75	90.87	35.55
A + BCD	14.58	0.90	15.79
B + ACD	3.78	1.64	7.54
C + ABD	-7.80	0.58	0.25
D + ABC	2.53	-0.79	-2.33
AB + CD	2.55	-0.05	-0.45
AC + BD	2.28	0.27	1.46
AD + BC	-0.31	-1.32	0.41

3.2. Factors influencing extractability of heavy metals from MIFA S specimen

Table 3 shows the leached concentrations of lead, cadmium, and chromium from MIFA S by six extractants of 0.1 N in concentration under an L/S ratio of 10, but different in extraction time. From this table, it was found that NaOAc (pH = 3) had the highest extraction yields for Pb and Cd and the second highest yield for Cr. Thus, NaOAc was selected as the sole extractant for later studies in this work. Namely, NaOAc was used for the extractability study (see Table 1).

The extractability of Pb, Cd, and Cr based on the experimental design indicated in Table 1 are shown in Table 4. These experimental results can be further processed by the effect analysis, as shown in Table 5. Fig. 2 presents the results of the effect analysis in a manner of the normal probability plot. From this figure, it is clear that points of ($A + BCD = 14.58$) and ($C + ABD = -7.80$) are the extreme outliers of the linear relationship for Pb. Namely, L/S ratio and extraction time had the main effects on Pb

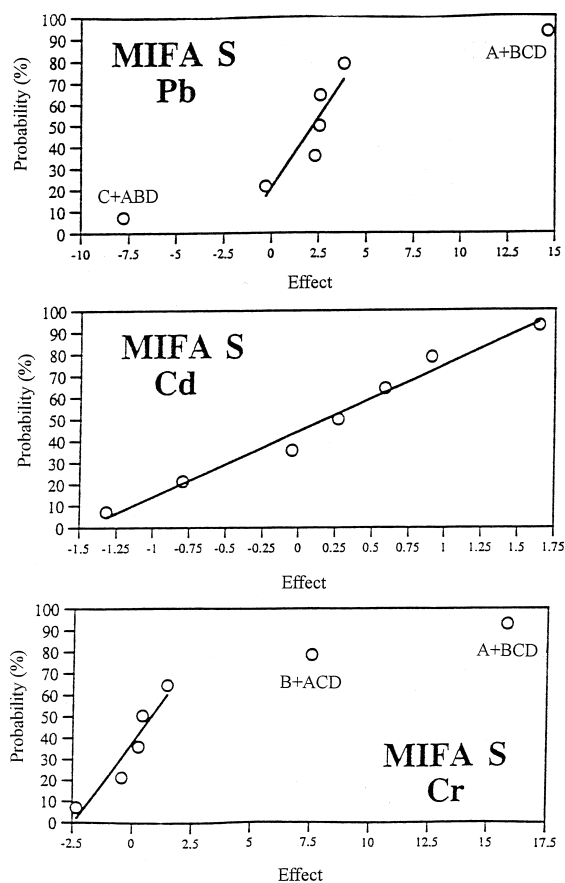


Fig. 2. The normal probability plots for the extractability of Pb, Cd, and Cr from MIFA S specimen by NAOAc.

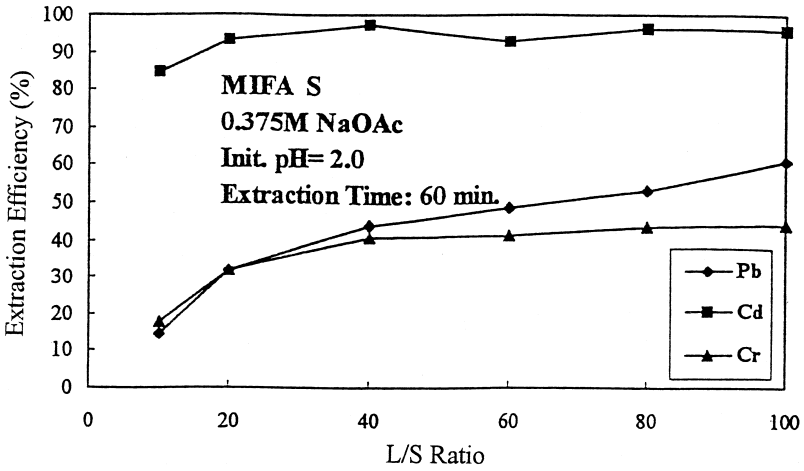


Fig. 3. The effect of liquid-to-solid ratio on extraction efficiency of MIFA S specimen.

extraction. In other words, these two are the controlling parameters for Pb extraction under the experimental conditions employed. More specifically, an upper level of L/S ratio (e.g. 40) is preferred because $(A + BCD)$ is positive in value while a lower level of extraction time (e.g., 60 min) is preferred because $(C + ABD)$ is negative in value (see Table 1). Based on the same principle, L/S ratio ($A + BCD = 15.79$) and extractant concentration ($B + ACD = 7.54$) are the controlling parameters for Cr extraction in this study. Namely, upper levels of L/S ratio (e.g. 40) and extractant concentration (e.g. 0.5 M) are preferred for Cr extraction. Under the experimental conditions used, however, no controlling parameter could be determined for Cd extraction because each parameter had a similar effect.

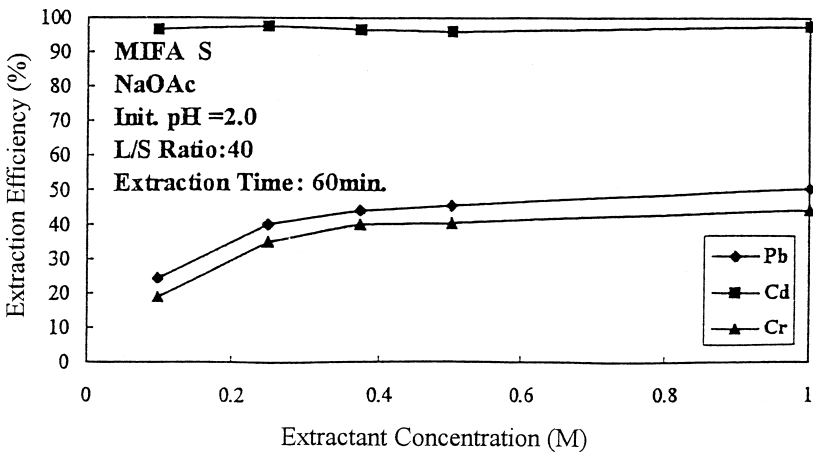


Fig. 4. The effect of extractant concentration on extraction efficiency of MIFA S specimen.

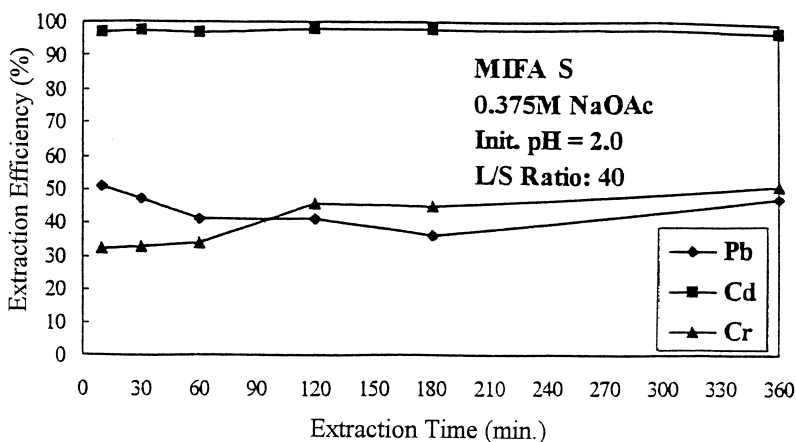


Fig. 5. The effect of extraction / time on extraction efficiency of MIFA S specimen.

The effects of L/S ratio, extractant concentration, extraction time, and initial pH can be further verified by the experimental results shown in Figs. 3–6. By using 0.375 M NaOAc as the extractant, an initial pH of 2, and an extraction time of 60 min, it was found that the extraction efficiency of Pb increased with increasing L/S ratio while the extraction efficiencies of Cd and Cr increased with increasing L/S ratio only up to 40 then leveled off (see Fig. 3). By using NaOAc as the extractant, an initial pH of 2, and an L/S ratio of 40, it was found that the extraction efficiencies of Pb and Cr increased with increasing extractant concentration up to 1 M while the extraction efficiency of Cd was independent of the extractant concentration (see Fig. 4). By using NaOAc with a concentration of 0.375 M, an initial pH of 2, and an L/S ratio of 40, it was found that the extraction efficiency of Pb decreased with increasing extraction time up to 180 min

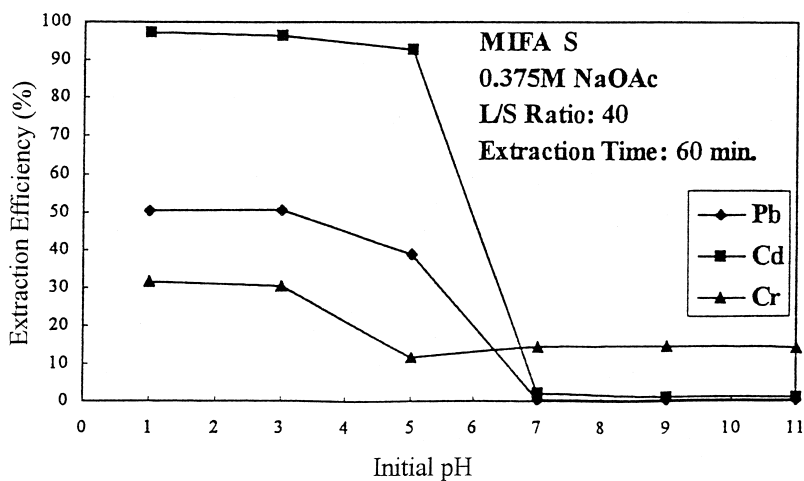


Fig. 6. The effect of initial pH on extraction efficiency of MIFA S specimen.

while the extraction efficiency of Cr increased with increasing extraction time up to 120 min. In this case, however, the extraction efficiency of Cd was independent of the extraction time (see Fig. 5). By using NaOAc with a concentration of 0.375 M, an L/S ratio of 40, and an extraction time of 60 min, it was found that extraction efficiencies of Pb, Cd, and Cr began to decrease from pHs greater than 3. This is more obvious for pHs between 5 and 7 in the cases of Pb and Cd (see Fig. 6). Accordingly, an initial pH of greater than 3 is detrimental to the extraction of these three metals from MIFA S specimen.

3.3. Cyclic voltammetry

Fig. 7 shows the sweep pattern of the leachate of MIFA S specimen. Two characteristic peaks were observed at -470 mV and -86 mV (vs. Ag/AgCl), respectively. Lead and copper were identified on the sweep pattern if these two characteristic peaks were compared with the characteristic peaks for each solution containing only a metal like Pb, Cd, Cu, and Zn [39]. This implies that Pb and Cu in the leachate are able to be recovered via the electrolysis process. Therefore, electrolytic recovery of Pb and Cu from the leachate of MIFA S specimen was conducted in this work. Whether it is feasible to recover Cd and Zn from the leachate by this technology is not studied here. More intensive study may be warranted.

3.4. Factors influencing electrolytic recovery of heavy metals from the leachate of MIFA S specimen

Based on the result of cyclic voltammetry obtained above, only Pb and Cu were studied for their removal efficiencies by using the electrolysis process in a fluidized-bed cell. The experimental factors influencing the removal efficiency and the experimental conditions employed are indicated in Table 2.

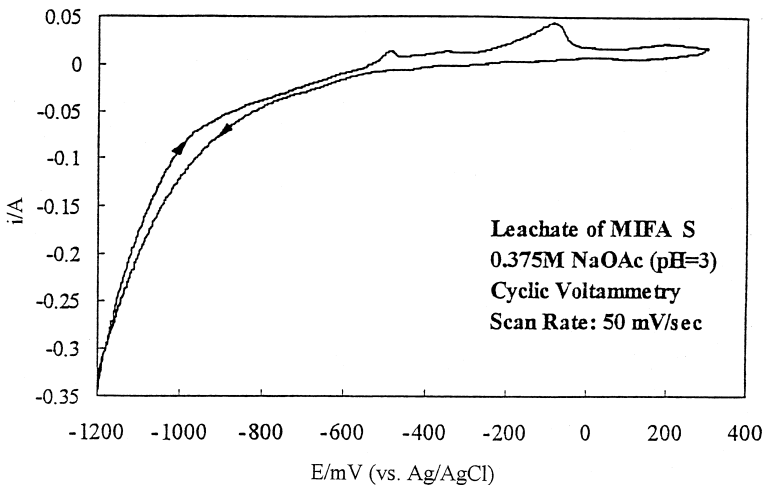


Fig. 7. The sweep pattern of cyclic voltammetry for the leachate of MIFA S specimen.

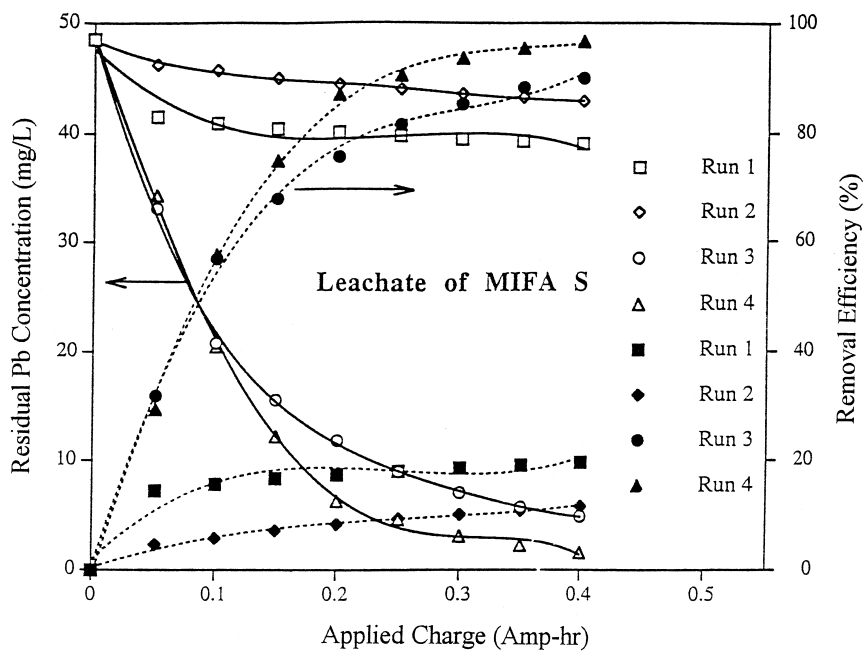


Fig. 8. The results of electrolytic recovery of Pb under various experimental conditions indicated in Table 2.

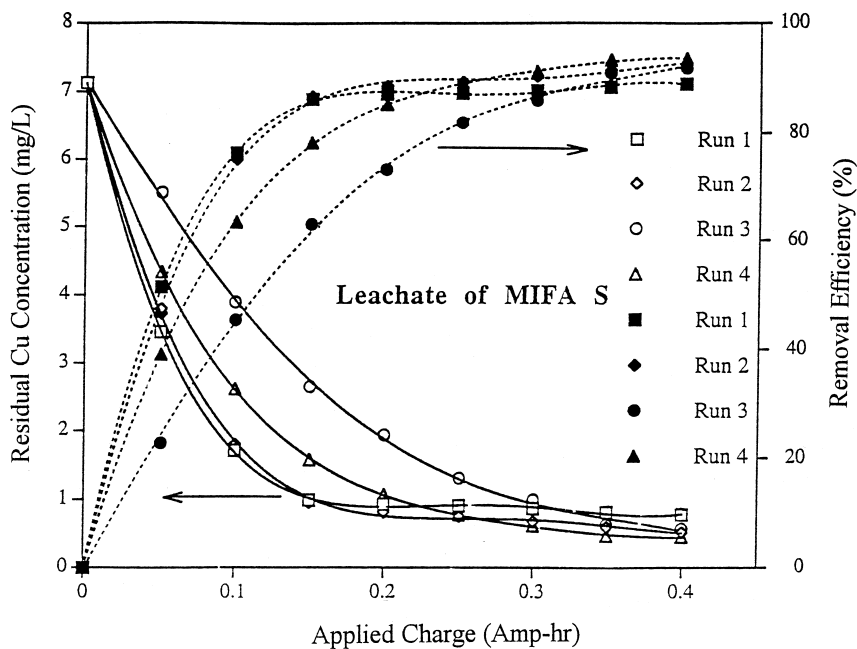


Fig. 9. The results of electrolytic recovery of Cu under various experimental conditions indicated on Table 2.

Table 6

The removal efficiency, current efficiency, and energy consumption for the electrolytic recovery of Pb and Cu with an applied charge of 0.2 A h based on the experimental conditions indicated in Table 2

Experimental run no.	Electrolytic recovery of Pb and Cu with an applied charge of 0.2 A h		
	Removal efficiency (%)	Current efficiency (%)	Energy consumption (kw h/kg)
1	17.35	2.33	5.23
	86.96*	5.58*	7.10*
2	8.37	1.12	15.69
	88.50*	5.68*	10.10*
3	75.68	10.14	3.27
	72.79*	4.67*	23.10*
4	87.10	11.67	2.35
	84.99*	5.46*	16.39*

Note: figures with an asterisk are for Cu, otherwise for Pb.

Figs. 8 and 9 present the results of electrolytic recovery of Pb and Cu, respectively. Evidently, Runs 3 and 4 gave rise to much greater removal efficiencies of Pb comparing with the results of Runs 1 and 2. Conversely, Runs 1 and 2 were found to be slightly better than the other two runs for removing copper. In fact, it is technically feasible to recover 96.70% of Pb and 93.69% of Cu from the leachate of MIFA S specimen if an applied charge of 0.4 A h is employed (see Figs. 8 and 9).

For an applied charge of 0.2 A h, the performance of electrolytic recovery of Pb and Cu based on the experimental design indicated in Table 2 are shown in Table 6. These experimental results were further analyzed to determine their effects, as shown in Table 7. Figs. 10 and 11 are the normal probability plots for the results of Pb and Cu in Table 7, respectively. In the case of Pb, it showed that current density had a main effect on

Table 7

The effect analysis for the removal efficiency, current efficiency, and energy consumption based on the results indicated in Table 6

Item of effect	Estimate of effect		
	Removal efficiency	Current efficiency	Energy consumption
Average	47.13	6.32	6.64
	83.31*	5.35*	14.17*
<i>E</i> + <i>FG</i>	68.53	9.18	-7.65
	-8.84*	-0.57*	11.15*
<i>F</i> + <i>EG</i>	1.22	0.16	4.47
	6.87*	0.45*	-1.86*
<i>G</i> + <i>EF</i>	10.20	1.37	-5.69
	5.33*	0.35*	-4.86*

Note: figures with an asterisk are for Cu, otherwise for Pb.

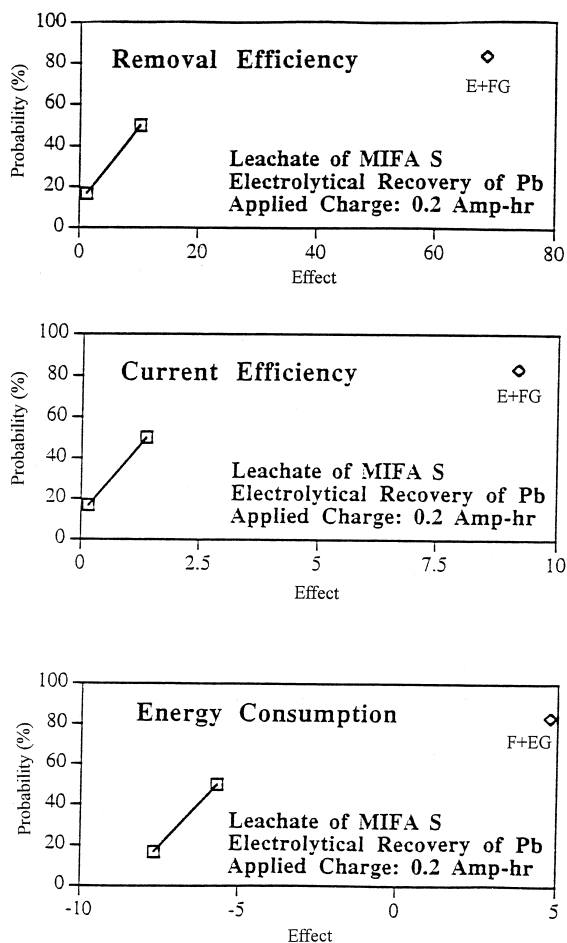


Fig. 10. The normal probability plots for the removal efficiency, current efficiency, and energy consumption of the leachate of MIFA S specimen by electrolytic recovery of Pb.

removal efficiency ($E + FG = 68.53$) and on current efficiency ($E + FG = 9.18$). More specifically, an upper level of current density (e.g. 0.5 mA/cm^2) is preferred to achieve a greater removal efficiency of Pb and a better current efficiency. In the case of Cu, it indicated that current density also had very significant effects on removal efficiency ($E + FG = -8.84$), current efficiency ($E + FG = -0.57$), and energy consumption ($E + FG = 11.15$). More specifically, a lower level of current density (e.g. 0.25 mA/cm^2) is preferred to achieve a greater removal efficiency of Cu, a better current efficiency, and a lower energy consumption. Regarding the effect of initial pH, an upper level of this experimental factor (e.g. $\text{pH} = 4$) would result in a higher energy consumption in the case of Pb removal (see Table 7 and Fig. 10). In the case of Cu removal, however, the effect of initial pH was found to be insignificant under the experimental conditions employed. With regard to the operating temperature, it had no marked effect

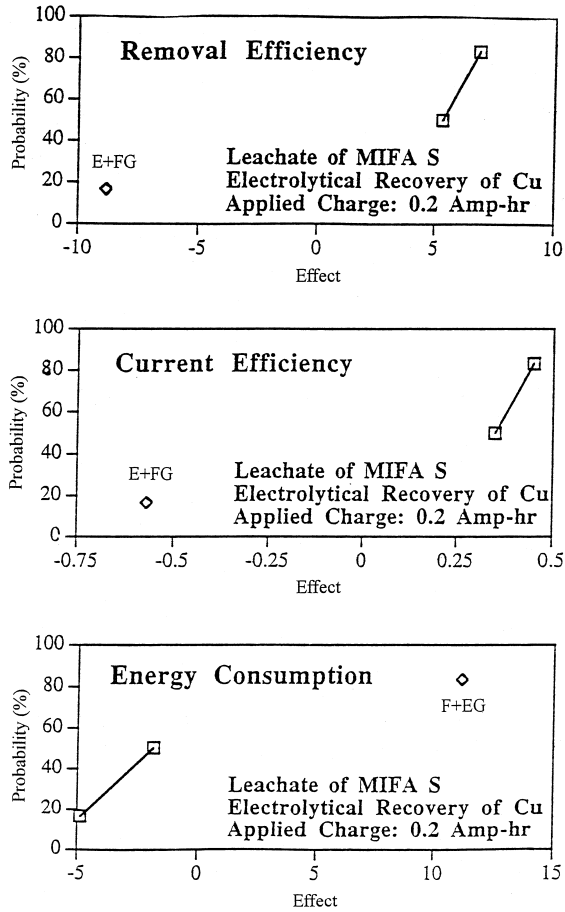


Fig. 11. The normal probability plots for the removal efficiency, current efficiency, and energy consumption of the leachate of MIFA S specimen by electrolytical recovery of Cu.

on removal efficiency, current efficiency, and energy consumption in both cases of Pb removal and Cu removal. But it is likely that a lower level of operating temperature (e.g. 27°C) would result in a higher energy consumption.

4. Conclusions

In this work, a specimen of municipal incinerator fly ash (designated MIFA S) from a modern waste-to-energy plant was used for studying its extractability of heavy metals (Pb, Cd, Cr, and Cu) by six extractants and subsequent recovery of Pb and Cu by electrolysis in a fluidized-bed cell. These two types of experiments were conducted according to 2^{4-1} and 2^{3-1} fractional factorial designs respectively. The most important factors for controlling the extractability and the subsequent electrolytic recovery were

determined from the effect analysis and normal probability plot. Based on the experimental results obtained, the following conclusions can be drawn.

(1) Technically, it is feasible to treat MIFA via solvent extraction and electrowinning for the removal of heavy metals. By using proper experimental conditions, more than 96% of Pb and 93% of Cu could be recovered from the leachate of MIFA S specimen.

(2) The extractability and electrolytic recovery of different metals vary with the change of experimental conditions.

(3) Cyclic voltammetry is a useful technique for determining which metals in the solution are suitable for electrolytic recovery.

(4) For Pb extraction, a higher level of L/S ratio and a lower level of extraction time are preferred. For Cr extraction, higher levels of L/S ratio and extractant concentration are preferred. However, no controlling parameters could be determined for Cd extraction in this investigation. An initial pH lower than 5 is preferred for the extraction of all metals studied.

(5) For electrolytic recovery of Pb, the removal efficiency increases with current density, while the recovery of Cu requires a lower level of current density.

Acknowledgements

This study was sponsored by the National Science Council of R.O.C. under the project No. NSC 85-2211-E-110-003.

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