Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin

I. Hsien Lee, Yu-Chung Kuan, Jia-Ming Chern *

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Sec., Taipei 10452, Taiwan

Abstract

Wastewaters containing heavy metals are usually treated by chemical precipitation method in Taiwan. This method can remove heavy metals form wastewaters efficiently, but the resultant heavy metal sludge is classified as hazardous solid waste and becomes another environmental problem. If we can remove heavy metals from sludge, it becomes non-hazardous waste and the treatment cost can be greatly reduced. This study aims at using ion-exchange resin to remove heavy metals such as copper, zinc, cadmium, and chromium from sludge generated by a PCB manufacturing plant. Factorial experimental design methodology was used to study the heavy metal removal efficiency. The total metal concentrations in the sludge, resin, and solution phases were measured respectively after 30 min reaction with varying leaching agents (citric acid and nitric acid); ion-exchange resins (Amberlite IRC-718 and IR-120), and temperatures (50 and 70 °C). The experimental results and statistical analysis show that a stronger leaching acid and a higher temperature both favor lower heavy metal residues in the sludge. Two-factors and even three-factor interaction effects on the heavy metal sorption in the resin phase are not negligible. The ion-exchange resin plays an important role in the sludge extraction or metal recovery. Empirical regression models were also obtained and used to predict the heavy metal profiles with satisfactory results.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Heavy metal; Sludge; Ion-exchange resin; Factorial design

1. Introduction

Industrial wastewaters containing heavy metals are usually treated by adjusting solution pH to form metal precipitates, followed by coagulation, clarification, and filtration. Although the precipitation method is quite effective to remove the heavy metals from industrial wastewaters, the resultant heavy metal sludge is classified as hazardous waste and generates other disposal problems. Several methods including solidification [1–6], extraction [7–10], bio-leaching [11–16], electrodialysis [17–19], microwave radiation [20,21], and ion-exchange have been used for detoxifying of metal sludge. Ion-exchange is another possible and effective method to recover heavy metal species from solution or solids by directly contacting with ion-exchange resin [22–26]. For the recovery processes by metal dissolution, an essential limit of the recovery efficiency is the thermodynamic equilibrium, i.e., the solid dissociates to such an extent that traces of heavy metal species are saturated in the solution. For example, the thermodynamic equilibrium during heavy metal leaching is:

$$M(OH)_{2(s)} \leftrightarrow M^{2+} + 2OH^- \tag{1}$$

Fortunately the sludge solid and the slightly dissolved metal ions equilibria in the solution can be disturbed in the presence of cationic ion-exchange resin according to the Le Chatelier principle. The hydrogen ions released from the cationic ion-exchange resin will neutralize the hydroxide ions so that the equilibrium will shift until all the metal ions are leached into solution and adsorbed onto the ion-exchange resin.

Design of experiments (DOE) has become one of the most popular statistical techniques since 1990s. The main advantage of experimental design is that it can cover a larger area of experimental statistics and obtain unambiguous results at minimum expense. 2^k full factorial design is a standard technique and widely use for studying a random response to a set of k possible factors [27]. With the full factorial design methodology,

---

* Corresponding author. Tel.: +886 2 27002737x23; fax: +886 2 27087819.
 E-mail address: jmchern@ttu.edu.tw (J.-M. Chern).

Fig. 1. Triple layer pyrex-glass-jacketed reactor.

2. Materials and methods

2.1. Characterization of heavy metal sludge

Non-coagulated slurry after alkaline precipitation was taken from the wastewater treatment plant of an electroplating factory in Taiwan. The slurry was first dewatered and the sludge samples were oven-dried at $105\,^\circ$C in order to determine the water content and total solid content values. The dried sludge samples were homogenized by grinding and mixing. Following grinding and homogenization, the sludge samples were passed through a series of sieves in order to determine the particle size distribution and the $212\,\mu$m size particles were chosen for all the experimental test runs. To determine the initial metal content in the sludge solid, 1.0 g of the dried sludge solids were placed inside a microwave pressure vessel filled with 20 mL aqua regia in a microwave digestion system (Microwave 3000, Anton Paar). After digestion, the residual solution was carefully removed and the metal concentrations were measured by atomic absorption spectroscopy (Varian, Model 3000). The characteristics and heavy metal contents determined from five samples are summarized in Table 1.

2.2. Heavy metal extraction

All the heavy metal extraction experiments were conducted in a triple-layer Pyrex-glass-jacketed reactor equipped with an agitator as shown in Fig. 1. To separate the sludge slurry and ion-exchange resin, a semi-permeable membrane was used to prevent the mixing of these two solid phases. The reactor jacket was connected to a temperature controller (Deng Yng, D-630,

main and interaction effects can be easily evaluated. The main effect refers to the effect caused by the changed factor, while the interaction effect refers to when the effect of one factor is dependent on the value of another factor [28].

There are many processes involved during heavy metal removal from the sludge with an acidic leaching agent and ion-exchange resin. The leaching agent H^+ first diffuses to the sludge particle surfaces then diffuses through the "ash layer" to the unreacted core, followed by a surface reaction expressed in Eq. (1).

$$M(OH)_{2(s)} + 2H^+ \leftrightarrow M^{2+} + 2H_2O \qquad (2)$$
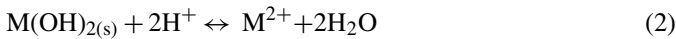
The heavy metal ions then diffuse through the ash layer to the sludge particle surface and finally release into the bulk solution [29]. In the presence of cationic ion-exchange resin, the released free heavy metal ions will be exchanged with the hydrogen ions in the resin to provide more hydrogen ions for the metal leaching from the sludge particles. The ion exchange between heavy metal ion and hydrogen ion is shown below:

$$M^{2+} + 2RH \leftrightarrow R_2M + 2H^+ \qquad (3)$$

Because the overall heavy metal removal process from sludge is very complicated, this study aims at using a DOE approach to remove heavy metal species such as copper, zinc, cadmium, and chromium from the sludge generated by an electroplating process.

Table 1
Characteristics and heavy metal composition of sludge

Water content (%)	Total solid content (g DSC/mL slurry)[a]	Cu (mg/g DSC)	Zn (mg/g DSC)	Cd (mg/g DSC)	Cr (mg/g DSC)	Total
85.97 ± 0.01	7.81 ± 0.14	6.2 ± 0.2	2.9 ± 0.2	<0.01	28.8 ± 5.0	37.9 ± 4.8

[a] Dry solid content.

Table 2
The high and low levels of experimental factors

Factor	Low level (−1)	High level (+1)
Leaching agent (A)	Citric acid	Nitric acid
Ion-exchange resin (B)	Amberlite IRC-718	Amberlite IR-120
Temperature, °C (C)	50	70

Taiwan) to maintain the desired reaction temperatures during reactions. Preliminary tests using varying agitation speeds were performed to select an agitation speed that is high enough to uniformly suspend the sludge particles and ion-exchange resin and to eliminate the external film mass transfer resistance. In addition to a constant agitation speed, the amounts of sludge and resin used per unit volume of leaching solution and the reaction time were kept constant to minimize the number of variables in the experimental design. In the experiments, reagent grade nitric acid (Nihon Shyaku Industrial, Ltd., Japan) or citric acid (Wako Pure Chemicals Industrial, Ltd., Japan) was used to prepare the leaching solution with desired acid concentration 0.01N. The weak acid cationic chelating exchange resin, Amberlite IRC-718 (Rohm Hass, USA) and the strong acid cationic exchange resin, Amberlite IR-120 (Rohm Hass, USA) were used in this study.

Before any experiments both types of resins were first washed to remove impurity and then conditioned to convert the exchange sites to the desired form. The first conditioning cycle used sodium hydroxide to convert the ion exchangers to Na^+ form, and then used deionized water to wash out the residual sodium hydroxide. The second conditioning cycle used hydrochloride acid to convert the exchange sites to the desired H^+ form, and then used deionized water to wash out the residual hydrochloride acid.

These two conditioning cycles were repeated several times to ensure the resins were completely converted to the desired H^+ form before use.

The type of leaching agent, type of ion-exchange resin, and temperature were selected as the factors with the high and low level shown in Table 2. The 2^3 factorial design cubical diagram with high and low level for three factors, leaching agent, ion-exchange resin, and temperature is shown in Fig. 2. After 30 min
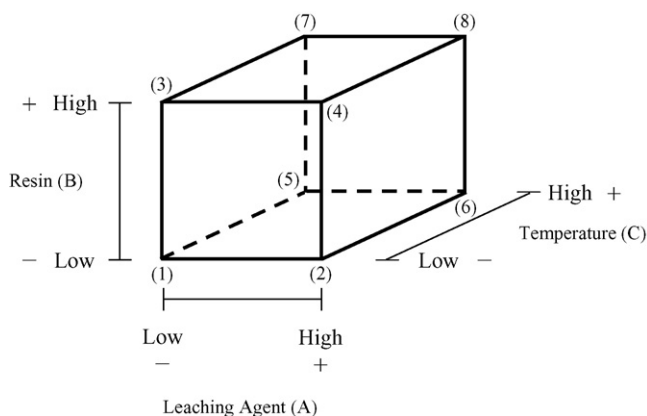

Fig. 2. The 2^3 factorial design with high and low level for three factors, leaching agent, ion-exchange resin, and temperature.

reaction, liquid samples were taken and filtered to measure the heavy metal concentrations by an atomic absorption spectrophotometer (Varian, Model 3000). The ion-exchange resin was then regenerated with 1N nitric acid and the regenerated solution was analyzed for heavy metal concentrations. The sludge particle residues were also digested with 20 mL aquaregia in the microwave digestion system and the digestion solution was also analyzed for heavy metal concentrations. Total sixteen duplicate experiments were carried out in the factorial design matrix with the high and low levels represented by +1 and −1, respectively.

3. Results and discussion

3.1. Total heavy metal extraction efficiency

The results listed in Table 1 indicate that copper, zinc, and chromium are the three measurable heavy metals in the sludge. Therefore only the concentrations of these three heavy metals were measured. For each experiment, after reaction the heavy metal concentrations in the sludge, resin, and solution phases were measured. The summation for individual heavy metal in the three phases is about 95% of the heavy metal in the original sludge. Before reaction, 100% of the heavy metals are in the sludge phase. After reaction for 30 min, some heavy metals are leached to the solution while some are exchanged to the resin phase. The heavy metal profiles in the three phases that can indicate the efficiency of heavy metal recovery are thus selected as the responses of the experimental design.

Table 3 shows the percentages of total heavy metal in the sludge, resin, and solution phases in the 2^3 full factorial design with duplicate tests in each design run. As shown by Table 3, the best combination of the factors for the lowest total heavy metal residue in the sludge phase occurs at run 8 where a stronger (nitric) acid, a strong cationic ion-exchange resin (IR-120), and a higher temperature are used. This result agrees with that obtained in the previous study [29] of the heavy metal sludge extraction by acid only. A stronger acid provides more hydrogen ion to penetrate through the sludge particles while a higher temperature facilitates overcome the energy barrier of the ash-layer diffusion and the surface reaction. The result about the acid effect on heavy metal removal efficiency also agrees with the study of Wu et al. [8] who used different acids to extract copper and

Table 3
Experimental design matrix and results in sludge, resin, and solution phase

Run no.	Factor			Total heavy metal percentage in					
	A	B	C	Sludge phase (%)		Resin phase (%)		Solution phase (%)	
1	−1	−1	−1	56.90	56.72	25.53	25.14	17.57	18.14
2	+1	−1	−1	54.54	54.54	18.57	20.13	26.89	25.33
3	−1	+1	−1	53.61	50.36	36.32	36.80	10.07	12.84
4	+1	+1	−1	50.97	48.99	36.69	39.08	12.34	11.93
5	−1	−1	+1	53.86	53.91	23.84	24.66	22.30	21.43
6	+1	−1	+1	55.53	56.36	20.52	20.07	23.95	23.57
7	−1	+1	+1	49.23	53.66	33.91	30.41	16.85	15.92
8	+1	+1	+1	44.39	48.46	39.30	37.80	16.31	13.74

Table 4
Experimental design results for individual heavy metal

Run no.	Copper			Zinc			Chromium		
	Sludge phase	Resin phase	Solution phase	Sludge phase	Resin phase	Solution phase	Sludge phase	Resin phase	Solution phase
1	43.68	44.69	11.64	38.47	45.18	16.35	63.93	16.78	19.28
	44.46	43.67	11.88	38.50	44.26	17.24	63.07	17.07	19.86
2	39.33	53.21	7.46	23.71	22.15	54.14	64.96	8.61	26.43
	36.71	53.46	9.84	23.74	28.50	47.76	67.55	6.61	25.84
3	40.46	50.26	9.28	25.04	66.13	8.83	64.12	25.50	10.38
	40.80	50.50	8.70	25.10	55.96	18.95	59.28	28.80	11.92
4	33.27	49.48	17.26	16.61	64.26	19.14	63.80	27.02	9.18
	32.79	48.96	18.25	16.59	62.62	20.79	60.98	30.36	8.67
5	40.25	49.65	10.09	29.37	54.05	16.59	61.93	11.47	26.60
	40.18	49.85	9.96	29.42	53.92	16.67	61.78	12.74	25.49
6	34.63	55.37	10.00	27.00	12.35	60.65	70.23	9.36	20.41
	35.71	53.99	10.29	26.92	21.64	51.44	69.86	8.16	21.98
7	31.96	58.76	9.28	12.75	80.04	7.21	63.69	14.89	21.42
	33.63	56.82	9.54	12.70	79.05	8.25	67.45	13.29	19.26
8	24.68	48.87	26.45	11.01	53.38	35.61	60.73	32.13	7.14
	26.54	51.71	21.75	10.98	54.81	34.20	64.33	29.54	6.14

nickel from a PCB plant sludge. They concluded that the heavy metal extraction mechanism was the reaction of acid with metals in the sludge by proton exchange and the dissolution of heavy metal hydroxides and the sequence of the extraction effectiveness was sulfuric acid ≥ nitric acid > hydrochloric acid > acetic acid > citric acid.

The functional group of the strong acid cationic exchange resin, Amberlite IR-120 is SO_3^{2-}, with the ion-exchange capacity independent of the solution pH. The functional group of the weak acid cationic chelating exchange resin, Amberlite IRC-718 is iminodiacetic acid with the ion-exchange capacity dependent on the solution pH. Although Amberlite IRC-718 could have a high exchange capacity at high pH, its capacity under the experimental conditions is lower than that of Amberlite IR-120. In separate measurements, the ion-exchange capacities of Amberlite IRC-718 and Amberlite IR-120 were determined by the method described by Helfferich [30] to be 1.87 ± 0.24 mequiv./mL resin and 3.79 ± 0.29 mequiv./mL resin, respectively. This capacity difference agrees with the results that a strong cationic ion-exchange resin provides more exchangeable sites for heavy metal ions and thus gives better heavy metal removal efficiency.

3.2. Individual heavy metal extraction

Although the result of run 8 only in Table 3 indicates the effects of the type of leaching agent, ion-exchange resin, and reaction temperature on the total heavy metal extraction efficiency, we need to look at individual heavy metal extraction results as shown in Table 4. The lowest heavy metal residue in the sludge phases for copper and zinc, and chromium are run 8 and run 4, respectively. Considering the measurement accuracy and experimental reproducibility, the results of run 4 and run 8 for chromium in the sludge phase probably have no significant

difference. Therefore, we can come to the same conclusion that a stronger acid, a strong cationic ion-exchange resin, and a higher temperature favor a lower heavy metal residue in the sludge for all the three heavy metals. Also shown in Table 4 are the heavy metal percentages in the resin phase. One can observe that the highest copper and zinc percentages in the resin phase occur at run 7 where a weaker (citric) acid, a strong cationic ion-exchange resin, and a higher temperature are used. The percentages of the heavy metal remained in the resin phase depends on the competition of all the cations including copper, zinc, chromium, and hydrogen ions. A strong acid of course facilitates leach the heavy metal ions from the sludge phase, but it also provides many hydrogen ions to compete the exchangeable sites with the heavy metals.

Because the overall heavy metal extraction and ion-exchange process is very complicated. We used the factorial experimental design methodology to analyze the results further with the assistance of statistics software. The results in Table 4 are ready to put into a regression model that can be used to predict the response at any point by the same factors in the design.

3.3. DOE result analysis

The significant factors in the regression model can be determined by performing an analysis of variation [28]. The sum of squares used to estimate the effect of the factors and the F distribution which is the distribution of the ratio of respective mean-square effect and mean-square error are shown in Tables 5–7. The F-ratio can be used to ensure the hypothesis of analysis and to compute the probability value in the analysis of variance is defined as:

$$F_i = \frac{MS_i}{MS_E} \tag{4}$$

Table 5
ANOVA analysis of variance of copper in sludge and resin phases

Factor	Sum of squares	Degrees of freedom	Mean square	F_0	p-Value	β-Coefficient
Sludge phase ($R^2 = 0.984$)						
Model	471.962	7	67.385	70.751	<0.0001	–
A	167.444	1	167.444	175.810	<0.0001	−6.470
B	161.417	1	161.417	169.482	<0.0001	−6.352
C	120.560	1	120.560	126.584	<0.0001	−5.490
AB	3.404	1	3.404	3.574	0.0953	−0.492
AC	0.504	1	0.504	0.529	0.4876	0.189
BC	18.276	1	18.276	19.189	0.0023	−1.140
ABC	0.087	1	0.087	0.091	0.7701	−0.0738
Intercept	20960	1	20960	24480	0.0000	36.193
Pure error	7.619	8	0.952			
Cor total	479.311	15				
Resin phase ($R^2 = 0.969$)						
Model	233.801	7	33.400	35.148	<0.0001	–
A	7.358	1	7.358	7.743	0.0238	1.356
B	8.223	1	8.223	8.653	0.0187	1.434
C	59.252	1	59.252	62.352	<0.0001	3.849
AB	129.334	1	129.334	136.101	<0.0001	−3.033
AC	27.905	1	27.905	29.365	0.0006	−1.409
BC	0.612	1	0.612	0.644	0.4453	0.209
ABC	1.118	1	1.118	1.177	0.3096	−0.264
Intercept	41950	1	41950	43290	0.0000	51.203
Pure error	7.602	8	0.950			
Cor total	241.403	15				

where i represents the symbol of the main effect or interaction in the 2^3-factorial design; MS_E represents the mean square of the error. A p-value is a measure of how much evidence we have against the null hypothesis. The smaller the p-value, the more evidence we have against H_0 and it is also a measurement of how likely we are to obtain a confident sample result assuming H_0 is true. In order to determine the important effects of the metal concentrations in the sludge, resin and solution phases, the F dis-

Table 6
ANOVA analysis of variance of zinc in sludge and resin phases

Factor	Sum of squares	Degrees of freedom	Mean square	F_0	p-Value	β-Coefficient
Sludge phase ($R^2 = 0.999$)						
Model	1183.6575	7	169.094	149475.3	<0.0001	–
A	187.622	1	187.622	165853.3	<0.0001	−6.849
B	706.895	1	706.895	624879.7	<0.0001	−13.294
C	141.670	1	141.670	125232.7	<0.0001	−5.951
AB	12.233	1	12.233	10813.3	<0.0001	0.933
AC	90.869	1	90.869	80325.8	<0.0001	2.542
BC	36.572	1	36.572	32329.1	<0.0001	−1.613
ABC	7.798	1	7.798	6893.3	<0.0001	−0.698
Intercept	8460	1	8460	9752	0.0000	22.994
Pure error	0.009	8	0.001			
Cor total	1183.667	15				
Resin phase ($R^2 = 0.980$)						
Model	5868.311	7	838.330	56.684	<0.0001	–
A	1577.678	1	1577.678	106.675	<0.0001	−19.86
B	3428.103	1	3428.103	231.792	<0.0001	29.275
C	25.452	1	25.452	1.721	0.2260	2.523
AB	277.722	1	277.722	18.778	0.0025	4.444
AC	516.198	1	516.198	34.903	0.0004	−6.059
BC	16.892	1	16.892	1.142	0.3164	1.096
ABC	26.266	1	26.266	1.776	0.2194	−1.281
Intercept	39830	1	39830	2479	0.0000	49.894
Pure error	118.317	8	118.317			
Cor total	5986.628	15				

Table 7
ANOVA analysis of variance of chromium in sludge and resin phases

Factor	Sum of squares	Degrees of freedom	Mean square	F_0	p-Value	β-Coefficient
Sludge phase ($R^2 = 0.640$)						
Model	117.121	7	16.732	4.051	0.0340	–
A	18.469	1	18.469	4.472	0.0674	2.149
B	22.397	1	22.397	5.423	0.0483	−2.366
C	9.471	1	9.471	2.293	0.1684	1.539
AB	44.189	1	44.189	10.699	0.0113	−1.773
AC	0.727	1	0.727	0.176	0.6859	0.227
BC	0.870	1	0.870	0.211	0.6586	0.249
ABC	20.999	1	20.999	5.084	0.0542	−1.146
Intercept	66010	1	66010	10990	0.0000	64.231
Pure error	33.041	8	33.041			
Cor total	150.162	15				
Resin phase ($R^2 = 0.984$)						
Model	1213.349	7	173.336	72.127	<0.0001	–
A	7.910	1	7.910	3.291	0.1072	1.406
B	766.321	1	766.321	318.879	<0.0001	13.841
C	53.181	1	53.181	22.129	0.0015	−3.646
AB	239.398	1	239.398	99.618	<0.0001	4.126
AC	112.095	1	112.095	46.645	0.0001	2.823
BC	13.1213	1	13.1213	5.461	0.0477	−0.966
ABC	21.321	1	21.321	8.872	0.0176	1.154
Intercept	5341	1	5341	1186	0.0000	18.271
Pure error	19.225	8	19.225			
Cor total	1232.574	15				

tribution and p-value tests were employed. Since $F_{0.051,8} = 5.32$, the value of 95.0% confidence level, all the effects in Tables 5–7 giving F_0 greater than 5.32 have statistical significance [28]. Based on the F-test and p-value test shown in Tables 5–7, some insignificant effects can be discarded, because these effects do not offer any statistical significance.

Table 5 shows the ANOVA analysis for copper in the sludge and resin phases, respectively. Because the summation of the copper percentages in the three phases is 100%, we only discuss the results in the sludge and resin phase. In Table 5, the F_0 values of the main factor A, B and C present the relatively higher statistical significance to other interactions. The p-values of the main factor A, B and C are also much smaller than the other interaction effects. If we consider only the main effects of A, B and C, we should run all the factors at the high level to minimize the residual copper in the sludge because all the three effects are negative. However, it is necessary to examine any interactions that are important in the experimental design analysis. Fig. 3a–c show that the interactions except BC interaction for copper in the sludge phase are inconspicuous. This conclusion is also proved by the ANOVA analysis shown in Table 5 where the F_0 values of AB and AC interactions are less than 5.32 at 95% confidence level. The interaction plots shown in Fig. 3a and b suggest that the high level of A favors the lower copper residue in the sludge no matter at low or high levels of B and C. Since the AB and AC interactions are not significant, the effect of leaching agent (A) is conclusive. The nitric acid (high level of A) provides more hydrogen ions that can penetrate the ash layer of the sludge particles to solubilize the copper ions. The interaction plot shown in Fig. 3c suggests the effect of B is more remarkable at the high

level of C. A stronger cationic exchange resin provides more exchangeable sites for copper and thus leads to a lower copper residue in the sludge, especially at a higher temperature.

In the resin phase, the amount of copper would be affected by the main factors A, B and C and the interactions AB and AC as shown by the F_0 value in Table 5. Although all the β-coefficients for factors A, B, and C are positive, we cannot conclude that high levels of A, B, and C will definitely lead to high copper fractions in the resin phases. Because the interactions AB and AC are significant, the effect of leaching agent (A) on the copper fraction in the resin is complicated as shown by Fig. 3d–f. Fig. 3d shows the copper fraction in Amberlite IRC-718 increases from 47.0% to 54.0% by using nitric acid instead of citric acid. But the copper fraction in Amberlite IR-120 decreases from 54.1% to 50.8% by using nitric acid instead of citric acid. Fig. 3e shows the copper fraction in the resin phase increases with the acid strength at a lower temperature but decreases with the acid strength at a higher temperature. At a lower temperature the energy barriers for ash layer diffusion and surface reaction are rather high so that we need a stronger acid to penetrate the ash layer to solubilize the copper ions before the copper ions can be released to the solution and finally exchanged to the resin phase. However, at a higher temperature where the energy barriers are negligible the stronger acid will provide more hydrogen ions to compete with copper for the exchangeable sites on the resin thus leads to a lower copper fraction in the resin.

Table 6 shows the ANOVA analysis for zinc in the sludge and resin phases, respectively. The F_0 values in Table 6 suggest that all the main effects, two-factor interactions, and even three-factor interaction are statistically significant for zinc in
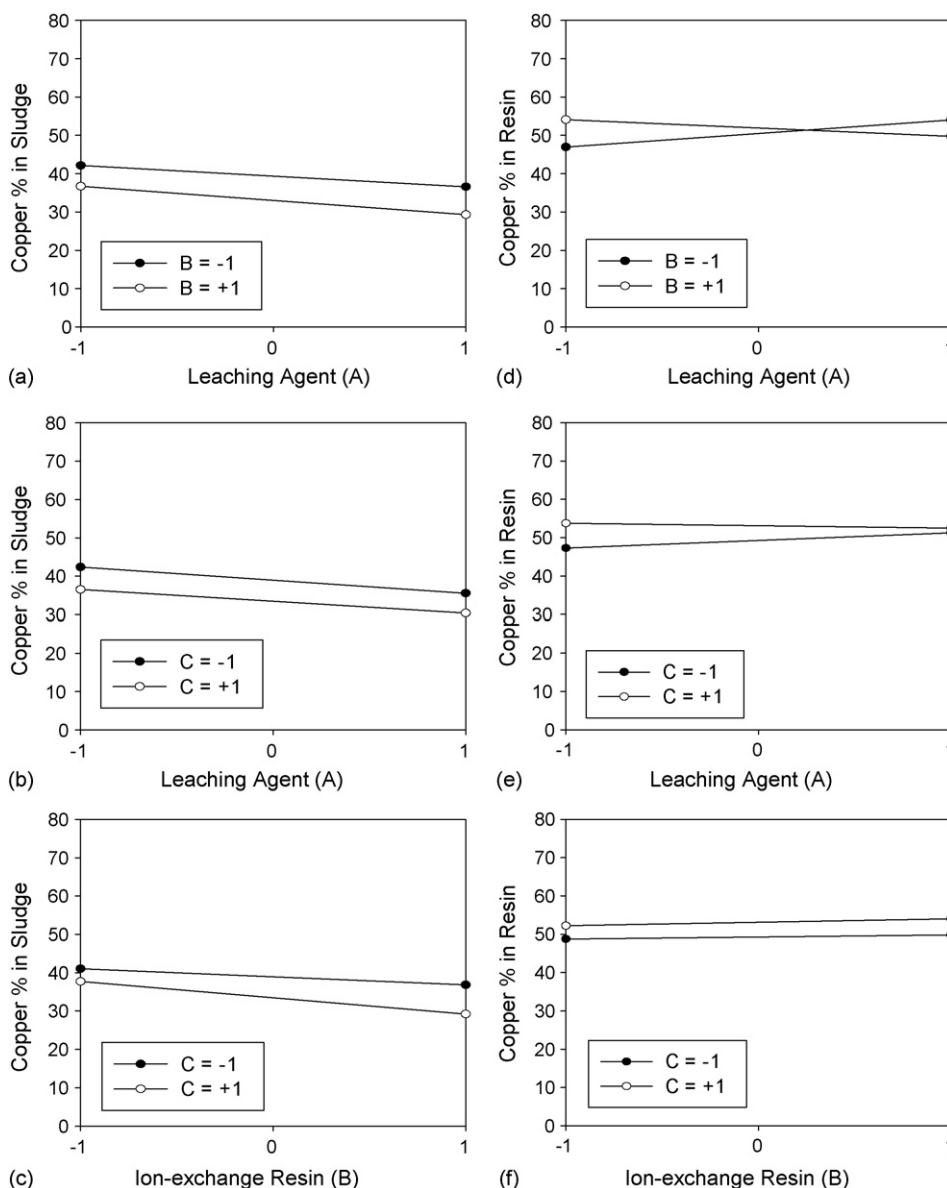
Fig. 3. Interaction plots of copper in the sludge and resin phases.

the sludge phase. Fig. 4a–c show that the two-factor interactions for zinc in the sludge are qualitatively similar to those for copper in the sludge as shown in Fig. 3a–c. The F_0 values in Table 6 suggest that the main effect of C, BC interaction, and the three-factor interaction are statistically insignificant for zinc in the resin phase. Comparing Figs. 3d and 4d, the acid–resin interaction effects on zinc in the resin phase are quite different from those on copper in the resin phase. For copper, if a weaker cation exchange resin is used, the copper residue in the resin phase increases with the acid strength as shown by Fig. 3d. For zinc, no matter what types of resins are used, zinc in the resin phases decreases with acid strength as shown by Fig. 4d. A comparison of Figs. 3e and 4e suggests that zinc in the resin phase is more sensitive to the acid strength than copper in the resin phase. Furthermore, at both high and low temperatures, copper in the resin phase slightly increases with the acid strength, but zinc in the resin phase decreases with the acid strength. The discrepancy

may be primarily caused by the different extractability of copper and zinc by different acids from the sludge [29]. Figs. 3f and 4f also show that zinc in the resin phase is more sensitive to the type of resin than copper in the resin phase. The discrepancy may be primarily caused by the different affinity of copper and zinc to the ion-exchange resins.

Table 7 shows the ANOVA analysis for chromium in the sludge and resin phases, respectively. In Table 7, only the main effect B and interaction effect AB represent the higher statistical significance in this case. Although the F_0 values of the main effect A is not statistical significant, it is still important when the AB interaction effect exists in this situation. Therefore we cannot choose to use Amberlite IR-120 to get a lower chromium residue in the sludge just because of a negative β-coefficient of B shown in Table 7. Fig. 5a shows Amberlite IR-718 should be used along with the citric acid while Amberlite IR-120 should be used along with the nitric acid to get a lower chromium
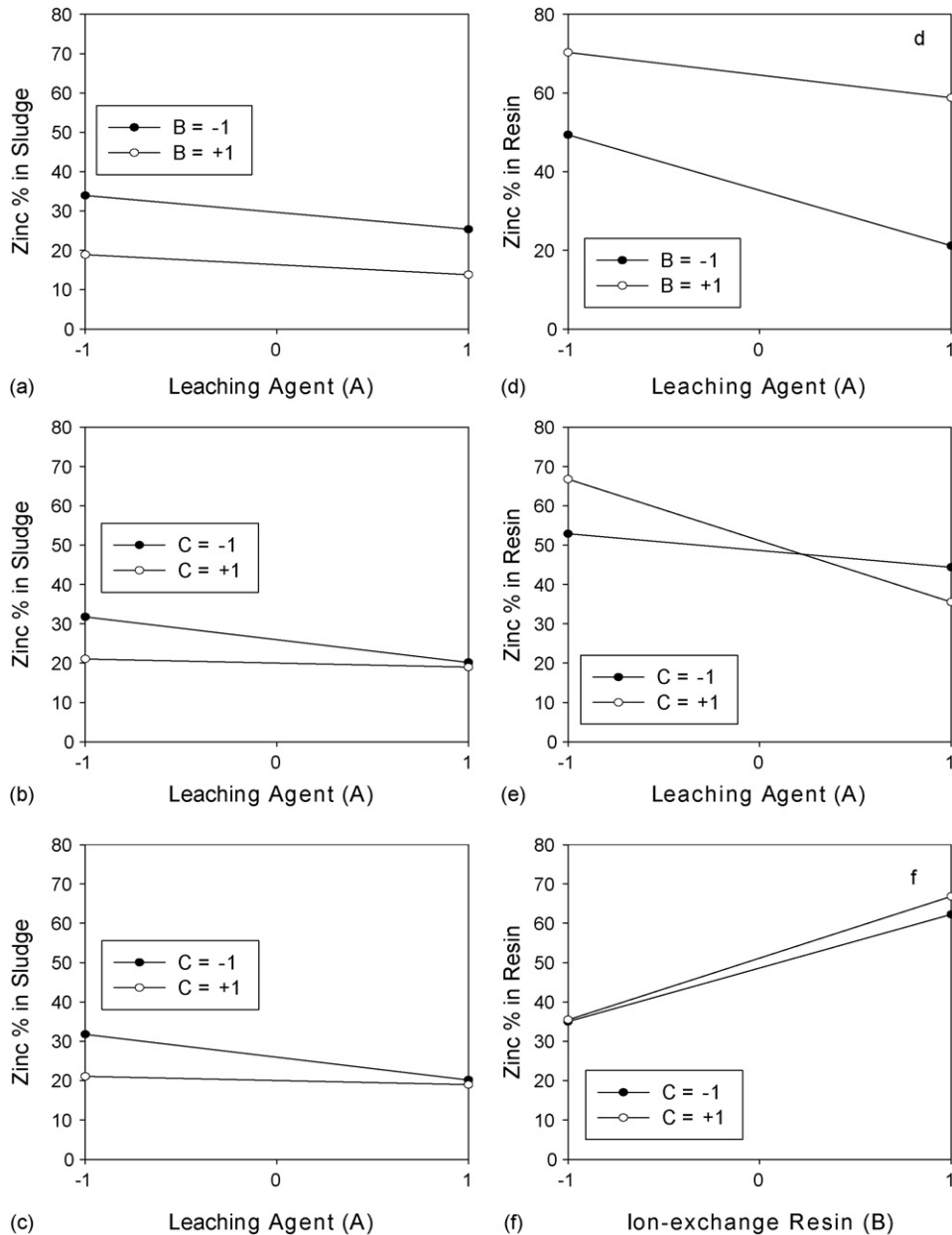
Fig. 4. Interaction plots of zinc in the sludge and resin phases.

residue in the sludge. Fig. 5b and c show that the reaction temperature has little influence on the chromium residue in the sludge.

The F_0 values in Table 7 suggest that all the main effects except for A, two-factor interactions, and even three-factor interaction are statistically significant for chromium in the resin phase. Because of the existence of significant interactions, we cannot choose to use low or high level of the single factors to obtain a higher chromium sorption in the resin phase. A higher heavy metal sorption onto the ion-exchange resin favors recovering the heavy metals by resin regeneration. Fig. 5d shows that the chromium sorption in the resin phase increases with the acid strength if Amberlite IR-120 is used while it decreases with the acid strength if Amberlite IR-718 is used. Similarly, Fig. 5e

shows that the chromium sorption in the resin phase increases with the acid strength at a higher temperature while it decreases with the acid strength at a lower temperature. Fig. 5f shows that the stronger acid favors a higher chromium sorption in the resin phase at both high and low temperatures.

3.4. Regression model of 2^3 designs

The above ANOVA analysis illustrates the effects and interactions of the factors on the heavy metal profiles in the sludge and resin phases respectively. In addition to know these effects and interactions qualitatively, we need quantitative models to predict the heavy metal profiles. For 2^3-factorial design in this study, the complete regression model would contain 7 ($=2^3 - 1$) degrees
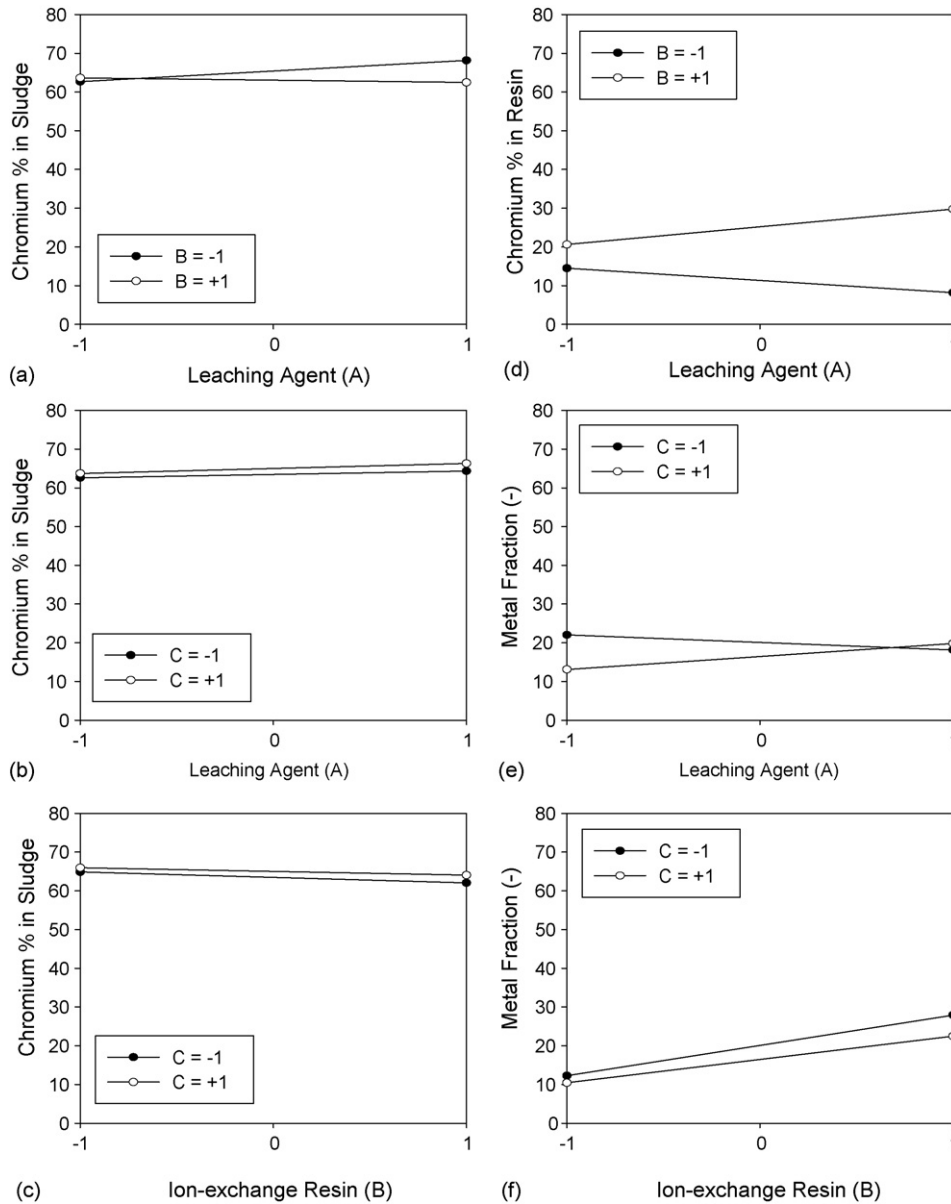
Fig. 5. Interaction plots of chromium in the sludge and resin phases.

of freedom between the eight-treatment combination including main effects and interactions. Three degrees of freedom are associated with the main effects and four degrees of freedom are associated with interaction. The mathematical model of the 2^3-factorial experimental design is as follow [27,28]:

$$\hat{y} = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{123} ABC \tag{5}$$

where A is the coded variable representing the leaching agent, B is the coded variable representing the ion-exchange resin, C is the coded variable representing the reaction temperature; the β's are the regression model coefficients, $\hat{y}$ represents the predicted response value using the regression coefficients and the coded variables. Using the method described in Box et al. [28] or the software of Design Expert (Stat-Ease, USA) to analyze

the results, some coefficients in Eq. (5) are negligible. The final empirical models for the heavy metals in the sludge and resin phases therefore become

$$\hat{y}_{copper,sludge} = 36.193 - 6.470A - 6.352B - 5.490C - 1.140BC \tag{6}$$

$$\hat{y}_{copper,resin} = 51.203 + 1.356A + 1.434B + 3.849C - 3.033AB - 1.409AC \tag{7}$$

$$\hat{y}_{zinc,sludge} = 22.994 - 6.849A - 13.294B - 5.951C + 0.933AB - 1.613BC - 0.698ABC \tag{8}$$

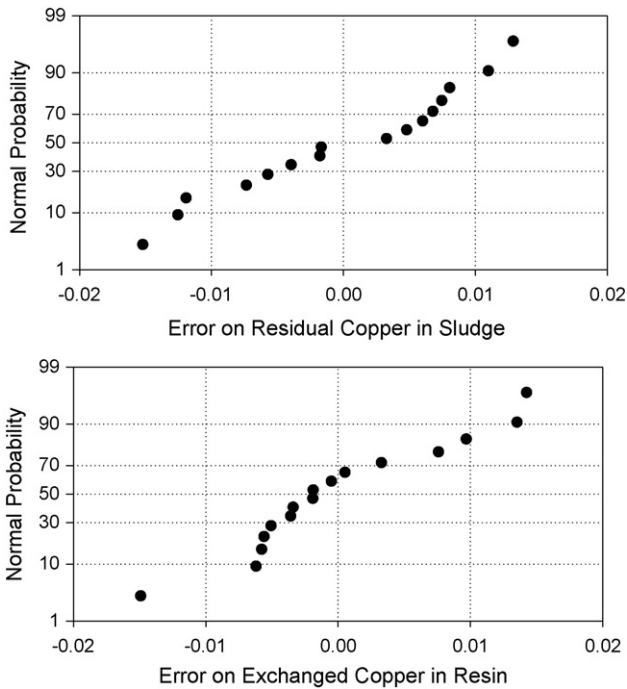$$\hat{y}_{zinc,resin} = 49.894 - 19.86A + 29.275B + 4.44AB - 6.059AC \tag{9}$$
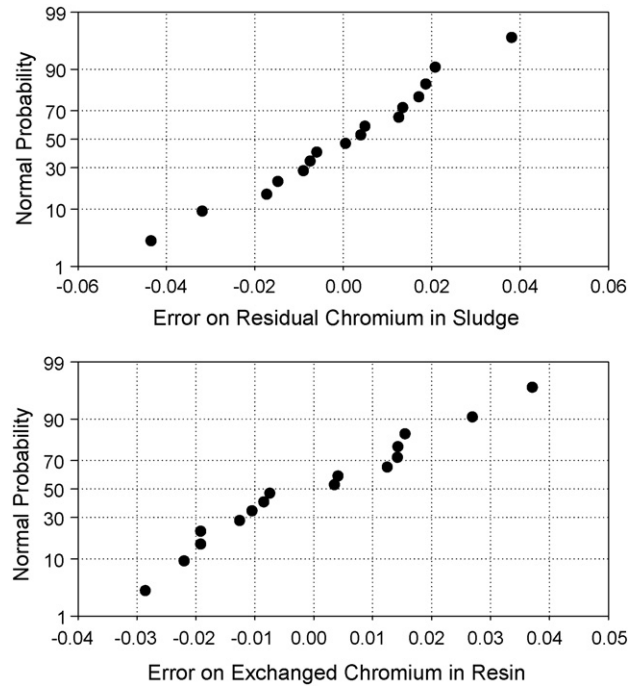
Fig. 6. Normal probability plots of error of copper.

Fig. 8. Normal probability plots of error of chromium.

$$\hat{y}_{\text{chromium,sludge}} = 64.231 + 2.149A - 2.366B - 1.773AB \tag{10}$$

$$\hat{y}_{\text{chromium,resin}} = 18.271 + 13.841B - 3.646C + 4.126AB$$
$$+2.823AC - 0.966BC + 1.154ABC \tag{11}$$

Eqs. (6)–(11) can be used to predict the heavy metal profiles in the sludge and resin phases. Figs. 6–8 show the normal distribution plots of the error predicted by the regression models for copper, zinc, and chromium, respectively. The error distributions along straight lines suggest that the model equations are adequate to predict the heavy metal profiles in the sludge and resin phases.
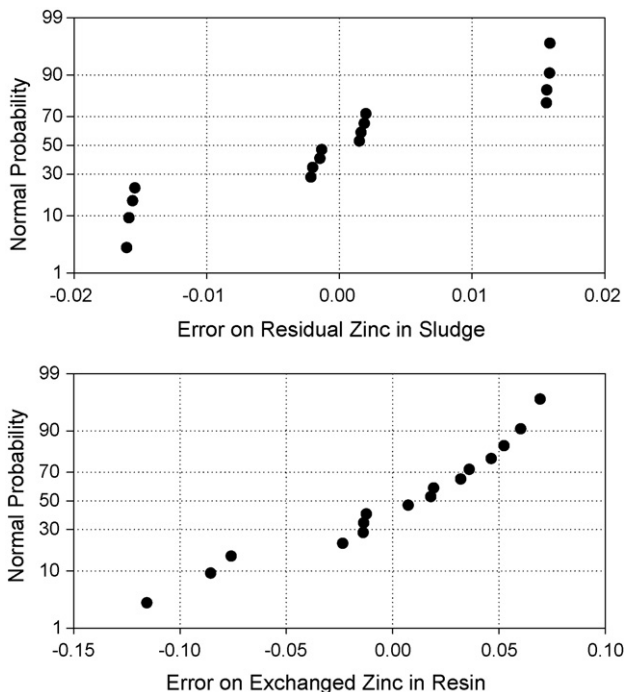
4. Conclusions

A series of full factorial experiments varying the leaching agent, ion-exchange resin, and reaction temperature were performed to study heavy metal removal from sludge. According to the experimental results and statistical analysis, the stronger leaching agent (nitric acid), a stronger cation exchange resin (Amberlite IR-120), and a higher reaction temperature favors a lower heavy metal residue in the sludge phase. After extracting the heavy metals from the sludge particles, the heavy metals in the extraction solution must be adsorbed onto the ion-exchange resin for metal recovery. The DOE results show that the heavy metal sorption onto the resin is strongly influenced by the type of resin and leaching agent–resin interactions. Empirical regression models are obtained and can be practically used to predict the heavy metal profiles in different phases. Although the simple DOE approach helps in understanding the mechanism of heavy metal extraction, the rate-limiting step of the metal recovery remains unknown. The role of the ion-exchange resin on the individual heavy metal sorption equilibrium and kinetics should be studied in more detail in the future to gain better insight of recovering the heavy metals from sludge with ion-exchange resin.

Fig. 7. Normal probability plots of error of zinc.

Acknowledgement

References

[1] V. Wong, G. Ho, Metal speciation and leachability of heavy metals from Enersludge™ ash in concrete, Water Sci. Technol. 41 (2000) 53–60.

[2] P.C. Hsiao, S.L. Lo, Extractability and fractionation of heavy metals in chemically treated sewage sludges, Water Sci. Technol. 44 (2001) 91–94.

[3] J.H. Tay, K.Y. Show, S.Y. Hong, Resource recovery from sludges: innovative applications as civil engineering materials, in: Proceeedings of the IWA Post-Conference, Taipei, Taiwan, 2001.

[4] X.D. Li, C.S. Poon, H. Sun, I.M.C. Lo, D.W. Kirk, Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials, J. Hazard. Mater. 82 (2001) 215–230.

[5] M. Balkan, G. Kocasoy, Industrial sludge solidification by using clinoptilolite, J. Environ. Sci. Health A39 (2004) 951–960.

[6] A.A. Zorpas, Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens, Greece, J. Hazard. Mater. B82 (2001) 291–298.

[7] S. Yoshizaki, T. Tomida, Principle and process of heavy metal removal from sewage sludge, Environ. Sci. Technol. 34 (2000) 1572–1575.

[8] C.H. Wu, C.Y. Kuo, S.L. Lo, Removal of heavy metals from industrial sludge by extraction with different acids, J. Environ. Sci. Health A39 (2004) 2205–2219.

[9] A.H.M. Veeken, H.V.M. Hamelers, Removal of heavy metals from sewage sludge by extraction with organic acids, Water Sci. Technol. 40 (1999) 129–136.

[10] K. Fischer, H.P. Bipp, P. Riemschneider, A. Kettrup, D. Bieniek, Method of decontaminating solid materials contaminated with heavy metals, US Patent, 5,849,567 (1998).

[11] L. Xiang, L.C. Chan, J.W.C. Wong, Removal of heavy metals from anaerobically digested sewage sludge by isolated indigenous iron-oxidizing bacteria, Chemosphere 41 (2000) 283–287.

[12] S.Y. Chen, J.G. Lin, Effect of substrate concentration on bioleaching of metal-contaminated sediment, J. Hazard. Mater. B82 (2001) 77–89.

[13] A.T. Lombardi, O. Garcia Jr., A.A. Mozeto, Bioleaching of metals from anaerobic sewage sludge: effects of total solids, leaching microorganism, and energy source, J. Environ. Sci. Health A36 (2001) 793–806.

[14] M. Chartier, G. Mercier, J.F. Blais, Partitioning of trace metals before and after biological removal of metals from sediments, Water Res. 35 (2001) 1435–1444.

[15] C. Solisio, A. Lodi, F. Veglio, Bioleaching of zinc and aluminium from industrial waste sludges by means of *Thiobacillus ferrooxidans*, Waste Manage. 22 (2002) 667–675.

[16] A.T. Lombardi, O. Garcia Jr., Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by *Thiobacillus ferrooxidans* and its effect on metal partitioning, Water Res. 36 (2002) 3193–3202.

[17] M.R. Jakobsen, J. Fritt-Rasmussen, S. Nielsen, L.M. Ottosen, Electrodialytic removal of cadmium from wastewater sludge, J. Hazard. Mater. B106 (2004) 127–132.

[18] L.M. Ottosen, I.V. Kristensen, A.J. Pedersen, H.K. Hansen, A. Villumsen, A.B. Ribeiro, Electrodialytic removal of heavy metals from different solid waste products, Sep. Sci. Technol. 38 (2003) 1269–1289.

[19] A.J. Pedersen, L.M. Ottosen, A. Villumsen, Electrodialytic removal of heavy metals from different fly ashes influence of heavy metal speciation in the ashes, J. Hazard. Mater. B100 (2003) 65–78.

[20] Q. Gan, A case study of microwave processing of metal hydroxide sediment sludge from printed circuit board manufacturing wash water, Waste Manage. 20 (2000) 695–701.

[21] J.A. Menendez, M. Inguanzo, J.J. Pis, Microwave-induced pyrolysis of sewage sludge, Water Res. 36 (2002) 3261–3264.

[22] P.G.R. de Villiers, J.S.J. Van Deventer, L. Lorenzen, The extraction of species from slurries of insoluble solids with ion-exchange resins, Miner. Eng. 8 (1995) 1309–1326.

[23] M. Ersoz, E. Pehlivan, H.J. Duncan, S. Yildiz, M. Pehlivan, Ion exchange equilibria of heavy metals in aqueous solution on new chelating resins of sporopollenin, React. Polym. 24 (1995) 195–202.

[24] R. Kiefer, W.H. Höll, Sorption of heavy metals onto selective ion-exchange resins with aminophosphonate functional groups, Ind. Eng. Chem. Res. 40 (2001) 4570–4576.

[25] M.H.L. Ribeiro, I.A.C. Ribeiro, Recovery of erythromycin from fermentation broth by adsorption onto neutral and ion-exchange resins, Sep. Purif. Technol. 45 (2005) 232–239.

[26] R.S. Juang, H.C. Kao, W. Chen, Column removal of Ni(II) from synthetic electroplating waste water using a strong-acid resin, Sep. Sci. Technol. 49 (2006) 36–42.

[27] R.H. Myers, D.C. Montgomery, Response Surface Methodology Process and Product Optimization Using Designed Experiments, Wiley, New York, 1995.

[28] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experiments: An Introduction to Design, Data Analysis, and Modeling, Wiley, New York, 1978.

[29] I.H. Lee, Y.J. Wang, J.M. Chern, Extraction kinetics of heavy metal-containing sludge, J. Hazard. Mater. B123 (2005) 112–119.

[30] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.