Extraction kinetics of heavy metal-containing sludge

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Abstract

In order to remove and recover copper, zinc, cadmium, and chromium from the wastewater treatment sludge generated by an electroplating process, the heavy metal extraction kinetics was studied in a batch reactor using two different extraction agents (nitric and citric acid) at constant agitation speed (150 rpm) and solid to liquid ratio (10 g/L), but varying acid concentrations (0.02–0.10N), temperatures (25–85 °C in nitric acid solution, 25–95 °C in citric acid solution), and sludge particle sizes. The shrinking-core model and empirical kinetic model were adopted to analyze the experimental data. Although both models could fit the experimental kinetic data well, the obtained parameters of the shrinking-core model did not show reasonable trends varying with the experimental variables while the empirical model parameters showed significant trends. The experimental and modeling results showed that the metal extraction rates increased with acid concentration, temperature, but decreased with increasing particle size. Nitric acid was found to be more effective than citric acid to extract the heavy metals from the sludge. The extraction activation energies obtained in this study suggested that both a physical diffusion process and a chemical reaction process might play important roles in the overall extraction process.
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1. Introduction

Heavy metal-containing wastewaters are usually treated by the chemical precipitation method. Although this method can efficiently remove heavy metals from wastewaters, it generates a lot of heavy metal sludge that is classified as hazardous industrial wastes and causes disposal problems. Sludge containing organic matter and metals may release harmful heavy metals when it is landfilled and pollute the soil and groundwater [1]. Concern of the pollution caused by heavy metal-contained sludge leads to develop different methods to stabilize the heavy metals. One popular method is to solidify the sludge by cement and other binders [2–8]. The solidified sludge however becomes very bulky and wastes too much landfill space. Another method is to remove the toxic heavy metals from the sludge by various methods,

e.g. ion exchange [9,10], electrochemistry [11], chemistry [12–21], or biology [22–26]. By using adequate chemical or biological methods, a selective removal of heavy metals to make sludge non-hazardous is possible and it is even possible to concentrate, recycle, and reuse the heavy metals [27].

Many wastewater treatment processes in the electronic and metal finishing industries have generated a large quantity of sludge that contains various heavy metals, classified as hazardous industrial waste and unacceptable for disposal without stabilization or detoxification. Although there exist many environmental laws to regulate the disposal of the hazardous industrial waste, effective treatment methods for heavy metal sludge are not available in Taiwan. In order to remove and recover copper, zinc, cadmium, and chromium from the wastewater treatment sludge generated by an electroplating process, a detoxification process is being developed. The detoxification process includes using acid to extract the heavy metals from sludge, followed by removing the extracted heavy metals by ion exchange. In the devel-

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Nomenclature

a_i	correlation parameter defined in Eq. (8)
A_i	pre-exponential factors for metal i defined in Eq. (10) ($\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$)
b_i	correlation parameter defined in Eq. (8)
c_i	correlation parameter defined in Eq. (11)
C_{acid}	acid concentration in the liquid phase ($\text{kmol}\,\text{m}^{-3}$)
C_{HI}	hydrogen ion concentration in the liquid phase ($\text{kmol}\,\text{m}^{-3}$)
$C_{\text{M}i}$	concentration of metal i in the liquid phase at time t ($\text{mol}\,\text{m}^{-3}$)
$C_{i\infty}$	saturation concentration of metal i in the liquid phase ($\text{mol}\,\text{m}^{-3}$)
d_i	correlation parameter defined in Eq. (11)
d_{P}	sludge particle diameter (m)
D_{e}	effective diffusion coefficient of the H^+ ions in the ash layer ($\text{m}^2\,\text{s}^{-1}$)
E_i	extraction activation energy for metal i defined in Eq. (10) ($\text{kJ}\,\text{mol}^{-1}$)
k	model parameter defined in Eq. (6) ($\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$)
k_1	external film mass-transfer coefficient ($\text{m}\,\text{s}^{-1}$)
k_{s}	surface reaction rate coefficient (s^{-1})
n	model parameter defined in Eq. (6)
R	gas constant ($\text{atm}\,\text{m}^3\,\text{mol}^{-1}\,\text{K}^{-1}$)
R_{p}	sludge particle radius (m)
t	extraction time (s)
T	solution temperature (K)
$X_{\text{M}i}$	extracted fraction of metal I

Greek letters

α_i	correlation parameter defined in Eq. (9) ($\text{kmol}\,\text{m}^{-3}$)
β_i	correlation parameter defined in Eq. (9) ($\text{kmol}\,\text{m}^{-3}\,\text{K}^{-1}$)
γ_i	correlation parameter defined in Eq. (12)
δ_i	correlation parameter defined in Eq. (12)
$\rho_{\text{M}i}$	molar density of metal i ($\text{mol}\,\text{m}^{-3}$)
τ_1	external film time constant (s)
τ_2	ash layer time constant (s)
τ_3	surface reaction time constant (s)

opment of the detoxification process, the extraction kinetics of heavy metals from the sludge is essential for reactor design and process optimization. Despite many studies using various methods to remove heavy metals from sludge, a suitable kinetic model for metal extraction is not available. This study therefore aims at developing a phenomenological model to describe the extraction kinetics of heavy metals from the sludge.

2. Extraction kinetics

2.1. Shrinking-core model

In municipal wastewater treatment sludge, heavy metals are mostly retained by extracellular polymeric substance (EPS) [21,28]. Degradation of the EPS was the primary mechanism to facilitate release heavy metals from the sludge. However, the main mechanism for the retention of heavy metals in the chemically precipitated sludge from electroplating factory is the heavy metal presence as hydroxide precipitates. In the presence of acid, the heavy metals retained in the sludge are exchanged by protons and the heavy metal precipitates are solubilized as follows.

$$M(OH)_{z(S)} + z\text{H}^+ \leftrightarrow \text{M}^{z+} + z\text{H}_2\text{O} \tag{1}$$
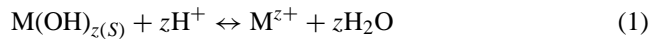
One can imagine that the H^+ ions first diffuse through the film surrounding the sludge particles to the surface of the solid. The H^+ ions further penetrate and diffuse through the blanket of an inert layer, i.e., the metal-depleted layer, to the surface of the unreacted core and react with the heavy metal precipitates. The heavy metal ions then diffuse out off the sludge particle to the surrounding fluid. The extraction kinetics with the above steps can be described by the shrinking-core model [27]. The resistances of the different steps usually vary greatly. One may consider the step with the highest resistance to be the rate-controlling step. For different rate-controlling steps, the conversion-time equations are different. With symbols as defined in the nomenclature, the equations are as follows:

- Film diffusion control:

$$\begin{cases} t = \tau_1 X_{\text{M}i} \\ \tau_1 = \dfrac{2\rho_{\text{M}i}R_{\text{p}}}{3k_1 C_{\text{HI}}} \end{cases} \quad i = 1, 2, \ldots, n \tag{2}$$

- Inert-layer diffusion control:

$$\begin{cases} t = \tau_2[1 - 3(1 - X_{\text{M}i})^{2/3} + 2(1 - X_{\text{M}i})] \\ \tau_2 = \dfrac{\rho_{\text{M}i}R_{\text{p}}^2}{3D_{\text{e}}C_{\text{HI}}} \end{cases}$$
$$i = 1, 2, \ldots, n \tag{3}$$

- Surface reaction control:

$$\begin{cases} t = \tau_3[1 - (1 - X_{\text{M}i})^{1/3}] \\ \tau_3 = \dfrac{2\rho_{\text{M}i}R_{\text{p}}}{k_{\text{s}}C_{\text{HI}}} \end{cases} \quad i = 1, 2, \ldots, n \tag{4}$$

In general, it may not be reasonable to consider that just one step controls throughout the extraction process. To account for the simultaneous action of these resistances one can express the time to reach any stage of extraction fraction as the sum of the times needed if each resistance acted alone:

$$t = \tau_1 X_{\text{M}i} + \tau_2[1 - 3(1 - X_{\text{M}i})^{2/3} + 2(1 - X_{\text{M}i})]$$
$$+ \tau_3[1 - (1 - X_{\text{M}i})^{1/3}] \tag{5}$$

In Eq. (5), the conversion can be expressed as the liquid-phase metal concentration at time t divided by the saturation concentration, i.e., $X_{Mi} = C_{Mi}/C_{i\infty}$. The parameters in the shrinking-core model can be obtained from fitting the experimental C_{Mi} versus t data to Eq. (5).

2.2. Empirical kinetic model

A careful examination of the extraction kinetic data reveals that the heavy metal concentration in the bulk liquid solution initially increases very fast, then slowly approaches a saturation value. This phenomenon suggests that the following empirical model may describe the extraction kinetics adequately:

$$\frac{dC_{Mi}}{dt} = k(C_{i\infty} - C_{Mi})^n \tag{6}$$

where k is the extraction coefficient, n is the reaction order, C_{Mi} and $C_{i\infty}$ are the heavy metal concentration at time t and saturation concentration, respectively. Similar equations with $n = 1$ or 2 have been frequently used in other applications. For example, Covelo et al. [29] used both first-order and second-order models to analyze the adsorption kinetic data of heavy metals by humic umbrisols.

Eq. (6) can be integrated with the initial condition $t = 0$, $C_{Mi} = 0$ as follows:

$$\begin{cases} C_{Mi} = C_{i\infty}\left(1 - e^{-kt}\right) & \text{for} \quad n = 1 \\ C_{Mi} = C_{i\infty} - [C_{i\infty}^{1-n} - k(1-n)t]^{1/(1-n)} \\ \quad\quad \text{for} \quad n \neq 1 \end{cases} \tag{7}$$

Similarly, the model parameters, k, n, and $C_{i\infty}$ can be obtained from fitting the experimental data to Eq. (7).

3. Experimental

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, sludge samples were passed through a series of sieves in order to determine the particle size distribution. Since the $212\,\mu$m particle was the most abundant fraction, we used this particle size for the majority of test runs.

To determine the metal contents in the sludge, 0.1 g of the dry sludge sample was placed inside a microwave transparent vessel filled with 10 mL nitric acid solution in a microwave digestion system (Anton Paar Multiwave 3000). The sample was subjected to a rapid heating with maximum microwave power of 700 W and continuous heating for 15 min. After digestion, the digested solution sample was carefully removed

and the metal concentrations were analyzed by atomic absorption spectroscopy (Varian, model 3000).

In heavy metal extraction experiments, reagent grade nitric acid (Nihon Shyaku Ind. Ltd., Japan) or citric acid (Wako Pure Chemicals Industrial Ltd., Japan) was used to prepare the extraction solution with desired acid concentrations. The extraction solution was first put in a Pyrex-glass jacketed reactor equipped with agitator and heated up to the desired temperature, then the desired weight of the dried sludge with known particle size was placed to start the extraction test runs. At different time intervals, liquid samples were taken and filtered. The filtrate was diluted, if necessary, and analyzed by atomic absorption spectroscopy for heavy metal concentrations.

4. Results and discussion

4.1. Effect of agitation speed

Before studying the effects of other factors that may influence the heavy metal extraction rate, the effect of the agitation speed was firstly studied. Fig. 1 shows the initial extraction rate of copper at different agitation speeds in 0.2N nitric acid solution at $25\,^\circ$C using 10 g/L solid concentration with sludge particle size 53 μm. As is shown in Fig. 1, the external mass-transfer resistance can be neglected for an agitation speed in excess of 150 rpm. Therefore, 150 rpm was used in other experiments (Table 1).
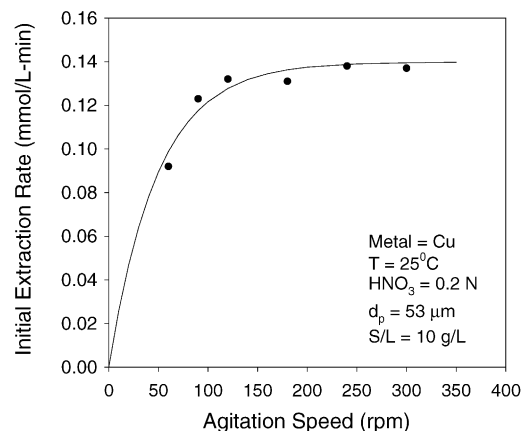

Fig. 1. Effect of agitation speed on copper initial extraction rate.

Table 1
Characteristics and heavy metal composition of sludge

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

[a] Dry solid content.

Table 2
Shrinking-core model parameters of heavy metal extraction at varying nitric acid concentrations and other experimental conditions[a]

[HNO$_3$]	0.02 (*N*)	0.04 (*N*)	0.06 (*N*)	0.08 (*N*)	0.10 (*N*)
Cu					
τ_1 (min)	0	0	0	0	0
τ_2 (min)	58.4	55.6	55.5	52.6	54.9
τ_3 (min)	0	0	0	0	0
$C_{i\infty}$ (mmol/L)	0.310	0.344	0.375	0.410	0.442
Zn					
τ_1 (min)	0	0	0	0	0
τ_2 (min)	80.3	58.1	59.5	54.2	57.3
τ_3 (min)	0	0	0	0	0
$C_{i\infty}$ (mmol/L)	0.300	0.299	0.333	0.331	0.382
Cd					
τ_1 (min)	0	0	0	0	0
τ_2 (min)	59.6	52.1	57.7	51.2	48.5
τ_3 (min)	0	0	0	0	0
$C_{i\infty}$ (mmol/L)	2.67	3.96	4.54	5.75	6.16

[a] $N = 150$ rpm, $d_p = 212$ μm, $T = 25\,^{\circ}$C, sludge/liquid = 10 g/L.

4.2. Effect of nitric acid concentration

The metal extraction kinetics for 212 μm particle size, 10 g/L solid to liquid ratio, at 150 rpm agitation speed and 25 °C with various nitric acid concentrations were experimentally measured. The experimental data were first fitted to Eq. (5) to obtain the model parameters of the shrinking-core model using the nonlinear regression method. The preliminary regression analysis gave very small τ_1 and τ_3 values for all the heavy metals at the different acid concentrations. Such small values are statistically insignificant compared with τ_2. Therefore, τ_1 and τ_3 were assumed to be zero in Eq. (5) and all the experimental data were re-analyzed to give the results shown in Table 2. All the correlation coefficients of the fit exceed 95%, suggesting that the shrinking-core model with the inert layer diffusion being the rate-determining step can be used to fit the metal extraction kinetic data satisfactorily.

The relative magnitude of the inert layer time constant for a constant nitric acid concentration τ_2 is Zn > Cu > Cr as shown in Table 2. Therefore a longer time is required to extract all the zinc contained in the sludge than copper and chromium. In the definition of the inert layer time constant τ_2 as shown in Eq. (3), the sludge particle radius, hydrogen ion diffusion coefficient, and nitric acid concentration are the same for the same test run. The only reasonable explanation for the differ-
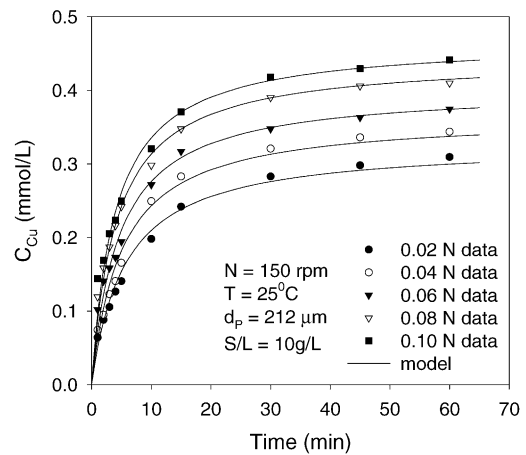

Fig. 2. Effect of nitric acid concentration on copper extraction kinetics.

ence in the inert layer time constant for different heavy metals is that the three heavy metals are not uniformly distributed in the sludge. The smaller τ_2 values for copper and chromium suggest that these two metal hydroxide precipitates should be located in outer layer, whereas zinc hydroxide precipitate is more uniformly distributed.

Although Eq. (5) fits the experimental data well, the variation of τ_2 with respect to the nitric acid concentration cannot reasonably be explained by the shrinking-core model. According to the definition of τ_2, τ_2 should be inversely proportional to the nitric acid concentration for a given heavy metal. But the τ_2 values listed in Table 2 do not show this trend; some τ_2 data at higher acid concentrations are even lower than those at lower acid concentrations. Therefore, the empirical kinetic model, Eq. (7) was used to fit the experimental data. It is interesting to notice that the apparent reaction order, *n* equals 2 for all heavy metals at varying nitric acid concentrations. Table 3 summarizes the parameters of the empirical kinetic model with correlation coefficients in excess of 98%. The extraction kinetics curves of the different heavy metals at varying nitric acid concentrations are in good agreement with the experimental data, as typically shown by Fig. 2 for copper. Although the apparent rate coefficients of the different heavy metals are independent of the nitric acid concentration, they have remarkably different rate coefficients as shown in Table 3. Fig. 3(a) shows that the saturation metal concentrations increase with the nitric acid concentration. The best-fit lines in Fig. 3(a) are calculated by the following correlation

Table 3
Empirical kinetic parameters of heavy metal extraction at varying nitric acid concentrations and given experimental conditions[a]

Concentration (*N*)	Saturation concentration (mmol/L)			Apparent rate coefficient (L/mmol min)			Apparent reaction order		
	Cu	Zn	Cr	Cu	Zn	Cr	Cu	Zn	Cr
0.02	0.328	0.250	3.12	0.54	1.08	0.039	2	2	2
0.04	0.366	0.293	4.52	0.54	1.08	0.039	2	2	2
0.06	0.403	0.321	5.00	0.54	1.08	0.039	2	2	2
0.08	0.444	0.331	6.29	0.54	1.08	0.039	2	2	2
0.10	0.468	0.404	6.55	0.54	1.08	0.039	2	2	2

[a] $N = 150$ rpm, $d_p = 212$ μm, $T = 25\,^{\circ}$C, sludge/liquid = 10 g/L.
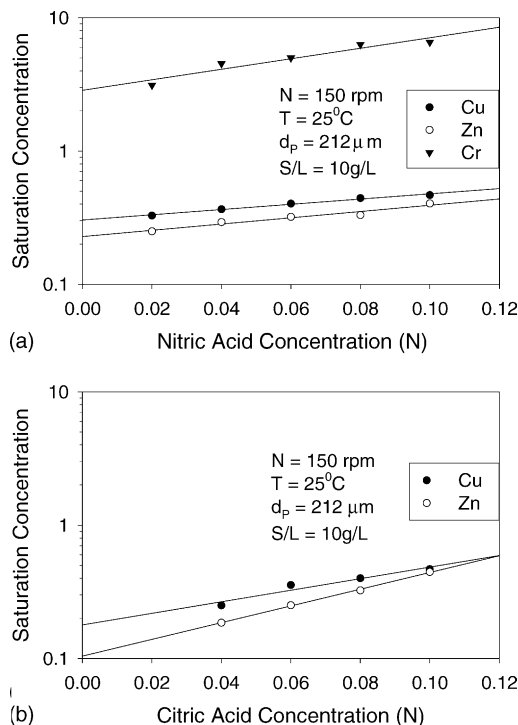
Fig. 3. Effect of acid concentration on heavy metal saturation concentration.

Fig. 4. Comparison of copper extraction kinetics using different acids.

equation:

$$\log C_{i\infty} = a_i + b_i C_{acid} \quad (8)$$

where $a_i = -0.16$, -0.64, and 0.46 and $b_i = 1.96$, 2.35, and 3.94 for copper, zinc, and chromium, respectively.

Unlike the shrinking-core model that cannot give model parameters showing a significant trend, the empirical kinetic model results in model parameters that have good correlations with the nitric acid concentration. Hereafter, we will use the empirical kinetic model to analyze other extraction data.

4.3. Effect of citric acid concentration

Since citric acid is a weaker acid, the ionized hydrogen concentration is actually lower than that in nitric acid for the same molar concentration. For the same acid molar concentration used, the ionized hydrogen concentration equals 100% of the nitric acid concentration, but the ionized hydrogen concentration only equals 1.3–2.1% of the citric acid concentration. Therefore, we can anticipate that the
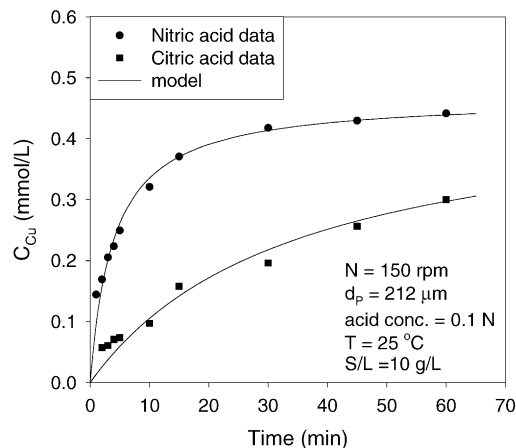
lower hydrogen ion concentration in the citric acid solution has a weaker penetrating capability in the sludge particles to dissolve the heavy metal hydroxide precipitates, particularly at low acid concentration. On the other hand, citrate can form complexes with the heavy metal ions; the formation of metal–citrate complex helps metal solubilization from the sludge. In order to compare the effectiveness of two different acids, additional extraction tests using different citric acid concentrations were also carried out under the same conditions.

Fig. 4 shows a typical comparison of the extraction kinetics using the two different acids. Obviously, the metal extraction rate using nitric acid is higher than using citric acid as we anticipated. All the experimental data were also satisfactorily fitted to Eq. (7) with the model parameters summarized in Table 4. As shown in Table 4, the rate of extraction increases with increasing citric acid concentration. A similar phenomenon was also observed by Veeken and Hamelers [16] who used citric acid to extract heavy metals from sewage sludge. Again, the apparent reaction orders for the different metals equal 2; the apparent rate coefficient for the same metal is independent of the citric acid concentration while the saturation metal concentrations increase with the citric acid concentration as shown in Fig. 3(b). The best-fit lines in Fig. 3(b) are also calculated by Eq. (8) with the parameters $a_i = -0.74$ and -0.98 and $b_i = 4.34$, 6.27 for copper and zinc, respectively.

Table 4
Empirical kinetic parameters of heavy metal extraction at varying citric acid concentrations and given experimental conditions[a]

Concentration (N)	Saturation concentration (mmol/L)		Apparent rate coefficient (L/mmol min)		Apparent reaction order	
	Cu	Zn	Cu	Zn	Cu	Zn
0.04	0.250	0.181	0.062	0.242	2	2
0.06	0.356	0.246	0.062	0.242	2	2
0.08	0.400	0.320	0.062	0.242	2	2
0.10	0.468	0.447	0.062	0.242	2	2

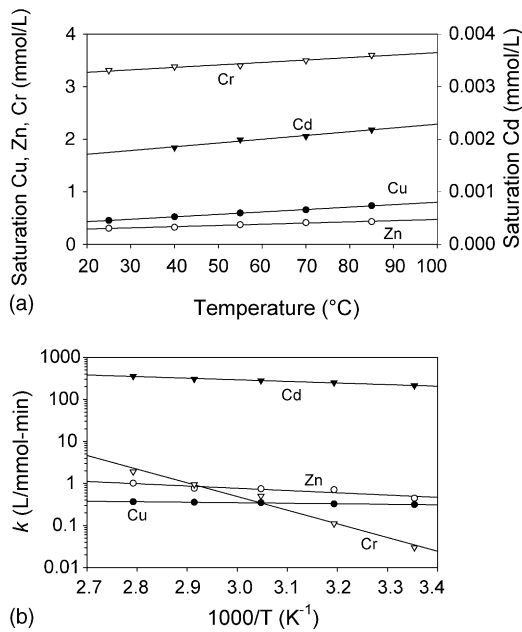[a] $N = 150$ rpm, $d_p = 212\,\mu m$, $T = 25\,°C$, sludge/liquid = 10 g/L.

Fig. 5. Effect of temperature on the heavy metal extraction parameters using nitric acid: $N = 150$ rpm, $d_p = 212 \,\mu$m, acid conc. $= 0.1$N, sludge/liquid $= 10$ g/L.

4.4. Effect of solution temperature

The effect of temperature was investigated using 0.1N nitric acid solutions. The experimental extraction data in a 0.1N nitric acid solution at 25, 40, 55, 70, and 85 °C were also successfully fitted by the empirical kinetic model, Eq. (7) and the obtained model parameters were found to be well correlated with the extraction temperature. It is interesting to find in this series of tests at a higher nitric acid concentration and higher temperatures that the cadmium concentrations are high enough to be detected. Nevertheless, the cadmium concentration is still much lower than the other metals. Fig. 5(a) shows that the saturation metal concentrations increase linearly with the extraction temperature.

$$C_{i\infty} = \alpha_i + \beta_i T \tag{9}$$

where the correlation parameters α_i for copper, zinc, cadmium, and chromium are 0.341, 0.245, 3.181, and 0.0016 mmol/L, respectively; the correlation parameters β_i for copper, zinc, cadmium, and chromium are 0.0046, 0.0023, 0.0047, and 7.17×10^{-6} mmol/L °C, respectively. The increase of the metal saturation concentration with the extraction temperature might be due to thermodynamic equilibria since solid solubilities generally increase with temperature [30].

Fig. 5(b) shows that the apparent rate coefficients increase with the extraction temperature and the correlation can be expressed as:
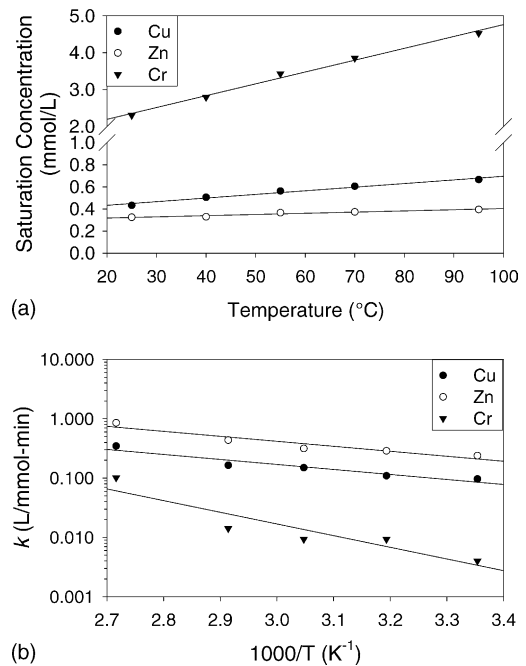
$$k = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{10}$$

Fig. 6. Effect of temperature on the heavy metal extraction parameters using citric acid: $N = 150$ rpm, $d_p = 212 \,\mu$m, acid conc. $= 0.1$N, sludge/liquid $= 10$ g/L.

where the pre-exponential factors A_i for copper, zinc, cadmium, and chromium are 0.811, 26.0, 4142, and 2.06×10^7 L/mmol min, respectively; the extraction activation energies for copper, zinc, cadmium, and chromium are 2.34, 9.75, 7.35, and 48.2 kJ/mol, respectively. In general, the activation energy of a physical process is less than 20 kJ/mol while that of a chemical process exceeds 40 kJ/mol. The lower activation energies for copper, zinc, and cadmium extraction suggests that the extraction rates might be controlled by a diffusion process while the higher value for chromium suggests that the rate might be controlled by chemical reaction.

Another series of sludge extractions in 0.1N citric acid solutions were performed at different temperatures 25, 40, 55, 70, 95 °C, respectively. Similarly, all the experimental extraction data were also successfully fitted by the empirical kinetic model with the apparent reaction order n being equal to 2 for all the different metals. The metal saturation concentrations and the apparent rate coefficient also increase with the extraction temperature as shown by Fig. 6(a) and (b), respectively. The extraction rates of Cu and Zn from sewage sludge by citric acid were also found to increase with increasing temperature [16]. Fig. 6(a) shows that the linear correlation of Eq. (9) is also applicable to this series of experiments with the correlation parameters α_i for copper, zinc, and chromium are 0.367, 0.297, and 1.552 mmol/L, respectively; the correlation parameters β_i for copper, zinc, and chromium are 0.0033, 0.00113, and 0.032 mmol/L °C, respectively. It is important to note that the cadmium concentration is so low that it cannot be detected in this series of experiments. This
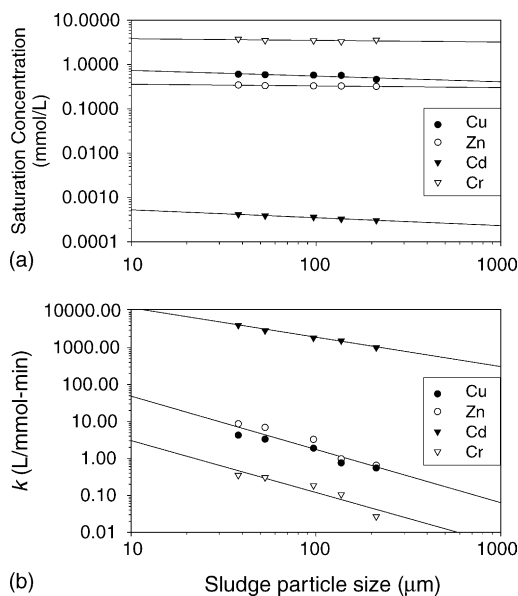
(a)

(b)

Fig. 7. Effect of sludge particle size on saturation extraction concentrations of heavy metals by nitric acid: $N = 150$ rpm, $T = 25\,°C$, nitric acid conc. $= 0.1$N, sludge/liquid $= 10$ g/L.

is because the citric acid is relatively weak compared with the nitric acid at the same concentration.

Eq. (10) was also used to satisfactorily correlate the apparent rate coefficients for the different metals with temperature, as shown in Fig. 6(b). The correlation parameters A_i for copper, zinc, and chromium are 257, 677, and 8.66×10^6 L/mmol min, respectively; the extraction activation energies for copper, zinc, and chromium are 20.4, 20.6, and 56.0 kJ/mol, respectively. The higher activation energies using citric acid instead of using nitric acid agree with the fact that citric acid is a weaker acid so that it has a weaker penetration capability within the sludge particles to solubilize the heavy metals.

4.5. Effect of sludge particle size

A series of extraction experiments in 0.1N nitric acid solutions were conducted at constant 150 rpm agitation speed, constant 25 °C temperature, constant 10 g/L solid to liquid, but varying sludge particle sizes. The experimental extraction data were also satisfactorily fitted by the empirical kinetic model, Eq. (7) with the apparent reaction order n being equal to 2. Fig. 7(a) shows that the metal saturation concentrations slightly increase with decreasing sludge particle size. A decrease in the amount of Zn and Cu leached from Municipal sewage sludge was also observed with increasing particle size [15]. The fitted lines in Fig. 7(a) can be expressed as:

$$C_{i\infty} = c_i d_p^{d_i} \tag{11}$$

where the correlation parameters are $c_i = 0.993$, 0.393, 7.91×10^{-4}, and 4.16 for copper, zinc, cadmium, and chromium, respectively; $d_i = -0.13$, -0.038, -0.18, and

-0.036, respectively. Note that the units used in Eq. (11) are mmol/L for $C_{i\infty}$ and μm for d_p.

Fig. 7(b) shows that the apparent rate coefficients are more significantly affected by the sludge particle size. The particle-size dependencies of the apparent rate coefficients for copper and zinc are very similar and all data of copper and zinc are grouped to be correlated by the following equation:

$$k = \gamma_i d_p^{\delta_i} \tag{12}$$

The correlation parameters in Eq. (12) are $\gamma_i = 1338$ for copper and zinc; 66,399 for cadmium; and 77.2 for chromium, respectively and $\delta_i = -1.44$ for copper and zinc, -0.78 for cadmium, and -1.40 for chromium, respectively. In general, the apparent rate coefficient in solid–liquid extractions is proportional to the total surface. For the extraction experiments with the same solid to liquid ratio, the test run with a smaller sludge particle size is in agreement with the fact that smaller particles have a greater total surface area available for extraction; thus the apparent rate coefficient increases with decreasing particle size.

All the experimental data with different sludge particles were also analyzed by the shrinking-core model and the inert-layer diffusion was found to be the rate-controlling step. But, the obtained inert layer time constant, τ_2 was not proportional to the square of the particle size, as show by Eq. (3). Although the extraction activation energies obtained suggest that the diffusion process plays an important role in the sludge extraction experiments, applying the shrinking-core model to fit the experimental data does not result in model parameters with significant trends that vary with the operating variables such as acid concentration and particle size. On the other hand, the empirical kinetic model successfully fits the experimental data and the model parameters show reasonable trends with the operating variables.

5. Conclusions

The heavy metal extraction kinetics of wastewater treatment sludge generated from an electroplating process was studied in nitric and citric acid solutions at a constant solid to liquid ratio. Preliminary tests showed that the agitation speed had no influence on the extraction rates for agitation speeds in excess of 150 rpm. The experimental results also showed that nitric acid was more effective than citric acid at the same acid concentration to extract the heavy metals from the sludge. All the experimental data were fitted to the shrinking-core model with the rate-controlling step being the diffusion of the acid through the inert layer. Although the results of data fitting were acceptable, the obtained inert-layer time constants did not show reasonable trends that vary with the acid concentration, temperature, and particle size. An empirical kinetic model was developed in this study to successfully fit all the experimental data. For copper, zinc, cadmium, and chromium, the apparent reaction order equal 2 at varying

acid concentrations, temperatures, and particle sizes. The saturation metal concentrations were found to increase with the acid concentration and the extraction temperature, but decrease with the particle size. The apparent rate coefficients were found to be independent of the acid concentration but increase with the extraction temperature and decrease with the particle size. According to the extraction activation energies obtained in this study, both physical diffusion and chemical reaction play important roles in the overall extraction process. The detailed extraction mechanism, involving both physical and chemical processes, needs to be future investigated.

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