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Regeneration of cobalt-contaminated activated carbon by supercritical carbon dioxide extraction

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Abstract A mixture of Di-(2-ethylhexyl) phosphoric acid (D2EPHA) and n-hexane or methanol is used as the extractant solution for extracting cobalt from activated carbon using supercritical carbon dioxide extraction technology. In this work, a semi-continuous pilot unit of SFE is employed to conduct the extraction. In order to feed the viscous extractant by HPLC pump, n-hexane or methanol is added as a diluent to reduce the viscosity of the extractant. The amount of cobalt removed along the time course of the extraction is recorded and plotted as an extraction curve. A kinetic model is also established and fit to the extraction curve, and the obtained parameters of the model are used to explain the regeneration mechanism. The effects of temperature ranged from 40 to 80 °C and the effect of the concentration of diluents on the extraction are investigated and discussed based on the established model. It is also found that the removal of cobalt ions reaches a maximum; this varies with the operational conditions and is known as maximum removal efficiency. It is presumed that the maximum removal efficiency is affected by the adsorption kinetics of the extractant and the rate of ion exchange between the extractant and metal ions on the surface of the activated carbon. After increasing the extraction temperature from 60 to 80 °C it is observed that the maximum removal efficiency is greatly increased, presumably resulting from the diminishing competitive adsorption between the extractant and diluents. The established model can help to reveal the extraction mechanism and to promote maximum removal efficiency for regenerating activated carbon without secondary pollution.

Keywords Supercritical carbon dioxide · Activated carbon · Metal extraction · Regeneration · Acid extractant

1 Introduction

Activated carbon is widely applied in wastewater treatment because of its high efficiency and easy regeneration. However, activated carbon is seldom regenerated in a nuclear power plant because the radioactive metal will dissolve into the washing liquid and create secondary pollution. Supercritical fluids have been widely applied to extract metal from aqueous solutions or from a solid matrix using various extractants (Wai and Wang 1997; Smart et al. 1977; Meguro et al. 1998; Dehghani et al. 1996; Joung et al. 1999; Laintz and Wai 1991). Metal extraction by supercritical carbon dioxide avoids using inorganic acid to dissolve metal ions from the solid phase. This can simplify downstream treatment for the separation of radioactive materials. Radioactive metal compounds, diluents and extractants can be easily collected and concentrated by precipitation, and carbon dioxide can be instantly recycled by vaporization. After using supercritical carbon dioxide for cleaning, decontaminated activated carbon can possibly be treated as normal waste or reused for wastewater. This is an environmentally benign decontamination process for an operating nuclear power plant. The application of supercritical carbon dioxide to regenerate activated carbon can further prolong the lifetime of activated carbon and reduce the total volume of nuclear waste.

The authors have used a lab scale setup and found that D2EHPA (Di-(2-ethylhexyl)Di-(2-ethylhexyl) phosphoric acid) in supercritical carbon dioxide can effectively extract cobalt from soil, activated carbon and perlite (Liang et al. 2011). D2EHPA is an acidic extractant widely used in the

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hydrometallurgical industry to extract and separate metals. The acid extractant is decomposed into a hydrogen ion and an ionic ligand in an aqueous phase, followed by complexing with metal ions in an aqueous phase. In the lipophilic phase, D2EHPA can directly coordinate with metal ions through ion exchange to form a coordinated complex. To investigate the mechanism and its feasibility of scaling up, in this study, the extraction of cobalt from activated carbon is conducted by a pilot SFE (supercritical fluid extraction) unit. The amount of extracted metal is monitored by periodically collecting samples from the separator in the pilot unit. Using information detailing how the extracted amount of cobalt varies over time, an extraction curve is obtained. Mechanisms and kinetic models are proposed and affirmed by curve fitting. The established model can provide useful information for studying the extraction mechanism and scale-up design.

In modeling, supercritical fluid extraction is a semi-continuous process and the assumption of a steady state is seldom met (Clifford et al. 2001). Literature and published models normally divide the extraction into several stages (Sovová 2005). The mechanism of metal extraction from solids involves a more complicated mechanism (Chen et al. 2011; Wadsworth 1979). Unlike traditional hydrometallurgy based on solvent extraction from the aqueous phase, the acidic extractant, D2EHPA, does not dissociate before the formation of a coordination complex on the surface of the activated carbon. It is assumed that metal adsorbs into the activated carbon and forms a coordination complex with D2EHPA through ion exchange. However, prior to the ion exchange, the D2EHPA in the supercritical fluid has to be adsorbed and diffused to the absorbed metal ions. After formation of the coordination complex, H^+ will remain on the surface because supercritical carbon dioxide does not dissolve ions, and the coordination complex will directly and rapidly be dissolved and removed from the surface by the supercritical carbon dioxide. The accumulation of H^+ on the surface will enhance the backward reaction and finally reach equilibrium. Based upon this assumption, both an extraction mechanism and a model derived to fit the extraction curves are proposed here.

2 Experiments and apparatus

Activated carbon, ranging from 20∼40 mesh, is currently used in the 2nd nuclear power plant in Taiwan. The apparent density is about 0.5 g/ml. One kilogram of activated carbon is soaked in five liters of cobalt nitrite solution (30,000 ppm) for two days. The presoaked activated carbon is filtrated and dried in an oven until the water content is below 3 wt%. Three hundred grams of the dried activated carbon is loaded into a basket for extraction. The basket is 10.2 cm in diameter and 11.3 cm in height, and is designed to fit the extractor so that the carbon dioxide can flow directly through to extract the metal ions.

Before conducting the experiments, several extractants were tested by the ISCO SFE system. Compared with TTA (thenoyltrifluoroacetone), TBP (tributyl phosphate), AA (acetylacetone) and CMPO (Octyl(phenyl)-N,N-diisobutylmethylcarbamoyl phosphine oxide), D2EHPA is the most effective extractant available at a reasonable price. It was also found that adding n-hexane or methanol can significantly improve the extraction. Therefore, in this study an extractant solution was prepared by mixing D2EHPA and hexane or methanol in various ratios.

Figure 1 illustrates the process flow of a supercritical fluid extraction unit. Supercritical carbon dioxide and an extractant solution are mixed and preheated by circulating hot water. This flows into the extractor where the metal is removed. The flow rate of carbon dioxide in this study is set as 60 g/min and is controlled by a Coriollis Flow Meter installed after the separator. The temperature of the extractor and separator are controlled by individual electric heaters. The pressure of the extractor is controlled by a back pressure regulator, and the pressure of the separator is dependent upon the temperature of the working tank, normally ranging from 38∼50 bars at extraction. A HPLC pump is used to feed and meter the extractant solution, which is a liquid mixture of extractants and diluents. The time course of the experiment starts as the HPLC pump begins to feed the extraction solution. Metal ions on the solid surface begin to react with the extractant to form a coordinated complex and dissolve into the supercritical fluid. The coordinated complex, and the unreacted extractant and diluents in the supercritical carbon dioxide, are precipitated in the separator by pressure reduction. In the separator, carbon dioxide is recycled and the precipitated liquid is periodically collected by evacuating the separator by opening the valve at the bottom of the separator.

If hexane is used as a diluent, cobalt in the collected liquid effluent is backwashed by ten times the volume of HNO_3 solution with a concentration of 1.472 M. When used as a diluent, methanol is replaced by hexane through vacuum drying followed by adding equal amounts of hexane. The mixture is then subjected to ultrasonic mixing for 30 min. After settling and decantation, the nitric acid in the bottom is ready for ICP-OES (Inductively Coupled Plasma–Optical Emission Spectrometer) analysis. The amount of cobalt in the collected liquid effluent is then evaluated to determine the amount of cobalt that has been removed from the activated carbon during the collection time interval. Variations in the amount of extracted cobalt accumulating over a period of time are calculated and plotted as an extraction curve. Later, the extraction curve is fitted to the established model.

In order to calculate the concentration of extractant and diluents in supercritical fluid, the composition of the supercritical fluids should first be evaluated. Since the HPLC

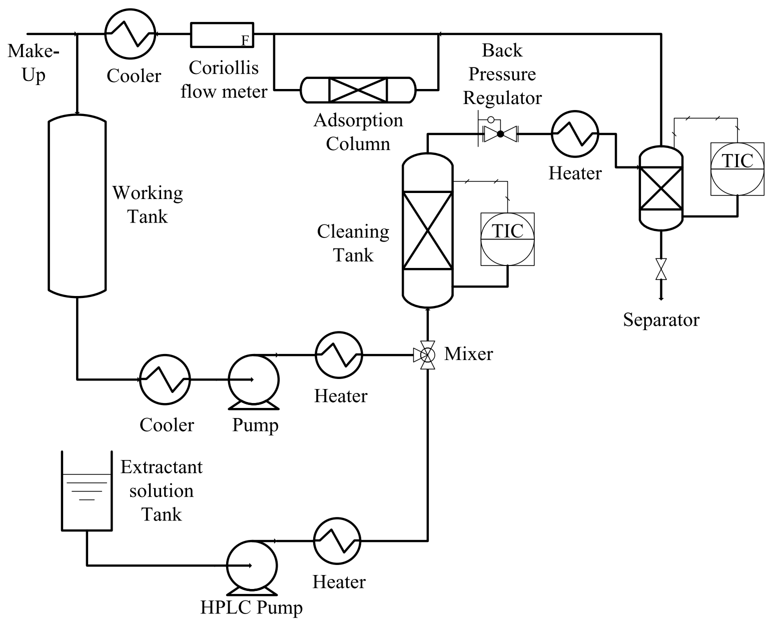

Fig. 1 Illustration of the pilot unit

Table 1 Operating conditions for extraction experiments

No	*P* (bar)	*T* (°C)	*F* (ml/min)	*r*	M_o (mg)	*V* (L/mol)	[HA] (mol/L)	[HX] (mol/L)	Diluents
3	339.9	82.2	6.1	3	1769	0.05280	0.06675	1.4474	Methanol
4	339.9	82.8	9.15	3	1915	0.05180	0.09831	2.1314	Methanol
5	341.5	82.2	12.2	3	1948	0.05098	0.12847	2.7853	Methanol
7	346.0	82.4	9.15	10	1591	0.05771	0.03463	0.7744	Hexane
8	349.7	59.8	9.15	10	1381	0.05293	0.03775	0.8442	Hexane
9	347.7	82.6	9.15	30	1320	0.05786	0.01221	0.8189	Hexane
10	349.0	59.8	9.15	3	1299	0.05312	0.01330	0.8920	Hexane
11	346.9	83.3	12.2	3	2074	0.05795	0.12620	0.8467	Hexane
12	348.5	40.3	9.15	3	1694	0.04840	0.11484	0.7698	Hexane
13	348.3	60.2	9.15	3	1733	0.05244	0.10590	0.7105	Hexane
14	348.3	83.1	9.15	3	1522	0.05730	0.09690	0.6501	Hexane
15	347.8	40.5	9.15	10	1063	0.04897	0.04081	0.9126	Hexane
16	347.0	40.0	9.15	30	1034	0.04917	0.01436	0.9630	Hexane

F: the flow rate of the mixture of hexane and D2EHPA (ml/min)

r: the volume ratio of diluents to D2EHPA

M_o: the total loading of cobalt

V: the molar volume of the supercritical fluid in the extractor (L/mole)

[HA]: the concentration of D2EHPA on extraction

[HX]: the concentration of diluents on extraction

feeds the liquid mixture of D2EHPA and diluents, and is metered by volumetric flow rate, the density of the liquid mixture must be accurately measured to calculate the mass flow rate of the D2EHPA and diluents. The liquid density of the mixture of hexane and D2EHPA is found in the literature (Biswas et al. 2003), and that of methanol and D2EHPA is measured by a density gauge. Once the mass flow rates of carbon dioxide, D2EHPA and diluents are calculated, the composition of the supercritical fluid phase is clearly defined, and the molar volume of the fluid phase inside the extractor can be calculated by the Peng-Robinson EOS (Equation of State). Because the content of D2EHPA in the supercritical fluid phase is usually less than 0.3 mol%, the molar volume of the supercritical solution, *V*, at the extracting temperature and pressure is simply calculated by the Peng-Robinson EOS without considering the contribution of D2EHPA. The concentrations of extractant and diluents are then calculated by dividing their molar fraction by the calculated molar volume. Table 1 lists the calculated concentrations of diluents and D2EHPA used in this study.

3 Kinetics of the reactive extraction

Once the extractant is adsorbed onto the activated carbon and remains in equilibrium with the fluid phase, the adsorption equilibrium can be expressed as:

$$HA^f \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} HA^s, \qquad K_1 = \frac{k_1}{k_1'} = \frac{[HA^s]}{[HA^f]}, \tag{1}$$

where HA is the extractant, superscripts s and f represent the solid and fluid phases respectively, the brackets represent the concentration, k_1 and k_1' are the rate constants for adsorption and desorption, and K_1 is the equilibrium constant of the adsorption, which is also called the Henry's constant for the adsorption if it is a constant. On the surface of the activated carbon, the extractant is expected to diffuse to the active site where the metal ions are already adsorbed. The surface diffusion of the extractants can be expressed as:

$$HA^s \xrightarrow{k_m} HA^*, \qquad \frac{d[HA^*]}{dt} = k_m\big([HA^s] - [HA^*]\big), \tag{2}$$

where the superscript $*$ represents the active sites, and k_m is the diffusion coefficient of the extractant on the surface. If HA^s is always in equilibrium with that in the fluid phase, Eq. (2) can be rewritten as:

$$\frac{d[HA^*]}{dt} + k_m[HA^*] = k_m K_1[HA^f]; \quad t = 0, \ [HA^*] = 0. \tag{3}$$

Solving the differential equation gives:

$$[HA^*] = K_1[HA^f]\big(1 - \exp(-k_m t)\big). \tag{4}$$

If the surface diffusion in Eqs. (2)–(4) is negligible, the diffusion coefficient k_m approaches an infinite number.

After reaching the active site, the extractant will react with the adsorbed metal ions through ion exchange. The ion exchange reaction can be expressed as:

$$nHA^* + M^{n+} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} MA_n^* + nH^+. \tag{5}$$

According to the mass conservation, the change in metal ion concentration is given by:

$$\frac{d[M^{n+}]}{dt} = -k_2[M^{n+}][HA^*]^n + k_2'[MA_n^*][H^+]^n \tag{6}$$

where M^{n+} and MA_n^* represent the metal ion and its coordinated complex, n is the number of valence electrons of the metal ion; k_2 and k_2' are the rate constants of the forward and backward reactions for the ion exchange, respectively. Because both M^{n+} and H^+ are highly charged species, they are not dissolvable in the fluid phase and will always remain on the surface; therefore, the superscripts of s and $*$ for the charged species are neglected for simplicity.

After formation of the coordinated complex, desorption of the complex can be expressed as:

$$MA_n^* \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} MA_n^f, \qquad K_3 = \frac{k_3}{k_3'} = \frac{[MA_n^f]}{[MA_n^*]} \tag{7}$$

where k_3 and k_3' are the rate constants of the desorption and adsorption for the coordinated complex, respectively, and K_3 is the equilibrium constant, which is the reciprocal of Henry's Constant for the coordinated complex. Because they are also not soluble in the fluid phase, the hydrogen ions released from the ion exchange will remain on the surface. Since all charged species always remain on the surface during extraction, the total charge on the surface will remain constant:

$$\big([M^{n+}] + [H^+]\big)F = C_T \tag{8}$$

where F is the Faraday Constant, and C_T is the total charge on the surface, which is equal to the initial concentration of cobalt ions times the number of valence electrons.

In the case of $n = 2$, and replacing $[H^+]$ and $[HA^*]$ by Eqs. (8) and (4), Eq. (6) can be rewritten as:

$$\begin{aligned}\frac{d[M^{2+}]}{dt} &= -k\big(K_1[HA^f]\big(1 - \exp(-k_m t)\big)\big)^2[M^{2+}] \\ &\quad + k_2'\frac{[MA_2^f]}{K_3}\left(\frac{C_T}{F} - 2[M^{2+}]\right)^2.\end{aligned} \tag{9}$$

With $[M^{2+}] = C_T/2F = [M^{2+}]_0$ at $t = 0$, the differential equation is rewritten as:

$$\begin{aligned}\frac{d[M^{2+}]}{dt} &= -k\big(K_1[HA^f]\big(1 - \exp(-k_m t)\big)\big)^2[M^{2+}] \\ &\quad + 4k_2'\frac{[MA_2^f]}{K_3}\big([M^{2+}]_0 - [M^{2+}]\big)^2.\end{aligned} \tag{10}$$

Once the extraction reaches its maximum removal efficiency, $d[M^{2+}]/dt = 0$, and the exponential term is ignored because of the great amount of time required, the maximum of extraction should satisfy:

$$\begin{aligned}\frac{([M^{2+}]_0 - [M^{2+}]_m)^2}{[M^{2+}]_m} &= \frac{[M^{2+}]_0 R_m^2}{1 - R_m} = \frac{k_2 K_3 (K_1[HA^f])^2}{4k_2'[MA_2^f]} \\ &= \beta_m[HA^f]^2\end{aligned} \tag{11}$$

where R_m represents the maximum value of removal efficiency. The removal efficiency is defined as:

$$R = 1 - \frac{[M^{2+}]}{[M^{2+}]_0}. \tag{12}$$

Substituting Eq. (11) into Eq. (10) gives:

$$\frac{d[M^{2+}]}{dt} = -k_2K_1^2\left\{[M^{2+}][HA^f]^2\left(1-\exp(-k_m t)\right)^2 + \frac{[M^{2+}]_0}{\beta_m}\left([M^{2+}]_0 - [M^{2+}]\right)^2\right\}. \qquad (13)$$

The nonlinear differential equation can then be solved by the Finite Difference Method. β_m in Eqs. (11) and (13) is related to the rate equilibrium between the forward and backward reactions, but not to the equilibrium constant of the ion exchange. In this study, this will be referred to as the maximum extraction constant.

Assuming that diffusion on the surface is a fast process, and the adsorption of extractant is a slow process, the rate of extraction is dominated by adsorption kinetics rather than by surface diffusion. If pseudo-first order adsorption is applied, the surface concentration of extractant (Febrianto et al. 2009; Vijayaraghavan et al. 2006; McKay et al. 1999) is expressed as:

$$[HA^s] = \begin{cases} \frac{c[HA^f]}{1+a[HA^f]+b[HX^f]}[1-\exp(-k_{ad}t)] & \text{Langmuir} \\ K_1[HA^f][1-\exp(-k_{ad}t)] & \text{Linear} \end{cases} \qquad (14)$$

where k_{ad} is the adsorption rate constant and a, b and c are parameters for the Langmuir Isotherms. If adsorption kinetics is the determining step and surface diffusion is the slow step, the rate equation expressed by Eq. (14) remains the same but k_m is replaced by k_{ad}. Therefore, Eq. (14) can be used to fit either the surface diffusion control or the adsorption kinetics control. If Langmuir Adsorption with competition is considered, Eq. (13) can be rewritten as:

$$\frac{d[M^{2+}]}{dt} = -k_2c^2\left\{[M^{2+}]\left(\frac{[HA^f]}{1+a[HA^f]+g[HA^f]}\right)^2 \times \left(1-\exp(-k_m t)\right)^2 + \frac{[M^{2+}]_0}{\beta_m}\left([M^{2+}]_0 - [M^{2+}]\right)^2\right\}. \qquad (15)$$

4 Results and discussion

4.1 Curve fitting of the extraction curves

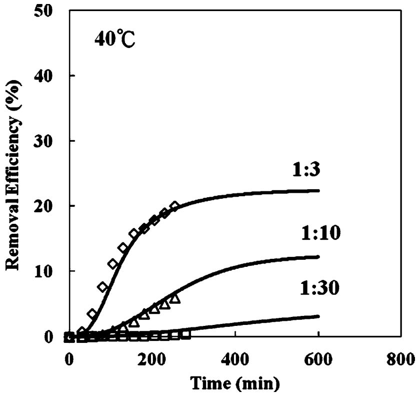

Fig. 2 Curve fitting at 40 °C with hexane as the diluent

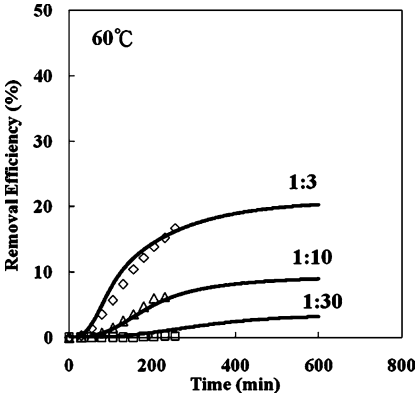

Fig. 3 Curve fitting at 60 °C with hexane as the diluent

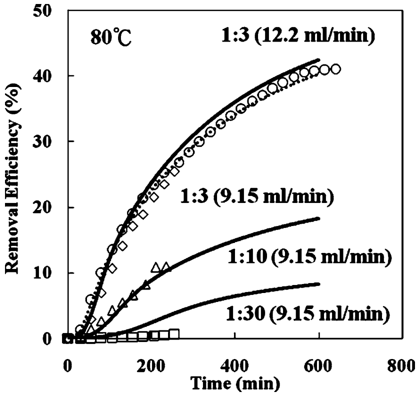

Fig. 4 Curve fitting at 80 °C with hexane as the diluent

Thirteen experiments were conducted at 40∼80 °C and 35 MPa of pressure using various diluents and compositions. The operating and feed conditions are summarized in Table 1. Figures 2, 3, 4 contain results from experiments conducted at 40, 60 and 80 °C applying hexane as the diluent. The symbols represent the experimental results, and the lines are those predicted by Eq. (15). Hexane was replaced by methanol, and the results at 80 °C are illustrated in Fig. 5. In Figs. 2–5, each curve is marked with the volume ratio of extractant to diluent. Three different volume ratios were conducted in this study, and the lower the volume ratio, the lower the concentration of extractant. As expected, increasing the volume ratio significantly increases the maximum removal efficiency and the slope of the extraction curve in the initial stage of the extraction.

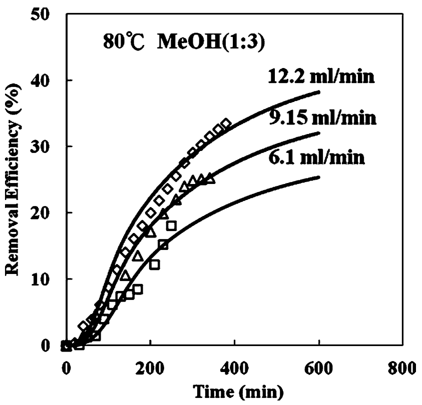

Fig. 5 Curve fitting at 80 °C with methanol as the diluent

Although the fitting is not optimized in Figs. 2–5, it is observed that the established model fits reasonably well with the experimental results here. The poor prediction at low concentrations of extractant, such as that marked by 1:30 in Fig. 4, is presumed to be due to the uptake time for unsteady state operation of the extraction being much greater than the uptake time required when there are high concentrations. The uptake time taken to reach a steady state usually leads to difficulty in modeling for the batch process, such as for supercritical fluid extraction. The parameters used for the curve fitting for Figs. 2–5 are listed in Table 2.

When modeling, the rate constant for ion exchange, k_2, and the parameter, c, for the Langmuir Isotherm are indistinguishable. Increasing k_2c^2 will speed up the extraction to reach maximum removal efficiency, R_m, but it does not change the extent of the maximum removal efficiency. The k_2c^2 mainly increases the removal efficiency, R, during the initial stage of the extraction. Increasing k_2c^2 will obviously increase removal efficiency during the initial stage of the extraction, but this influence is gradually reduced at a later stage. The surface diffusion coefficient, k_m, also affects the extraction curve on the slope of removal efficiency. For a large k_m, the slope of the curve increases. It is observed that the extraction is likely to reach a maximum, which will increase with the maximum extraction constant, β_m.

4.2 Effects of adsorption behavior on the extraction

Table 2 shows that the rate constant represented by k_m or k_{ad} decreases with temperature. While it is recognized that surface diffusion should increase with temperature, this is inconsistent with our observations. It is, therefore, presumed that the extraction process is dominated by the adsorption process rather than by the diffusion process. When methanol replaces hexane, the adsorption rate constant increases slightly. It is presumed that the diluents and their concentration have little effect on adsorption at 80 °C.

From Table 2, it is also observed that the experiments are all fitted by Langmuir Isotherms. In this study, the curve fitting by linear adsorption was also tried and failed to fit all of the experimental results. The metal extraction dependent on the adsorption isotherm is also observed when extracting cobalt from perlite (Liang et al. 2011). In Table 2, the parameters for the adsorption isotherms, a and b, vary with temperature. The parameter b becomes zero as the temperature increases to 80 °C. This implies that the competitive adsorption between extractants and diluents occurs at 40 and 60 °C and diminishes at 80 °C. It is also presumed that increasing the temperature to 80 °C can exclude the adsorption of hexane and provide more sites for the adsorption of extractant so that the maximum removal efficiency abruptly increases. If hexane is replaced by methanol, the results are similar. However, the maximum extraction constant for methanol is less than the extraction constant for hexane. This implies that hexane is the better diluent for removing cobalt from activated carbon.

Table 2 The parameters used for curve fitting

T (°C)	k_2c^2 (mol^2/L^2-sec)	k_m (or k_{ad}) (1/sec)	β_m (58.9^2 L^2/kg Co)	a	b	Remark
40	0.065	0.000140	1.00×10^8	1	2	Hexane
60	0.150	0.000095	0.95×10^8	1	2	Hexane
80	0.300	0.000040	1.60×10^8	1	0	Hexane
80	0.080	0.000050	1.00×10^8	1	0	Methanol

4.3 Effects of temperature on the extraction

Figures 6 and 7 illustrate the effect of temperature on the extraction curve. It is observed that the extraction curves do not simply increase with temperature. At high extractant concentrations, Fig. 6 shows that the removal efficiency decreases as the temperature increases from 40 to 60 °C, but increases as the temperature increases from 60 to 80 °C. It is presumed that the maximum removal efficiency is decreased after the temperature increases from 40 to 60 °C because of the decrease in adsorption of the extractant at high temperatures. After increasing the temperature from 60 to 80 °C, the competition adsorption is diminished and the maximum removal efficiency increases. The disappearance of competition adsorption can be realized by the parameter for adsorption isotherm, b, becoming zero at 80 °C, as shown in Table 2. At a low concentration of extractant, Fig. 7 shows a similar trend in the effect of temperature on the extraction curves. It is concluded that the effect of temperature on the extraction is contributed mainly from the adsorption equilibrium and adsorption kinetics, and that extraction can be significantly prompted by increasing the temperature from 60 to 80 °C .

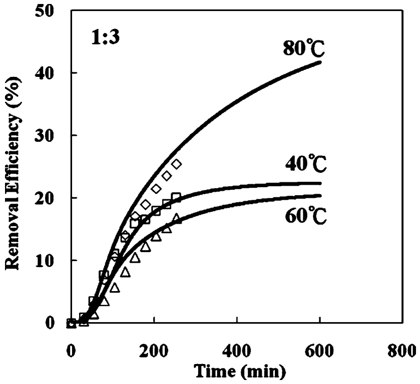

Fig. 6 Effect of temperature on extraction with a high extractant concentration

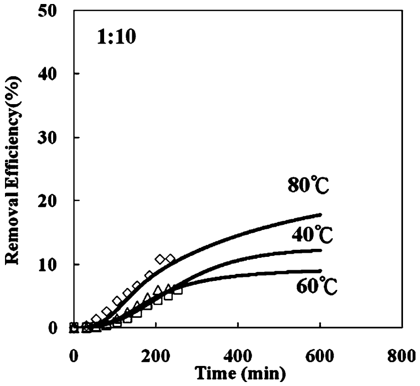

Fig. 7 Effect of temperature on extraction with a low extractant concentration

5 Conclusions

In this study, a kinetic model was established and used to explain the extraction of cobalt from activated carbon. The obtained parameters of this model were used to explain the extraction mechanism. It is presumed that the extraction was affected mainly by the adsorption kinetics of the extractant and the rate of ion exchange between the extractant and metal ions on the surface of activated carbon. By increasing the extraction temperature from 60 to 80 °C, the adsorption competition between diluents and extractants diminishes and the maximum removal efficiency is significantly increased. Further studies of the adsorption isotherm for the extractant in supercritical carbon dioxide will improve the model and its prediction accuracy.

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References

Biswas, R.K., Banu, R.A., Islam, M.N.: Some physico-chemical properties of D2EHPA Part 2. Distribution, dimerization and acid dissociation constants in n-hexane/1 M (Na$^+$, H$^+$)SO$_4^{2-}$ system, interfacial adsorption and excess properties. Hydrometallurgy **69**, 157–168 (2003)

Chen, Y., Mariba, E.R.M., Van Dyk, L., Potgieter, J.H.: A review of non-conventional metals extracting technologies from ore and waste. Int. J. Miner. Process. **98**, 1–7 (2011)

Clifford, A.A., Zhu, S., Smart, N.G., Lin, Y.H., Wai, C.M., Yoshida, Z., Meguro, Y., Iso, S.: Modelling of the extraction of uranium with supercritical carbon dioxide. J. Nucl. Sci. Technol. **38**, 433–438 (2001)

Dehghani, F., Wells, T., Cotton, N.J., Foster, N.R.: Extraction and separation of lanthanides using dense gas CO$_2$ modified with tributyl phosphate and di(2-ethylhexyl)phosphoric acid. J. Supercrit. Fluids **9**, 263–272 (1996)

Febrianto, J., Kosasih, A.N., Sunarso, J., Jua, Y.H., Indraswati, N., Ismadji, S.: Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. J. Hazard. Mater. **162**, 616–645 (2009)

Joung, S.N., Yoon, S.J., Park, J.U., Kim, S.Y., Yoo, K.P.: Single-phase limit for mixtures of tri-n-butyl phosphate + CO$_2$ and bis(2-ethylhexyl)phosphoric acid + CO$_2$. J. Chem. Eng. Data **44**, 1034–1036 (1999)

Laintz, C.R., Wai, C.M.: Solubility of fluorinated metal diethyldithiocarbamates in supercritical carbon dioxide. J. Supercrit. Fluids **4**, 194–198 (1991)

Liang, M.T., Liang, K.Y., Liang, R.C., Hus, P.J.: Kinetics of metal extraction by supercritical carbon dioxide. In: Supergreen 2011 (The 7th Internation Conference on Supercritical Fluids), Beijing, China, Aug. 2011 (2011)

McKay, G., Ho, Y.S., Ng, J.C.Y.: Biosorption of copper from waste waters: a review. Sep. Purif. Methods **28**, 87–125 (1999)

Meguro, Y., Iso, S., Sasaki, T., Yoshida, Z.: Solubility of organophosphorus metal extractants in supercritical carbon dioxide. Anal. Chem. **70**, 774–779 (1998)

Smart, N.G., Carleson, T., Kast, T., Clifford, A.A., Burford, M.D., Wai, C.M.: Solubility of chelating agents and metal-containing compounds in supercritical fluid carbon dioxide. Talanta **44**, 137–150 (1977)

Sovová, H.: Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation. J. Supercrit. Fluids **33**, 35–52 (2005)

Vijayaraghavan, K., Palanivelu, K., Velan, M.: Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles. Bioresour. Technol. **97**, 1411–1419 (2006)

Wadsworth, M.E.: Hydrometallurgical process. In: Wadsworth, M.E., Hong, Y.S. (eds.) Rate Processes of Extractive Metallurgy, pp. 133–185. Plenum Press, New York (1979)

Wai, C.M., Wang, S.F.: Supercritical fluid extraction: metals as complexes. J. Chromatorg. A **785**, 369–383 (1997)