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Supercritical Extraction of Phenols from Organically Modified Smectite

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ABSTRACT

Supercritical extraction has been performed in a fixed column to desorb phenol and 4-nitrophenol from organically modified smectite. The experiments were carried out in the sequence of adsorption of hexadecyltrimethylammonium (HDTMA) to montmorillonite, adsorption of phenols to organoclay in aqueous solutions, desorption of phenols from loaded organoclay using supercritical carbon dioxide, and adsorption of phenols to regenerated organoclay. The desorption characteristics of phenols were investigated at various pressures up to 420 bar; at temperatures of 40, 60, and 70°C, and at low concentrations of a cosolvent. The extraction percentages of phenols reached up to 90% in 3 hours of extraction. The results showed that under the experimental conditions investigated, the activity of HDTMA was intact during the supercritical extraction of phenols, and hence HDTMA-modified montmorillonite exhibited undiminished adsorption power toward phenols after several regeneration cycles.

INTRODUCTION

The interest in application of supercritical fluid technology in environmental control is increasing rapidly. Contaminated soils, wastewater, chemical industry sludges, and solid adsorbents are major environmental concerns, and supercritical extraction has been proposed as a remediation technology for

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liquid and solid matrices (1). The earliest application was regeneration of adsorbents, including activated carbon, as described by Krukonis in 1977 (2). Barna et al. (3) extracted biphenyl from soil using supercritical carbon dioxide, and the authors estimated thermodynamic and kinetic parameters by fitting mathematical models with experimental data. Firus et al. (4) investigated extraction of weathered and artificially contaminated soil, and they found that the removal efficiency of the former was far less than that of the latter. Macnaughton and Foster (5) measured adsorption isotherms and desorption profiles for DDT on activated carbon under supercritical conditions. In the case of the activated carbon regeneration, it has been shown that supercritical extraction is hindered by a strong affinity between organic compounds and a carbon surface, which diminishes the recovery yield.

Organically modified clays (organoclays) have been extensively studied as an alternative solid adsorbent for the adsorption of various ionic and nonionic organic contaminants from aqueous solutions (6, 7). Natural clays such as smectite, modified with amine cations which have an organophilic nature, provide dramatically enhanced immobilizing and adsorption power toward organic acids, phenols, VOCs, PCBs, and PAHs. Research has been focused on the adsorption kinetics and isotherms of organoclays. Zhang et al. (8) studied the sorption and desorption of quaternary amine cations on homoionic Na and K montmorillonite. They found that the sorption involved an exchange reaction and the adsorption of amines at nonexchangeable sites. Stapleton et al. (9) investigated the sorption of pentachlorophenol to organoclay as a function of ionic strength and pH, and developed a model that described the sorption across the experimental pH range. Nzengung et al. (10) measured isotherms for sorption of naphthalene and diuron by various organoclays modified by four different quaternary ammonium ions. Lo et al. (11) examined the use of a commercial organoclay to remove high-strength organic pollutants in leachate and to reduce its liquid flow. To our knowledge, little work has been done on the desorption and regeneration of organoclays loaded with organic species.

The objective of this study was to develop a methodology to regenerate smectite-based organoclay using supercritical fluid technology, and to examine the stability of an organic modifier on the organoclay after the supercritical extraction process. Montmorillonite was employed as a base clay, and hexadecyltrimethylammonium (HDTMA) was used as an organic modifier. The organoclay was loaded with various phenolic compounds through aqueous adsorption. Supercritical carbon dioxide, with and without cosolvent, was used to extract the phenolic compounds from the organoclay in a fixed column, and the processed organoclay was then reused for aqueous adsorption.

EXPERIMENTAL METHODS

Materials

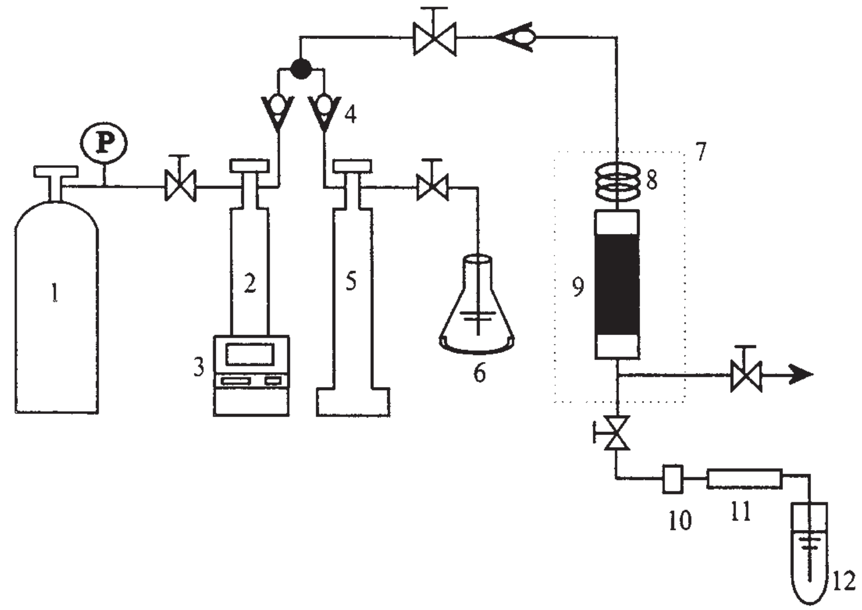
Montmorillonite was purchased from Aldrich Chemical Co. (Lot 06016PN). Impurities and clay organics were removed from the purchased montmorillonite through repeated washings and a digestion process using 35 wt% H_2O_2 solutions and distilled water. The cation-exchange capacity (CEC) of the clay sample was 50.4 meq/100 g-clay. The average diameter of the clay particles was 10 μm. Hexadecyltrimethylammonium (HDTMA), which is one of the quaternary amine cations of the form $[(CH_3)_3NR]^+$, was used as an exchange ion on montmorillonite. HDTMA (in the form of a 25 wt% solution in water) was purchased from Aldrich Chemical Co. (Lot 05226JN). Phenol and 4-nitrophenol were selected as model phenolic compounds, and they were purchased from Junsei Chemical Co. Carbon dioxide was used as a supercritical fluid with ethanol as a cosolvent.

Clay Modification and Adsorption of Phenols

Organically modified montmorillonite was prepared by adsorbing a CEC equivalent amount of HDTMA on the clay. The purified montmorillonite was added to an aqueous solution of HDTMA and agitated for 24 hours at 25°C. After mixing, the clay–HDTMA suspension was centrifuged, and the total organic carbon (TOC) of the solution was determined using a TOC analyzer (Shimadzu model TOC-5000). The modified clay was washed with distilled water and dried at 60°C. The resulting uptake of HDTMA on montmorillonite was 152.0 mg/g-clay. Phenols were adsorbed on HDTMA-modified montmorillonite from aqueous solutions. The uptake of phenols by the organoclay was measured by the batch adsorption equilibrium technique. Phenols were dissolved in water at concentrations of 50–3000 mg/L. A known amount of organoclay was added to 200 cm^3 of the phenol solution, and the mixture was agitated for 24 hours at 25°C. At equilibrium, the supernatant was centrifuged and the concentration was determined using a UV spectrophotometer (HP model 8452A). The uptake of phenols by natural clay was also investigated, and there was no measurable amount of phenol adsorbed. Adsorption isotherms of the organoclay were well described by the classical form of the Langmuir isotherm: $C/S = (1/ab) + (C/b)$, where C is the equilibrium solution concentration, S is the uptake per unit mass of organoclay, a is the affinity parameter or Langmuir constant, and b is the capacity parameter.

Extraction of Phenols from Organoclay

The reason for employing supercritical technology to extract phenols from organoclay was to utilize the fact that while phenol is soluble in supercritical



1. Carbon Dioxide Cylinder
2. Syringe Pump
3. Controller
4. Check Valve
5. Co-Solvent Pump
6. Co-Solvent Reservoir
7. Constant Temperature Chamber
8. Pre-Heater
9. Extraction Column
10. Filter
11. Capillary Restrictor
12. Solvent Trap

FIG. 1 Experimental apparatus for the extraction of phenols from organoclay.

carbon dioxide, HDTMA is practically insoluble. Therefore, the purpose of the extraction was to extract only phenol from the HDTMA–montmorillonite matrix, and to investigate the stability of HDTMA on the clay surface under supercritical conditions.

Figure 1 shows the experimental apparatus used in this study. The extraction unit was purchased from Isco Co. (model SFX2-10). The system consisted of two high-pressure syringe pumps (Isco model 260D), an extraction column (2.5 cm^3 volume), and a stainless steel capillary restrictor (300 μm OD). The two syringe pumps were used for carbon dioxide and ethanol cosolvent supply, respectively. The system was designed to maintain a constant pressure and flow rate during extraction. Normally, the column was charged with 1.5 g of organoclay. Before the extraction, the system was vented with gaseous carbon dioxide for 5 minutes to remove air from the extraction system. The extraction of phenol was performed in the column by flowing carbon dioxide continuously. The experiments were carried out at pressures of 206.8, 275.8, 344.7, and 413.6 bar and at temperatures of 40, 60, and 70°C. The flow rate of carbon dioxide was maintained at 1.3–2.3 cm^3/min with cosolvent concentrations of 0–5 vol%. The extract was collected in a trap which contained ethanol solution. In order to obtain extraction profiles with time, the traps were changed every 5 minutes for the first 30 minutes and every 30 minutes for the next 3 hours. The ethanol solution was analyzed by a UV spectrophotometer to determine phenol concentration.

RESULTS AND DISCUSSION

Adsorption of Phenols

The adsorption isotherms of phenol and 4-nitrophenol on the HDTMA-modified montmorillonite are shown in Fig. 2. Greater adsorption was exhibited by 4-nitrophenol which is the more organophilic compound. The uptakes of the two compounds were well represented by the Langmuir isotherm with constants of $a = 0.0333$, $b = 0.0003092$ for phenol and $a = 0.0575$, $b = 0.0007105$ for 4-nitrophenol. The result agreed well with data in the literature (7). For the extraction experiments, phenol-loaded organoclays with uptakes of 34 mg phenol/g-clay and 41 mg 4-nitrophenol/g-clay were generated.

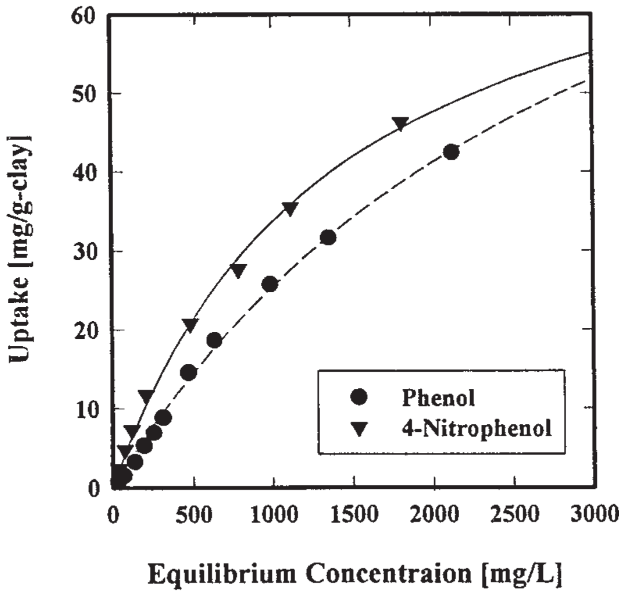


FIG. 2 Adsorption isotherms of phenols on the HDTMA-modified montmorillonite. The line represent Langmuir adsorption isotherms.

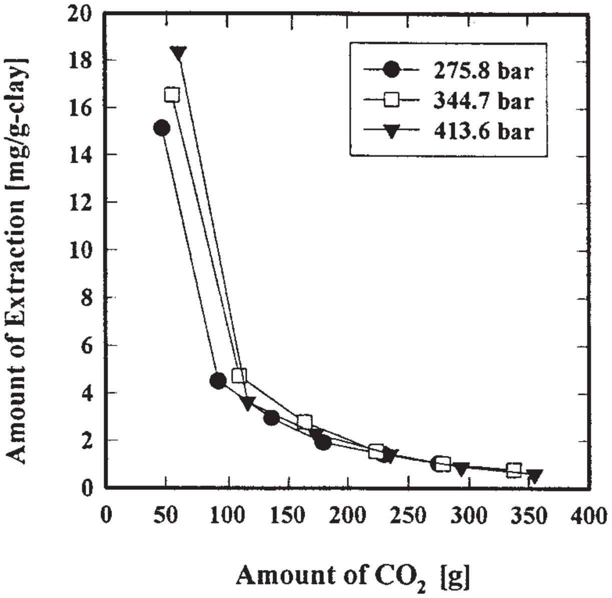


FIG. 3 Typical extraction profiles of phenol as a function of carbon dioxide consumed at 70°C.

Extraction of Phenols

Figure 3 displays typical extraction profiles of phenol at 70°C as a function of carbon dioxide consumed at various pressures. The profiles show that the amount of extraction decreases dramatically at the first stage of extraction. The three isobars indicate that higher pressure provides better extraction during the initial stage of the extraction, and the profiles tend to collapse to almost a single curve. This result shows that the extraction might be influenced by the solubility of carbon dioxide only at the very beginning of the extraction, where the extraction of weakly adsorbed phenol on the surface of the organic modifier occurs. The extraction is then rapidly shifted to desorption control, in which the internal mass transfer limitation governs the major process of extraction. Figure 4 shows the effect of temperature on the extraction percentage of phenol at 413.6 bar. The enhanced extraction percentage at the elevated temperature indicates that the higher temperature accelerates the desorption of phenol, the result of a change in the sorption isotherm at the high temperature. Table 1 shows the effects of pressure, temperature, and cosolvent concentration on the percentage recovery. The recovery represents the percentage amount of phenol extracted per unit mass of organoclay based on the amount of carbon dioxide, with or without cosolvent, consumed. At constant pressure the recovery increased with temperature, which resulted from the high vapor pressure of phenol and enhanced desorption from organoclay. At constant

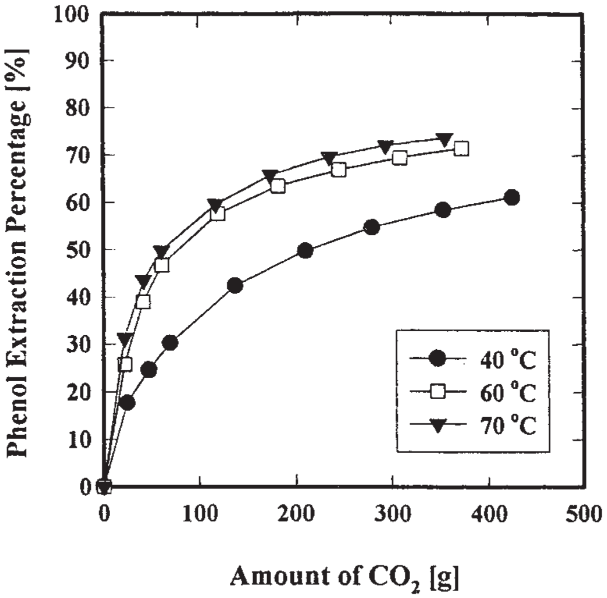


FIG. 4 Effect of temperature on the extraction percentage of phenol at 413.6 bar.

temperature the recovery increased with pressure. The results show that the effect of pressure on the interaction of adsorbent and adsorbate on organoclay can be neglected. The phenol recovery effectively increases with the concentration of ethanol cosolvent.

TABLE 1
Phenol Recovery under Various Experimental Conditions

Solvent	*T* (°C)	*P* (bar)	Amount of solvent used (g)	Percentage recovery
CO_2	40	413.6	350	58.0
CO_2	60	413.6	350	70.0
CO_2	70	413.6	350	73.6
2.5% EtOH	60	206.8	230	78.1
2.5% EtOH	60	344.7	230	88.7
2.5% EtOH	60	413.6	230	90.8
CO_2	60	275.8	270	68.8
1.0% EtOH	60	275.8	270	70.0
2.5% EtOH	60	275.8	270	79.6
5.0% EtOH	60	275.8	270	92.6

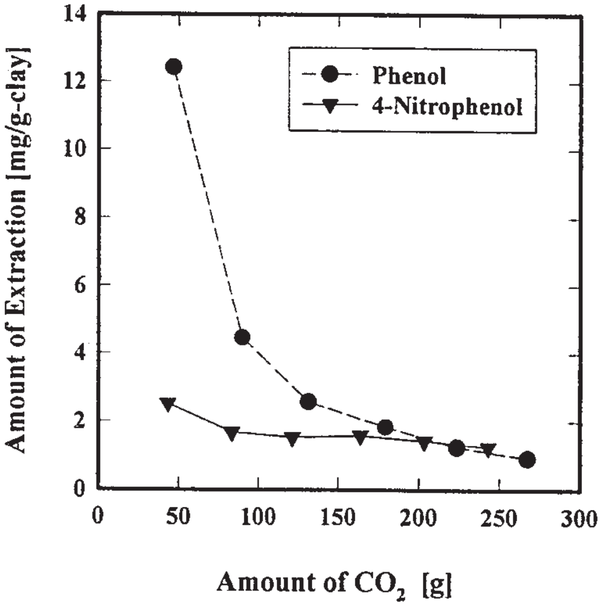


FIG. 5 Extraction profiles of phenol and 4-nitrophenol at 60°C and 275.8 bar.

The extraction profiles for 4-nitrophenol exhibit trends similar to those of phenol. However, the extraction efficiency of 4-nitrophenol was much lower than that of phenol (Fig. 5), which resulted from the strong affinity of 4-nitrophenol to organoclay. Figure 6 shows the effect of ethanol cosolvent on the extraction percentage of phenol and 4-nitrophenol at 275.8 bar. In the cosolvent concentration range of 0–5%, the extraction percentage of phenol and 4-nitrophenol increased up to 87.0 and 96.8%, respectively, in 3 hours of extraction, which corresponds to the use of 270 g of pure carbon dioxide. The results demonstrate that the ethanol cosolvent accelerates the extraction of ‘hard to extract’ material.

Prediction of Extraction Profiles

The extraction profiles of phenols from organoclays in a fixed column were predicted by adopting two different models suggested by Brady et al. (12) and Tan and Liou (13). First, the system was simplified by assuming that the content in the column is efficiently mixed with carbon dioxide. Therefore, the concentration gradient and mass transfer resistances inside the column were negligible, with equilibrium being the only factor contributing to the extraction process (12). A material balance over the extraction column yields

$$W \frac{d\theta}{dt} = -QC \tag{1}$$

where W is the clay weight, θ is the phenol concentration in the clay phase in g/g-clay, Q is the volume flow rate of carbon dioxide in cm^3/min, and C is the phenol concentration in the carbon dioxide phase in g/cm^3. Phenol concentrations of the two phases are linearly related as follows:

$$\theta = KC \tag{2}$$

where K is the distribution coefficient in cm^3/g-clay. The solution of Eq. (1) becomes

$$\ln(\theta/\theta_0) = \left(-\frac{Q}{KW}\right)t \tag{3}$$

where θ_0 is the initial concentration in clay. Equation (3) allows calculation of the distribution coefficient K by fitting the experimental data to predict the extraction profiles (12). This simplified linear model might be inaccurate for modeling fixed-bed column extraction. However, the column used in this study was of short length and large diameter, and the flow rate of the mobile phase was relatively low, hence, equilibrium could possibly be attained in the column.

Second, a material balance in the column (neglecting the axial dispersion effect) can be written as (13)

$$\epsilon \frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = -(1 - \epsilon)\frac{\partial S}{\partial t} \tag{4}$$

where ϵ is the bed porosity, u is the superficial velocity of carbon dioxide in

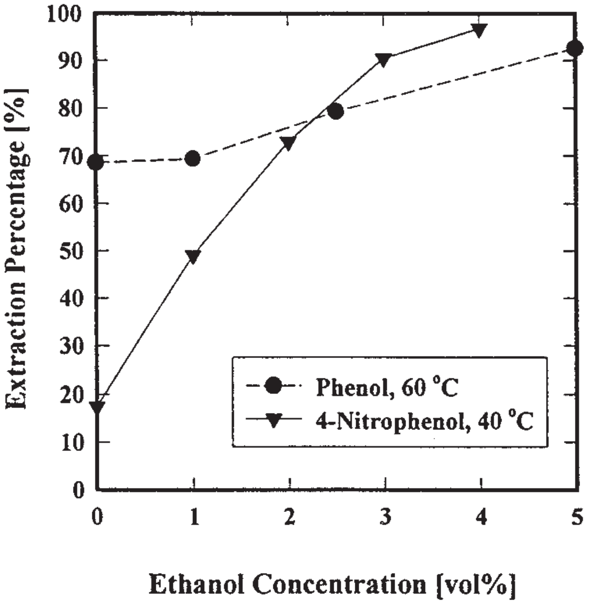


FIG. 6 Effect of the concentration of ethanol cosolvent on the extraction of phenol and 4-nitrophenol.

cm/min, and S is the phenol concentration per unit volume of clay in g/cm^3. The initial and boundary conditions are at $t = 0$, $C = 0$ and at $z = 0$, $C = 0$. The linear desorption kinetics used is as follows:

$$\partial S/\partial t = -kS \tag{5}$$

where k is the desorption rate constant in min^{-1}. The initial condition is at $t = 0$, $S = S_0$. The solution of Eqs. (4) and (5) with the initial and boundary conditions gives the expression for the concentration at the exit of extraction column C_e.

$$C_e = \frac{1-\epsilon}{\epsilon} S_0 \left\{ \exp\left[-k\left(t - \frac{\epsilon L}{u} \right) \right] - \exp(-kt) \right\} \tag{6}$$

where L is the column length in cm. The amount of extraction can be calculated by integrating C_e with respect to time. The desorption rate constant k is determined by regression of Eq. (6) with the experimental data (13).

The experimental and the calculated extraction profiles of phenol and 4-nitrophenol are shown in Figs. 7 and 8, respectively. The utilized models could reasonably fit the extraction profiles by employing the two adjustable parameters, which is essential in these calculations. The evaluated values of the distribution coefficient K and the desorption rate constant k were 82.60

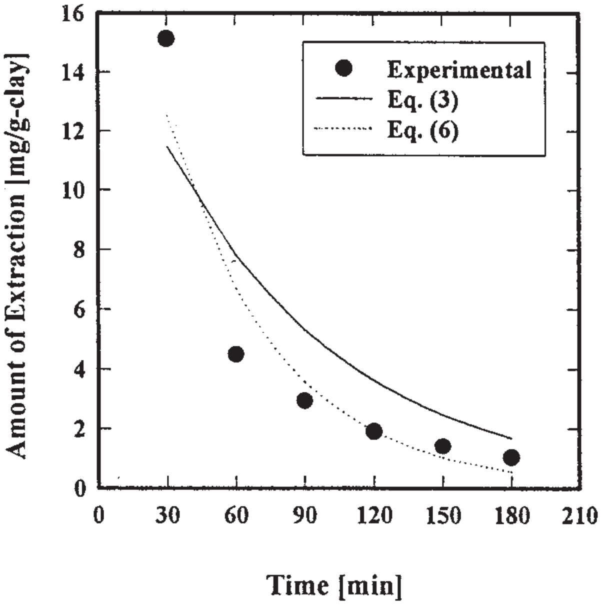


FIG. 7 Predicted extraction profiles of phenol by Eqs. (3) and (6) at 70°C and 275.8 bar when pure carbon dioxide is used.

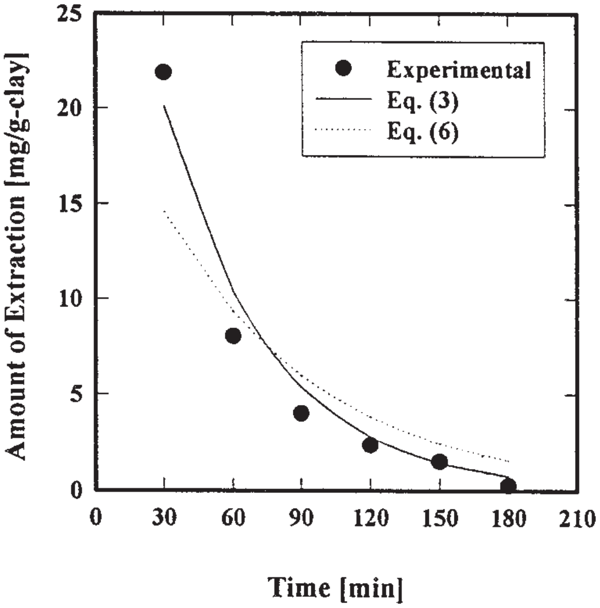


FIG. 8 Predicted extraction profiles of 4-nitrophenol by Eqs. (3) and (6) at 40°C and 275.8 bar when 3 vol% ethanol cosolvent is used.

cm^3/g and 0.021 min^{-1} for phenol and 40.46 cm^3/g and 0.015 min^{-1} for 4-nitrophenol, respectively.

Adsorption of Regenerated Organoclays

The extracted organoclays were recycled for adsorption of phenols, and the corresponding adsorption isotherms were measured. The extraction–adsorption cycles were repeated up to 3 times. Figures 9 and 10 show the adsorption isotherms of phenol and 4-nitrophenol on the virgin and the regenerated organoclays in aqueous solutions, respectively. In the case of 4-nitrophenol, all the extractions were performed using 3 vol% ethanol cosolvent. The results show that the regenerated organoclays exhibit an undiminished adsorption power toward phenols after a couple of regeneration cycles. The phenols were also extracted from the loaded organoclay by shaking 24 hours in pure ethanol at 24°C. The adsorption power of the ethanol-processed organoclay markedly decreased as shown by data points in Figs. 9 and 10. This result indicates that if an organic solvent such as ethanol is employed as an extraction medium, the organic modifier as well as phenols are desorbed from the clay surface. The supercritical fluid, on the other hand, enables the organic modifier, HDTMA, to remain intact during extraction, and hence the organoclay can maintain its adsorption power after the extraction–adsorption cycles. There is the possibility that the ethanol cosolvent used in supercritical extraction will

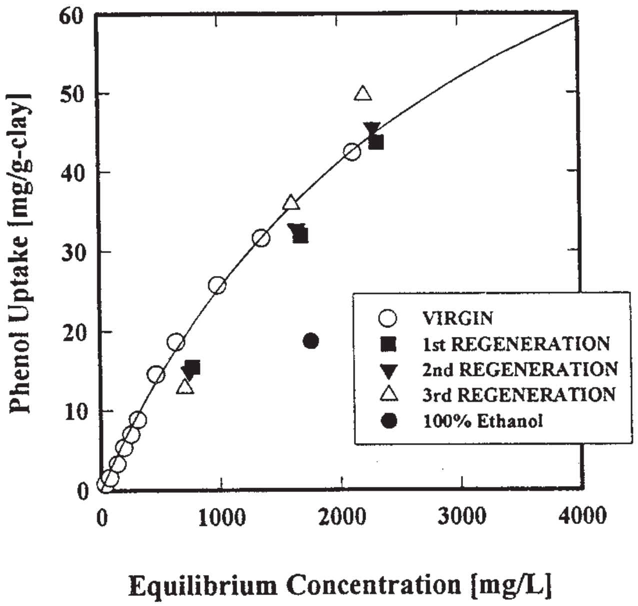


FIG. 9 Effect of regeneration cycles on the adsorption of phenol on organoclay.

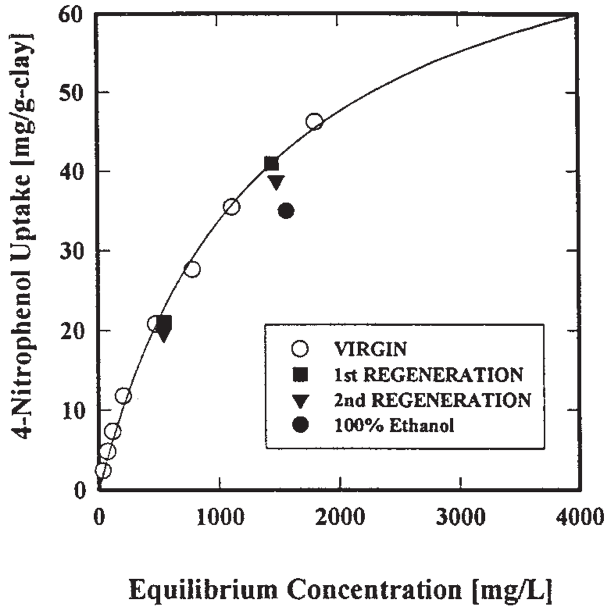


FIG. 10 Effect of regeneration cycles on the adsorption of 4-nitrophenol on organoclay.

degrade the organic modifier. However, under the experimental conditions investigated, no degradation of HDTMA due to the low concentration of cosolvent was observed up to 3 regeneration cycles.

The motivation for this research was that supercritical extraction will provide high desorption efficiency from organoclays which exhibit relatively weak adsorption power compared to activated carbon. Therefore, when an organoclay is utilized as an alternative adsorbent toward hazardous or useful organic compounds, supercritical extraction can be expected to be a favorable technology for the regeneration of the organoclay as well as for the recovery of the adsorbed materials from the organoclay.

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REFERENCES

1. A. Akgerman, *Waste Manage.*, *13*, 403 (1993).
2. V. J. Krukonis, *EPA Report R804-554-010* (1977).
3. L. Barna, J. M. Blanchard, E. Rauzy, C. Berro, and P. Moszkowicz, *Chem. Eng. Sci.*, *51*, 3861 (1996).
4. A. Firus, W. Weber, and G. Brunner, *Sep. Sci. Technol.*, *32*, 1403 (1997).
5. S. J. Macnaughton and N. R. Foster, *Ind. Eng. Chem. Res.*, *34*, 275 (1995).
6. S. A. Boyd, S. Shaobai, J. F. Lee, and M. M. Mortland, *Clays Clay Miner.*, *36*, 125 (1988).
7. Y. S. Kim, D. I. Song, Y. W. Jeon, and S. J. Choi, *Sep. Sci. Technol.*, *31*, 2815 (1996).
8. Z. Z. Zhang, D. L. Sparks, and N. C. Scrivner, *Environ. Sci. Technol.*, *27*, 1625 (1993).
9. M. G. Stapleton, D. L. Sparks, and S. K. Dentel, *Ibid.*, *28*, 2330 (1994).
10. V. A. Nzengung, E. A. Voudrias, P. Nkedi-Kizza, J. M. Wampler, and C. E. Weaver, *Ibid.*, *30*, 89 (1996).
11. I. M. C. Lo, R. K. M. Mak, and S. C. H. Lee, *J. Environ. Eng.*, p. 25 (January 1997).
12. B. O. Brady, C-P. C. Kao, K. M. Dooley, and F. C. Knopf, *Ind. Eng. Chem. Res.*, *26*, 261 (1987).
13. C-S. Tan and D-C. Liou, *Ibid.*, *27*, 988 (1988).

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