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Desorption Processes: Supercritical Fluid Regeneration of Modified Clays

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Abstract. The main objective of this work is the study of the regeneration capacity of modified clays using carbon dioxide. These modified clays are used as organic compounds adsorbents. Modified clays were used to remove ethyl acetate from aqueous solutions. Structural changes on the montmorillonite clay after a treatment with quaternary amines were investigated. The experimental step was also done using a packed column with the clay contaminated by ethyl acetate and toluene. Different pressures and temperatures were employed, leading to different fluid conditions (gas, liquid and supercritical). The results obtained showed the influence of the density of the supercritical CO_2 and of the organic modifier in the desorption process. These data were modeled with a simple model and with models of first and second orders. The better results were reached using the second-order model. This study allows the scale-up of the desorption process for the regeneration of solid matrices using supercritical fluids. The modified clay capacity as a pollutant attenuator remained almost unchanged after a regeneration cycle.

Introduction

The reverse process by which the adsorbed molecules are removed from the surface to the bulk fluid phase is called desorption. Energy must be supplied to the adsorbed phase (endothermic) for the desorption process. Both adsorption and desorption form vital steps in a practical adsorptive process where the adsorbent is repeatedly used for carrying out the separation of a fluid mixture. This concept of regenerative ad/desorption is key to the practical use of this technology (Garside, 1994).

The application of supercritical fluid (SCF) as a regeneration solvent for adsorbents has been extensively studied. The most important adsorbent is activated carbon prepared by partial volatization or combustion of a carbonaceous (Walas, 1985). Regeneration of spent activated carbon by desorption with supercritical carbon dioxide was first proposed as an alternative to conventional thermal regeneration. Normally, the activated carbon is used to reduce and/or to recover organic compounds in effluent streams commonly emitted in the chemistry industry. Clay minerals as adsorbents, especially smectite, are of particular interest because of their large specific surface areas (Park and Yeo, 1999).

An alternative adsorbent is modified clay. In spite of the significant number of studies attesting the high capacity that the organically modified clays have to adsorb organic compounds, its commercial application have been rarely observed. The main difficulty on this application lies on the regeneration process.

In this article, we report on the utilization of modified organoclay to remove organics compounds (ethyl acetate/toluene) from aqueous solutions. The suitable model was used to describe the desorption kinectics of each compound.

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Literature Review

Researches carried out over the last years has shown that the supercritical extraction of organic compounds from soils (Dooley et al., 1987) or solid matrix may become an interesting alternative to classical treatments such as solvent extraction or incineration (Barna et al., 1996). The most employed supercritical solvent is carbon dioxide because of its special characteristics and physicochemical properties, e.g., nonflammability, nontoxicity, relatively inexpensive, higher mass-transfer rate and adjustable extraction power for organic compounds depending on the density. It has proved to be an effective solvent for the regeneration of the activated carbon loaded with organic compounds (Modell et al., 1979). In order to know the adsorption and desorption process, researches regarding new adsorbents for the removal of pollutants have also been extensively done. The study of the regeneration of these adsorbents is also very important. The regeneration of activated carbon by SC-CO_2 after adsorption of toluene had already been studied experimentally (Tan and Liou, 1990). Normally, the activated carbon is used to reduce and/or to recover organic compounds in effluents streams (Srinivasan et al., 1990; Kikic et al., 1996). The use of clay minerals as adsorbents is of particular interest because of their large specific surface areas. An alternative adsorbent is the modified clay proposed by Coelho et al. (2001). In this work, the regeneration of organoclays loaded with toluene and ethyl acetate using SC-CO_2 at different pressures and temperatures was studied. The employed clay was montmorillonite and tetramethylammonium (TMA^+) was used as organic modifier, which gave a better organophilic nature to the clay. This kind of study is so important to make a possible scale-up of the regeneration process for the application on solid matrices or contaminated soils (Alonso et al., 2002).

Experimental Methods

The experimental program included the steps as follows: Clay purification (montmorillonite); Quaternary amine impregnation (TMA^+ and $HDTMA^+$ as modifiers); X-ray diffraction analysis (monitoring the basal spacings); Adsorption experiment (batch); Adsorption experiment (continuous), Supercritical fluid extraction (the collected samples were analyzed by gas chromatography (GC) and SPME-GC (Coelho et al., 2001).

The experimental apparatus used for the regeneration measurements at elevated pressures is illustrated in Figs. 1 and 2, for the toluene and ethyl acetate, respectively.

The clay used (montmorillonite) and the TMA^+ chloride were purchased from Sigma-Aldrich Canada Ltd. The TMA^+ used without further purification was employed in the clay modification. The extraction of toluene was done by passing the pure supercritical carbon dioxide through a stainless steel tube charged with prevently contaminated clay with 134 μl of organic contaminant. The desorption column (2.7 cm^3) was packed with about 1.26 g of the modified clay for the toluene experiments and 1.0 g for the ethyl acetate experiments and glass beads were also packed above and below the clay packing, both with height of about 1.5 cm in order to uniform the flow rates. Stainless steel frits were used to contain the organoclay in the column. A HP 5890 gas chromatograph with a flame ionization detector (silica column type SE-54, 25 m, col. 70°C, inj. 250°C and det. 250°C) was used for this task.

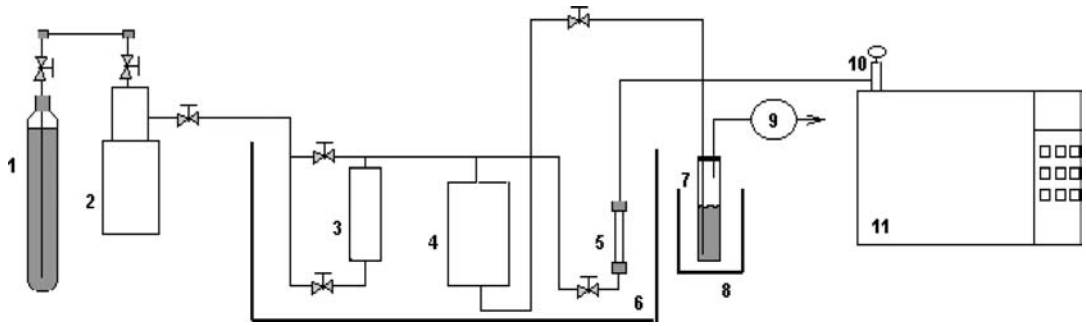

Figure 1. Schematic diagram of the apparatus used for toluene desorption experiments, where 1—gas cylinder, 2—high pressure pump, 3—saturator, 4—mixing tank, 5—desorption column, 6—heating bath, 7—trap, 8—ice bath, 9—gas meter, 10—six way valve and 11—gas chromatography.

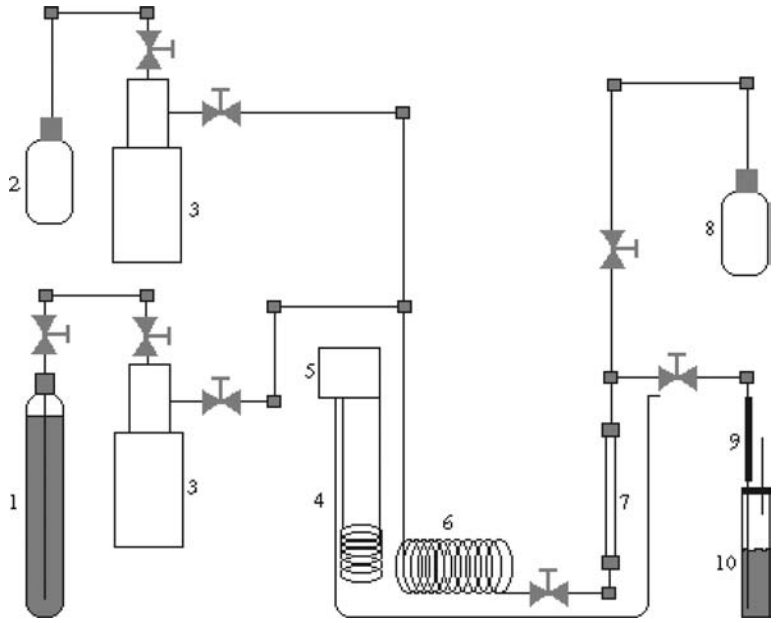

Figure 2. Sketch of the apparatus used for adsorption and supercritical extraction of ethyl acetate from organoclays: 1—liquid CO_2 tank; 2—ethyl acetate solution; 3—syringe pump; 4—water bath; 5—heating; 6—preheating coil; 7—adsorption/desorption column; 8—effluent collector; 9—restrictor; 10—collector trap.

An ethyl acetate solution (2.6 g/L) was pumped (syringe pump, ISCO model 100D) through the column packed with the organoclay (Fig. 2). Approximately 800 mL of ethyl acetate solution, at a temperature of 308 K, were circulated through the packed bed. The concentration of the effluent was measured using SPME-GC.

The same apparatus developed for the adsorption experiments was operated on the supercritical fluid extractions (Fig. 2). The extractions were performed with a syringe pump (ISCO, model 260D) that continuously supplies the column with CO_2. The temperature was controlled with a constant temperature bath. The CO_2 stream, before entering the column, circulated through a preheated coil reaching the bath temperature. The extracted ethyl acetate was collected through a stainless steel capillary restriction in a cold trap containing 2-propanol. Nine samples were collected for each experiment. Over the first 30 min a time interval of 5 min between samples was adopted; for the following 2 hours the time interval was increased to 30 min. Desorption profiles were obtained at several pressure-temperature combinations. This allowed us to study the desorption efficiency with CO_2 at different operational conditions.

Modeling of the Desorption Process

The modeling of the toluene desorption process was done based on the model proposed by Chiou and Li (2002). The desorption quantities, time and the equilibrium constant of the process are the variables of the models containing first-order and second-order equations. The first-order expression is expressed as

$$\log(q_e - q) = \log(q_e) - \frac{K_1}{2,303} \times t \qquad (1)$$

where q_e is the desorbed amount in the equilibrium, q the desorbed amount at any time, t is the operational time of the process and K_1 is the constant of the first-order equation that must be estimated.

Rewriting the equation above in function of the desorption amount and time

$$\left(1 - \frac{q}{q_e}\right) = 10^{\left(-\frac{K_1}{2,303} \times t\right)} \qquad (2)$$

A straight line of the right term in function of the left term of the Eq. (2) suggests the applicability of this kinetic modelto represent the experimental data. The

coefficients of this correlation were low that do not give representative values.

The second-order model has the same principle of the first-order model, although it was expressed in function of q_e

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

After dividing all the equation by q_e and due to q_e is equal to 100% because of the conduction of the experimental step and known the q/q_e values with the time, so

$$\left(\frac{q_e}{q} - 1\right) = \frac{1}{t \times K_2} \tag{4}$$

The straight lines were plotted in terms of $(q/q_e - 1)$ in function of time and show a good agreement in comparison with the experimental data using the second-order kinetic model for the regeneration process (Carneiro et al., 2004).

For the ethyl acetate desorption process, the packed bed has been considered perfectly mixed with carbon dioxide. The mass transfer resistances are negligible in this case with equilibrium being the only contributing factor to the extraction process. A mass balance in the extraction column is expressed by

$$W\left(\frac{d\theta}{dt}\right) = -QC \tag{5}$$

where W is the clay weight, θ is the ethyl acetate concentration in the clay phase in g/g-clay, Q is the flow rate of carbon dioxide in cm^3/min and C is the ethyl acetate concentration in the carbon dioxide phase in g/cm^3. It will be considered a linear partition relationship between the phases

$$\theta = KC \tag{6}$$

where K is the distribution coefficient in cm^3/g-clay.

The solution of Eqs. (5)–(6) is given by

$$\ln\left(\frac{\theta}{\theta_0}\right) = \left(-\frac{Q}{KW}\right)t \tag{7}$$

where θ_0 is the initial ethyl acetate concentration in the clay. A linear regression of the extraction data, $\ln(\theta/\theta_0)$ vs t, allows the determination of the distribution coefficient and the prediction of the extraction profiles (Coelho et al., 2001).

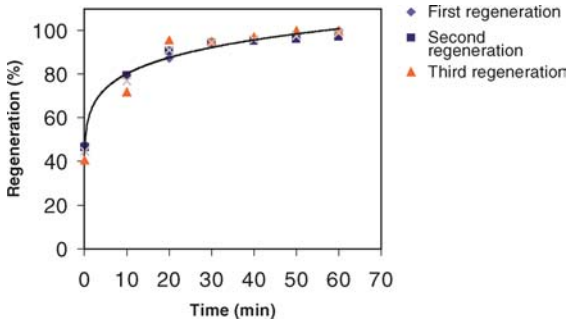

Figure 3. Desorption of toluene at more than one regeneration in the same matrix at 310 K and 75 bar.

Results and Discussion

The results obtained for the experiments with toluene show that more than one regeneration in the same matrix of adsorbent did not really change the kinetic of the process and this behavior can be observed in Fig. 3. The experiments were done in the same conditions of pressure and temperature (75 bar and 310 K) and the experimental points were almost equals.

Figure 4 illustrates that the desorption process increases with the increase of the density of the supercritical CO_2. At 310 K and 75 bar, the density of the CO_2 is 0.25438 g/cm^3 and at 323 K and 100 bar, is 0.44944 g/cm^3. This indicates that at higher values of density or pressure, the interaction forces between toluene and carbon dioxide molecules are larger than the bonding forces between toluene and modified clay surface. This fact illustrates that a higher regeneration efficiency of the organoclay loaded with toluene can be obtained when the density is increased.

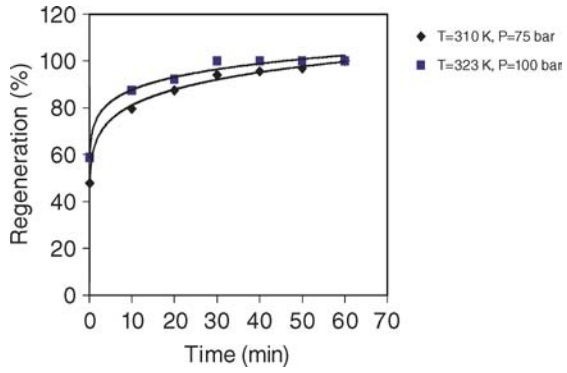

Figure 4. Desorption of toluene at different operational conditions using supercritical carbon dioxide.

Table 1. Experimental and calculated data using the first and second-order models.

T (K)			First-order	Second-order
310	310		$K_1 = -0.0605$	$K_2 = 0.3959$
q/qe	qe/q		$R = 0.7013$	R = 0.9811
		t (min)	1 − (q/qe)	(qe/q) − 1
0.795	1.257	10	0.248274	0.252580
0.874	1.144	20	0.061640	0.126290
0.940	1.064	30	0.015304	0.083351
0.956	1.046	40	0.003799	0.063145
0.968	1.033	50	0.000943	0.050516
323	323	t	$K_1 = -0.0844$	$K_2 = 14.1286$
q/qe	qe/q	min	$R = 0.8698$	$R = 0.9672$
			1 − (q/qe)	(qe/q) − 1
0.873	1.145	10	0.143277	0.707776
0.921	1.086	20	0.020528	0.007078
1.0	1.0	30	0.002941	0.003539
1.0	1.0	40	0.000421	0.002336
1.0	1.0	50	0.000060	0.001769
1.0	1.0	60	0.000009	0.001416

The experimental data of the desorption process were modeled using first-order and second-order models. The first-order model did not give reasonable values. The differences between experimental and calculated data can be observed in Table 1. The second-order model shows a good agreement behavior in comparison to the experimental data at 310 K and 323 K.

The results obtained for the ethyl acetate experiments have the same behavior of the toluene. In the batch sorption experiments, the mass of adsorbent, the sorbate and its concentration, and the temperature were all kept constant. Thus, the only factor affecting the adsorption was the type of modification suffered by the clay (the adsorbent nature). Figure 5 shows the results of the batch sorption experiments, where it is possible to compare the adsorptive capacity (mg of ethyl acetate/g of clay) of modified and unmodified clays. As expected, the presence of quaternary amines on the montmorillonite changed the surface properties from hydrophilic to organophilic, increasing the capacity of the clays to adsorb organic compounds. On the original montmorillonite the adsorptive capacity was 6.2 mg/g while on the TMA-montmorillonite it was 15.6 mg/g and on the HDTMA-montmorillonite it was 35.6 mg/g.

It is also observed that the montmorillonite saturated with TMA^+ ions presented a weak sorption capacity when compared with the clay modified with the ion $HDTMA^+$. This ion is more hydrophobic and it is widely known that, in general, the more hydrophobic the group associated with the quaternary ammonium is, the greater the sorption of the sorbate is.

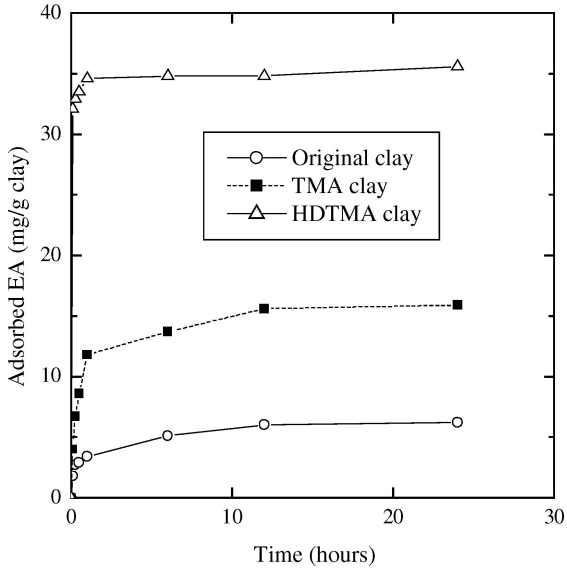

Figure 5. Adsorption capacity of modified and unmodified clays.

Willing to explain the observed adsorption capacity of the clays the determination of d_{001} spacings by X-ray diffraction analysis was carried out. These results can be seen on Figs. 6–8. The first peak of the diffraction results represents the d_{001} spacing of an intercalated layer of the sample. Table 1 presents the properties of the clays, relating the adsorption capacity with the basal spacing. The d_{001} spacing of the original clay is 14.79 Å at 5.89 and the d_{001} spacing of HDTMA-clay

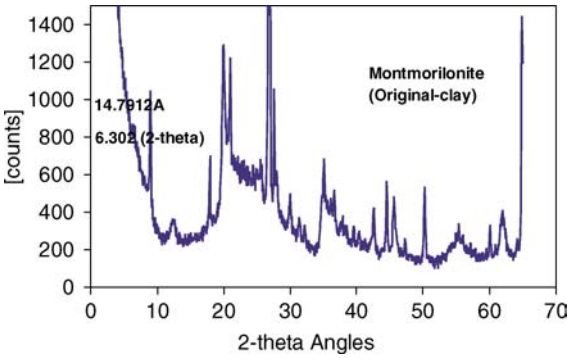

Figure 6. Unmodified montmorillonite X-ray diffraction.

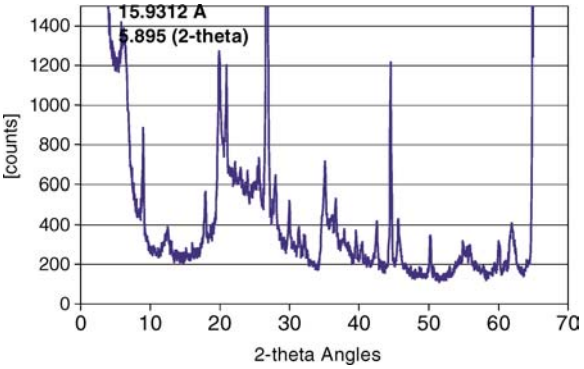

Figure 7. TMA-montmorillonite X-ray diffraction.

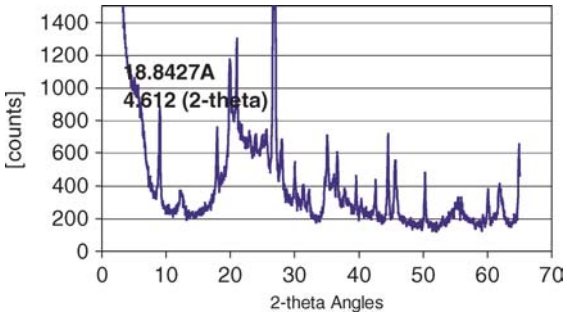

Figure 8. HDTMA-montmorillonite X-ray diffraction.

is 18.84 Å at 4.61. The presence of the $HDTMA^+$ ion inside the intercalated layer increases considerably the d_{001} spacing of the original clay. The modified clay containing a small organic ion (TMA^+) behaved almost like the original clay (Cavalcante et al., 2005).

Aiming the regeneration of the porous matrix the recuperation of the ethyl acetate adsorbed on the HDTMA-montmorillonite was performed. These experiments were carried out with carbon dioxide at different combinations of temperature and pressure, allowing the search for the optimal operating conditions. A mass balance for the ethyl acetate was performed at the end of the adsorption/desorption experiments. The total volume of the carbon dioxide applied for the recovery of the adsorbed ethyl acetate from the organoclay was 266 mL. The influence of the temperature on the regeneration was studied at pressures ranging from 69 to 413.8 bar. On the other hand, the effect of operating pressure on the cumulative amount of ethyl acetate desorbed was studied at temperatures ranging from 301 to 333 K.

The best operational conditions were found with CO_2 in the supercritical region (333 K and 413.8 bar)

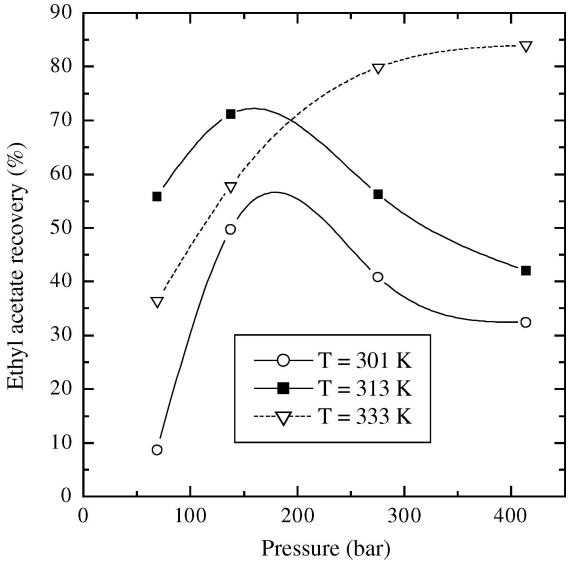

Figure 9. Isothermal desorption of ethyl acetate from HDTMA-clay with supercritical carbon dioxide—Influence of the pressure.

where 84% of the adsorbed ethyl acetate could be recovered from the HDTMA-clay. The worst result was found in the liquid phase (301 K and 69.0 bar) where the recovery of ethyl acetate reached 8.6%. For the two gaseous conditions studied in this work, when the pressure was kept at 69.0 bar, the recovery efficiency decreased with the increase of the temperature. The same behavior was observed when the pressure was kept at 137.9 bar. On the other hand, this effect cannot be seen at pressures of 275.9 bar and 413.8 bar. Figure 9 clearly depicts this unusual phenomenon that is similar to that followed by the solubility in a supercritical solvent, where the solubility decreases with an increasing temperature, at low supercritical pressures. This behavior is known as the crossover effect. A crossover effect has also been found for supercritical fluid desorption from activated carbon (Srinivasan et al., 1990).

Besides its unique solubility characteristics, a supercritical fluid owns certain physicochemical properties that increase its attractiveness. As an example, even though it owns a liquid-like density over much of the range of industrial interest, it exhibits gas-like transport properties of diffusivity and viscosity. Additionally, the very low surface tension of supercritical fluid provides an easy penetration into microporous materials. Such properties can provide different effects. Higher density may enhance the solubility, and higher viscosity may slow down the rate of diffusion.

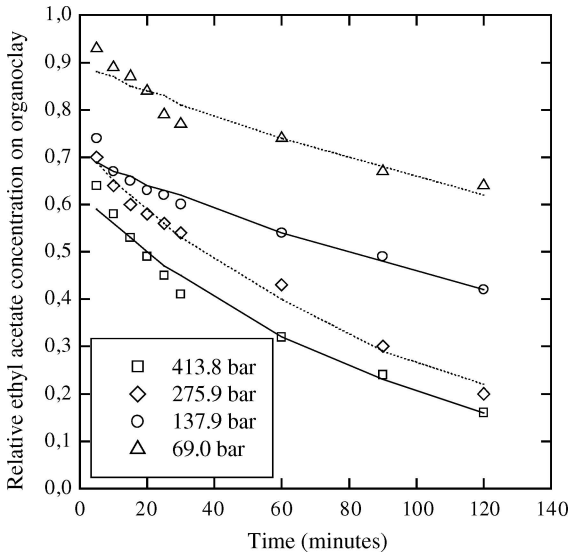

Figure 10. Experimental and predicted extraction profiles for the extraction of ethyl acetate with supercritical carbon dioxide at 333 K. The solid curves were obtained with the simplified model.

The isothermal curves (Fig. 9), at a temperature of 301 K in the liquid phase and 313 K at the beginning of the gas phase going into the supercritical region, show analogous behavior where the recovery efficiency increases at low pressures and decreases at high pressures. In these cases the viscosity effect seems to be dominant.

Results computed with this simplified model are presented in Fig. 9 together with some experimental data. It can be observed in this figure that for isothermal conditions the increase on the pressure causes a decrease on the ethyl acetate concentration in the clay. This result could be explained by the dependency between desorption and carbon dioxide density. In isothermal conditions, the increase on the pressure increases the carbon dioxide density leading to a greatest solvating power and, consequently, a fastest desorption.

As the results in Fig. 10 indicate, despite the different adsorptive capacities of the original and modified clays, there was no significant difference in regeneration efficiency between the two modified and the original montmorillonite.

It is worthwhile to mention that, having some desirable physicochemical properties, CO_2 could induce considerable swelling in the clay at moderate pressures. This is analogous to the swelling already reported for polymeric matrices (Wissinger and Paulaites, 1987). The results confirm that ethyl acetate is soluble in supercritical CO_2 and is not strongly adsorbed on the modified or on the original montmorillonite. These characteristics make the regeneration of all montmorillonites an easy process.

A last experiment was done to verify if the regenerated clays (the modified and the original) had its adsorption capacity altered after the adsorption/desorption cycle.

Conclusions

The regeneration of modified and original clays with supercritical carbon dioxide was experimentally studied. Amongst the many types of clay available, montmorillonite was employed because its high cation exchange capacity facilitates the surface modifications. Two quaternary amine modifiers ($HDTMA^+$ and TMA^+) were used. As a result, the surface properties of montmorillonite clay are changed considerably from highly hydrophilic to increasingly organophilic. Considering the ethyl acetate adsorption the most effective form of montmorillonite clay was the one modified with $HDTMA^+$. The effect of pressure and temperature on the regeneration process was characterized under different phase conditions (gas, liquid and supercritical). It was found that supercritical carbon dioxide led to the best regeneration results. Therefore, when an organoclay is utilized as an alternative adsorbent, 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. The desorption occurs according to a more complex mechanism. A crossover effect for desorption was observed, i.e., desorption decreases with an increasing temperature. A related crossover effect is well known for equilibrium solubility (solubility decrease with increasing temperature). The roles of the density and viscosity were observed to be determinants for the optimal conditions.

The supercritical regeneration with carbon dioxide of a modified clay loaded with toluene was experimentally studied. The data showed that the fluid density has an important influence in the process. The condition that gives a better regeneration of the clay is at 323 K and 100 bar where the density of the solvent is higher enough to give an efficient extraction power.

In order to know the equilibrium constant that represents the desorption process, the modeling of the process was done using the first-order and second-order models, which had already been used in the literature.

Only the second-order model represented properly a good agreement to experimental data. It means that the models are highly dependent of the operational conditions, therefore is necessary a specific equilibrium constant to each experimental point. Keeping in mind the knowledge of the isotherm equilibrium constant, the new data could be predicted.

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