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ADSORPTION OF ETHYL ACETATE ONTO MODIFIED CLAYS AND ITS REGENERATION WITH SUPERCRITICAL CO_2

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Abstract - Modified clays were used to remove ethyl acetate from aqueous solutions. These clays were regenerated using supercritical CO_2. Structural changes in the montmorillonite clay after treatment with quaternary amines were studied. The surface properties of the modified clay changed from highly hydrophilic to highly organophilic.

The clay was regenerated by percolation of a stream of CO_2 through the porous montmorillonite matrix. Different pressures and temperatures were employed, resulting in different fluid conditions (gas, liquid, and supercritical). The experimental data was fitted with a simplified model. The best desorption result was found under supercritical conditions. A crossover effect was observed. The capacity of the modified clay as a pollutant attenuator remained almost unchanged after a regeneration cycle.

Keywords: Ethyl acetate adsorption; Regeneration of modified clays; Supercritical CO_2.

INTRODUCTION

The increasing use of organic detergents and agricultural chemicals is dramatically accelerating the pollution of water. The removal of organic contaminants from wastewater via several physicochemical and biological techniques has been extensively researched. In this area of research, the removal of organic contaminants by means of adsorption onto organically modified clays, has attracted much attention (Kim et al., 1996).

In spite of the significant number of studies attesting to the high capacity of the organically modified clays to adsorb organic compounds, their commercial application is rarely seen. The main difficulty in their application lies in the regeneration process.

If a clay has metallic ions occupying cationic-exchange sites, its surface will be hydrophilic due to the water molecules in the hydration shell solvating the ions. This type of surface is not a good adsorbent for removing hydrophobic organic molecules, which have poor water solubility (Boyd et al., 1988). When the metallic ions are replaced by large organic ions, such as those from surfactants, the nature of the clay surface is drastically altered, becoming hydrophobic or organophilic. In this work, this sort of replacement is achieved through an ion-exchange reaction. A quaternary amine ion is introduced on the inorganic clay surface. The addition of amine enhances the capacity of the clay to remove organic contaminants.

Due to their large specific surface area and a cationic-exchange capacity, smectites are among the clays most frequently used as adsorbents. The quaternary amines used to modify smectites are cationic surfactants that have carbon chains with more than ten carbon atoms.

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In their study on adsorption of aromatic compounds onto modified clays, Kim et al. (1996) emphasized that surfactants with the highest organic carbon content should have the largest partition coefficient.

In this work, the use of modified and unmodified montmorillonite clays as adsorbent agents was studied. Montmorillonite is a special type of smectite clay. The removal of ethyl acetate found in aqueous solutions as an organic pollutant was the main goal of this study. Ethyl acetate is a chemical compound frequently discharged by chemical industries. The clay regeneration step is of key importance; therefore the use of supercritical CO_2 as regenerating agent was also studied in our work. The extraction of contaminants from solid matrices using a supercritical stream has several potential applications (e.g. analytical extraction, activated carbon regeneration, and soil recuperation) (Macnaughton and Foster, 1995).

EXPERIMENTAL METHODS

Clay Purification

Initially, the montmorillonite clay (Sigma-Aldrich, particle size of about 15 μm) was pretreated to remove impurities. The dry powder clay was dissolved for 24 h in hydrogen peroxide. The excess peroxide was decomposed by gently heating the mixture in a boiling water bath (Olphen, 1977). The purified clay was suspended in deionized water and then allowed to settle; the water was siphoned off and the clay was dried for further use.

Quaternary Amine Impregnation

Tetramethylammonium (TMA^+) chloride and hexadecyltrimethylammonium ($HDTMA^+$) bromide (Sigma-Aldrich) were used as modifiers. An amount of surfactant equal to the cation-exchange capacity of the clay (0.504 mequiv/g of clay) was introduced into different reactors. For the preparation of the clay with TMA^+, excess salt was added to achieve saturation. Excess organic salt was not used for the preparation of clay with $HDTMA^+$ because it could be retained by the clay above the exchange capacity (Boyd et al., 1988). A total amount of 30 g of pretreated montmorillonite was added to this container and then stirred with a magnetic stirrer for 24 h. After stirring, the treated clay was filtered, washed twice with 500 mL of deionized water, dried in an oven at 60ºC for 24 h, and kept in a brownish bottle for use.

X-Ray Diffraction Analysis

The structural changes in the montmorillonite after modification with the quaternary amines were studied using a powder X-ray diffractometer (Siemens D-500). The property monitored was basal spacings (d_{001}).

Adsorption Experiment (Batch)

A batch experiment was designed to compare the adsorptive capacity of organically modified clays with that of unmodified clays. Ethyl acetate was dissolved in deionized water at concentrations of 0.1 to 2.6 g/L and 40 mL of ethyl acetate solution were added to three different bottles containing 1g of the adsorbent material (unmodified clay, TMA montmorillonite, or HDTMA montmorillonite). The bottles were kept at a temperature of 308 K and were vigorously stirred with a magnetic stirrer. Samples were taken for analysis at regular time intervals until the concentration of ethyl acetate attained a constant value. The concentration of the samples was determined by SPME-GC (solid-phase microextraction – gas chromatography).

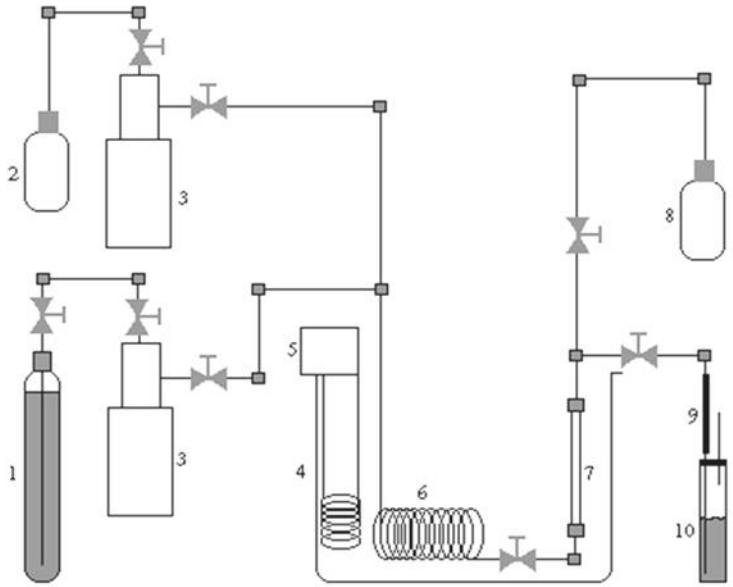
Adsorption Experiment (Continuous)

A column (2.7 cm^3) was charged with 1.0 g of organoclay and both ends were packed with1.0 cm of 20-30 mesh glass spheres. This was done to allow a homogeneous flow distribution, thus avoiding possible end effects. Porous stainless steel supports were used to hold the porous matrix in the column. An ethyl acetate solution (2.6 g/L) was pumped (syringe pump, ISCO model 100D) through the column packed with the organoclay (Figure 1). 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.

Supercritical Fluid Extraction

The apparatus developed for the adsorption experiments was also used in the supercritical fluid extractions (Figure 1). 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 heated bath at

constant temperature. Before entering the column, the CO_2 stream passed through a preheated coil, reaching bath temperature. The extracted ethyl acetate was collected through a stainless steel capillary tube in a cold trap containing 2-propanol. Nine samples were collected for each experiment. Over the first 30 minutes a time interval of 5 minutes between samples was adopted; for the following 2 hours the time interval was increased to 30 minutes. Desorption profiles were obtained at several pressure-temperature combinations. This allowed us to study desorption efficiency with CO_2 under different operational conditions. The samples collected were analyzed by gas chromatography (GC).



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.

Figure 1: Sketch of the apparatus used for adsorption and supercritical extraction of ethyl acetate from organoclays:

EXPERIMENTAL RESULTS AND DISCUSSION

In the adsorption of solutions, the amount of adsorbed material depends on several characteristics: adsorbent material, nature of the solute, adsorbent superficial area, solution concentration, and temperature.

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 adsorption was the type of modification undergone by the clay (the nature of the adsorbent).

Figure 2 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 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 can also be observed that the montmorillonite saturated with TMA^+ ions had a weaker sorption capacity than the clay modified with the $HDTMA^+$ ion. 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.

In order to explain the observed adsorption capacity of the clays, d_{001} spacings were determined by X-ray diffraction analysis. These results can be seen in Figures 3, 4, and 5. The first peak of the diffraction results represents the d_{001} spacing of an intercalated layer of the sample. In Table 1 the properties of the clays, relating adsorption capacity with basal spacing, are shown. The d_{001} spacing of the original clay is 14.79 Å at 5.89º and the d_{001} spacing of the HDTMA clay is 18.84 Å at 4.61º. The presence of the $HDTMA^+$ ion in 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.

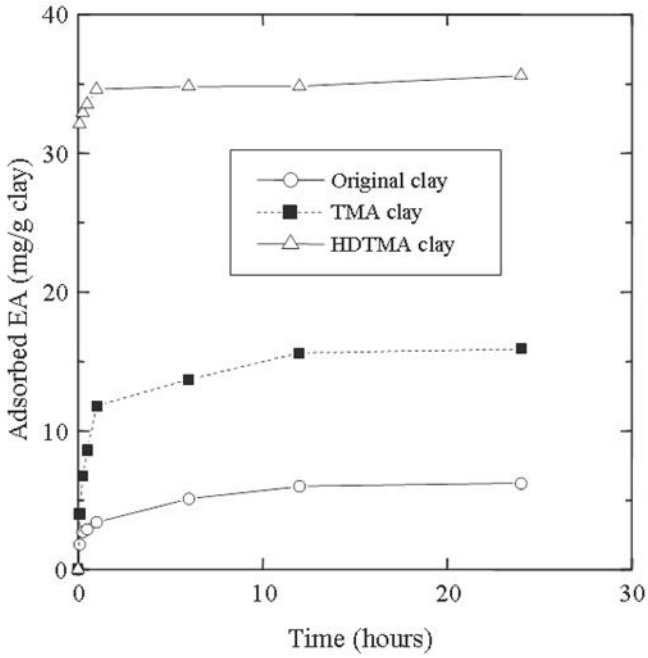


Figure 2: Adsorption capacity of modified and unmodified clays.

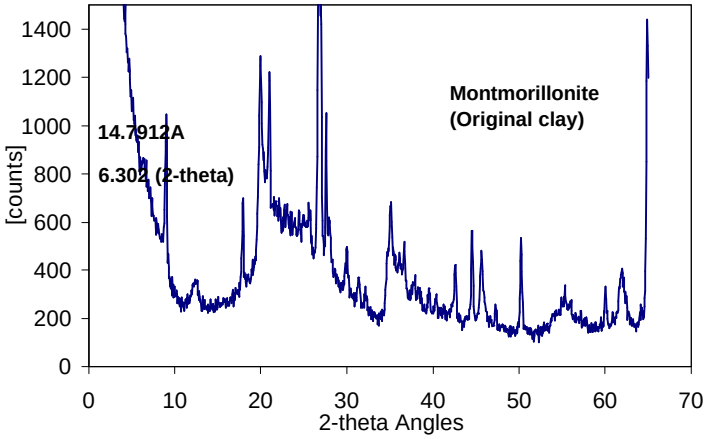


Figure 3: Unmodified montmorillonite X-ray diffraction.

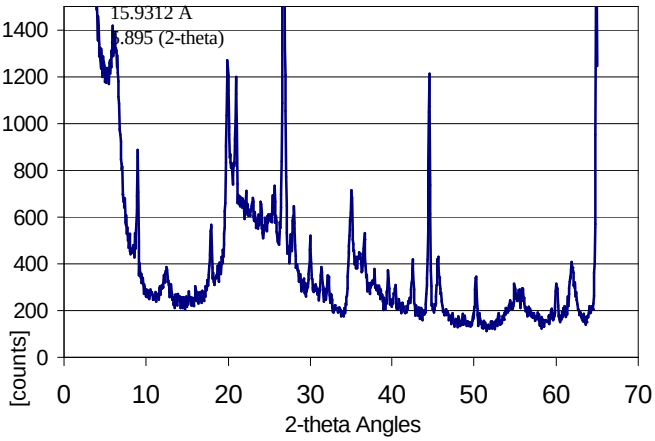


Figure 4: TMA montmorillonite X-ray diffraction.

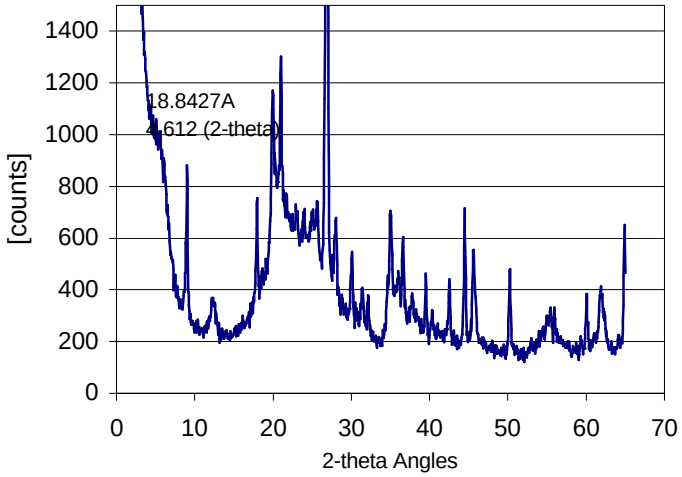


Figure 5: HDTMA montmorillonite X-ray diffraction.

Table 1: Properties and adsorption capacity of the clays.

Properties*	Original clay	TMA^+ clay	$HDTMA^+$ clay
Basal spacings d_{001} (Å)	14.79	15.93	18.84
Adsorption of EA (mg/g-clay)	6.20	15.60	35.60

(*) The regenerated clay does not change the properties.

Aiming to regenerate the porous matrix, the ethyl acetate adsorbed on the HDTMA montmorillonite was recovered. These experiments were carried out with carbon dioxide at different combinations of temperature and pressure, in a search for the optimal operating conditions. A mass balance for the ethyl acetate was calculated at the end of the adsorption/desorption experiments. The total volume of the carbon dioxide applied for recovery of the adsorbed ethyl acetate from the organoclay was 266 mL. The influence of temperature on 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. These results are presented in Figure 6 and Table 2.

The best operational conditions were found with CO_2 in the supercritical region (333 K and 413.8 bar), 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 gas conditions studied in this work, when the pressure was kept at 69.0 bar, the recovery efficiency decreased with the increase in 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 6 clearly depicts this unusual phenomenon, which is similar to that of solubility in a supercritical solvent, where solubility decreases with an increase in 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 has certain physicochemical properties that increase its appeal. As an example, even though it has a liquid-like density over much of the range of interest to industry it has the gas-like transport properties of diffusivity and viscosity. Additionally, the very low surface tension of supercritical fluid allows easy penetration into microporous materials. These properties can provide different effects. Higher density may enhance solubility, and higher viscosity may slow down the rate of diffusion (Table 2).

The isothermal curves (Figure 6), 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 efficiency of recovery increases at low pressures and decreases at high pressures. In these cases the effect of viscosity seems to be dominant.

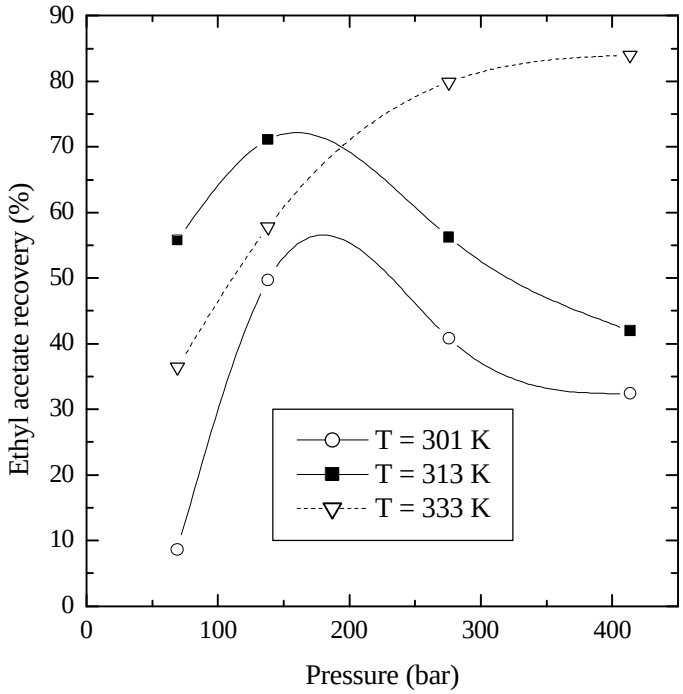


Figure 6: Isothermal desorption of ethyl acetate from HDTMA clay with supercritical carbon dioxide – The influence of pressure.

Table 2: Ethyl acetate recovery and carbon dioxide properties under several experimental conditions.

Temperature (K)	Pressure (bar)	Density (g/mL)	Viscosity (g/(cm.s))10^4	Recovery** (%)	Region
301	69.0	0.706	2.27	8.6	L
	137.9	0.834	7.79	49.7	L
	275.9	0.948	10.22	40.8	L
	413.8	0.998	12.01	32.4	L
313	69.0	0.211	2.03	55.8	G
	137.9	0.745	6.52	71.1	SF
	275.9	0.908	9.18	56.2	SF
	413.8	0.967	11.03	42.0	SF
333	69.0	0.160	1.99	36.4	G
	137.9	0.474	4.25	57.8	SF
	275.9	0.822	7.37	79.9	SF
	413.8	0.901	9.36	84.0	SF

Key: L – liquid; G – gas; SF – supercritical fluid
(**) All values are averages from replicate analyses ± 1 standard deviation.

For modeling the desorption process the packed bed was assumed to be perfectly mixed with carbon dioxide. The mass transfer resistances are negligible in this case with equilibrium being the only factor contributing to the extraction process. A mass balance in the extraction column is expressed by

$$W\left(\frac{d\theta}{dt}\right) = -QC \qquad (1)$$

where W is the clay weight, q 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. A linear partition relationship between the phases is assumed

$$\theta = KC \qquad (2)$$

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

The solution of Equations (1-2) is given by

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

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 determination of the distribution coefficient and prediction of the extraction profiles (Coelho et al., 2001). Results computed with this simplified model are presented in Figure 7 together with some experimental data. It can be observed in this figure that under isothermal conditions the increase in pressure causes a decrease in the ethyl acetate concentration in the clay. This result can be explained by the mutual dependence of desorption and carbon dioxide density. Under isothermal conditions, the increase in pressure increases the density of the carbon dioxide resulting in a greater solvating capacity and, consequently, a faster desorption.

As the results in Figure 8 indicate, despite the different adsorptive capacities of the original and modified clays, there was no significant difference in efficiency of regeneration between the two modified and the original montmorillonite.

It is worth mentioning that, because it has some desirable physicochemical properties, CO_2 can induce considerable swelling in the clay at moderate pressures. This is analogous to the swelling already reported for polymeric matrices (Wissinger and Paulaites, 1990). 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.

The last experiment was done to verify whether adsorption capacity of the regenerated clays (the modified and the original) was altered after the adsorption/desorption cycle. Another adsorption experiment was conducted with the regenerated clays and the efficiency of adsorption found was similar to that in the original experiment also shown in Figure 2.

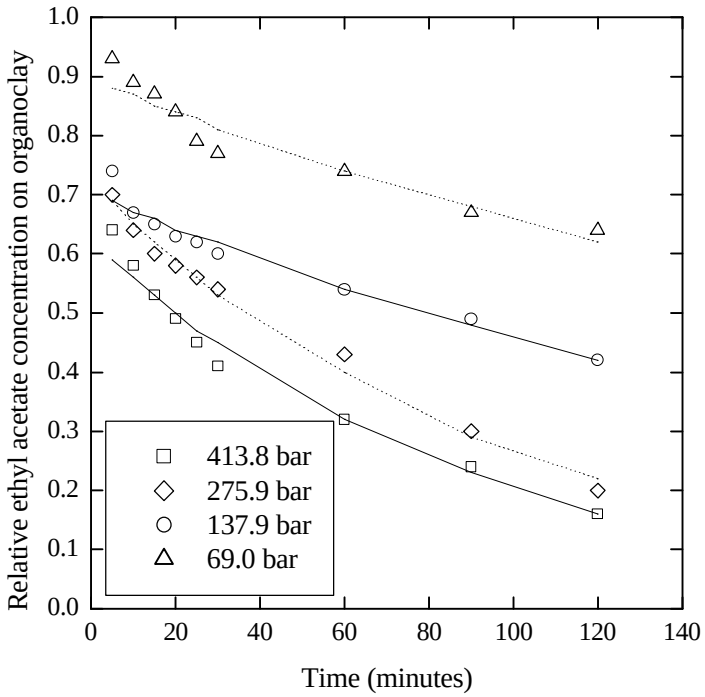


Figure 7: Experimental and predicted extraction profiles for the extraction of ethyl acetate with supercritical carbon dioxide at 333 K. The lines were obtained with the simplified model (Eq. 3).

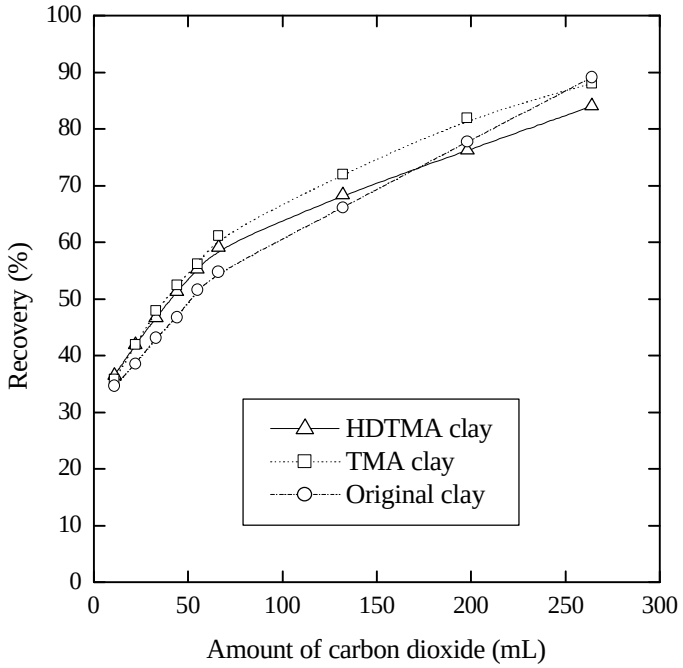


Figure 8: Regeneration of modified and original clays loaded with ethyl acetate with supercritical CO_2 at 413.8 bar and 333 K.

CONCLUSIONS

The regeneration of modified and original clays with supercritical carbon dioxide was studied experimentally. Of the many types of clay available, montmorillonite was chosen because its high cation-exchange capacity facilitates surface modifications. Two quaternary amine modifiers ($HDTMA^+$ and TMA^+) were used. As a result, the surface properties of montmorillonite clay were changed considerably from highly hydrophilic to increasingly organophilic. For 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 produced the best regeneration results. Therefore, when an organoclay is utilized as an alternative adsorbent, supercritical extraction can be an effective technology for regeneration of the organoclay as well as for recovery of the adsorbed materials from the organoclay. Desorption occurs according to a more complex mechanism. A crossover effect for desorption was observed, i.e., desorption decreases with an increase in temperature. A related crossover effect is well known for equilibrium solubility (solubility decreases with an increase in temperature). The roles of density and viscosity were observed to be determinants under optimal conditions.

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