DESORPTION OF TOLUENE FROM MODIFIED CLAYS USING SUPERCRITICAL CARBON DIOXIDE

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Abstract - The main objective of this work is to study the regeneration capacity of modified clays using supercritical fluid. These modified clays are used as organic compound adsorvents. The experimental step was done using a packed column with the clay contaminated by toluene. 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 first- and second-order models. Better results were obtained using the second-order model. This study makes possible the scale-up of the desorption process for regeneration of solid matrices using supercritical fluids.
Keywords: Supercritical fluid, desorption process, organic compound adsorvents.

INTRODUCTION

Environmental control is an area of great interest for application of supercritical fluid extraction technology which is constantly improving, by soils contaminated. Industrial solid, liquid and gas residues are currently the biggest environmental worry (Macnaughton and Foster, 1995). Research carried out over the last few 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 frequently employed supercritical solvent is carbon dioxide because of its special characteristics and physicochemical properties, e.g., nonflammability, nontoxicity, relatively low cost, higher mass-transfer rate and adjustable extraction ability of organic compounds depending on density. It has proved to be an effective solvent for regeneration of activated carbon loaded with organic compounds (Modell et al., 1979). In order to understand the adsorption and desorption process, extensive research on new adsorbents for the removal of pollutants has also been carried out. The study of regeneration of these adsorbents is also very important. The regeneration of activated carbon by SC-CO_2 after adsorption of toluene has already been studied experimentally (Tan and Liou, 1990). Normally, the activated carbon is used to reduce and/or to recover organic compounds in effluent 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 using SC-CO_2 at different pressures and temperatures was studied. The clay used was montmorillonite and tetramethylammonium

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(TMA⁺) as organic modifier, which gave a better organophilic nature to the clay. This kind of study is very important for making it possible to scale-up the regeneration process for application to solid matrices or contaminated soils (Alonso et al., 2002).

EXPERIMENTAL METHOD

The experimental apparatus used for the regeneration measurements at elevated pressures is illustrated in Figure 1.

Preparation of the organoclay: the clay used (montmorillonite) and the TMA⁺ chloride were purchased from Sigma-Aldrich Canada Ltd. The

TMA⁺ was used without further purification for modification of the clay.

Regeneration: the toluene was extracted by passing the pure supercritical carbon dioxide through a stainless steel tube charged with clay previous contaminated with 134 μl of organic contaminant. The desorption column (2.7 cm³) was packed with about 1.26 g of the modified clay and glass beads were packed above and below the clay packing, both at a height of about 1.5 cm in order create uniform flow rates. Stainless steel frits were used to hold the organoclay in the column.

Gas chromatographic analyses: a HP 5890 gas chromatograph with a flame ionization detector (silica column type SE-54, 25m, col. 70 °C, inj. 250 °C and det. 250 °C) was used for this task.
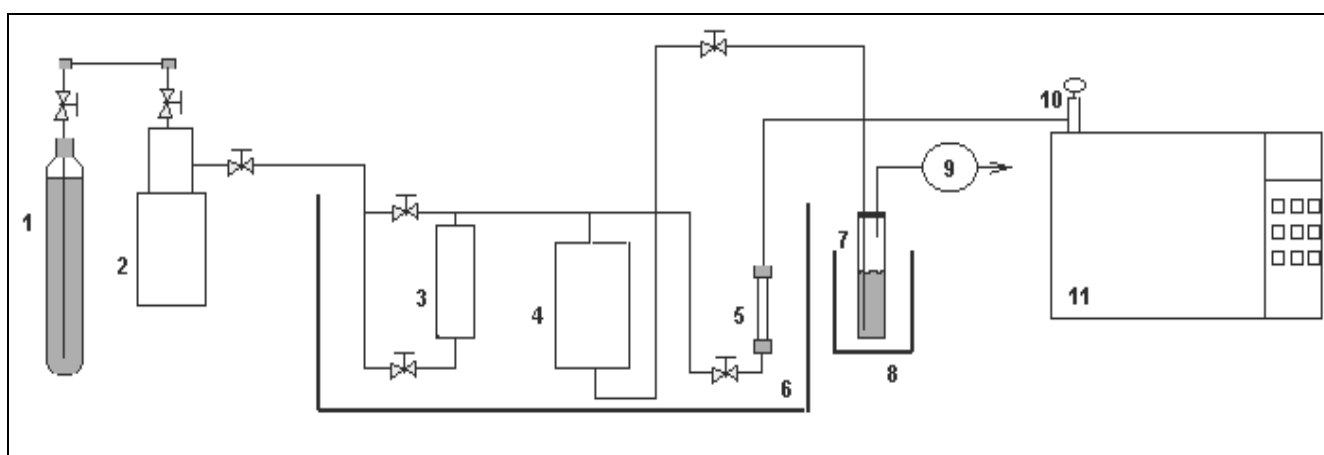
Figure 1: Schematic diagram of the apparatus used for desorption experiments were: 1) gas cylinder (minimum purity of 99.9%, AGA); 2) high pressure pump; 3) saturator; 4) mixing tank (Berghof Labortechnik, Germany); 5) desorption column; 6) heating bath (FALC FA90, ± 0.1ºC); 7) trap, 8) ice bath; 9) gas meter; 10) six-way valve and 11) gas chromatography.

MODELING OF THE DESORPTION PROCESS

The modeling of the desorption process was 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

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

where q_e is the desorbed amount in the equilibrium, q is 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 as a function of the desorption amount and time

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

A plot of the logarithm of the lefthand side of equation (2) as a function of time suggests the

applicability of this kinetic model to represent the experimental data. The correlation coefficients were so low that they do not give representative values.

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

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Dividing the equation and rewriting it,

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

Since q_e is equal to 100% because of the experimental step and the q/q_e values with time are known, then

$$\left(\frac{q_e}{q} - 1 \right) = \frac{1}{t \cdot K_2} \qquad (5)$$

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

RESULTS AND DISCUSSION

The results obtained in the clay regeneration process are shown in Figures 2, 3 and 4. The data show that more than one regeneration in the same matrix of adsorbent did not really change the kinetics of the process and this behavior can be observed in Figure 2. The experiments were done under the same conditions of pressure and temperature (75 bar and 310 K) and the experimental points were almost the same.

Figure 3 illustrates that the desorption process increases with the increase in density of the supercritical CO_2. At 310K and 75 bar, the density of the CO_2 is 0.25438 g/cm^3 and at 323K and 100 bar, it 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 stronger than the bonding forces between toluene and the modified clay surface. This illustrates that a higher efficiency of regeneration can be obtained for the organoclay loaded with toluene when density is increased.

Figure 4 shows the large difference between the desorption kinetics of TMA-clay and the unmodified clay. The curve that represents the regeneration of unmodified clay is almost a line, which characterizes it as a drag instead of a regeneration process. This probably happened due to the contamination method used. The unmodified clay has a low adsorption capacity.
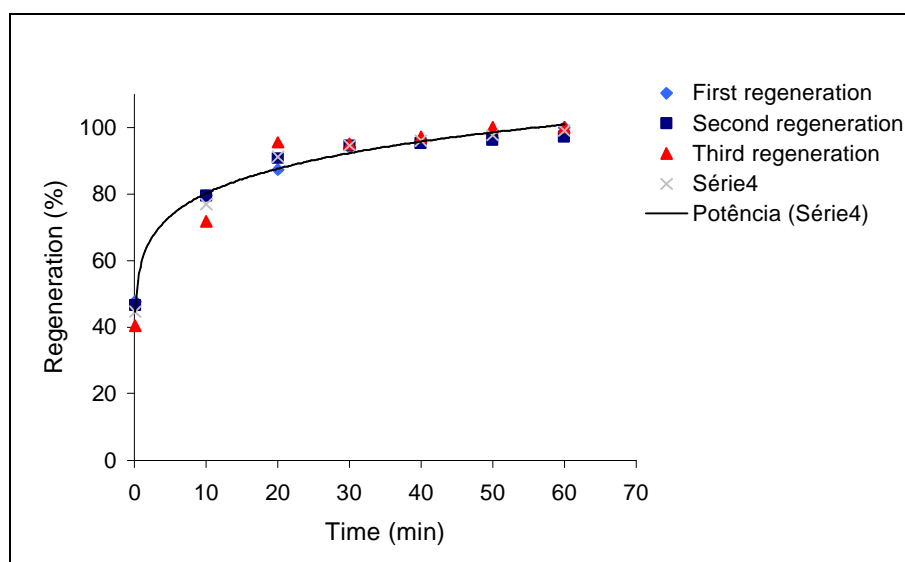
Figure 2: Desorption of toluene after regeneration of the matrix at 310 K and 75 bar.
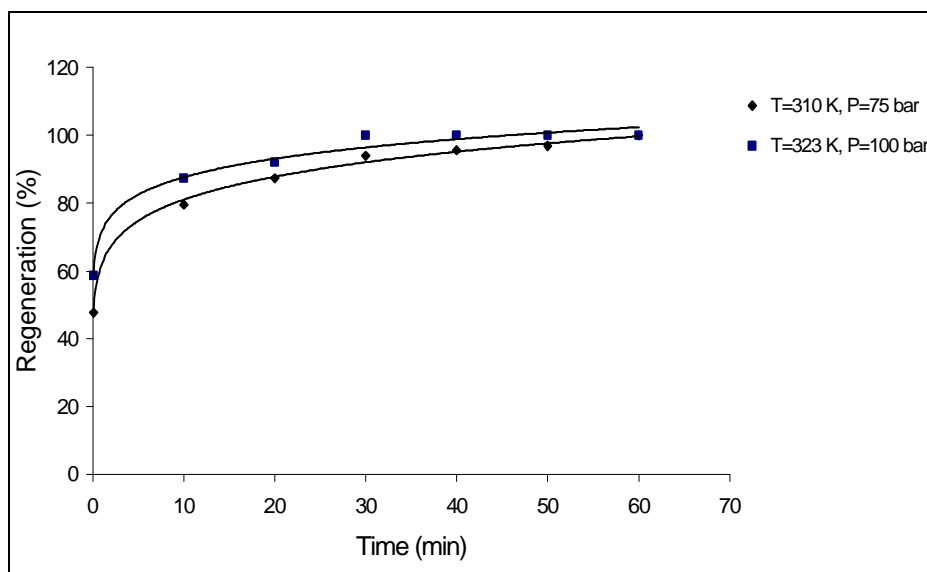
Figure 3: Desorption of toluene under different operational conditions using supercritical carbon dioxide.
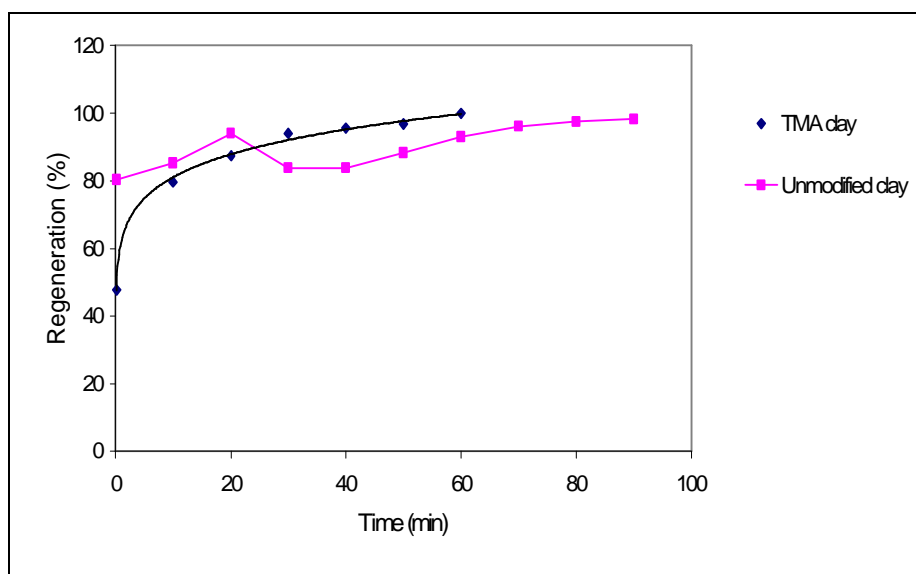
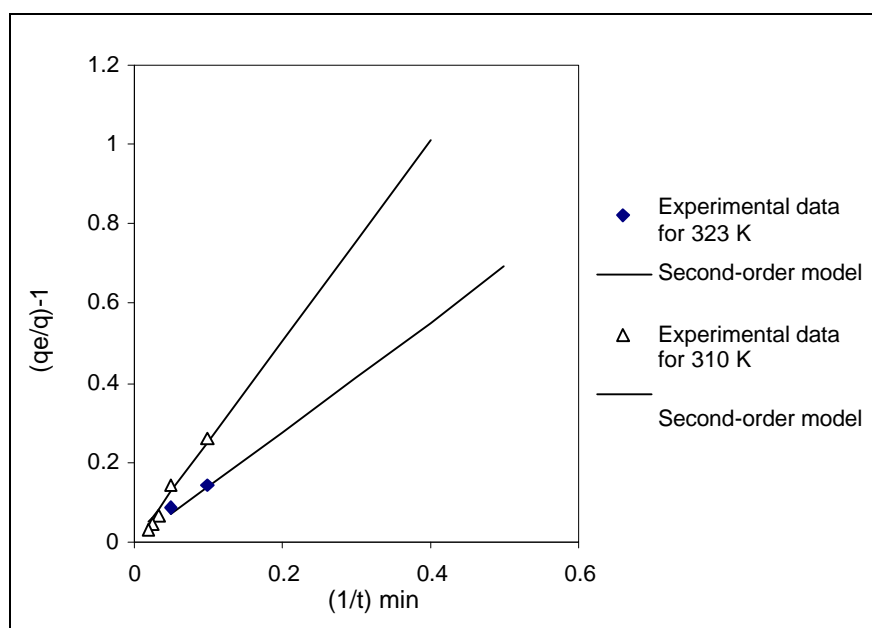**Figure 4:** Desorption of toluene comparing TMA[+] clay with the unmodified clay.

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

Only two experimental points were obtained at 323K; these are presented in Figure 5. This happened because the clay is totally regenerated at this temperature within 30 minutes. In addition to the data fitted by the model using the experimental data, Figure 5 shows the correlated experimental data and predicted points for times shorter than 10 minutes, which is the initial time of the desorption process. Prediction of new adsorption data is possible using the model with the estimated parameters and knowledge of the regeneration process profiles at the same conditions of temperature and pressure.

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

T (K)			First-order	Second-order
310 **q/qe**	**310** **qe/q**	**t** **min**	**K₁ = -0.0605** **R= 0.7013** **1-(q/qe)**	**K₂ = 0.3959** **R= 0.9811** **(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 **q/qe**	**323** **qe/q**	**t** **min**	**K₁ = -0.0844** **R= 0.8698** **1-(q/qe)**	**K₂ =14.1286** **R= 0.9672** **(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

Figure 5: Modeling of the desorption process using the second-order
model for experimental data at 310 and 323 K.

CONCLUSIONS

The supercritical regeneration with carbon dioxide of a modified clay loaded with toluene was experimentally studied. The data showed that fluid density has an important influence on the process. The best regeneration of the clay is at 323K and 100 bar, where the density of the solvent is high enough to provide an efficient extraction ability.

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 adequately provided good agreement with experimental data. This means that the models are highly dependent on the operational conditions; therefore it is necessary to determine a specific

equilibrium constant for each experimental point. Given the knowledge of the isotherm equilibrium constant, the new data could be predicted.

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