

SUPERCRITICAL CARBON DIOXIDE DESORPTION OF XYLENE FROM ZEOLITE

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ABSTRACT

Emissions of organic vapors from industrial and commercial sources need to be controlled because they are a source of photochemical smog and nuisance odors. Several methods, such as condensation, absorption, adsorption, contact oxidation and incineration are used for removal and/or recovery of organic vapors. The adsorption process is one of the most effective methods. Activated carbons are the conventionally adsorbents used but highly dealuminated Y zeolites have been successfully tested in adsorption pilot plant as a good alternative. After the exhaustion of the full adsorption capacity, zeolite is subject to treatment not only to recover the solvents but also to re-use of the adsorbent. Because supercritical carbon dioxide possesses several special characteristics and physicochemical properties, it has proved to be an effective solvent for regenerating adsorbents loaded with volatile organic compounds (VOC). However, the existing experimental database of DAY zeolite supercritical carbon dioxide desorption is limited.

In this study, the m-xylene, chosen as a representative product of the volatile organic compounds, was adsorbed on dealuminated Y zeolite. The main objective of this work is to demonstrate the ability of supercritical carbon dioxide to regenerate the zeolite loaded at low pressure with m-xylene and to study the effect of temperature, pressure and CO₂ flow rate on regeneration efficiency.

INTRODUCTION

The increasing awareness of the necessity for environmental safety and pollution control has opened new prospects for the adsorption/desorption process in many industrial chemical plants such as printing, coating, textile dyeing, spray painting and polymer processing. In such plants, volatile organic compounds (VOC) are commonly used and emitted. To recover organic pollutants such as VOC, activated carbon are customarily employed but they show some inconveniences. The activated carbon is a flammable material, it does not desorb efficiently high-boiling solvents and it is a hygroscopic material.

In this study, a relatively new adsorbent is used: a dealuminated Y zeolite (DAY zeolite). This zeolite exhibits the FAU (faujasite) structure. The advantages of this are essentially its incombustibility, its great stability, its hydrophobic character and its regenerability at low temperature. A comparison of the properties of this material with those of the activated carbon was given by Otten et al. [1]. In this work, the m-xylene, chosen as a representative product of the volatile organic compounds, was adsorbed on dealuminated Y zeolite. The m-xylene adsorption isotherms on this zeolite were studied by El Brihi et al. [2].

The steam regeneration method is customarily employed to regenerate adsorbents but, in recent years, supercritical fluid extraction has received widespread attention for the removal of VOC from liquid and solid matrices. Several studies have investigated the supercritical desorption characteristics of activated carbon systems [3-8]. However, there has been very limited study concerning the supercritical regeneration of the selected zeolite.

The aim of this paper is to study the regeneration by supercritical carbon dioxide of DAY zeolite loaded at low pressure with m-xylene at different operating conditions. The effects of temperature, pressure and CO₂ flow rate on regeneration were investigated.

MATERIALS AND METHODS

m-xylene was used as the adsorbate in this study because it is frequently used as the solvent in petrochemical and polymer industries. m-xylene (98% purity) was purchased from Aldrich.

DAY zeolites samples were supplied by Degussa-Hüls in the form of solid extrudates (diameter = 2 mm). This zeolite allows the adsorption of VOC from polluted air without exhausting the capacity by adsorbing water vapor. The loss on ignition was measured by thermogravimetry, the low measured value (3.38%) is due to the hydrophobic character of this zeolite. DAY zeolites are nonflammable and stable at temperatures up to 1000 °C. The measured physical properties of the DAY zeolite are listed in Table 1.

Table 1. Zeolite Properties

Properties	Values
Loss on ignition/%	3.38
BET surface area/m ² .g ⁻¹	800
Micropore volume/cm ³ .g ⁻¹	0.3
Pore diameter/nm	0.74

Adsorption

Since the adsorption has been studied by El Brihi et al. [2], adsorption theory is not detailed in this work. To prepare samples of saturated zeolite, a flow type apparatus based on a chromatographic technique with frontal analysis was build up. This dynamic method allows us to measure vapor adsorption equilibria for m-xylene. A schematic diagram of the experimental set-up is shown in figure 1. Nitrogen was used as a carrier gas for the organic pollutant. The nitrogen flow rate equal to 3.10⁻⁴ m³.min⁻¹ at 0.1 Mpa and 293.15 K was regulated using a mass flow controller. The m-xylene was introduced into the system using a syringe pump and the partial pressure of m-xylene in the gas mixture entering the adsorption column was approximately 144 Pa. The adsorption column temperature was kept constant by using a thermostated bath and the pressure was controlled by the manometer located at the exit of the adsorption column.

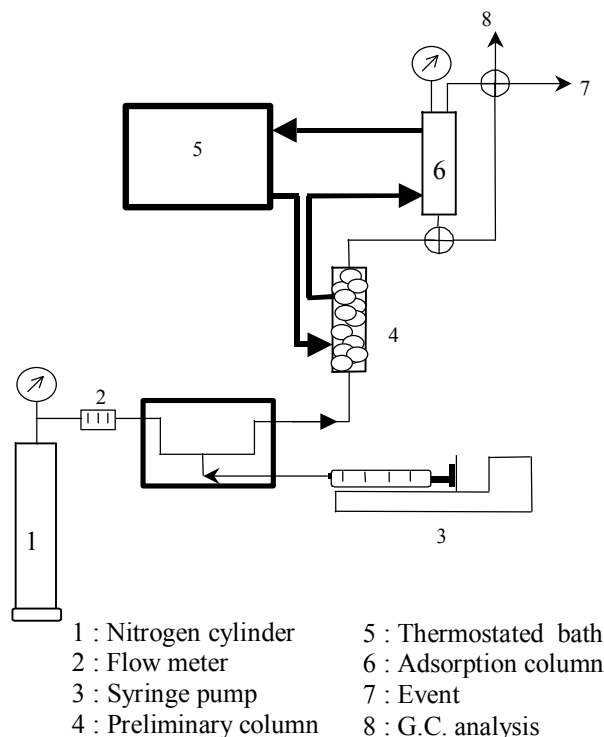


Figure 1. Schematic flow sheet of the adsorption apparatus.

In order to render homogeneous the mixture of nitrogen and m-xylene, a preliminary column, thermostated at the same temperature as the adsorption column and filled with glass beads, was introduced in our apparatus. For each adsorption, 4 g of zeolite was introduced in the column (zeolite was located in the middle of the column meaning that the top and the bottom of the column were filled with glass beads). The selected adsorption temperature was 328.15 K whereas the column pressure was maintained constant and equal to 0.12 Mpa. Before starting an adsorption experiment, the gas entering the adsorption column is analysed by gas chromatography. Once the gas composition is constant, it is sent to the adsorption column and the leaving gas is periodically analysed by the on-line gas chromatograph to measure the m-xylene concentration. Typically, an adsorption ends when the outlet concentration equals the inlet concentration, meaning that the equilibrium has been achieved (the zeolite is saturated with m-xylene at the selected temperature). The plot of outlet concentration against time (breakthrough curve) yields the equilibrium data and information on the adsorption dynamics. The adsorption loading is obtained by numerical integration of the area behind the breakthrough curve.

To prepare equivalent samples of zeolite loaded with m-xylene for the regeneration, adsorption conditions were maintained constant. Under these experimental conditions, the average amount of absorbed m-xylene (expressed in mole of m-xylene per kilogram of zeolite) is $q \approx 1.40 \text{ mol.kg}^{-1}$.

Desorption

After the adsorption step, the loaded zeolite was taken out of the adsorption column and was packed in the desorption column to study the regeneration. The schematic flow sheet of the experimental apparatus used is presented in figure 2. In order to make the supercritical fluid uniform in the regeneration column, glass beads were also packed in the regions above and below the zeolite sample.

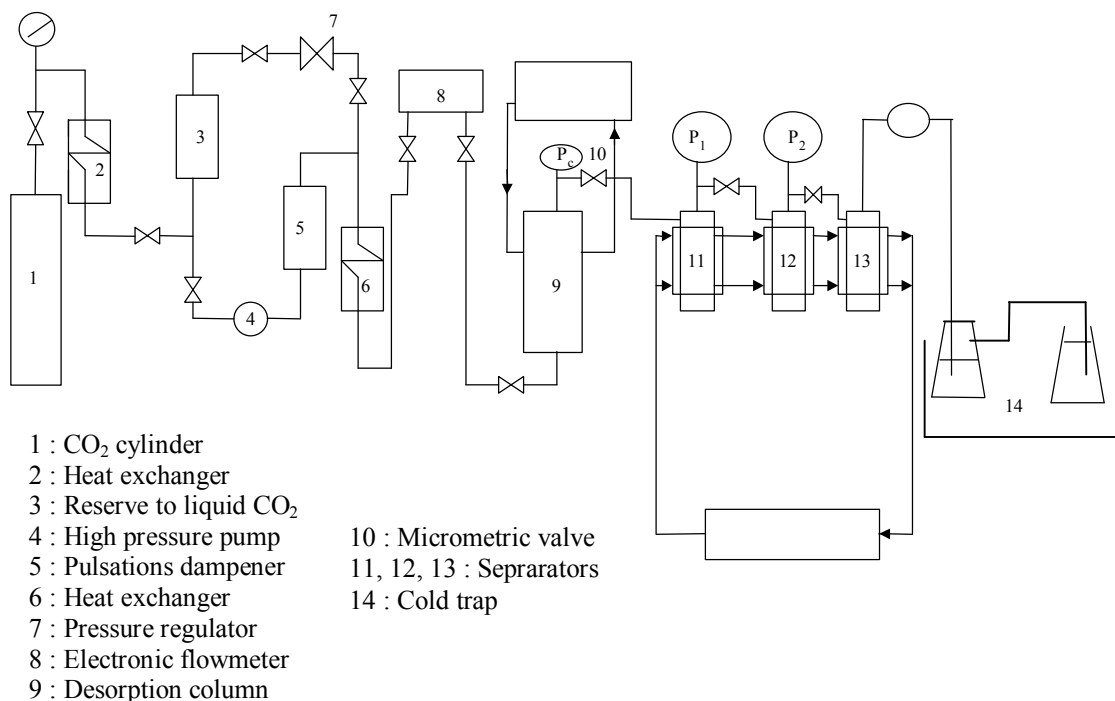


Figure 2. Schematic flow sheet of the desorption apparatus.

The carbon dioxide exiting the cylinder is cooled, pumped, heated and by the end sent into the thermostated desorption column containing the zeolite to regenerate. The supercritical CO₂ flow rate is measured by a flow meter. In each desorption experiment, the pressure, the CO₂ flow rate and the temperature were maintained constant. The gas coming out of the desorption column (a mixture CO₂/m-xylene) passes through three cyclonic separators (used only to expand the mixture) and the desorbed m-xylene was collected in a cold trap (14) containing 1.3 L of ethanol. The ethanol allows the dissolution of the m-xylene desorbed by the CO₂. Samples of 1 μ L were frequently taken out for gas chromatography analysis (FID detector) in order to obtain the desorption curves. When the concentration of m-xylene in the cold trap did not change any longer, the desorption experiment was stopped.

RESULTS AND DISCUSSION

The desorption experiment described above was conducted many times in order to study the regeneration under different conditions of temperature, pressure and CO₂ flow rate.

Pressure effect

The effect of regeneration pressure on the desorption amount at 313.15 K is shown in figure 3. For each experiment, the CO₂ flow rate was maintained constant at 6.7 g.min⁻¹. From this figure, it obviously can be concluded that regeneration efficiency increases with the operating pressure. This trend was also observed by Tan and Liou [3-4] and Benkhedda et al. [8] concerning the regeneration of activated carbon. The pressure effect may be due to the increase of the density.

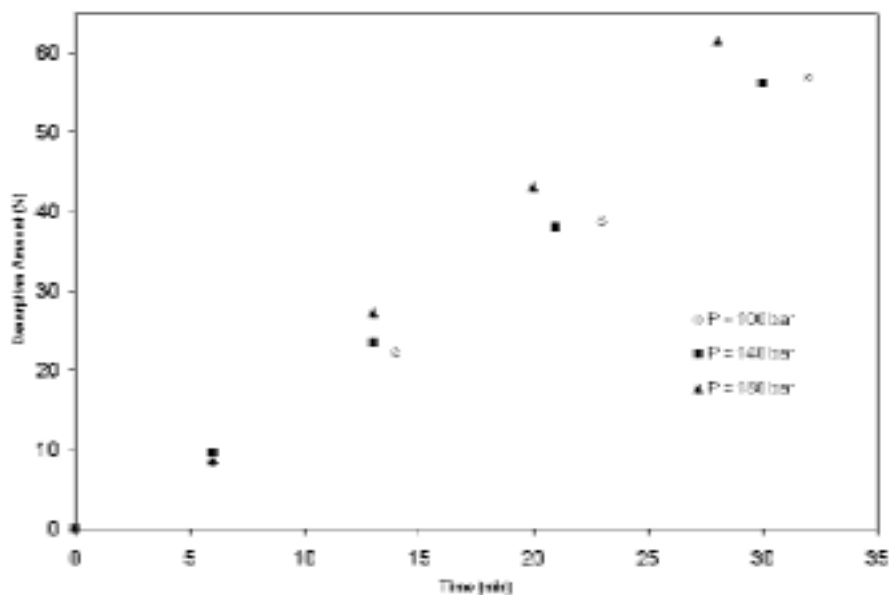


Figure 3. Pressure effect on regeneration at 313.15 K (CO_2 flow rate = $6.7 \text{ g}\cdot\text{min}^{-1}$).

Temperature effect

The effect of temperature on the desorption is shown in figure 4.

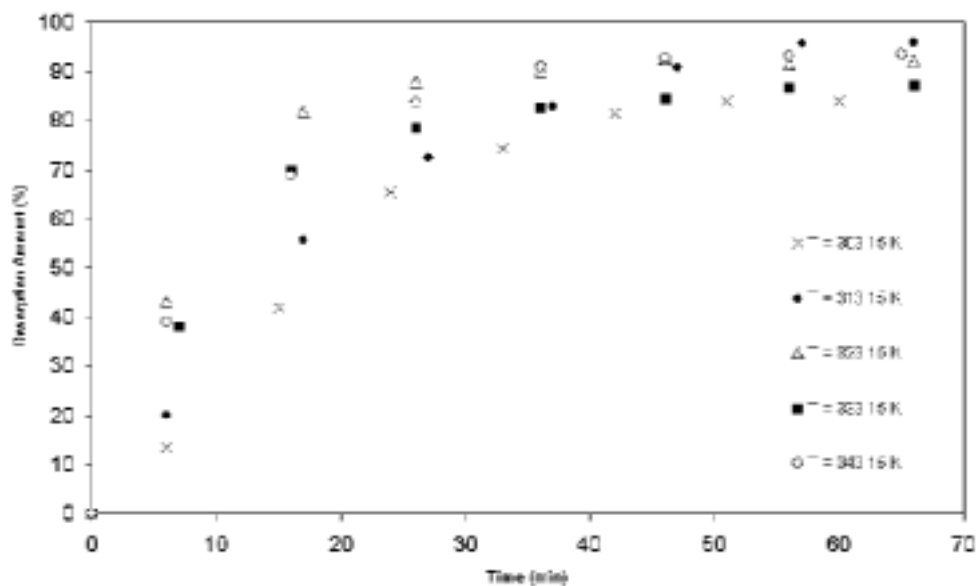


Figure 4. Temperature effect on regeneration at 100 bar (CO_2 flow rate = $15 \text{ g}\cdot\text{min}^{-1}$).

The effect of temperature was studied at 100 bar when the CO_2 flow rate was fixed at $15 \text{ g}\cdot\text{min}^{-1}$. The figure indicates that an optimal operating temperature exists. The existence of an optimal operating temperature might be explained in terms of density and viscosity of the fluid. In general, higher density may enhance the solubility of a solute in a supercritical fluid but higher viscosity may have an adverse effect on diffusion rate. At 100 bar, it seems that the viscosity effect in addition to density is also important; hence an optimal temperature exists in the critical region.

Flow rate effect

The importance of the supercritical CO_2 flow rate on the regeneration of zeolite was studied at $T = 313.15 \text{ K}$ and $P = 100 \text{ bar}$.

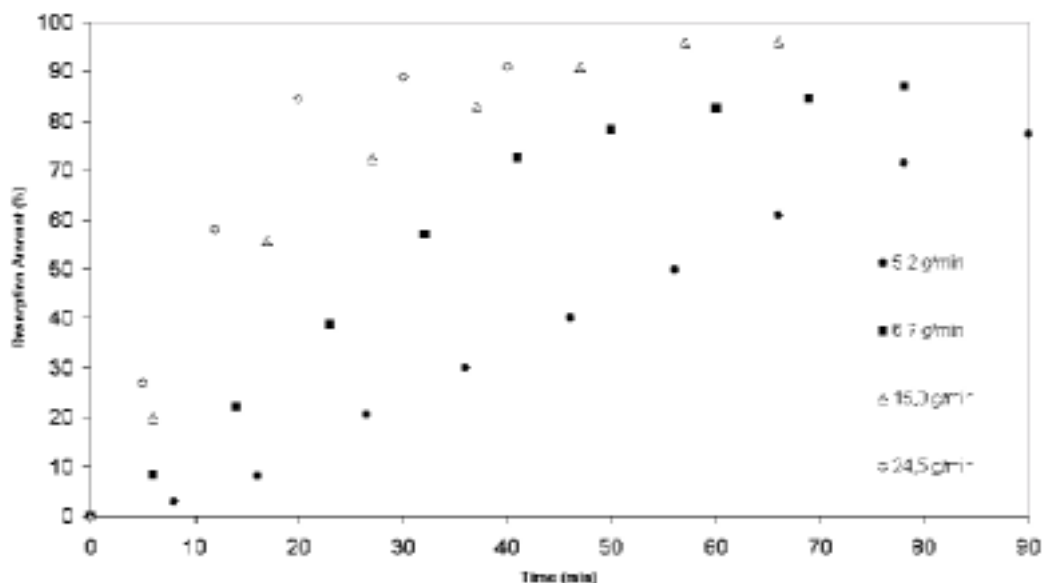


Figure 5. Flow rate effect on regeneration at 100 bar and 313.15 K.

Four different flow rate between $5.2 \text{ g}\cdot\text{min}^{-1}$ and $24.5 \text{ g}\cdot\text{min}^{-1}$ were tested. Obviously, an increase of the supercritical carbon dioxide flow rate involves a decrease of the desorption time. In other words, the desorption amount increases with the flow rate at fixed time. However, if we plot the desorption amount in function of the total quantity of CO_2 , the result is quite surprising: about 500 g of CO_2 are needed to reach 80% of regeneration, whatever the CO_2 flow rate used! It means that, in this range of flow rate ($5\text{-}25 \text{ g}\cdot\text{min}^{-1}$), the mass-transfer coefficient is more or less constant and it is not influenced by the flow rate.

CONCLUSION

In this study, the regeneration of DAY zeolite loaded with m-xylene by supercritical carbon dioxide was investigated. It was found that the higher operating pressure was more favorable for regeneration and an optimal desorption temperature was observed for a pressure of 100 bar. The regeneration efficiency increases with the CO_2 flow rate but the mass-transfer coefficient is more or less constant in the studied range of flow rate.

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