

MODELLING OF EQUILIBRIUM SORPTION OF M-XYLENE ON DAY ZEOLITE AND SUPERCRITICAL DESORPTION

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ABSTRACT

Adsorption isotherms of m-xylene, on dealuminated Y zeolite (DAY) were measured by the gravimetric static method at four temperatures (25, 35, 45, 55 °C) and by the dynamic method at two temperatures (45 and 55°C). The m-xylene isotherms obtained by the both methods are compared in order to check the accuracy of our measures. The experimental data obtained by the gravimetric static method were correlated with the very simple Langmuir model.

In the second step, the method of the regeneration of the saturated zeolite by supercritical carbon dioxide was exposed.

INTRODUCTION

Environmental protection regulations for volatile organic compounds (VOC) emission control have been accelerating the development of VOCs abatement systems. Among numerous method of removal and/or recovery of VOC, the adsorption method is investigated in this study. Activated carbons are the conventionally adsorbents used but highly dealuminated Y zeolites (DAY zeolites) have been successfully tested in adsorption pilot plants as a good alternative. A comparison of the properties of the both adsorbents was given by Otten et al [1].

The design of any adsorption process requires the knowledge of adsorption equilibrium. In particular, VOCs adsorption equilibrium data on DAY zeolite is becoming increasingly important in engineering and environmental studies. For measuring VOCs adsorption equilibrium data, three types of experimental techniques can be used: gravimetric, volumetric, and dynamic method [2]. The volumetric and gravimetric methods are static type, that is, the adsorbate and the adsorbent are in equilibrium in a closed system. The number of moles adsorbed is found either by weight measurements (gravimetric method) or by appropriate P-V-T measurements (volumetric method). In the dynamic type of experiment, a gas chromatograph (GC) is used for measuring adsorption equilibrium data by frontal analysis.

Because supercritical carbon dioxide possesses several special characteristics and physicochemical properties (non-flammable, non-toxic, relatively inexpensive, high mass-transfer rate, and adjustable extraction power for organic compounds depending on the

density) it has proved to be an effective solvent for regenerating activated carbon loaded with VOCs [3-5]. However the existing experimental database of DAY zeolite supercritical carbon dioxide desorption is limited [6].

In this study, the m-xylene, chosen as a representative product of the volatile organic compound, was adsorbed on DAY zeolite. Adsorption isotherms were measured by using the gravimetric method at $t = (25, 35, 45, 55) ^\circ\text{C}$ and by the dynamic method at $t = (45 \text{ and } 55) ^\circ\text{C}$. The experimental data obtained by the gravimetric static method were correlated by the Langmuir model. Another main objective of this paper was to expose the method of the regeneration of DAY zeolite loaded with m-xylene.

I. MATERIALS AND METHODS

DAY zeolites samples were supplied by Degussa-Hüls, which uses a special silicon tetrachloride treatment yields an Y-zeolite with almost all of the aluminium sites occupied by silicon. The samples were in the form of solid extrudates (diameter = 2 mm). This zeolite was found to be thermally stable up to 1000°C , non-inflammable and acid resistant [7]. The loss on ignition was measured by thermogravimetry under helium flow using a SeTaram Tag 24 apparatus. The low measured value (3.38 %), obtained after water vapor equilibrium, is due to the hydrophobic character of this zeolite. The BET surface area, micropore volume and the binder amount of the DAY zeolite sample used were measured with a ϕ -Sorb from GIRA Society using liquid nitrogen at $T = 77 \text{ K}$. The apparent density, the macropore and mesopore volume, the external void porosity, the particle porosity, the bed porosity and the particle density were determined by porosimetry using a Micromeritics apparatus. The measured physical properties of the DAY zeolite are listed in Table 1.

Table 1. Adsorbent properties.

Property	Value
loss on ignition/%	3.38
BET surface area/ $\text{m}^2 \cdot \text{g}^{-1}$	615
micropore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$	0.250
macropore and mesopore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$	0.539
binder amount/mass %	17
bulk density/ $\text{g} \cdot \text{cm}^{-3}$	0.496
particle density/ $\text{g} \cdot \text{cm}^{-3}$	0.809
external void porosity (ϵ_I)	0.387
particle porosity (ϵ_P)	0.436
bed porosity (ϵ_B)	0.654

The VOC, chosen for the study, was m-xylene (98 % purity) and it was purchased from Aldrich. The physical properties of this VOC are listed in Table 2.

Table 2. Physical properties of m-xylene

Property	Unit	Value
Molecular weight	$\text{g} \cdot \text{mol}^{-1}$	106.7

Normal boiling point	°C	139.1
Vapor pressure		
25 °C		1.126
35 °C	Pa	1.962
45 °C		3.279
55 °C		5.283
Liquid density at 20 °C	$g \cdot cm^{-3}$	0.836

Adsorption

The gravimetric static method. A SARTORIUS 4201 electromagnetic suspension microbalance was installed for the measurement of the adsorbed quantities of vapors in zeolites. It has a ± 0.01 mg resolution and a ± 0.02 mg precision, for a measuring full scale of 100.00 mg. A schematic diagram of the apparatus is shown in Figure 1. The temperatures of the VOC vapor, of the sorption chamber and of the magnet chamber were separately controlled.

In a typical experiment, about 15 mg of DAY zeolite was evacuated at 60 °C under 0.01 Pa during two days. Then the VOC vapor source was connected to the sorption chamber. The mass was digitized and monitored as a function of time by a computer. The mass was obtained by averaging five mass values acquisitioned at 0.1 s intervals around the time point (one point every 1 second). The background noise, averaged by means of statistical function in the assistant software was subtracted from the measured values. By this way, smooth, reproducible sorption curves were obtained. The sorption experiments were carried out below atmospheric pressure and the sample mass was measured over a large range of vapor pressures. In this study the adsorption equilibrium data of m-xylene on DAY zeolite were measured at $t = (25, 35, 45, 55)$ °C.

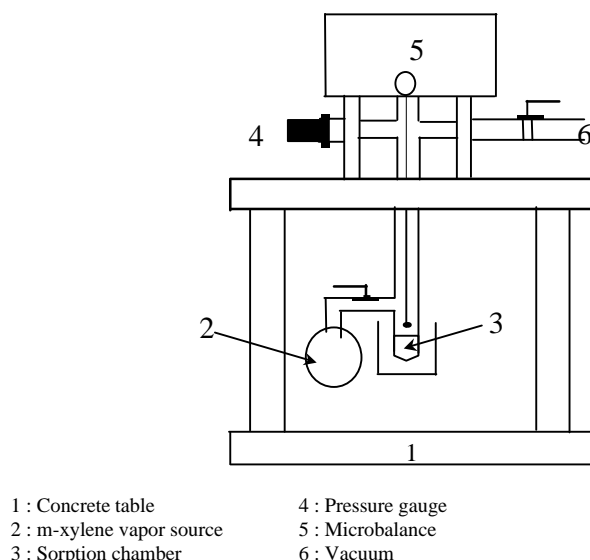


Figure 1. Schematic description of the electromagnetic suspension microbalance

The dynamic method. A flow type apparatus based on a chromatographic technique with frontal analysis was built up to measure vapor adsorption equilibria for m-xylene. A schematic diagram of the experimental set-up is shown in Figure 2.

All experiments were performed at atmospheric pressure. Nitrogen was used as a carrier gas for the organic pollutant. The m-xylene was introduced using a syringe pump. By changing the flow rate different concentrations of m-xylene in nitrogen can be obtained. During each experiment, the adsorption column is thermostated, whereas the column pressure is controlled by the manometer located at the exit of the Nitrogen cylinder.

In this study, 2 temperatures were studied (45, 55°C) and the column pressure was maintained constant and equal to 1.4 bar. Before an adsorption experiment, the gas entering the adsorption column is analyzed by using gas chromatography (GC) via the three-way valves located at the top and at the bottom of the column. An on-line gas chromatograph (Chrompack capillary column, CP-sil 5 CB), which was connected with a six-way valve (volume is equal to 500 μ l), and a flame ionization detector were used for the analyze. Consequently, a calibration curve giving the m-xylene concentration as a function of its area peak was first determined using mixtures of nitrogen and m-xylene the composition of which were known. Typically, an experiment ends when the outlet concentration equals the inlet concentration, meaning that the equilibrium has been achieved. The plot of outlet m-xylene concentration versus time (breakthrough curve) yields the equilibrium data information on the adsorption dynamics. In this study, the breakthrough curves were obtained with successive step changes of increasing concentrations (Figure 3). The adsorption loading is obtained by numerical integration of the area behind the breakthrough curve.

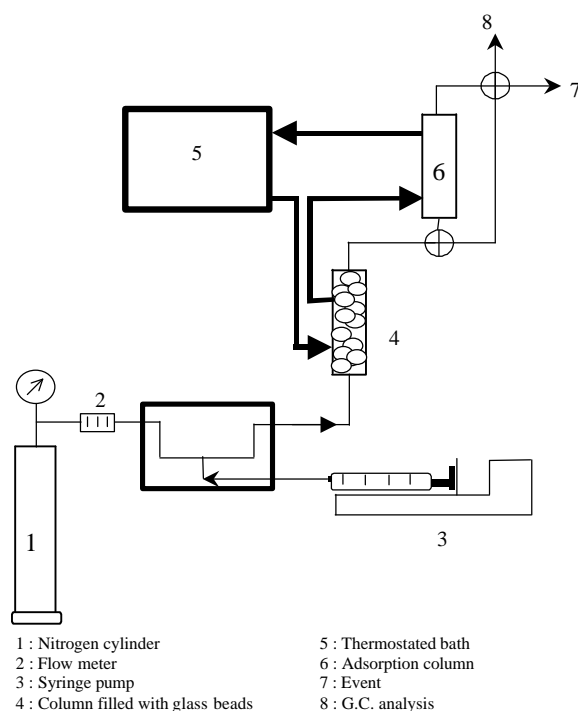


Figure 2. Schematic flow sheet of the home made apparatus

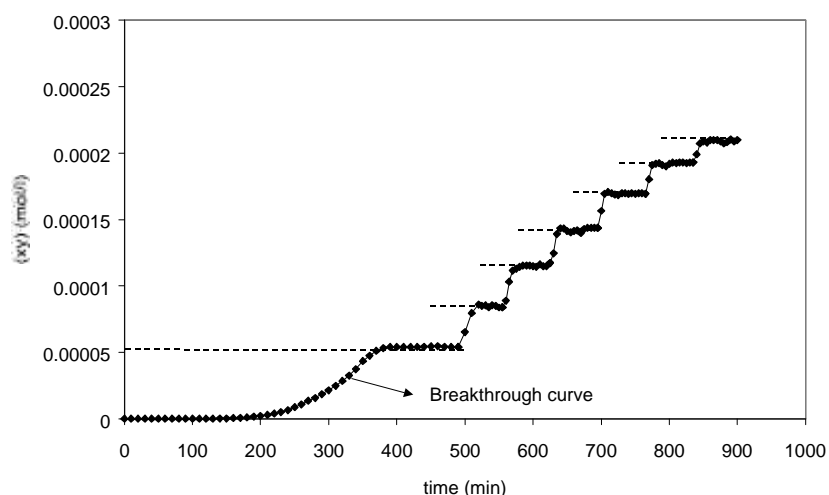


Figure 3. Breakthrough curves obtained with successive step changes of increasing concentrations at $t = 45^{\circ}\text{C}$.

Desorption

The schematic flow sheet of the experimental apparatus used in this study is presented in Figure 4. The CO_2 exiting the bottle at 50 bar is gaseous, it is liquefied in a heat exchanger and then pumped. At the exit of the pump, the liquid CO_2 is warmed by means of a heat exchanger to reach the supercritical state. It flows through a thermostated desorption column containing the adsorbent to regenerate (4 grams). The internal diameter and the height of the adsorption column are respectively equal to 22 mm and 290 mm. The CO_2 flow is measured with a flowmeter ("Micro Motion" model supplied by Separex-Champigneules-France). The relaxation of the working pressure to the atmospheric pressure is made with a micrometric valve. The stream then crosses a cold trap containing 400 ml of ethanol, which allows the dissolution of the m-xylene desorbed by the CO_2 . A sample of $1\ \mu\text{l}$ was frequently taken to be analyzed by gas chromatography. A flame ionization detector, a Split-Splitless injector and a Chrompack capillary column (CP-sil 5 CB) were used. The oven temperature was 75°C . Injector and detector temperatures were both at 250°C .

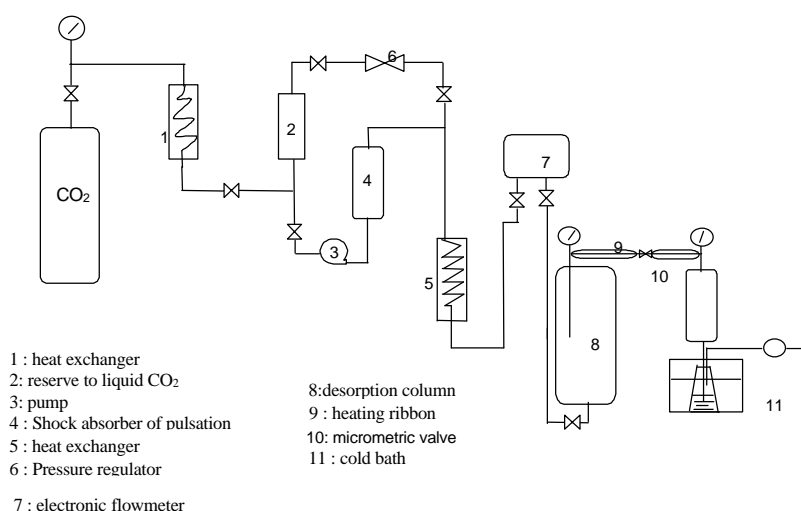


Figure 4. Schematic diagram of experimental apparatus for desorption.

II. RESULTS AND DISCUSSION

Adsorption

As previously explained, m-xylene adsorption experiments were performed using the gravimetric static method at $t = (25, 35, 45, 55 \text{ } ^\circ\text{C})$ and using the dynamic method at $t = (45 \text{ and } 55) \text{ } ^\circ\text{C}$.

Correlation of the adsorption isotherms. The Langmuir model [8] was used to correlate our data points. The Langmuir equation is represented as:

$$q = q_m \frac{bP}{1 + bP} \quad (\text{i})$$

The different parameters (q_m , b) were determined by using a non-linear curve fitting procedure. The parameters obtained are summarized for the four temperatures in Table 3 and the corresponding calculated adsorption isotherms are shown in Figure 5.

Table 3. Langmuir parameters for the adsorption of m-Xylene on DAY zeolite

t ($^\circ\text{C}$)	Langmuir parameters	
	q_m (mol/kg)	b (Pa^{-1})
25	1.747	0.111
35	1.461	0.299
45	1.332	0.255
55	1.296	0.206

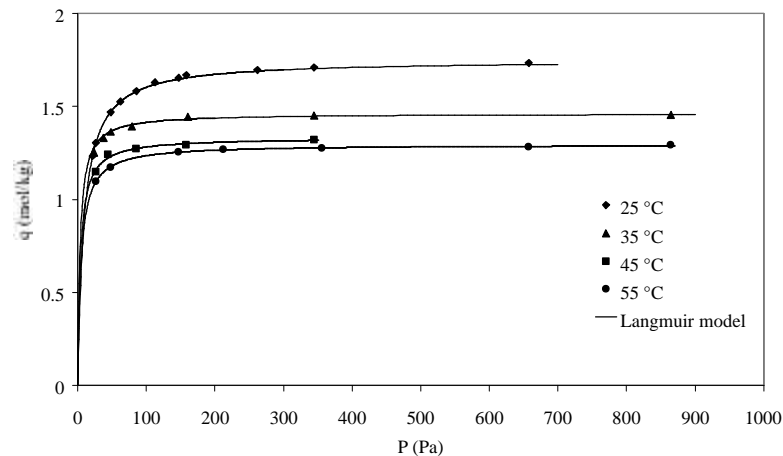


Figure 5. Correlation of the experimentally determined adsorption isotherms with the Langmuir model.

Comparison of the dynamic and of the static methods. The m-xylene adsorption equilibria obtained by the dynamic method were compared with those obtained by the gravimetric static method at $t = (45 \text{ and } 55) \text{ } ^\circ\text{C}$. Indeed, it is interesting to compare the results because in the literature, some disagreement between the both methods has been reported for a pure adsorbate [9]. To make the comparison easy, a relative deviation between data obtained by the static method and the dynamic method was established according to:

$$\Delta q(\%) = 100 \cdot \frac{|q_i^{\text{static method}} - q_i^{\text{dynamic method}}|}{q_i^{\text{static method}}} \quad (\text{ii})$$

For the two temperatures considered in this study (45 and 55) °C, the relative deviation remains lower than 2 %. The example of the comparison of the obtained adsorption isotherms at 45 °C by the both methods may be seen in figures 6.

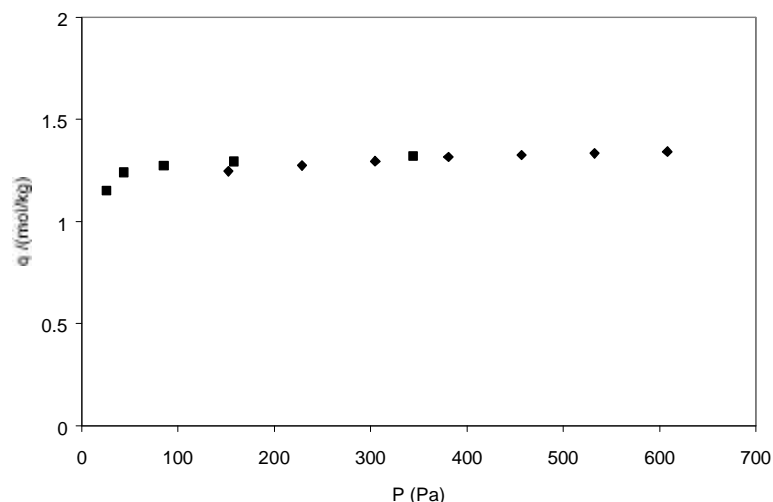


Figure 6. Comparison between adsorption isotherm of m-Xylene on DAY zeolite measured at 45 °C using either the gravimetric static method (■) or the dynamic method (v).

CONCLUSION

The equilibrium adsorption data showed that, when the temperature increased, the amount was reduced. The data obtained by the gravimetric static method were correlated with the Langmuir model. From this study, it can be concluded that the Langmuir model leads to a nice correlation of the data.

The perspectives opened by this work of the desorption viewpoint is to study the effect of the supercritical CO₂ flow rate on regeneration efficiency.

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