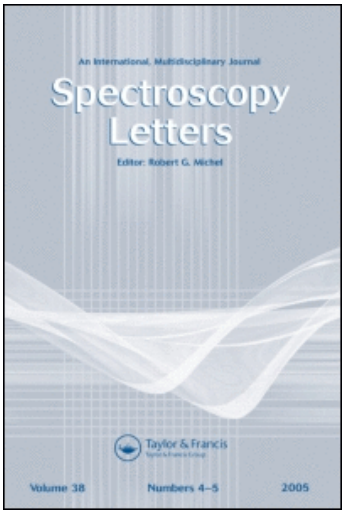

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Determination of the Heat of Adsorption and Desorption of a Volatile Organic Compound Under Dynamic Conditions Using Fourier-Transform Infrared Spectroscopy

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Abstract: Quantitative Fourier-transform infrared spectroscopic analysis was used for the determination of adsorption capacity of a model volatile organic compound (VOC) under dynamic conditions. The analytical method used also offers the possibility of distinguishing between reversible and irreversible adsorption as well as further detection of adsorbed VOC transformation. The obtained adsorbed amounts have been used for the determination of the heat of adsorption and the activation energy of desorption using, respectively, isosteric and temperature programmed desorption methods. The approach has been applied to explore the potential use of local clay as an adsorbent material for VOC pollutants.

Keywords: Adsorption heat, desorption energy, FTIR spectroscopy, isosteric, temperature programmed desorption (TPD), volatile organic compounds (VOCs)

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INTRODUCTION

Adsorption is well established as a unit operation for pure gas production and also for waste-stream treatment. The process is attractive regarding its cost/performance ratio. The choice of a potential adsorbent should avoid chemical bonding with adsorbate so that adsorbed species can be removed easily (lower desorption energy).[1] For this purpose, determination of the heat of adsorption and desorption energy could be very useful for the estimation and the prediction of the potential use of an adsorbent material.[2]

The isosteric method was found to be efficient for the determination of the heat effects generated by adsorption processes for systems involving relatively weak interaction.[3,4] High accuracy of the experimental method for determining the adsorbed quantities is required; otherwise, the values of the heats are adversely affected.[5] Moreover, the analytical method must be able to differentiate the reversible and irreversible quantities. For example, only an average value of adsorption heat can be obtained using micro-calorimetry measurements.[6,7]

When the adsorption process involves significant irreversible fraction, the temperature programmed desorption (TPD) method was found to be appropriate and efficient for the investigation of thermal behavior.[8–10] The results are of interest for adsorbent regeneration and for security of industrial plants. For instance, volatile organic compound (VOC) desorption from an activated carbon bed, the most frequently used material, may induce local temperature rises that may cause fire hazards.[11]

Fourier Transform Infrared spectroscopy (FTIR) is a proven technique for qualitative and quantitative analysis particularly in the case of heterogeneous catalysis and gas adsorption studies.[12–16] Recently, we have presented an experimental approach for measurement of adsorbed and desorbed amounts under dynamic conditions using spectroscopy.[17] The method has been shown to be particularly efficient for distinguishing between reversible and irreversible adsorption by quantitative analysis of IR bands. The technique offers further detection of adsorbate dissociation through simultaneous detection of new IR bands that may originate from adsorbate dissociation during the adsorption or desorption processes.

In the current work, the obtained reversible and irreversible adsorbed amounts were used to determine the heat of adsorption and desorption, respectively, according to isosteric and TPD methods. The approach was applied to explore the potential use of local clay as an adsorbent of VOC pollutant. The current study could be a starting point for further development of innovative materials involved in environmental engineering control with a perspective of local sustainable development through scientific research activities with potential economic added value.

MATERIALS AND METHODS

Materials

The clay tested in the current work comes from deposits located in the north of Morocco (Nador area). The results corresponding with its textural and mineralogical composition have been published.[18] The clay was found to be a mixture of phases, namely, opal, montmorillonite, kaolinite, muscovite, topaz, rutile, calcite, and dolomite, suggesting a bentonite type clay. Textural studies perfomed with N_2 adsorption desorption at 77 K have shown a BET (Brunauer, Emmett, and Teller) specific surface area of 79 $m^2\ g^{-1}$ and a negligible micropore volume of 0.002 $cm^3\ g^{-1}$ compared with total pore volume of 0.205 $cm^3\ g^{-1}$. The pore size distribution obtained following BJH (Barrett, Joyner, and Halenda) method revealed the presence of a wide pore size in the mesopore range with a significant contribution of pore widths between 10 and 50 nm.

Procedure of Adsorption and Desorption Experiments

Adsorption/desorption experiments were performed under dynamic conditions at atmospheric pressure with a homemade apparatus as recently reported.[17] The bentonite adsorptive properties were investigated with respect to *o*-xylene vapor, which has been selected as a model VOC pollutant because of its use in local industry. Prior to adsorption, a model mixture with a given concentration of *o*-xylene vapor in nitrogen flow was prepared by means of a saturator connected to a condenser that was immersed in a thermostatically controlled bath. This temperature was carefully checked to maintain constant *o*-xylene vapor pressure and consequently keep the *o*-xylene concentration unchanged. The resulting concentration is expressed as molar fraction (or partial pressure; P/P_0), where P is the vapor pressure of *o*-xylene obtained from the Antoine equation and P_0 the atmospheric pressure taken as 760 torr. Hence, fixing condenser temperature between $-8^{\circ}C$ and $40^{\circ}C$ permitted obtaining a value of concentration at reactor inlet (C_{in}) in a range of 700–11,000 ppm.[19,20]

The sample pretreatment as well as adsorption and desorption experiments were performed with a flow rate of 100 $cm^3\ min^{-1}$ that was passed through a quartz reactor (U-type) containing 1 g of bentonite meshes. The sample was first pretreated under N_2 flow at 473 K for 30 min, then adsorption was carried out using the model mixture flow until saturation was reached in order to obtain breakthrough curves. The model gas mixture was switched again to pure N_2 flow, to proceed with isothermal desorption until *o*-xylene concentration at the reactor outlet reached zero. This step was followed by a subsequent linear heating in order to perform the TPD experiment.

The *o*-xylene concentrations at reactor outlet during adsorption and desorption were monitored with a FTIR spectrometer (Jasco 410, resolution

4 cm^{-1}, Japan Spectroscopic Co., Ltd.) using a Pyrex gas cell equipped with CaF_2 windows. The quantitative analysis is, currently, facilitated by FTIR instrumentation and programs that allow high-frequency spectra acquisition and manipulation (substraction, multiplication, smoothing). This operation is particularly easy when there are no IR bands overlapping, and the application of Beer–Lambert law permits relating IR bands area to concentration. In the current work, the quantitative treatment was achieved by integrating characteristic *o*-xylene IR bands located between 2600 and 3200 cm^{-1}. Preliminary calibration with *o*-xylene/
N_2 mixtures of known composition was carried out using reactor bypass, in order to correlate bands area with concentration. Figure 1 shows the calibration curve representing the area integral of *o*-xylene IR bands between 2600 and 3200 cm^{-1} as a function of concentration. The FTIR response was found to produce a linear plot in the studied concentration range, and its accuracy was checked over three experiments and was represented as mean value.

RESULTS AND DISCUSSION

Determination of Adsorption Capacity as well as Reversible and Irreversible Amounts

The monitoring of *o*-xylene IR bands during adsorption at 300 K shows gradual increase of IR bands until equilibrium was reached, which corresponds with adsorbent saturation (Fig. 2A). Following this step, the gas mixture was switched to pure nitrogen flow (0.36% *o*-xylene/$N_2 \rightarrow N_2$) to perform isothermal desorption giving rise to a gradual decrease of IR bands

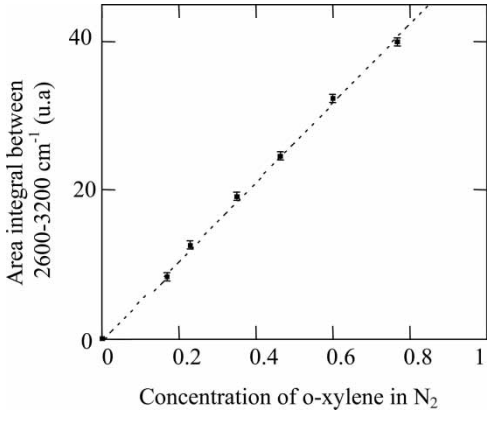

Figure 1. Calibration curve of *o*-xylene IR band area integral (2600–3200 cm^{-1}) versus its concentration in N_2 (molar fraction %).

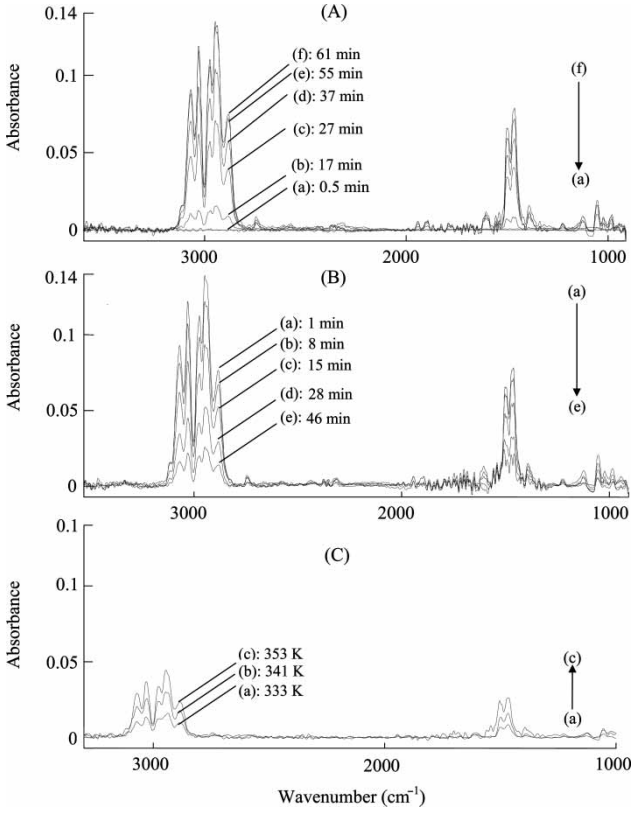

Figure 2. Evolution of *o*-xylene IR bands during the following successive experiments: (A) isothermal adsorption at 300 K, (B) isothermal desoprtion and (C) TPD under N_2 at linear heating rate of 5 K/min.

with time, as shown in Fig. 2B. The sample was then linearly heated up to 473 K to carry out a TPD experiment under N_2 flow (Fig. 2C). It is to be noted that the recorded FTIR spectra do not reveal any new species formation originating from *o*-xylene transformation involving adsorbent catalytic activity. This information provided by the use of FTIR analysis technique can be considered as an advantage of the experimental approach.

The evolution of *o*-xylene concentration at the reactor outlet (C_{out}) obtained from FTIR spectra permitted the monitoring of adsorbent loading as a function of time during adsorption (i.e., breakthrough curve) and desorption processes. Figure 3 shows the profile of the variation of *o*-xylene concentration in the gas flow at reactor outlet, represented as relative values (C_{out}/C_{in}) during the aforementioned cycle of successive steps (adsorption at 300 K until saturation followed by isothermal desorption then TPD).

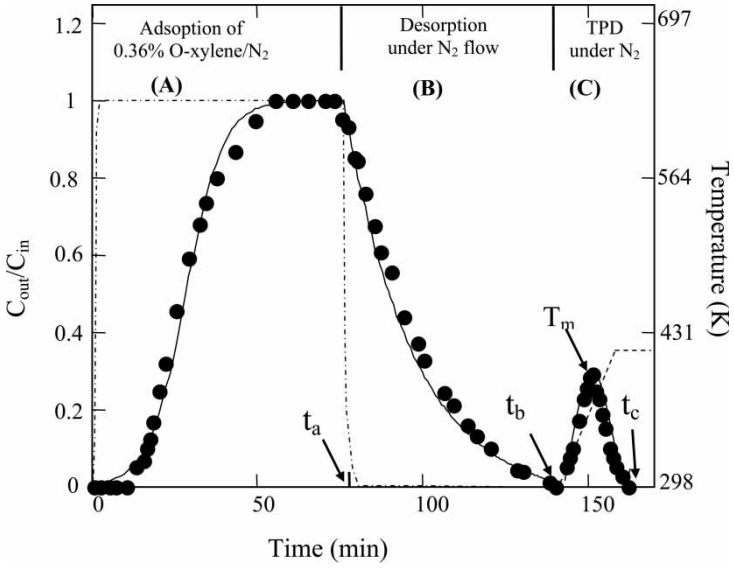

Figure 3. Profile of the variation of *o*-xylene concentration in the gas flow at reactor outlet, represented as relative values (C_{out}/C_{in}), during the aforementioned cycle of successive steps; adsorption performed with a mixture of 0.36% xylene in N_2 at 300 K until saturation followed by isothermal desorption then temperature programmed desorption carried out with a linear heating rate of 5 K/min (—·—·, without adsorbent; – – – –, heating profile during TPD experiment).

The adsorbed amount measured from the breakthrough curve is generally used to indicate adsorbent performance in terms of a given constituent removal from a flowing stream. In the current study, the adsorption capacity is obtained by integration of the breakthrough curve, according to the following equation (1) and considering the curve corresponding with the reactor response in the absence of solid:

$$Q = \frac{FC_{in}}{m}\left[t_a - \int_0^{t_a} \frac{C_{out}}{C_{in}}dt\right], \tag{1}$$

where Q is the adsorbed amount of *o*-xylene at saturation (adsorption capacity in μmole/g), C_{in}, C_{out} the molar fractions of *o*-xylene at reactor inlet and outlet, m the mass of absorber, t_a the saturation time, and F the gaseous molar flow rate.

It should be stated that this equation is valid only if the gas velocity is constant across the reactor bed.[21] This limitation was overcome by performing the adsorption test in a microreactor under isothermal conditions with a high flow rate to ensure negligible pressure drop. Accordingly, the numerical integration of the breakthrough curve using MathCAD software yields a total adsorbed amount of 420 μmol g^{-1}, in the case of the experiment

carried out with a flow containing 0.36% *o*-xylene in N_2 (Fig. 3A). This amount is lower than the adsorption capacity of 1958 μmol g^{-1} reported in our previous work for SiO_2 Degussa (200 m^2 g^{-1}).[17] In comparison with the literature, substantially higher values of 4666, 2800, 1800, and 2050 μmol g^{-1} are reported for xylene adsorption, respectively, for activated carbon AC40 (1300 m^2/g)[22] and zeolithes[23] [Al-Meso 100 (915 m^2/g) UL-ZSM5-100-2 (840 m^2/g), UL-ZSM5-100-6 (780 m^2/g)].

The numerical integration of the desorption curve (Fig. 3B) using equation (2) and considering the curve in the absence of solid permitted quantification of reversibly adsorbed fraction of 370 μmol g^{-1}:

$$Q_{\text{rev}} = \frac{FC_{\text{in}}}{m}\left[\int_{t_a}^{t_b} \frac{C_{\text{out}}}{C_{\text{in}}}dt\right], \tag{2}$$

where t_a and t_b correspond with starting and ending time of isothermal desorption. It is to be noted that although the *o*-xylene desorption curve reached zero, the calculated reversible fraction represents 88% of the total adsorbed amount. The remaining *o*-xylene adsorbed amount corresponds with the irreversible fraction. It was removed with thermal treatment using linear heating according to a TPD method. The integration of the corresponding curve, shown in Fig. 3C, using equation (3), permits obtaining an irreversible amount of 60 μmol g^{-1}

$$Q_{\text{irrev}} = \frac{FC_{\text{in}}}{m}.\left[\int_{t_b}^{tc} \frac{C_{\text{out}}}{C_{\text{in}}}dt\right], \tag{3}$$

where t_b and t_c correspond with the starting and the ending of the TPD curve.

Therefore, the data corresponding with total adsorbed quantity, reversible and irreversible amounts were found to fit the mass balance equation ($Q_{\text{tot}} \approx Q_{\text{rev}} + Q_{\text{irrev}}$) with a precision of 2%, which gives an indication of the accuracy of the analytical methodology used (the best result of three measurements). The above values of adsorbed and desorbed amounts do not suffer major changes during three successive cycles of adsorption/desorption; the precision remains at best around 2%. However, for bentonite sample used more than three successive cycles of adsorption/desorption experiments, a treatment under N_2 flow at 473 K for 30 min is enough for recovering its initial performances.

Other important information given by the TPD experiment concerns the desorption performance indicated by the temperature at the peak maximum. The T_m value of 353 K shown by Fig. 3 is slightly, lower than the T_m value of 368 K given by the TPD peak obtained using the same heating rate for SiO_2 Degussa (200 m^2 g^{-1}).[17]

The current results reveal adsorptive properties of bentonite clay that might be of interest for adsorbent regeneration and adsorbate recovery under industrial operating conditions such as larger reversibly adsorbed fraction and lower temperature for complete thermal desorption. Even with

its lower BET surface area, bentonite's potential use as an adsorbent material deserves to be investigated because adsorbent with higher specific surface area, such as active carbon, is not usually the best.[2] The efficiency of an adsorbent destined to physisorption process application depends also on the size and the shape of adsorbate molecules, which affect their diffusion and interaction within the adsorbent pore structure. Thus, investigation of adsorption energies is also needed for selection of efficient adsorbent material, particularly if collecting and reusing VOCs is targeted.

Isosteric Heat of Adsorption

The amounts adsorbed at equilibrium, which correspond with adsorbent saturation obtained from breakthrough curves, were determined at different adsorption temperatures and for different xylene pressures and yield isotherms shown in Fig. 4. The isotherms are represented in the form of $N = f(P)$ where N is the adsorbed amount per adsorbent weight at equilibrium and P the *o*-xylene partial pressure in the mixture flow. The experimental isotherms were modeled with Langmuir and Freundlich equations using a nonlinear regression method (MathCAD software). The fitting curves are shown as solid and dashed lines, respectively, for Langmuir and Freundlich models (Fig. 4). Apparently, the experimental data were well represented by the Langmuir model while the Freundlich equation deviates at pressures higher than 4 torr.

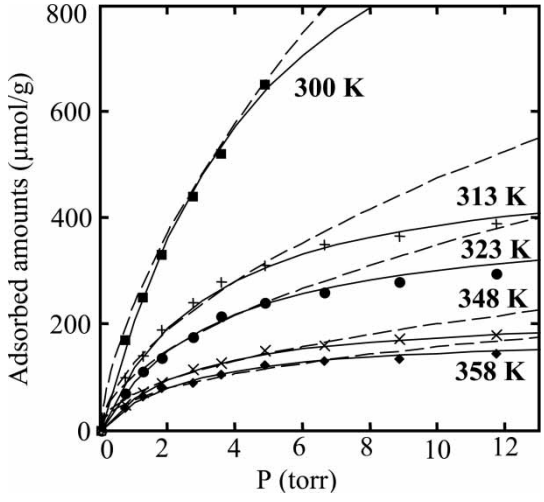

Figure 4. Experimental and modeled adsorption isotherms of *o*-xylene at different temperatures (——, Langmuir equation; – – – –, Freundlich model).

The adsorption isotherms presented in Fig. 4 were used for determination of isosteric heat (Q_{st}) of adsorption by extrapolation at different temperatures and for a given coverage according to the Clausius–Clapeyron equation:[21]

$$Q_{st} = -R\left(\frac{\partial \ln P}{\partial(1/T)}\right), \tag{4}$$

where R is the perfect gas constant, and P and T correspond, respectively, with partial pressure and temperature at equilibrium.

This approach does not require an assumption about model fitting with experimental data even though we have shown that the Langmuir equation well described the adsorption process in the studied T, P ranges. Thus, Q_{st} values were extracted from the slopes of isosteres (Fig. 5) representing the plot of $\ln(P) = f(1/T)$. One has to check very carefully whether the resulting isosteres correspond with straight lines, which depends strongly on the accuracy of experimental conditions. Hence, a temperature measurement error of ± 2 K may yield to an uncertainty of ± 8 kJ/mol for the isosteric heat calculation.[4,5] For temperatures ranging from 300 to 363 K, values of isosteric heat of adsorption in range of 40 to 44 kJ/mol were obtained for *o*-xylene loading between 100 and 250 μmol/g corresponding with a coverage between $0.05 \leq \theta \leq 0.125$ ($\theta = Q/Q_m$, where Q is the adsorbed amount and Q_m is the adsorbed amount at monolayer). Nevertheless, these values do not exceed the heat of vaporization (55 kJ/mole)[20] indicating a weak physisorption adsorption.

Determination of the Heat of Desorption by TPD Method

In the following section, we are going to use the irreversible adsorbed fraction (obtained after adsorbent saturation followed by isothermal desorption) for determination of desorption activation energy. The resulting data may be

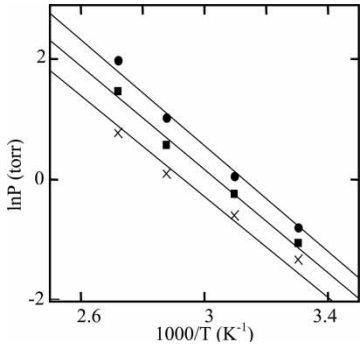

Figure 5. Plot of isostere corresponding with $\ln(P)$ versus $1/T$ corresponding with the following adsorbed amounts: ●, 206; ■, 133; ×, 100 μmol g^{-1}.

useful for prediction of thermal behavior of a potential adsorbent, which is of interest in terms of industrial security and energy savings (thermal desorption). The determination of the desorption energy according to TPD method developed by Cvetanovic et al.[8] has recently been validated and used by several authors.[24–27] Regardless of whether there is readsorption or not and assuming that there is no limitation by diffusion of the desorbed species within the pores during TPD process, the energy of desorption E_d is, generally, derived from the following equation:[28]

$$2 \ln T_m - \ln \beta = E_d / R T_m + \text{constant}, \quad (5)$$

where T_m is the desorption temperature at peak maximum (K), β is the linear rate of temperature rise (K s^{-1}), E_d is the desorption energy (kJ mol^{-1}), and R is the perfect gas constant (kJ mol^{-1} K^{-1}).

The experimental approach on which TPD method is based consists on the analysis of TPD curves collected at different linear heating rates (β), by exploiting the shift of the temperature maximum T_m "desorption temperature at peak maximum" as a function of β. Therefore, in order to provide reliable determination on activation desorption energy, the TPD curves have to be well defined, with clearly detectable T_m positions. This was the case of our experiment as shown in Fig. 3C. Table 1 summarizes β values and the corresponding temperature maximum T_m (K) obtained from an additional set of experiments; saturation and desorption at 300 K followed by TPD performed with different linear heating rate β (curves not shown).

The desorption activation energy is deduced from equation (5) using the slope of the line "Cvetanovic curve" representing ($2 \ln T_m - \ln \beta$) as a function of T_m^{-1} and results in a value of 75 kJ/mol (Fig. 6). This value is higher than the one obtained using an isosteric method. We have previously mentioned that the use of the Clausius–Clapeyron law is efficient and accurate when the adsorption process is essentially reversible because the heat of adsorption is considered roughly equal to desorption activation energy. This approach is no longer valid for systems with significant irreversible adsorption, which requires higher activation energy for its desorption because it was adsorbed with higher adsorption energy, as shown in the current work. Thus, when the total adsorption amount is used for determination of the heat of adsorption, the analytical method must be able to quantify different adsorbed fractions (i.e., reversible and irreversible) or else, at best, only an average of the heats of adsorption is obtained, as it is

Table 1. Linear heating rate β used for TPD experiments and its corresponding temperature at peak maximum T_m (K)

β (K/min)	4	5	7	10	12
T_m (K)	350	353	356	361	364

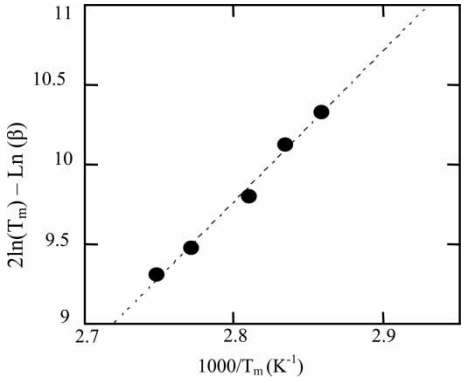

Figure 6. Cvetanovic curve obtained with TPD experiments performed with β and T_m values presented in Table 1 for an adsorption test performed with a flow containing 3600 ppmv of xylene.

the case of integral or differential heat of adsorption provided by microcalorimetric methods.[29,30]

CONCLUSIONS

The use of FTIR spectroscopy was found to permit accurate quantitative analysis that allows determination of adsorbent saturation loading from breakthrough curves and differentiation between reversible and irreversible adsorption. Also, the technique provides the possibility of simultaneous detection of further adsorbate dissociation through appearance of new IR bands. The data obtained using this analytical approach have been used to derive useful thermodynamic parameters related to heat involved during adsorption and/or desorption processes.

The approach has been used to investigate the potential use of local clay as an adsorbent material for pollutants of the VOC type, in a context of sustainable development. The obtained data suggest bentonite is a promising adsorbent candidate because it exhibits properties that are generally required in gas purification, such as a large amount of reversible adsorption capacity, no catalytic activity, and easy regeneration performance.

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