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Thermodynamic study of adsorption alcohols on natural clay by inverse gas chromatography

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Abstract

The adsorption of VOCs onto porous clays has been considered as an innovative research of environmental treatment. This work was performed to investigate the adsorption properties of alcohols vapors (ethanol and methanol) on natural clay using inverse gas chromatography (IGC). This method was based on the principle of the chromatography of elution in gas phase. From the IGC data, the adsorption isotherms of alcohols on natural clay were determined. These isotherms were used to calculate the thermodynamic parameters such as enthalpy and entropy and to find the appropriate adsorption model. Finally, the adsorptive performance in terms of adsorption of alcohols by natural clay has been compared to activated carbon.

Keywords: Adsorption, Elution chromatography, isotherms, enthalpy, entropy.

1. Introduction

There has been an everlasting interest of research at a global level, in the valuation of natural and industrial adsorbents. Bentonite clay, a widely available natural adsorbent in Tunisia, has caught our attention due to its numerous important physic-chemical properties which have rendered it an industrially useful and commercially valuable substance. Indeed, the several studies realized locally on this material whether in its natural or chemically activated state show that it can adsorb various chemical substances, discolor vegetable and mineral oil, treat waters, etc… [1-11].

These promising results have encouraged us to follow their path and to prepare a voucher adsorbing alcohols vapors in particular the ethanol and the methanol. These alcohols are used in the chemical, pharmaceutical and food industries. These are volatile compounds. The exposure to these alcohols vapors produce irritation of the eyes and a trouble breathing. Furthermore, these compounds are highly flammable. Their vapors may form explosive mixtures with air.

Our study on this clay material consists exactly in experimentally determining, the maximal adsorption capacities - isotherms of adsorption- of alcohols vapors on natural clay at different temperatures using the inverse gas chromatographic method.

This technique is a dynamic method that has been developed for years to easily obtain the isotherms of adsorption and show its validity like the other methods of determining isotherms of solid fluid adsorption to know the static and volumetric methods [12-17].

We distinguish two techniques of inverse gas chromatography, which allow to obtain the isotherms of adsorption: i) the frontal analysis method which consists in sending alternately a pure carrier gas to a fixed and constant concentration of solute to the column [13] and (ii) the method of elution characteristic point (ECP), which involves injecting a known amount of adsorbate on the adsorbent column and to deduct the retention volume.

Here, the determination of the isotherms of adsorption is made using the second method because it is a very simple technique, requiring no special equipment other than a commercial analytical chromatograph.

2. Theory

2.1. The adsorption isotherms

Using the method of elution characteristic point (ECP), the adsorption isotherms can be determined from chromatograms.

Starting from a matter assessment on the volume of the chromatographic column, we established the existing relation between the adsorbed quantity and the relative pressure of the adsorbate.

$$q(c) = \frac{M_a * D}{m_b}\int_0^c (t_{ra} - t_{rg})dc = \frac{M_a * D}{m_b * U}\int_0^c (x_a - x_g)dc \qquad (1)$$

The output volumetric rate of the carrier gas is corrected at the temperature and the pressure of the column.

$$D = D_m * \frac{T}{T_a} * \frac{(P - P_{H_2O})}{P} \qquad (2)$$

For a given detector, the concentration of the solute is proportional to the height on the peak (Fig. 1).

$$c = k * h \qquad (3)$$

With $$k = \frac{m_a * U}{M_a * D}\int_0^\infty h\,dx = \frac{m_a * U}{M_a * D} * S_{pic} \qquad (4)$$

And for perfect gases, we have:

$$P = c * R * T \qquad (5)$$

So, to calculate the amount adsorbed according to the partial pressure of solute from chromatograms, we will use the equations below [11-12].

$$q = \frac{m_a}{m_b} * \frac{S_{ads}}{S_{pic}} \qquad (6)$$

$$P = \frac{m_a * U * h * R * T}{M_a * D * S_{pic}} \qquad (7)$$

According to Kiselev [15], the criterion for achieving equilibrium in the column is attributed to the coincidence of the diffuse part of the chromatographic peaks for different amounts of fluid injected and for different gas velocity vector.

2.2. Isosteric enthalpy and entropy of adsorption

The isosteric enthalpy and entropy of adsorption are usually determined using isosteres obtained from adsorption isotherms at different temperatures. These isosteres are based on the Clausius-Clapeyron equation:

$$\frac{\partial\, Ln\,P}{\partial\,(\frac{1}{T})} = \frac{\Delta H_{ads}}{R} \qquad (8)$$

The integration of (8) gives:

$$Ln(\frac{P}{P^\circ}) = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \qquad (9)$$

In the equations (8) and (9), ΔHads and ΔSads respectively indicate the isosteric enthalpy and the entropy of adsorption. These two thermodynamic functions can be given starting from the slope and of the ordinate at the origin of isosteres Ln (P/P°) according to 1/T.

3. Experimental study

3.1. Materials

As we have already noted above, the solutes used are ethanol and methanol with a purity of 99.85%. The adsorbent tested in the present work is the gray natural clay which comes from the strata of EL HICHA (governorate of Gabes of the Tunisian South). It belongs to the family of bentonites. Its chemical composition and structural characteristics are represented in previous works [1-11]. A granular activated carbon type chemviron is used for the comparison of experimental adsorption isotherms on this industrial adsorbent and natural clay advocated. The characteristics of the two adsorbents are given in Table 1.

3.2. Instrumentation

A chromatograph in gas phase commercial series IGC 10 M, mono-column and mono-detector is used to experimentally determine the thermodynamic equilibrium data comprising primarily a column of adsorption which is a stainless tube filled with adsorbent, and a system of acquisition connected to the chromatograph.

In order to standardize the properties of clay at the beginning of each experiment, an experimental protocol is followed during regeneration: the adsorbent is swept by a helium current during one night at 150 °C by means of the electric oven ordered by a regulator of precision both assembled with the chromatograph. Then, for each injection it is necessary to equilibrate the catharometer and check the equality of the gas outputs vector in the column of reference and adsorption. Finally, the amount of the injected alcohol and the gas flow vectors are fixed satisfying the conditions of thermodynamic equilibrium in the column and for each adsorption temperature. An adequate mathematical program of numerical integration allows the exploitation of the data of thermodynamic equilibrium and it leads to the calculation of adsorption isotherms, basing on equations (6) and (7).

2. Results and discussions

4.1. Adsorption isotherms

For: (i) a mass of dry natural clay of 2.8874 g, (ii) a temperature of adsorption of T = 80 °C, (iii) an amount injected of ethanol of 100 µl and (iv) a carrier gas flow rate of 0.003 m^3/h thermodynamic equilibrium is achieved in the column. Thereafter, a volume of ethanol of 100 µl and a minimum gas output of 0.003 m^3/h will be taken during experimental measurements of the isotherms of adsorption at various temperatures. After having fixed the equilibrium conditions of the column we determined the adsorption isotherms at different temperatures illustrated in Fig. 2. The experimental protocol, which was followed during the determination of the isotherms of division of the couple ethyl alcohol- natural clay, is adopted while studying the couple methyl alcohol- natural clay (Fig. 3). After that, we determined the adsorption isotherms of this alcohols on activated carbon for a mass of 1.1666 g (Fig. 4 and 5). From Fig. 2 and 3, we noted that the amount of methanol adsorbed by this clay is higher than ethanol. This can be explained by the influence of the difference in carbon-chains. Moreover, it is shown that temperature influences the adsorbed amount: for the same partial pressure, the more the temperature increases, the more the quantity of methanol adsorbed decreases. Hence, the phenomenon of adsorption of methanol is exothermic. Opposite effect of temperature is noted in the case of ethanol adsorption. So, the phenomenon of adsorption of ethanol on natural clay is endothermic.

We also notice that the activated carbon has a capacity of adsorption of alcohols approximately twice that of the natural clay. The isotherms found are of type II according to the classification of Brunauer, Deming, Deming and Teller (BDDT). Consequently, a strong interaction between the surface of the adsorbents and the molecules of alcohols.

4.2. Modeling

At this stage, we sought the adequate model which better describes the experimental data of the isotherms of adsorption.

4.2.1. Langmuir Model

This model is characterized by the following equation:

$$\frac{q}{q_{\infty}} = \frac{K_L * \frac{P}{P_0}}{1 + K_L * \frac{P}{P_0}} \tag{10}$$

To determine the parameters of this model (K_L, q_{∞}□) we have resorted to trace 1/q according to P_0/P, shown in Fig.6 and 7. The variation of these parameters according to the temperature was illustrated in Table 2. From Fig. 6, we noted that this model is not valid for the temperatures 150°C and 166°C. Also, Fig.7 shows that this model describes appropriately the isotherms studied but it is not valid for T=102°C.

4.2.2. BET Model

Equation (11) is the linearized form of model BET chosen for smoothing the experimental data of adsorption.

$$\frac{x}{q * (1 - x)} = \frac{1}{c * q_m} + (\frac{c - 1}{c * q_m}) * x = y \tag{11}$$

The results of smoothing of the experimental data of adsorption on natural clay by this model are related to Fig. 8, 9 and Table 3. This model is the most appropriate model for the description of the equilibrium data. The values of the constant C of this model are large. This verifies that the isotherms obtained are classified as type II of BDDT.

4.3. Isosteric enthalpies and entropies of adsorption

The enthalpies and the entropies of adsorption calculated from the adsorption isotherms at different temperatures for the couples studied are shown in Fig. 10, 11 and 12.

These different values of H_{ads} (Fig. 10 and 12) are due to the influence of the surface heterogeneity of natural clay. These values correspond to weak bounds such as hydrogen bounds and dipole-dipole interactions (Van der Waals). The most active sites were covered preferentially.

Fig.10 shows that the enthalpies of adsorption for the couple ethanol/natural clay are positive: Hence an endothermic phenomenon of adsorption unlike the phenomenon of adsorption of ethanol/activated carbon is exothermic.

Moreover, the values of H_{ads} of methanol get close to the melting point (-35.2 kJ/mol) when the adsorbed quantity increases (Fig.12). Therefore, the adsorption of methanol on natural clay is a physical one.

Also, the values $|\Delta H_{ads}|$ of methanol are lower than the enthalpies of ethanol. This may be related to the strong interaction forces between the ethanol molecules and the large surface area of bentonite.

3. Conclusions

This work presented the efficiency of local bentonite to adsorb alcohols. The isotherms found were of type II according to the classification of BDDT. Consequently, a strong interaction between the surface of the clay and the alcohols molecules. In addition, the process of adsorption is proved to be physical type. On the other hand, activated carbon adsorbs alcohols better than the natural clay. Eventually, we may conclude that the relevant adsorbent, natural clay, has low adsorption capacity to alcohols and that its extensive industrial use is attributed to its being more economical, even it is used in large quantities, than using small quantities of other expensive adsorbents, such as (activated carbon, silica gel, activated alumina ...).

Therefore, this natural clay can be used as an abundant adsorbent of alcohols for its adsorptive performance and its lower cost.

Nomenclature

q: the amount adsorbed (kg/kg).
m_a : mass of the adsorbate (kg).
m_b: mass of the adsorbent (kg).
S_{ads}: the surface of the peak relative to m_a (m^2)
S_{pic}: surface of the chromatographic peak (m^2)
P: pressure partial of the solute (Pa)
U: speed of paper (m/s)
h: height on peak relative to m_a (m)
R: constant of perfect gases (J/mol.K).
D: volumetric rate (m^3/s).
M_a: mass molar of solute (kg/mol).
ΔS_{ads} : entropy of adsorption (J/mol.K).
q_∞: the quantity adsorbed necessary to cover full-course with adsorbate
q_m: quantity necessary to form the full- course

t_{ra}: retention time of the adsorbate (s).
t_{rg}: retention time of carrier gas (s).
x_a-x_g: the distance between the elution time of the carrier gas and that the adsorbate (m).
T_a: ambient temperature (K).
P_{H2O}: saturation pressure of water vapor at ambient temperature (Pa).
T: temperature of adsorption (K).
D_m: carrier gas flow rate measured at the outlet of the column at ambient temperature (m^3/h).
ΔH_{ads} : isosteric enthalpy (J/mol).
P_0: saturated vapor pressure (Pa).
K_L: constant of Langmuir
$x = P/P_0$
C: constant of BET

(g/g).

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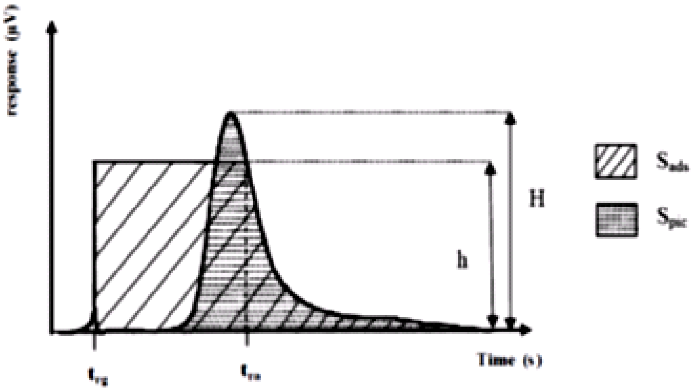

Figure 1. The principle of the measurement of surfaces S_{pic} and S_{ads} for a point characteristic of the chromatogram.

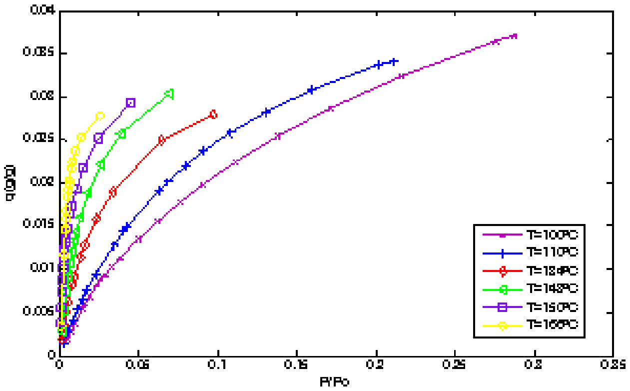

Figure 2. Adsorption isotherms of ethanol on natural clay for an injected volume of 100 µL and carrier gas flow of 0.003 m^3/h.

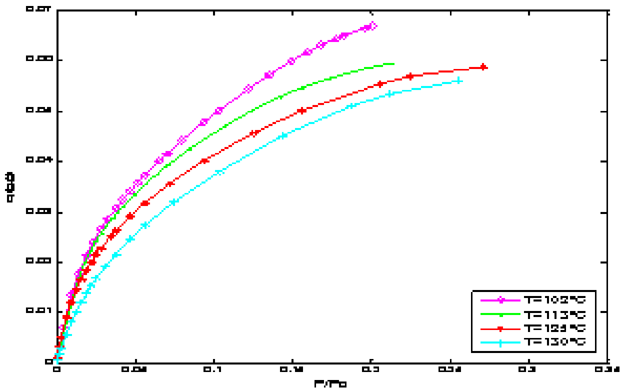

Figure 3. Adsorption isotherms of methanol on natural clay for an injected volume of 200 µL and carrier gas flow of 0.0016 m^3/h.

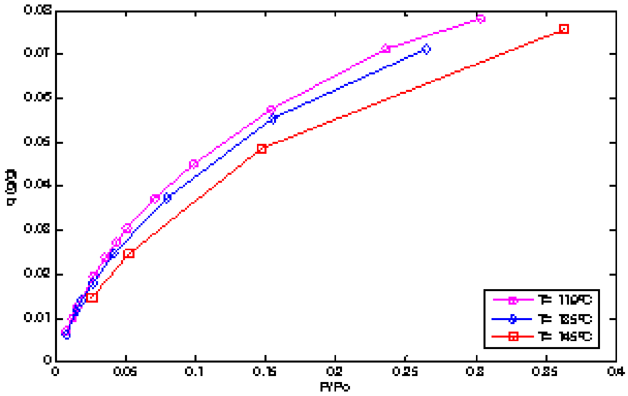

Figure 4. Adsorption isotherms of ethanol on activated carbon for an injected volume of 100 µL and carrier gas flow of 0.00139 m^3/h.

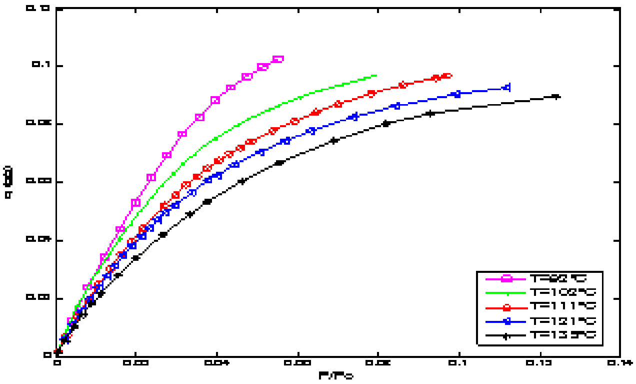

Figure 5. Adsorption isotherms of methanol on activated carbon for an injected volume of 120 µL and carrier gas flow of 0.0016 m^3/h.

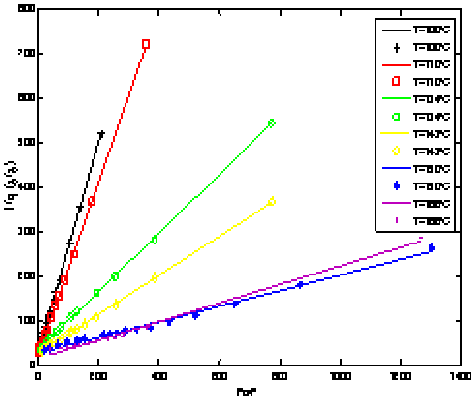

Figure 6. Langmuir model: ethanol/ natural clay

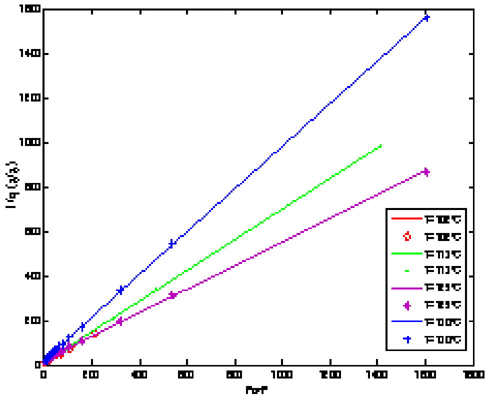

Figure 7. Langmuir model: methanol/natural clay

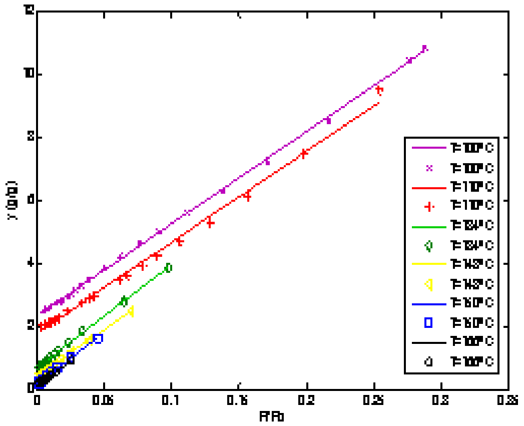

Figure 8. Model of BET: ethanol/ natural clay

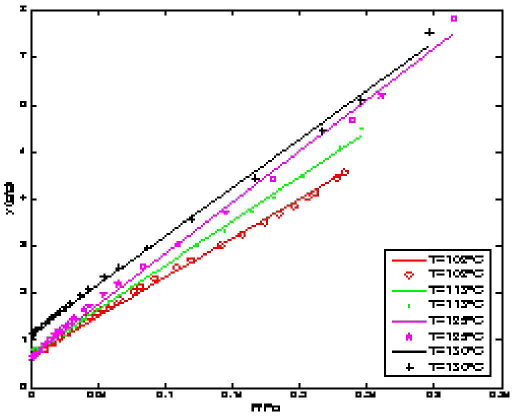

Figure 9. Model of BET: methanol/ natural clay

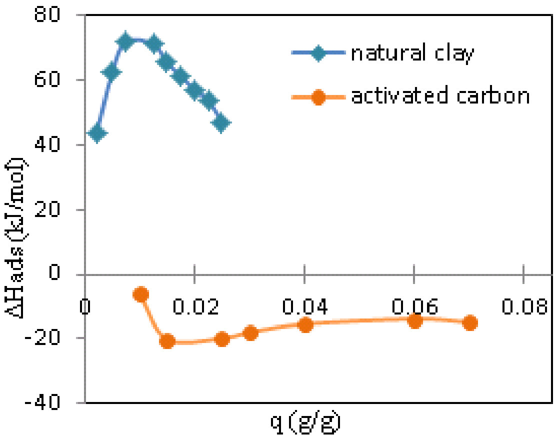

Figure 10. Enthalpies of adsorption of ethanol

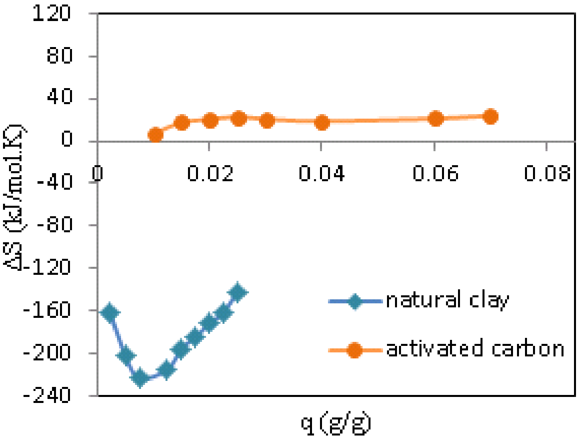

Figure 11. Entropies of adsorption of ethanol

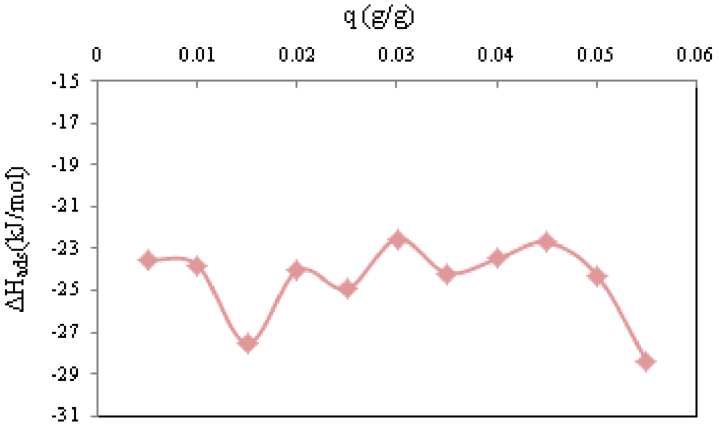

Figure 12. Enthalpies of adsorption of methanol / natural clay.

Table 1. Structural characteristics of the natural clay and the chemviron.

Adsorbent	Specific surface BET (m^2/g)	Pore volume (cm^3/g)	Micro pore volume (cm^3/g)	Mesopore volume (cm^3/g)
Natural clay	86	0.1207	-	-
Chemviron	879	0.540	0.470	0.070

Table 2. Langmuir Parameters for alcohols adsorption on natural clay.

Adsorbate	T (°C)	(g/g)	K_L
Ethanol	100	0.0438	9.6002
	110	0.0493	10.4316
	134	0.0301	50.4623
Methanol	102	0.0688	25.1600
	113	0.0780	18.6458
	130	0.0493	21.0867

Table 3. BET Parameters for alcohols adsorption on natural clay.

Adsorbate	T (°C)	(g/g)	C
Ethanol	100	0.0316	13.5975
	110	0.0325	17.2190
	134	0.0299	48.8475
Methanol	102	0.0604	28.1198
	113	0.0536	29.9550
	130	0.0489	20.2480

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