

Sorption study of organic contaminant on raw and modified clay materials

N. Dammak^{1,2,a}, N. Fakhfakh^{1,2}, S. Fourmentin^{3,4} and M. Benzina^{1,2}

¹ *University of Sfax, 3029 Sfax, Tunisia*

² *Laboratory of research Water, Energy and Environment – code: AD-10-02, National School of Engineers of Sfax, BP. 3038, Sfax, Tunisia*

³ *Université Lille Nord de France, 59000 Lille, France*

⁴ *ULCO, UCEIV, 59140 Dunkerque, France*

Abstract. The adsorption of volatile organic compound VOC (*o*-xylene) was studied by a static headspace coupled to gas chromatography in natural and intercalated clay. Vapor–solid adsorption isotherms of *o*-xylene were measured at 20 °C, 30 °C and 40 °C. Clay was modified with hexadecyl trimetyl ammonium bromide (HDTMA). Absolute values of the amounts of *o*-xylene adsorbed in intercalated clay were about eighteen times higher than natural clay.

The adsorption isotherm were analysed with Langmuir, Freundlich, Langmuir–Freundlich and Toth models. Langmuir–Freundlich model describes well the equilibrium adsorption data. The evaluation of thermodynamic parameters presents an exothermic and spontaneous adsorption process.

1. INTRODUCTION

Volatile organic compounds (VOCs) are organic substances characterized by their high vapor pressure at ambient temperature and their low boiling point [1]. Many VOCs are hazardous to human health and the environment. Adsorption is one of the most practical methods for separating and recovering VOCs from industrial gas streams [2]. *O*-xylene was selected as a VOC model since it was known to be among the most harmful VOCs [3].

In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent materials for dealing with the treatment problem of contaminated industrial effluents. Natural Tunisian clays are very abundant materials with a low cost and porous texture. Such characteristics make them of capital interest for a possible use in the adsorption of VOCs for their removal from waste gases [4].

In this work, natural clay was modified with the cationic surfactants, HDTMA, to increase its sorptive capabilities on single VOC component. The adsorption isotherms of *o*-xylene on the modified clay materials showed that intercalation of HDTMA could significantly improve the *o*-xylene adsorption, indicating that intercalated materials have the better capacities to adsorb VOC than natural clay materials. Thus, HDTMA can be used to modify clay to improve its sorption capability. A successful response to this synthetic challenge was given by several authors who prepared organobentonites by using cations of alkylammonium for the adsorption of VOCs [5,6].

2. EXPERIMENTAL

2.1. Materials

O-xylene (98%) obtained from Fluka Chemical and used without further purification, was chosen as model

^a e-mail: dammak.nes@gmail.com

compound in this study. The clay material used in this study was taken from Jebel Sbih deposits located in the south of Tunisia from the area of Skhira. For intercalation we use Hexadecyltrimethylammonium bromide obtained from fluka Analytical.

2.2. Preparation of intercalated clay

Natural clay (NC) with a cationic exchange capacity (CEC) of 0.85 mmol.g⁻¹, was purified. The Na saturated clay was prepared by the treatment of the <2 μm fraction with NaCl solution by leaving the material in agitation during 24 h with a NaCl solution (1 mol L⁻¹) for three times. After complete exchange, the sample underwent several dialyses until the complete elimination of chloride, confirmed by the AgNO₃ test.

Organoclay (OC) was prepared by dispersing the cationic surfactant (HDTMA), equal to twice the CEC of the clay, into Na saturated clay under stirring at 80 °C for 10 h [3,7]. Then, the suspension was washed three times to remove any excess surfactant, dried at 90 °C. Afterwards, the OC was ground with a mortar and particles of size less than 63 μm were collected for the VOC adsorption.

2.3. Characterisation methods

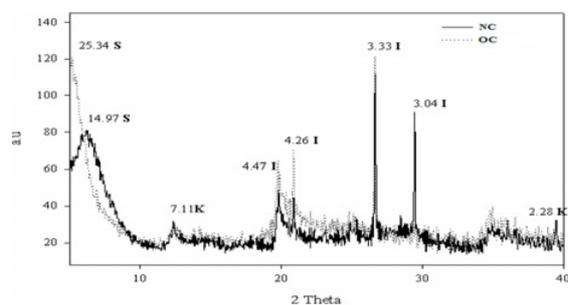
To determine the various species constituting the clay materials, a scanning electron micrograph (SEM; Model MEB LEO 438VP equipped with EDS system) was used. Normative mineral composition was calculated from the quantitative chemical analysis obtained by X-ray powder diffractometer (Rigakud-Max 2200 model). FTIR spectra were acquired on a Bruker Spectra.

2.4. Adsorption experiments

The adsorption experiments were carried out using the batch equilibration technique. A mass of adsorbent

Table 1. Elemental analysis of NC and OC.

	Si	Al	C	O	Ca	Fe	Mg
NC	42.13	13.34	9.29	25.54	2.91	3.39	2.13
OC	40.54	12.92	17.8	21.83	0.91	3.34	1.73

**Figure 1.** Diffraction of X-ray of NC and OC.

material (200 mg of NC or 10mg of OC) was introduced into a vial of 22 mL. It was covered with glass wool to avoid direct contact with *o*-xylene. The last one with a concentration of 10000 ppm was introduced in variable amounts (1, 2, 4, 6, 8, 10 and 12 μ L). The suspensions were mixed on a rotary tumbler for 24h at desired temperature (20, 30 and 40 $^{\circ}$ C). The adsorbed quantities were determined by calculation of concentration of *o*-xylene in the supernatant with static headspace coupled to gas chromatography.

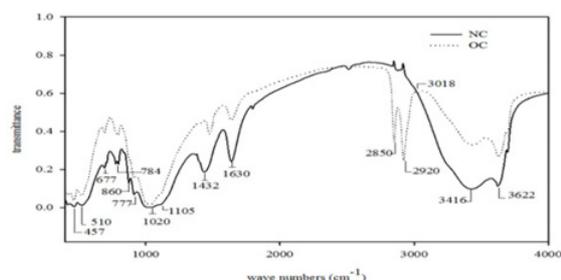
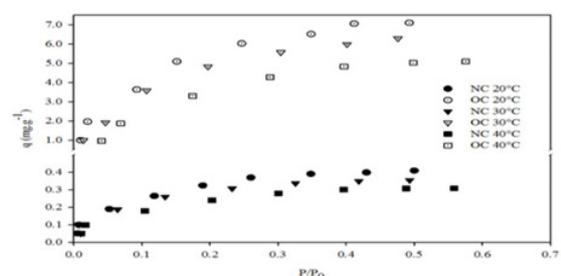
3. RESULTS AND DISCUSSION

3.1. Physical properties of the clays

Energy dispersion spectrum (EDS) showed increase in carbon counts due to substitution of surfactant with long carbon chain (Table 1). In addition a considerably decrease in oxygen, aluminium, silica and calcium amounts in OC. Diminution of silica was due to purification of clay and elimination of many silica oxides. Aluminum differences occurred mainly on the amount of tetrahedral aluminium layer [8]. Calcium decrease indicated that the interlayer cation in the smectite component was made of Ca^{2+} [9].

The XRD patterns of the NC and OC are given in Figure 1. The spectrum shows that this clay is composed mainly of smectite (S) by the appearance of peaks at 14.97 \AA , kaolinite (K) by the appearance of peaks at 7.11 \AA and illite (I) which is proved with peaks at 4.47, 4.26, 3.33 and 3.04 \AA [3,6]. The peak of smectite in NC was 14.97 \AA , and it expanded to 25.34 \AA for OC. Thus, the basal space was increased.

As shown in Figure 2, the characteristic absorption band at 3622 cm^{-1} is assigned to the stretching vibration of AlOH and SiOH and band at 3416 cm^{-1} was due to the stretching vibration of H_2O proved the smectitic nature of clay. The attributions of absorption in the range of 470–1120 cm^{-1} can be due to Si–O–Si and Si–O–Al bending and stretching [10]. In addition to this, the infrared spectra of OC showed a strong bands at 2920 and 2850 cm^{-1} attributed to asymmetric and symmetric

**Figure 2.** FTIR spectra of NC and OC.**Figure 3.** Adsorption isotherms of *o*-xylene on NC and OC (20, 30, 40 $^{\circ}$ C).

stretching vibrations of C–H groups and the peak around 3018 cm^{-1} was assigned to the anti-symmetric stretching modes of the trimethyl ammonium head group of HDTMA [10]. However, after exchange treatment, quaternary ammonium salt apparently entered the interstitial spaces of montmorillonite and was adsorbed on its mineral surfaces.

3.2. Adsorption isotherms

The effect of temperature on adsorption of *o*-xylene onto OC and NC was investigated at 20, 30 and 40 $^{\circ}$ C. The experimental results (Figure 3) showed that adsorption capacity of *o*-xylene on NC and OC decreased from 0.476 to 0.356 mg.g^{-1} and from 8.765 to 7.299 mg.g^{-1} respectively with increasing temperatures from 20 to 40 $^{\circ}$ C, indicating the exothermic nature of VOC adsorption on clay. This slight change could be related to the higher collision frequencies at higher temperature and therefore lower adsorption capacity. Thus, 20 $^{\circ}$ C was chosen as the best temperature for the removal of VOCs in the subsequent study.

The isotherms show that the intercalation of HDTMA can remarkably improve the *o*-xylene adsorption of smectite. For example, at temperature of 20 $^{\circ}$ C, the adsorption capacity of *o*-xylene on NC is 0.476 mg.g^{-1} , and is 18.42 times the value of OC, 8.765 mg.g^{-1} . Our results showed also that the removal of *o*-xylene increased with the increase of the pressure ranges (P/P_0) due to the free reactive sites available for the adsorption of *o*-xylene until saturation. However, the adsorbed amount (q) was higher at high pressure ranges (Figure 3) due to the larger driving forces for mass transfer at higher pressure. These forces increased the loading capacity of the studied clay samples [11]. Furthermore, the saturation of the surface adsorption sites was favoured due to the higher pressure

Table 2. Fitted parameters of four models to the experimental data of *o*-xylene isotherm on NC and OC at 20 °C.

Langmuir $q = q_0 K_L (P/P_0) / (1 + K_L (P/P_0))$									
Natural clay				Organo clay					
q_0	K_L	R^2	χ^2	q_0	K_L	R^2	χ^2		
0.476	12.195	0.990	0.098	8.765	8.855	0.996	0.415		
Freundlich $q = K_F (P/P_0)^{1/n}$									
K_F	n	R^2	χ^2	K_F	n	R^2	χ^2		
0.182	2.909	0.987	0.023	420.950	2.663	0.980	0.432		
Langmuir-Freundlich $q = q_0 (b (P/P_0))^n / (1 + (b (P/P_0))^n)$									
q_0	b	n	R^2	χ^2	q_0	b	n	R^2	χ^2
0.536	3.551	1.815	0.999	0.013	9.341	4.543	1.413	0.999	0.104
Toth $q = q_0 K_T (P/P_0) / (1 + (K_T (P/P_0))^t)^{1/t}$									
q_0	K_T	t	R^2	χ^2	q_0	K_T	t	R^2	χ^2
0.731	25.438	0.476	0.998	0.020	10.500	11.218	0.700	0.998	0.154

Table 3. Thermodynamic parameters at 20 °C.

clay	K_L	ΔG^0 (kJ.mol ⁻¹)	ΔH^0 (kJ.mol ⁻¹)	ΔS^0 (J.mol ⁻¹ K ⁻¹)
NC	18.325	-7.085	-25.390	-30.407
OC	8.333	-5.165	-11.609	-1.034

of *o*-xylene. The isotherm data were fitted to four models described in Table 2 by non-linear regression.

Where q is the equilibrium adsorption capacity (mg.g⁻¹); P is the vapor pressures of VOC (Pa); P_0 is the saturated vapor pressures of VOC (Pa); q_m is the maximum adsorption capacity (mg.g⁻¹); K_L is Langmuir constant; K_F and n are Freundlich constants; b Langmuir-Freundlich constant; K_T and t are Toth constants. The parameters obtained and the corresponding correlation coefficients R^2 and χ^2 are summarized in Table 2.

$$\chi^2 = \sum \frac{(q - q_m)^2}{q_m}$$

Where q and q_m are experimental and calculated equilibrium capacity, respectively. All the data demonstrate almost perfect agreement with Langmuir-Freundlich and Toth models. Toth model over estimated the adsorption of *o*-xylene since the *o*-xylene adsorbed amount always increases with pressure. Thus, the Langmuir-Freundlich model fitted best the *o*-xylene adsorption isotherms. However, the Langmuir-Freundlich model is an empirically development of Langmuir equation which is suitable to describe the adsorptive behaviour of homogeneous surfaces, and the Freundlich isotherm which endorses the heterogeneity of the surface. This result suggests that *o*-xylene is adsorbed by different ways on the surface of the natural and OC. Thus, for *o*-xylene, the interaction with the clay can occur between the surface of the clay and the molecule of *o*-xylene or between methyl group of *o*-xylene and the adsorption clay sites [12].

3.3. Thermodynamic studies

The adsorption capacities of *o*-xylene on both NC and OC suggest that the interaction of *o*-xylene and clays is exothermic in nature. The thermodynamic parameters

such as change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), were calculated from the slope and intercept of van't Hoff plots of $\ln K_L$ vs $1/T$.

$$\Delta G^0 = -RT \ln K_L$$

$$\ln K_L = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303R} \left(\frac{1}{T} \right)$$

Where R is the gas constant and is equal to 8.314 J.mol⁻¹, K_L the equilibrium constant obtained from Langmuir equation and T is the temperature (K). The thermodynamic parameters for *o*-xylene adsorption on NC and OC are presented in Table 3. The negative values of ΔG^0 indicate the spontaneous nature of *o*-xylene adsorption. The negative value of ΔH^0 which are -25.39 kJ.mol⁻¹ for NC and -11.61 kJ.mol⁻¹ for OC confirms the exothermic nature of adsorption. The negative value of ΔS^0 indicates a decrease in disorder of *o*-xylene adsorption. Generally, the absolute magnitude of the change in free energy for physisorption is between -20 and 0 kJ.mol⁻¹; chemisorption has a range of -80 to -400 kJ.mol⁻¹ [13]. The results obtained are -7.08 and -5.17 kJ.mol⁻¹ at 20 °C for NC and OC, respectively. Considering that these values are in the typical standard free energy range for physisorption, one can conclude that *o*-xylene adsorption on NC and OC mainly physically.

4. CONCLUSION

The surface of natural clay is not a more effective adsorbent for the removal of organic compounds from gas stream. However, natural clay may be modified with organic cations (HDTMA) in a manner that significantly improves its capability of sorption.

The results of present investigation indicate that natural clay and organo clay prepared from low-cost

natural material have suitable adsorption capacity of *o*-xylene. organo clay showed a higher adsorption capacity toward *o*-xylene than natural clay. The isotherm data were well represented by the Langmuir-Freundlich model. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG^0 at 20 °C indicated spontaneity and the negative values of ΔH^0 and ΔS^0 showed the exothermic nature and decrease in disorder of *o*-xylene adsorption, respectively.

References

- [1] P. Hunter, and S.T. Oyama, Wiley, New York (2000).
- [2] M. Guillemot, and all., Ind. Eng. Chem. Res. 46, 4614–4620 (2007).
- [3] H. He , et al., J. Theo K, Appl. Clay Sci. 31, 262-271 (2006).
- [4] I. Jarraya, and all., Chem. Geol. 275, 1–8 (2010).
- [5] S.H. Lin, and M.J. Cheng, Waste Manag. 22, 595–603 (2002).
- [6] C.Y. Ryu, and S.D. Yeo, J. Ind. Eng. Chem. 16, 441–447 (2010).
- [7] Z. Li, and W.T. Jiang, Thermochem. Acta. 483, 58–65 (2009).
- [8] S.J. Chipera, and D.L. Bish, Clays and Clay Minerals. 49, 398–409 (2001).
- [9] H.L. Hong, and all., Appl. Clay Sci. 42, 292–299 (2008).
- [10] Darder, M., Colilla, M., Ruiz-Hitzky, E., Appl. Clay Sci. 28, 199–208 (2005).
- [11] F. Qu, and all., J. Hazard. Mater. 170, 7–12 (2009).
- [12] H. Zaitan, and all., J. Hazard. Mater. 153 852–859 (2008).
- [13] Y. Yu, and all., J. Colloid Interface Sci. 242 (2) 288 (2001).