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An effective functionalized Moroccan bentonite: Application for a green remediation of m-Cresol

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Abstract

An organo-clay complex was synthesised from Moroccan bentonite and hexadecyltrimethyl ammonium bromide (HDTMA-Br) *via* ion-exchange reaction. The resulting hybrids were used for m-cresol removal from aqueous solutions as model of organic pollutant. Structure and chemical composition of the studied clays were characterized by means of elemental analysis, N2 adsorption, thermal analysis, (TGA/DTG), X-Ray diffraction (XRD) and Fourier transform infrared spectroscopie (FTIR). The adsorption capacities of bentonite and organo-bentonite towards m-cresol were investigated in aqueous solution in a batch system with respect to contact time and initial concentration. The influence of surfactant amount on pollutant adsorption was also estimated. Pseudo-first order and pseudo-second order models were used to determine the adsorption kinetics parameters and to understand the reaction pathways. The performance and the adsorption capacity of the organo-bentonite were predicted by the Langmuir and Freundlich isotherms. The maximum adsorption capacity of organo-bentonite to adsorb m-cresol was 17 times higher than that of natural bentonite. It was obtained with bentonite modified with an amount *equivalent* to 100% of *cation exchange capacity* (*CEC*).

1. Introduction

For several decades, the development of efficient and low-cost adsorbents of highly toxic compounds constituted a real challenge for many industries and researchers. Because of their low cost, local availability and their special physicochemical properties, clay minerals have gained significant interests as adsorbents of a wide variety of pollutants (heavy metals, organic and inorganic molecules) [1-3]. Phenol and phenolic derivatives are major pollutant in several industrial wastewaters released into the *environment*. Thus, there is a need to treat these *wastewaters* to recycle process water. Various processes were developed such as adsorption technology. Previous investigation showed that activated carbon displayed a good affinity for m-cresol adsorption at pH 2.5 [4]. Moreover, hybrid diatomite/ carbon composites are more adequate materials to be used in the removal p-cresol from aqueous solution than clays and Fly ash [5]. Activated charcoal and activated alumina *were also efficient to the removal of* p-cresol [6]. However, the use of these materials is limited due to its high cost.

Several decades of research have shown that the retention of organic compounds from aqueous solution correlates strongly with soil organic matter and ignores the contribution of the mineral fraction [7,8]. In this context, organo-clays, in particular organo-bentonites have been proved to be a potential solution of removing pollutants from aqueous solution due to their high hydrophobic properties which are far higher than those of natural clay [9,10]. The isomorphous substitutions in the tetrahedral and / or octahedral layer generate negative layer charge balanced by exchangeable cations which influence significantly the surface properties of bentonite. Organo-clays are often produced via non-equivalent ion-exchange reactions. Actually, several studies showed that when an organic cation is placed on the exchange complex by ion exchange, the long-chain alkyl groups are able to impart hydrophobic character to the mineral surface which become organophilic [11,12]. Hence, the interlayer space increase and the adsorption capacity towards organic compounds are improved. Among several surfactants that have been used to modify clays and to enhance their adsorption capacity, the quaternary ammonium (ex. HDTMA) attracted special attention, notably because of its long-chain alkyl and its cationic nature that is not affected by the pH [13,14].

In this work, we aimed to improve the adsorption capacity of natural Moroccan bentonite towards m-cresol by intercalation of HDTMA on the clay interlayer space. M-cresol was selected as a model of toxic water contaminants. This pollutant has a potential public and ecological threat because of his toxic effect and its ability to accumulate in terrestrial and aquatic food chain [15]. As such, the United States Environmental Protection Agency and the International Program on Chemical Safety reported this organic compound as a priority pollutant due to its low biodegradability and its potential toxicity [16,17]. Moreover, only a little attention has been paid on elimination of cresols by adsorption.

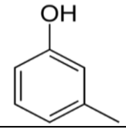
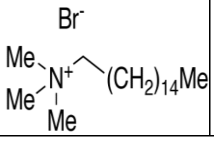
2. Material and methods

2.1. Preparation of organo-bentonite

The bentonite used in this study originated from Segangane-Nador, Morocco. The organo-bentonite was prepared by dispersing 0.5 g of bentonite (particle size < 200 µm.) in 200 ml of distilled water to which amounts of HDTMA (Sigma-Aldrich, St. Louis, MO, USA) equivalent to 0.5 and 1 cation exchange capacity (CEC) of the natural bentonite was added. The mixture was stirred for 2 hours at room temperature. The product was then filtered and sufficiently washed with distilled water until complete removal of bromide ions as indicated by $AgNO_3$. The resulted samples were dried at 50°C for 24 hours and stored at room temperature for the characterization and the adsorption study. The bentonite and organo-bentonite at 0.5 and 1 time CEC were labelled hereafter as BN, BM0.5 and BM1 respectively. M-cresol was purchased from Sigma-Aldrich. Molecular Structures and some chemical properties of m-cresol and HDTMA are given in **Table 1**.

Table 1: Structure and chemical properties of m-Cresol and HDTMA

2.2.

Compound (IUPAC Name)	Structure	Molecular weight	Molecular formula	Log Kow	Solubility
m-cresol: 3-methylphenol		108.14 g/mol	C_7H_8O	1.96	22.7 g/L
HDTMA-Br: Hexadecyltrimethyammonium bromide		364.45 g/mol	$C_{19}H_{42}BrN$	3.23	0.44 g/L

Analytical methods

Cation exchange capacity (CEC) was measured by the hexamino-cobalt method described elsewhere [18] X-ray diffraction (XRD) patterns of natural bentonite and organo-bentonite were obtained with $CuK\alpha$ radiation ((λ = 1.5406 Å).) on a PW1710 Philips Analytical diffractometer controlled by X'Pert Quantify software (EA Almelo, The Netherlands) and a scanning speed of 0,016°/s. For the swelling test, the oriented aggregate of fine bentonite fraction was treated under ethylene glycol vapours into a desiccator during 24 h, and finally, the sample was treated at 500 °C during 2 h before XRD analysis. The chemical composition was evaluated using an X-ray fluorescence spectrometer WDXRF, S4 Pioneer from BRUKER. Particle outer surface areas were determined by the N_2 adsorption–desorption method at – 196 °C according to the Brunauer-Emmet-Teller (BET) procedure using a Micomeritics Multi-point Beckman Coulter surface analyzer SA 3100. Thermal analysis was conducted using a model SDT Q600 TA Thermogravimetric Analyzer (New Castle, USA) operating under the following conditions: approximately 10 mg of sample was performed in ceramic pans with a heating rate of 20 °C/min from 40 °C to 800 °C in air atmosphere. Fourier transform infrared FTIR spectra were recorded in the transmission mode using a FTIR spectrometer (model FTIR/4100, Jasco). The samples were ground into powder and dried in an oven at 60 °C for 1 hour, and the potassium bromide pellet press method was used to improve the signal. Concentrations of m-cresol in aqueous solution were measured by UV-vis spectroscopy method at a maximum wavelength of 271 nm (Jasco 630).

2.3. Adsorption Procedure

The aqueous solutions of m-cresol were prepared by dissolving a pre-calculated amount of liquid m-Cresol with deionised water in the volumetric flasks. The stock solutions were stored in darkness at room temperature (22°C) and then diluted to desired concentrations. Adsorption experiments were conducted in a batch mode to obtain equilibrium data. 100 mg of adsorbent (bentonite or organo-bentonite) was contacted with a 20 mL of m-cresol aqueous solution in glass-stoppered tubes with initial concentration ranging from 10 to 200 mg/L at pH 6.5. The glass tubes were then shaken at room temperature until the equilibrium condition was attained. At the predetermined equilibrium time, the liquid and the solid phases were separated by centrifugation for 20 min at 6500 rpm. Samples of supernatant were taken and the concentration of unabsorbed m-cresol in aqueous phase was analyzed using UV-visible spectrophotometer.

2.4. Kinetic models

Kinetics experiments are helpful to predict *the equilibrium time necessary* for the adsorption of the pollutant and to control the adsorption conditions. The adsorption data were fitted using the pseudo-first-order and the pseudo-second-order kinetic models ([19, 20]. The linear forms of these models are expressed by the equations (1) and (2):

$$Ln\,(q_e - q_t) = \ln q_e - K_1 t \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

Were k_1 (min^{-1}) and k_2 (g/min/mg) are the rate constants of the pseudo first-order and the pseudo second-order models respectively, q_t (mg/g) is the adsorbate amount on the surface of the adsorbent at time t and q_e (mg/g) is the adsorbate amount at equilibrium time.
The amount of m-cresol adsorbed per gram of solid (q, mg g^{-1}), was determined from a mass balance, as follows:

$$q_e = \frac{(\mathrm{C_i} - \mathrm{C})\mathrm{V}}{\mathrm{m}} \qquad (3)$$

where C_i (mg L^{-1}) and C (mg L^{-1}) are m-Cresol concentrations at the initial and at equilibrium or specific time, respectively. m is the mass of adsorbent (g), and V is the total volume of liquid (L).
The results were modelled by the Freundlich and the Langmuir isotherms [21,22].

2.5. Adsorption equilibrium isotherms

The Freundlich model is one of the more widely used models for describing pollutant adsorption as reported in many literatures [23,24]. This isotherm is applicable for a multilayer adsorption on heterogeneous surface. The linear form of Freundlich isotherm can be expressed as follows:

$$\mathrm{Log}\,\mathrm{q_e} = LogK_f + \frac{1}{n} LogC_e \qquad (4)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L*)*, while K_f and 1/n are Freundlich constants related to the adsorptive capacity and the adsorption intensity of the adsorbent, respectively.
According to Okeola and Odebunmi [25], the efficiency of an adsorbent is even as high as the coefficient 1/n is small. Consequently, a high value of n indicates a strong bond between the adsorbent and the adsorbate.

The Langmuir isotherm model is valid to describe the adsorption on a solid surface at homogeneous definite sites. Therefore, adsorption is restricted to a monolayer [26]. In this model, each site on the adsorbent surface can hold only one adsorbate molecule and therefore adsorption is restricted to a monolayer [24].
The linear equation of the Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_m\, bC_e} + \frac{1}{q_m} \qquad (5)$$

Where q_m (mg/g) is the maximum monolayer capacity, C_e (mg/L) is the equilibrium concentration of the adsorbate and b (L/mg) is adsorption energy constant of Langmuir adsorption isotherm. The higher b is the affinity of the adsorbent for the adsorbate [22].

3. Results and discussion

3.1. Characterization of the natural bentonite

3.1.1. Analysis by X-ray fluorescence (XRF)

Elementary chemical analysis by X-ray fluorescence (**Table 2**) shows that aluminium oxide (Al_2O_3) and silicon oxide (SiO_2) are the predominant constituents with a ratio SiO_2/Al_2O_3 equal to 2.3. This value and the low content of K_2O (0.65%) indicate that the clay used in this work belongs to the family of smectite. The presence of exchangeable cations such calcium (Ca^{2+}), sodium (Na^+) and magnesium (Mg^{2+}) indicates that the analysed sample has a high cation exchange capacity. These results are completely consistent with those reported by Er-ramly and Ider [27] for a Moroccan bentonite.

Table 2: Chemical composition of bentonite analyzed by XRF

Elemental oxides	wt.%
SiO_2	57.32
Al_2O_3	24.87
Fe_2O_3	3.90
MnO	0.00
MgO	2.42
CaO	1.10
Na_2O	1.90
K_2O	0.65
TiO_2	0.27
P_2O_5	0.04
SO_3	0.12
SrO	0.02
LOI	11.36
(%)	103.95

3.1.2. Cation exchange capacity (CEC)

Cation exchange capacity (CEC) is the total capacity of a sample to bind or hold exchangeable cations. These cations are held by the negatively charged clay layers through electrostatic forces. This parameter is one of the most important properties of clays which are mainly related to the cation adsorption ability and surface functionalization. Various methods have been used to determine CEC of clays. Therefore, an estimation of the CEC value by the hexamino-cobalt method as described elsewhere [18] is given in **Table3**. The calculated CEC value was about 84.7 meq/100 g in good agreement with previous works [28]. Generally the CEC of bentonite is > 60 meq/100 g. The organic matter content given in **table 2** is very Low (1.22%) and the suspension pH is *slightly alkaline with a pH value* of 7.4.

Table 3: Texture and cation exchange capacities of the studied clay

pH	**CO %**	**MO %**	**CEC meq/100g**	**Sandy %**	**Loam %**	**Clay %**
7.4	0.71	1.22	84.7	12.3	24.7	57.4

3.1.3. Specific surface area (SSA)

The specific surface area (SSA) of the natural bentonite was determined from the nitrogen adsorption-desorption isotherms using the standard BET method [29]. The surfaces measured correspond to the outer surfaces because nitrogen has no access to interlayer spaces. Thus, the surface accessible to the nitrogen will depend on the texture and the particle size of materials. The SSA value of the natural bentonite was about 68 m^2/g. However; the total surface area of montmorillonite can exceed 800 m^2/g if all the clay layers are totally exfoliated [30].

Figure 1 shows that adsorption/desorption isotherms of nitrogen are of type IV according to the IUPAC classification [31].The hysteresis loops observed are generally associated with a slow filling and emptying of mesopores. Furthermore, a significant increase in the volume adsorbed at low relative pressure indicates the presence of narrow micropores as expected for a clay material. Similar findings were reported by several authors for another bentonite samples [32,33].

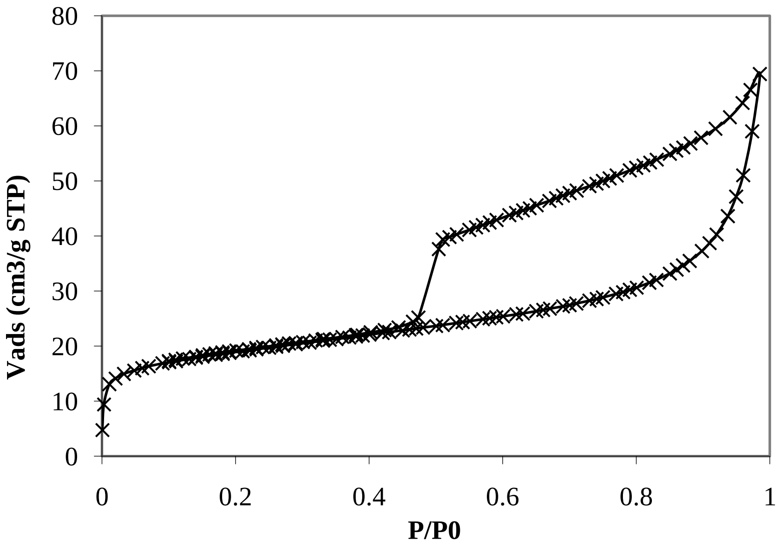


Figure 1: Isotherms of N_2 adsorption/desorption at - 196 °C of natural bentonite.

3.1.4. Thermal analysis (TGA- DTG)

Thermal characterization of bentonite was also carried out to determine its stability. The DTG and TGA curves of the natural bentonite are presented in **Figure 2**. These curves showed an important mass loss between 110 and180°C related to physisorbed and interlayer water loss (2.5%) followed by a small second peak (DTG) between 380°C-550°C due to the gradual departure of the lattice water [27,34, 35]. In these intervals, the removal of water is not associated with destruction of clay mineral structure suggesting the high thermal stability of the selected clay which related to crystalline structure. A second important mass loss event corresponding to the dehydroxylation of the sample was observed at high temperature (680-710°C) associated with the breakdown of the clay crystal structure. All these results indicate that smectite is the predominant clay mineral in the clay fraction analysed [12].

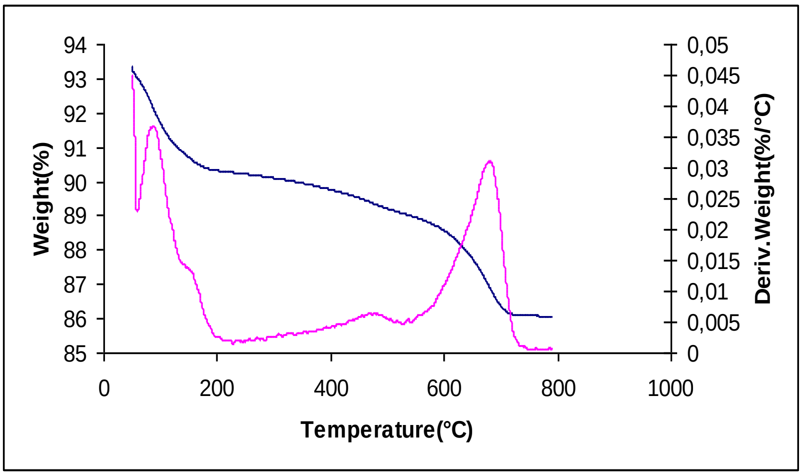


Figure 2: The DTG (▬) and TGA (▬) curves of the natural bentonite

3.1.5. Analysis by XRD

The clay particle size is very small in the order of microns and the degrees of crystal perfection are variables, making their *adequate characterization very difficult*. The XRD patterns of natural bentonite sample are given in **Figure 3**. A typical smectite d_{001} basal spacing is observed at 12.2 Å and d_{020} at 4.45 Å indicating the presence of one layer of water molecules [36,37]. Ethylene glycol treatment substitutes the interlayer water with a layer of big organic molecules and the 001-peak shifts to 16.9 Å. This reflection moves to 9.89 Å and its height decreases after thermal treatment at bellow 550 °C. The examination of the positions and intensities of this XRD patterns suggests that this clay is predominantly composed of montmorillonite. The other peaks are impurities corresponding to quartz, with reflection at 4.45 Å and 3.33 Å and feldspar at 3.74 Å.

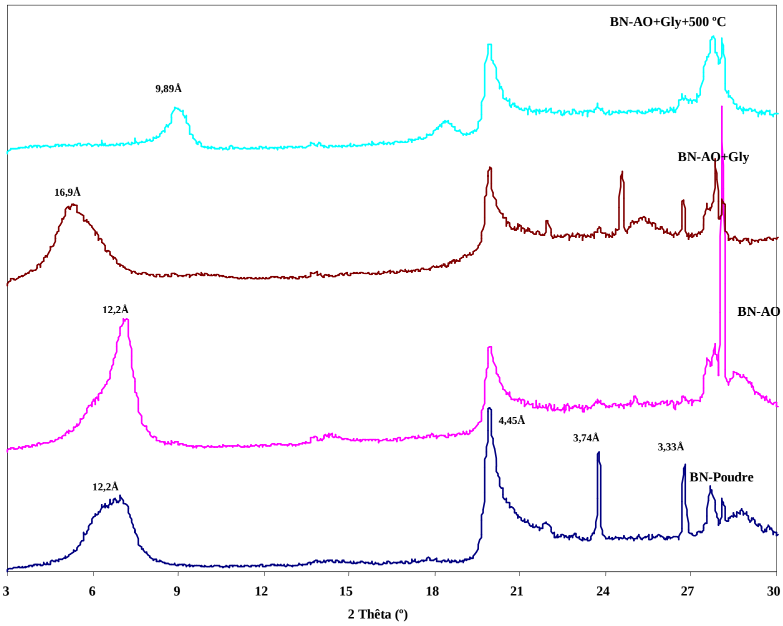


Figure 3: XRD pattern of natural bentonite

3.1.6. FTIR spectrum analysis

The FTIR spectrum of natural bentonite is ~~are~~ shown in **Figure 4**. The absorption bands at 3450 cm^{-1} and 1610 cm^{-1}are assigned to the stretching vibration and bending mode of the water molecules associated with the exchangeable cations in the interlayer spaces, of bentonite. The AlAlOH and AlFeOH streching bands are respectively situated at 920-930 cm^{-1} and 875-885 cm^{-1} [36,38]. The Si-O stretching bands are situated at the 1100 cm^{-1} region. No intense bands corresponding to organic matter was observed which is in agreement with low content of organic matter (1.22 %) reported in **Table 3**.

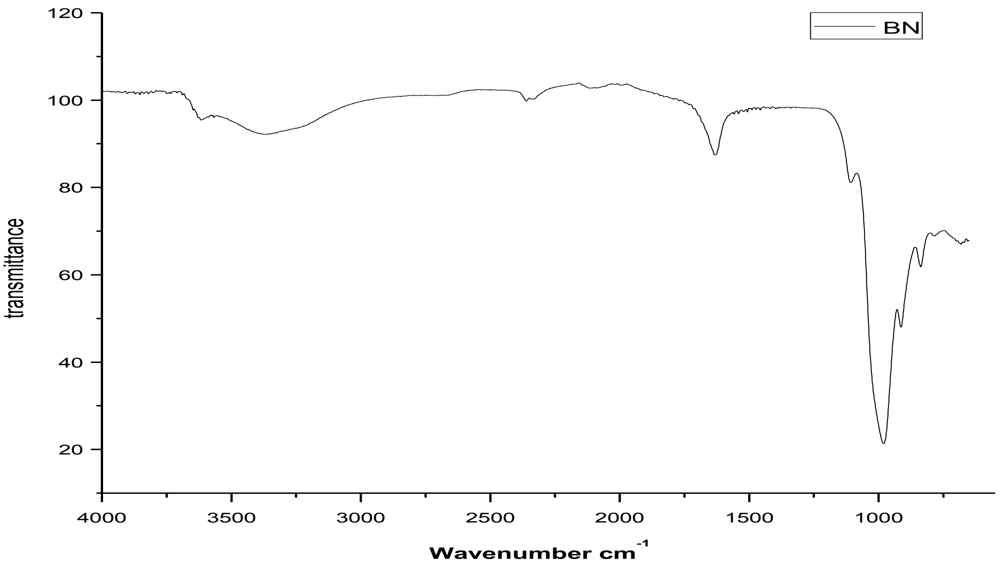


Figure 4: FTIR spectrum of the natural bentonite

3.2. Characterization of organo-bentonite

The organo-bentonites complex synthesized using hexadecyltrimethyl ammonium bromide (HDTMA-Br) as cationic surfactant were characterized by XRD and Infra Red analysis methods and the individual patterns were compared.

Generally, intercalation of cations into the clay interlayer spaces can be reflected by the increase of its basal spacing. **Figure 5** shows that d_{001} value shifts from 12.2 Å to 23.2 Å. This clearly confirms that the HDTMA cations were successfully intercalated into the interlayer spaces gallery of bentonite.

In order to obtain complementary evidence for the interactions between the cationic surfactant and the bentonite, FTIR measurements were carried out. **Figure 6** shows the apparition of new bands in the organo-bentonite attributed to stretching vibrations and deformation of the various groups of HDTMA molecules [39,40]. Absorption bands assigned to antisymmetric and symmetric stretching vibrations of C-H groups of the amine chain were observed only on the modified bentonite spectrum at about 2919 cm^{-1} and 2838 cm^{-1} respectively. These bands were less intense in BM0.5 than BM1 spectrum. A remarkable attenuation of the intensity of the bands at 1610 cm^{-1} and 3450 cm^{-1} relative to interlayer water was observed. This attenuation increased with the initial surfactant amount surfactant loading. This result confirms the substitution of hydrated cations by those of HDTMA [41] which is in perfect agreement with the literature [39,42]

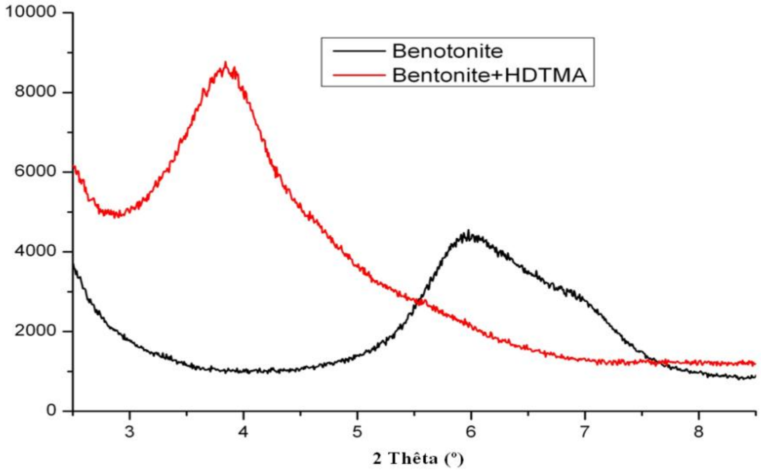


Figure 5: XRD patterns of bentonite and organo-bentonite

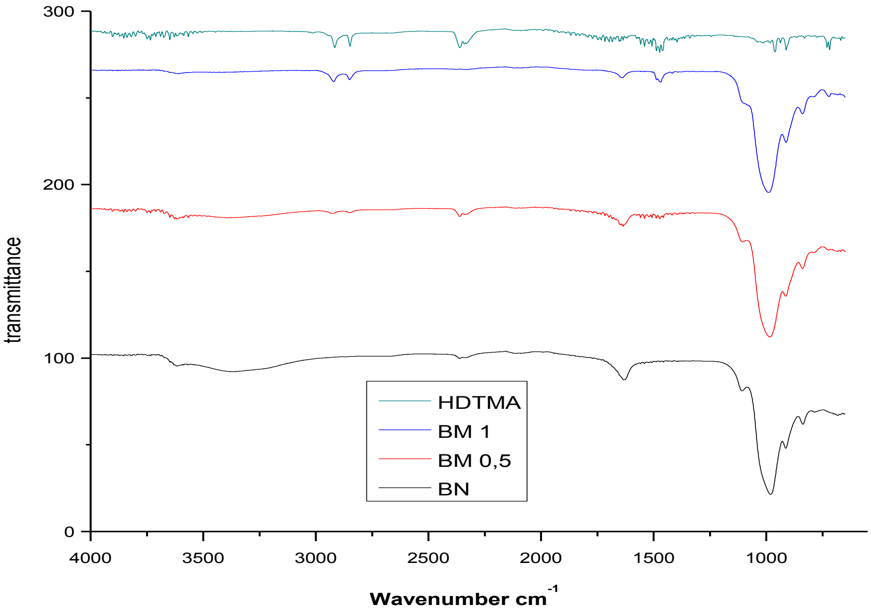


Figure 6: FTIR spectra of HDTMA, bentonite and organo-bentonites

3.3. Kinetic adsorption

The adsorption kinetic is an important step in any adsorption study since it allows to the determination of the contact time necessary to reach adsorption equilibrium. The effect of contact time on the adsorption efficiency of bentonite and organo-bentonite for m-cresol is depicted in **Figure 7**.

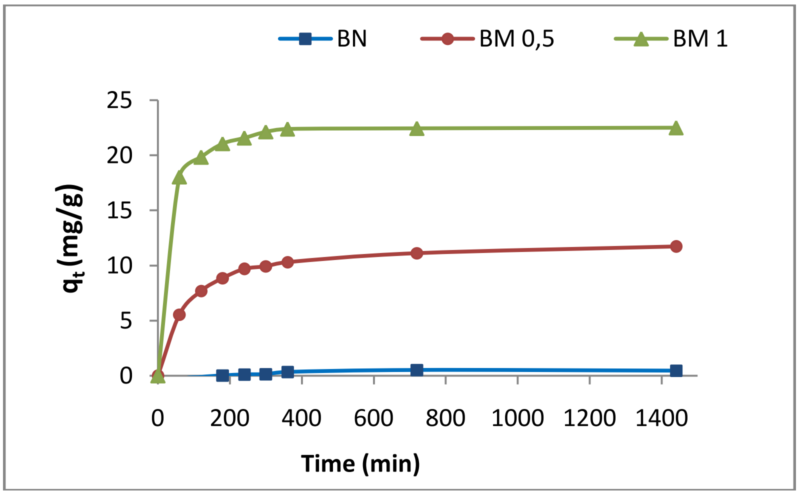


Figure 7: Effect of contact time on m-Cresol adsorption on BN, BM0.5 and BM1, C_i = 200 µg/mL, pH=6.5

For all the examined systems, the required time for reaching the equilibrium stage is almost identical (about 7 hours). The adsorption kinetics has approximately the same shape and shows three-stage process: a rapid initial phase at low concentrations followed by a second slower process until reaching equilibrium state. This phenomenon can be interpreted by the existence, in the first step, of outer adsorption sites easily accessible for m-cresol molecules. In the second phase, the pollutant diffuses slowly to the less accessible sites before reaching the equilibrium until all the sites become occupied [43]. It is worth noting that the adsorption capacity increases with the amount of HDTMA, which implies that the presence of the surfactant improves the interaction of organo-bentonite with hydrophobic compounds [44,45]

The adsorption kinetics of m-cresol onto the bentonite and organo-bentonite has been investigated in terms of pseudo-first-order kinetic (**Figure 8**) and pseudo-second-order kinetic models (**Figure 9**). The parameters were calculated and summarised in **Table 4**.

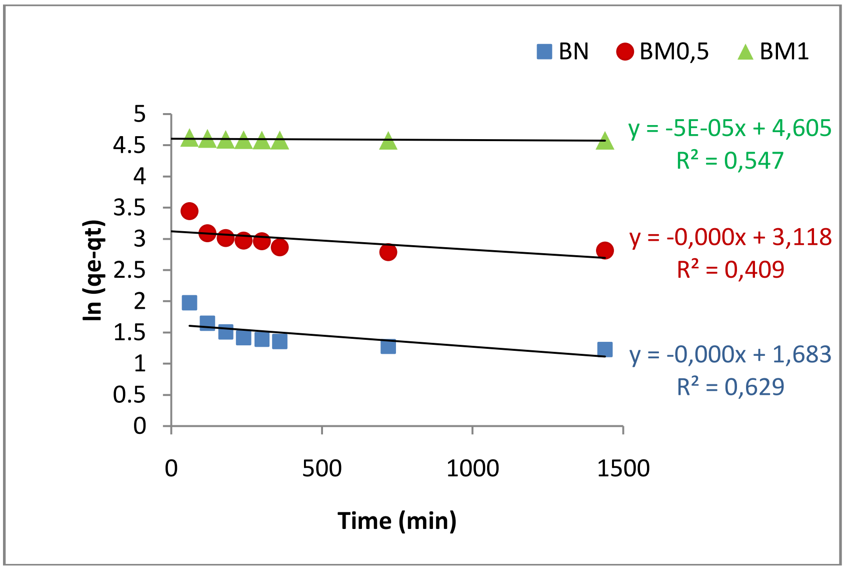


Figure 8: Pseudo-first-order kinetics for the adsorption of m-Cresol on BN, BM0.5 and BM1

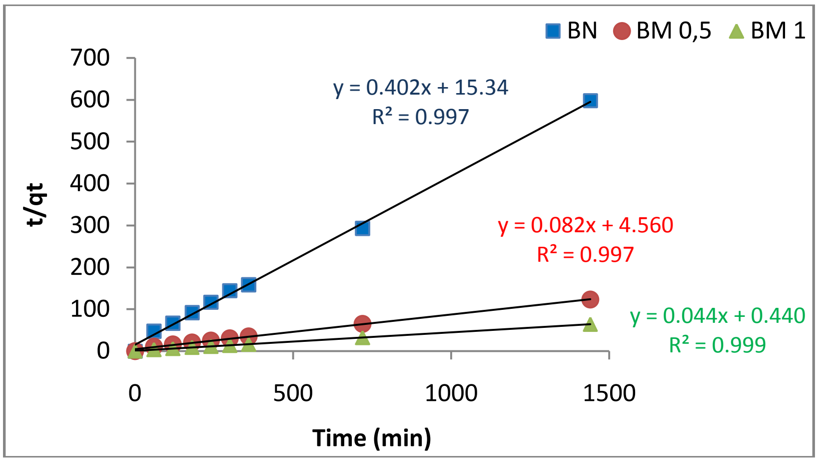


Figure9: Pseudo-second-order kinetics for the sorption of m-Cresol on BN, BM0.5 and BM1

By comparing the correlation coefficients, the pseudo-second-order model seems to be more suitable to represent the kinetic data in the ongoing adsorption process (R^2 higher than 0.99). According to Ahmad et al. [46] this tendency indicates that chemisorption might be the rate-limiting step in adsorption process. Furthermore, the rate constants of adsorption and theoretical adsorption capacities predicted by the pseudo-second-order equation agree very well experimental results. Similar results were also obtained for adsorption of certain pesticides by caprylate intercalated layered double hydroxide as adsorbent [47].

Table 4: Kinetic parameters of pseudo-first-order and pseudo-second-order models for adsorption of m-Cresol by bentonite and organo-bentonites

Samples	Pseudo-second-order model			Pseudo-first-order model		
	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2	q_e (mg/g)	K_2 (g/mg min)
BN	0.997	2.56	0.0104	0.629	0.139	0.0312
BM0.5	0.997	11.76	0.0011	0.409	2.251	0
BM1	0.999	23.25	0.004	0.547	9.535	0

3.4. Adsorption isotherms

The adsorption isotherm gives crucial data about adsorbent/adsorbate interactions during the adsorption process. This allows determining *the amount of* removed from solution to adsorbent. **Figure 10** *shows the results of adsorption study* of m-cresol onto unmodified and modified bentonite.

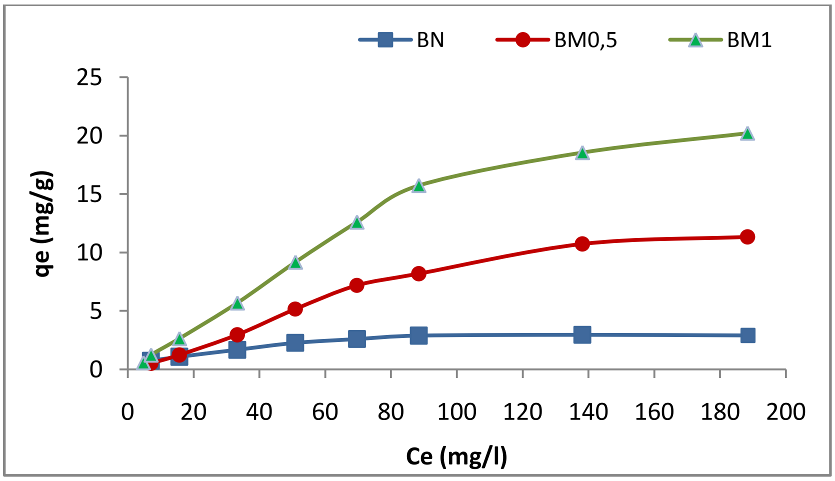


Figure 10: Adsorption isotherms of m-Cresol on BN, BM0.5 and BM1; pH 6.5

The equilibrium adsorption data were adjusted to Langmuir and Freundlich isotherm models [21,22]. Langmuir parameters can be calculated from the intercept and the slope of the linear plot of experimental data of $\frac{1}{q_e}$ *versus* $\frac{1}{C_e}$ (**Figure 11**). The Freundlich isotherm is given in **Figure 12**.

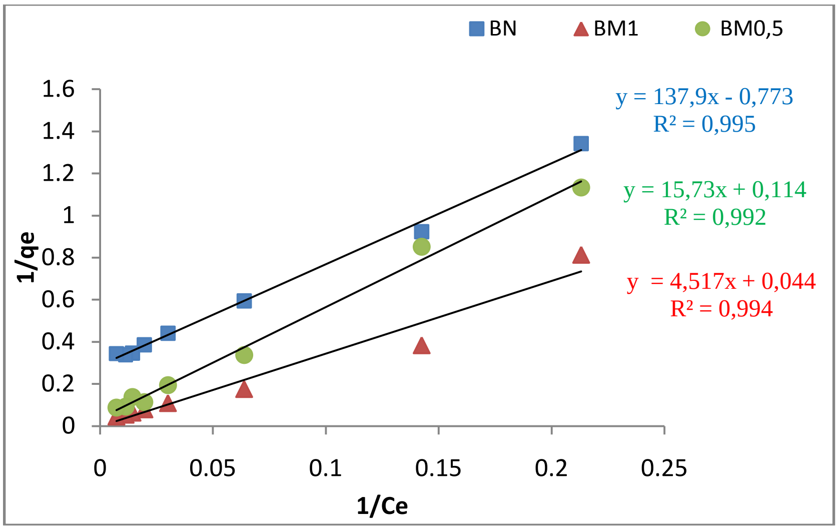


Figure 11: Langmuir isotherms for m-cresol adsorption on BN, BM0.5 and BM1

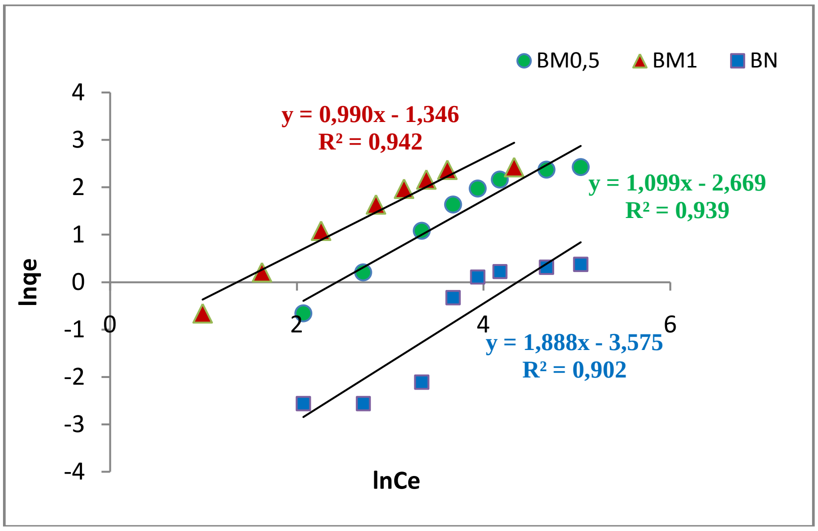


Figure 12: Freundlich isotherms for m-cresol adsorption on B, BM0.5 and BM1

The models parameters were evaluated through the linearized forms and presented in **Table 5**.We can clearly observe that both Langmuir and Freundlich models can predict m-cresol adsorption data, but a better fit has been given to the Langmuir model. At lower equilibrium concentrations, the Freundlich model seems to be most appropriate to describe m-cresol adsorption. This suggests the existence of heterogeneous energetic active sites on the organo-bentonite surface which consists of organic and inorganic components. However, at extremes concentrations, the experimental adsorption isotherms presented in **Figure 10** exhibited a long plateau indicating that monolayer saturation (q_m) values is reached. Thus, the Langmuir model could be the most convenient to describe the adsorption equilibrium data at higher concentrations involving less energetic sites [48].

Adsorption performance of adsorbents can be easily known by comparing their maximum adsorption capacities (q_m). **Table 5** shows that the removal capacity of organo-bentonite was greatly improved. The natural bentonite possesses very low adsorption capacity and removes only 1.29 mg of m-cresol per gram of adsorbent. The adsorption mechanism of m-cresol should be a low interaction with the siloxane surfaces and the hydrated inorganic interlamellar cations through the hydrogen bounds [48]. However, the maximum amount of m-cresol adsorbed by BM0.5 and BM1 was 8.77 and 22.72 mg/g respectively. This last value exceeds by more than 17 times that reached by natural bentonite. In addition, the affinity of binding sites for m-cresol increases in organo-bentonite samples as the surfactant loading increase. The efficiency of studied clays for m-cresol increases in this order: BN<BM0.5<BM1. This result confirmed that adsorption of m-cresol is catalyzed by strong hydrophobic interactions, hydrogen bonding, and electrostatic interaction [5,,44,49]. The value obtained with BM1 was similar to that cited with activated carbon (21.70 mg/g) [4]. However the bentonite presents advantage in term of cost and availability. The average price of bentonite is 0.06 US$/kg, very lower than of the activated carbon with an average price of 10·US$/kg [50].

Table 5: Langmuir and Freundlich parameters for m-Cresol adsorption on bentonite and organo-bentonite

	Langmuir isotherm model			Freundlich isotherm model		
	R^2	q_m (mg/g)	b	K_f	N	R^2
BN	0.995	1.29	0.005	0.02	0.53	0.902
BM0.5	0.982	8.77	0.007	0.06	0.91	0.939
BM1	0.994	22.72	0.009	0.26	1.01	0.942

4. Conclusion

In this work, an efficient hybrid material for removal of phenolic compounds was developed. The organophilic modification of the Moroccan bentonite improved markedly its affinity towards m-Cresol, judging by the high adsorption yield obtained by these materials. A maximum rate of m-Cresol was removed by the bentonite modified with an amount of HDTMA equivalent to 100% of cation exchange capacity. DRX and FTIR organo-bentonite characterization shows successful intercalation of the cationic surfactant in the interlayer spaces. The stabilization of surfactant into bentonite interlayer spaces, converts the hydrophilic surface to hydrophobic. The pseudo-second-order model was found more suitable to explain the adsorption kinetics more effectively as was demonstrated from the higher value of R^2. The equilibrium adsorption data fitted well to the Langmuir and Freundlich models, but gave a better fit to the Langmuir model.

The results obtained show clearly that Moroccan organo-modified bentonite could be a potential alternative low cost, eco-friendly and easy-to-prepare adsorbent for m-Cresol adsorption from aqueous solutions. This hybrid material appears to *be a promising adsorbent* for the removal of nonionic *organic* contaminants.

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