J. Chem. Eng. Data **2007,** *52,* 1621−1625

Adsorption of Methylene Blue from Aqueous Solutions on a Moroccan Clay

Y. El Mouzdahir,[†] A. Elmchaouri,*[,†] R. Mahboub,[†] A. Gil,[‡] and S. A. Korili[‡]

Université Hassan II Mohammedia, Faculté des Sciences et Techniques, Laboratoire d'Electrochimie et Chimie Physique, BP 146, 20650 Mohammedia, Morocco, and Department of Applied Chemistry, Los Acebos Building, Public University of Navarre, Campus of Arrosadia, E-31006 Pamplona, Spain

---

In this work, an equilibrium adsorption isotherm for the removal of a basic dye, Methylene Blue (MB), from aqueous solution on a natural Moroccan clay mineral has been investigated. Equilibrium data are mathematically modeled using the Freundlich and Langmuir adsorption models. The adsorption kinetics of MB has also been studied in terms of pseudo-first-order and pseudo-second-order. A maximum adsorption capacity of 135 $mg\cdot g^{-1}$ at equilibrium is achieved, indicating that the material could be used as a low-cost alternative in wastewater treatment for the removal of color and dyes.

Introduction

Major contaminants found in wastewater include biodegradable, volatile, and recalcitrant organic compounds; toxic metals; microbial pathogens; and parasites[1] causing deterioration of the surrounding medium that can present a great danger to the environment and human health.[2,3] Several studies have been undertaken on the toxicity of dyes and their impact on ecosystems.[4,5] These studies show that certain dyes degrade and that their derived products can be toxic and carcinogenic even at low concentrations.[5] Consequently, there is considerable need to treat these effluents prior to their discharge into receiving waters.[2,3]

Biological treatment[6] has been shown to be very efficient for the decrease of biological and chemical organic demand (BOD and COD), but it is ineffective for the elimination of dyes from wastewater.[6] Several techniques such as ultrafiltration,[7] catalytic photodegradation,[8,9] oxidation by UV/H_2O_2,[10,11] direct precipitation and separation of the pollutants by membrane processes,[12] and adsorption methods[6] have been studied. Among them, adsorption processes have been reported as a low-cost technique for the treatment of textile industry effluents and pigments.

The most common adsorbents used for dye removal from wastewater are activated carbons.[13] Natural materials have also been investigated as potential industrial adsorption media.[10,11,14−16] Regarding the adsorption of dyes using clay minerals, bentonites, montmorillonites, and sepiolites have been described as adsorbents.[17−21]

The first study about the adsorption behavior of a cationic dye on clay particles was reported by Bergman and O'Konski.[22] The authors observed the presence of four distinct bands near (575, 610, 670, and 760) nm, using visible spectroscopy analysis, which were related to dye aggregates. Many other studies have been reported on dye−clay systems, relating the adsorption bands to several species. Yariv and Lurie[23] assigned the bands at (575 and 610) nm to the interaction between the π-system of the dye and the lone pair of electrons of the oxygen atoms on the clay surface. Cenens and Schoonheydt[24] proposed that the band near 575 nm can be related to trimers on the external surface and that the band at 610 nm corresponded to dimers at the outer and inner surfaces of the clay. The investigators confirmed that the band at 670 nm was due to the adsorption of monomers and showed that the band at 765 nm is due to the protonated Methylene Blue (MB) adsorbed on the clay. Many of the aggregation and adsorption properties of clays can be related to the layer charge density.[25] Bujdak and Komadel[26] studied the interaction between modified clays with various layer charges and MB in aqueous suspensions. The authors concluded that the strong aggregation and redistribution of the molecules in the negative sites of clay surfaces suggests that the dye is adsorbed initially only on a small fraction of the clay particles, followed by a redistribution with time.

In the current work, we address the issue of Methylene Blue adsorption on Moroccan clay fractions from aqueous solutions to investigate and evaluate its adsorptive capacity. The adsorption kinetics of the cation exchange of MB with the clay mineral is also studied.

Materials and Methods

Adsorbent. The material adsorbent used in the present study was prepared with a purified Moroccan clay mineral from mid Moulouya (Morocco) known as a ghassoulite or rhassoulite. Chemical analysis was carried out by X-ray fluorescence spectrometry using a Philips PW 1400 spectrometer. The results, shown in Table 1, refer to dried solids (0 % water). These results were compared to those of various investigators.[27,28] The presence of a significant amount of silicon and a minimum aluminum quantity leads to the supposition that this sample can be classified in the silicates family. It also contains a large quantity of magnesium, thus it can be considered as a magnesian montmorillonite. Faust et al.[28] considered it as a stevensite or a magnesium smectite. The name of ghassoulite was proposed for the mineral extracted by Jbel Ghassoul.[29]

Experiments on the adsorption of dyes will take place only after a series of preliminary treatments carried out on the starting material. The principal objective of this pre-processing is the conversion of the ghassoulite into its homocationic form. All the exchangeable cations of rough, crushed, and filtered clay are exchanged by Na^+ after elimination of carbonates by acid

---

* Corresponding author. E-mail: elmchaouri@hotmail.fr.
[†] Université Hassan II Mohammedia.
[‡] Public University of Navarre.

10.1021/je700008g CCC: $37.00

Table 1. Chemical Composition of Na-ghassoulite (Metal Oxides in wt %)[a]

SiO_2	Al_2O_3	MgO	MnO	Li_2O	K_2O	CaO	Na_2O	Fe_2O_3	SO_3
64.57	2.06	23.63	0.41	0.28	2.84	1.84	1.52	0.84	1.91

[a] Results refer to dried solids (0 % water).

Table 2. Structural and Physical Properties of Na-ghassoulite

BET surface area	414 $m^2 \cdot g^{-1}$
cation exchange capacity	0.49 $meq \cdot g^{-1}$
porosity BJH	0.004 $cm^3 \cdot g^{-1}$
particle size	< 50 μm

attack, oxidation of the organic matter by leaching with H_2O_2 (30 % v/v) in a temperature less than 60 °C, and calcination at a heating rate of 10 $°C \cdot min^{-1}$ to 600 °C and kept at this temperature for 2 h to reduce the negative charge of the structure. The sodium clay samples were washed 4 times at 95 °C with 1 $mol \cdot dm^{-3}$ NaCl solutions under continuous stirring. The particles obtained were washed several times with bidistilled water to remove residues of NaCl and dried at 100 °C. The structural characteristics were estimated from nitrogen adsorption employing a volumetric technique. The structural and physical properties of the obtained material are given in Table 2.

Adsorption Procedure. The basic dye used in this work was Methylene Blue from Merck. It was used as received without further purification. A stock solution of MB (1000 $mg \cdot dm^{-3}$) was prepared and suitably diluted to the required initial concentrations. The concentrations of the dye in stock solutions and all samples during the experimental tests were measured using a UV−visible spectrophotometer at a wavelength corresponding to the maximum absorbance, 663 nm. To determine the equilibrium adsorption capacity of the dye by the clay material, a 100 cm^3 stoppered conical flask was placed in a temperature-controlled water bath shaker at 27 °C. Exactly 50 cm^3 of adsorbate solution was placed in the flask, and 0.1 g of clay was added. The flasks were sealed with a stopper and then shaken for 2 h at 350 rpm. The pH was controlled to 7.2, by addition of solutions of HCl (0.1 $mol \cdot dm^{-3}$) or NaOH (0.1 $mol \cdot dm^{-3}$). After 2 h of reaction, the flasks were taken out and the dye concentrations of the aqueous solutions were determined. After centrifugation, for 10 min at 4500 rpm, the MB concentration in the supernatant (C_{eq}) was measured. The specific adsorbed amount of MB was calculated according to the equation

$$q_e = V(C_0 - C_{eq})/m \qquad (1)$$

where C_0 and C_{eq} are the initial and equilibrium liquid-phase concentrations ($mg \cdot dm^{-3}$) of MB; *m* is the amount of adsorbent (g); and *V* is the volume of the solution (dm^3).

Batch experiments were repeated at least twice to ensure the accuracy of the obtained data. The kinetic study of adsorption was carried out at several intervals of time according to the above procedure using an initial concentration of 1000 $mg \cdot dm^{-3}$.

Results and Discussion

Methylene Blue Adsorption Isotherm. The equilibrium distribution of MB between the adsorbent and the solution is very important to determine the capacity of the adsorbent for the dyestuff. The adsorption isotherm is given in Figure 1, and the experimental adsorption data are summarized in Table 3. The adsorption efficiency and effectiveness of the clay material increases with increasing initial dye concentration. When MB is added to the clay suspension, the dye molecules readily adsorb on the clay particles and the state of saturation appears after very strong initial variations of the adsorbed quantity explaining the great affinity in the field of low concentrations of the dye for this smectite, MB being adsorbed to a capacity of 135 $mg \cdot g^{-1}$. It has been suggested[25] that MB molecules can migrate from the external surfaces to the interlamellar region, resulting in the disaggregation of the aggregates and restoring monomers. At a high load of MB, agglomerates are expected to be predominant, whereas monomers and dimers are practically absent in MB−clay complexes.[26] The capacity of adsorption is important in comparison to other adsorbents (see Table 4).[15,18,30,31] It depends on several parameters such as the specific surface area, the expansible character,[32−35] the ionic exchange phenomenon of the adsorbent material,[36] the mobility of the dye molecules in the liquid phase and in the interior of the solid, and the forces of attraction between the surface of the solid and the molecules of MB.

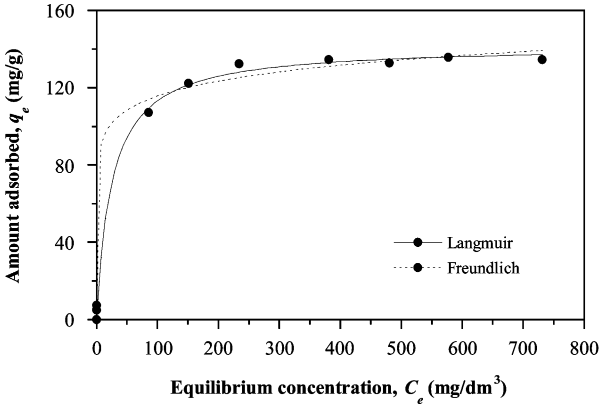

Figure 1. Equilibrium adsorption data of Methylene Blue on Na-ghassoulite.

Table 3. Equilibrium Adsorption Data of Methylene Blue On Na-ghassoulite

run A			run B		
C_0[a]	C_{eq}[b]	q_e[c]	C_0[a]	C_{eq}[b]	q_e[c]
$mg \cdot dm^{-3}$	$mg \cdot dm^{-3}$	$mg \cdot g^{-1}$	$mg \cdot dm^{-3}$	$mg \cdot dm^{-3}$	$mg \cdot g^{-1}$
0	0	0	0	0	0
10	0	5	10	0	5
15	0	7.5	15	0	7.5
300.02	85.6	107.21	300	80.8	109.6
395.08	150.62	122.23	400	160	120
498.14	233.68	132.23	500	236.2	131.9
650	381.04	134.48	650	385.6	132.2
746.01	480.13	132.94	750	482.2	133.9
848.59	576.99	135.80	850	581	134.5
1000.52	731.52	134.5	1000	731	134.5

[a] C_0, initial concentration of Methylene Blue. [b] C_{eq}, equilibrium concentration of Methylene Blue. [c] q_e, amount of Methylene Blue adsorbed.

Table 4. Adsorption Capacity of MB and Comparison with Other Adsorbents

adsorbent	adsorption capacity ($mg \cdot g^{-1}$)
kaolinite[18,30]	76.9; 20.5
tanned solid wastes[15]	84
Na-ghassoulite [this work]	135
activated carbon[31]	521

Modeling of MB Adsorption Isotherms. The parameters of the isotherm model equations can be related to the structural properties of the materials. These properties are crucial to the selection of the solids used as adsorbents. The adsorption equilibrium data of MB on clay material were fitted by applying the Freundlich and Langmuir isotherm models.

Table 5. Freundlich and Langmuir Equation Parameters for the Methylene Blue Adsorption

Langmuir				Freundlich		
K_L		q_m		K_F		
$dm^3 \cdot mg^{-1}$	R^2	$mg \cdot g^{-1}$	R_L	$mg \cdot g^{-1}$	n	R^2
0.0395	0.996	142	0.025	75.2	10.7	0.993

The equation of Langmuir, based on the assumption of an adsorption on a homogeneous surface containing a number of sites with the same adsorption energies,[37] supposes that there is no migration of the adsorbate on the surface of the adsorbent solid.

$$q_e = \frac{K_L q_m C_{eq}}{1 + C_{eq} K_L} \tag{2}$$

where q_e ($mg \cdot g^{-1}$) is the equilibrium amount of MB adsorbed for the adsorbent; C_{eq} ($mg \cdot dm^{-3}$) is the equilibrium concentration of the dye; and q_m ($mg \cdot g^{-1}$) and K_L ($dm^3 \cdot mg^{-1}$) are the Langmuir constants, which are the monolayer adsorption capacity and the energy of adsorption, respectively. The Langmuir equation parameters for the MB adsorption are summarized in Table 5.

For the Langmuir-type adsorption process, the influence of the isotherm shape on whether adsorption is *favorable* or *unfavorable* can be classified by the separation factor R_L, which is considered as a more reliable indicator of the adsorption capacity.[38] This constant is evaluated as

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where K_L ($dm^3 \cdot mg^{-1}$) is the Langmuir constant and C_0 ($mg \cdot dm^{-3}$) is the initial concentration in the liquid phase. Favorable adsorption is reported when the R_L values are between 0 and 1.[39] In the present work, the value of R_L calculated is 0.025 (see Table 5), indicating that the Langmuir model can describe the adsorption process. The maximum of adsorption estimated from the Langmuir model is 142 $mg \cdot g^{-1}$, in accordance with the experimental value obtained, 135 $mg \cdot g^{-1}$.

The Freundlich equation is applicable to adsorption on heterogeneous surfaces, i.e., surfaces with nonenergetically equivalent sites.[40] The model gives a representation of the adsorption equilibrium between an adsorbate in solution and the surface of the adsorbent.

$$q_e = K_F {C_{eq}}^{1/n} \tag{4}$$

where q_e ($mg \cdot g^{-1}$) is the equilibrium amount of MB adsorbed for the adsorbent. K_F and $1/n$ are empirical constants, being indicative of the extent of adsorption and an indicator of adsorption effectiveness, respectively. The Freundlich equation parameters for the MB adsorption are summarized in Table 5.

Kinetic Studies of Methylene Blue Adsorption. To evaluate the effectiveness of an adsorbate, studies of kinetics of adsorption equilibria are also needed. The evolution of the amount of MB adsorbed, q_t, as a function of the time of adsorption is presented in Figure 2. The experimental adsorption data are summarized in Table 6. The maximum of adsorption is obtained after 5 min of contact between MB and the clay.

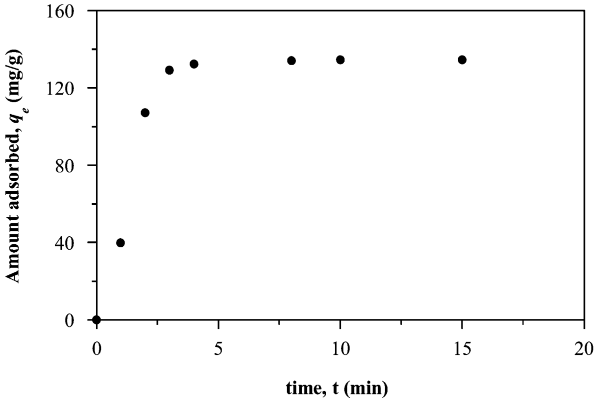

Figure 2. Adsorption of Methylene Blue as a function of the contact time at room temperature.

Table 6. Kinetic Adsorption Data of Methylene Blue on Na-ghassoulite

data A			data B		
t^a	$C_t{}^b$	$q_t{}^c$	t^a	$C_t{}^b$	$q_t{}^c$
min	$mg \cdot dm^{-3}$	$mg \cdot g^{-1}$	min	$mg \cdot dm^{-3}$	$mg \cdot g^{-1}$
0	1000	0	0	1000	0
1	920.1	39.95	1	929	35.5
2	785.78	107.11	2	783.4	108.3
3	741.5	129.25	3	738	131
4	735.52	132.24	4	735.6	132.2
8	731.6	134.2	8	731	134.5
10	731	134.5	10	731	134.5
15	731.2	134.4	15	731.2	134.4

[a] t, time of contact. [b] C_t, concentration of Methylene Blue in the solution. [c] q_t, amount of Methylene Blue adsorbed.

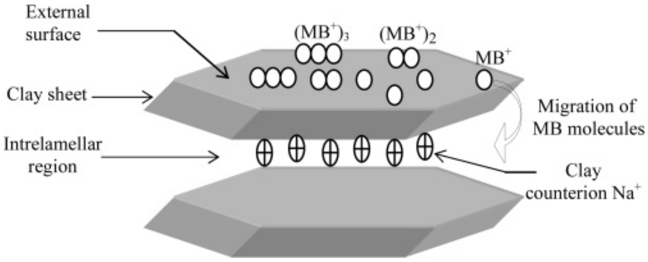

Figure 3. Sorption mechanism of Methylene Blue (MB) molecules on clay.[25]

The initial process, when a dye is added to the clay suspension, is the adsorption of the molecules on the external surface of the particles. This increases significantly the local concentration, giving rise to the formation of MB aggregates such as trimers $(MB^+)_3$ and dimers $(MB^+)_2$. With time, the dye molecules can migrate to the interlamellar region resulting in the disaggregation of the aggregates and restoring protonated monomers because of the higher acidity in this region, and so the adsorption proceeds through an ion pairing mechanism.[25,41] A possible mechanism of this process is summarized in Figure 3.[25]

Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data. The rate constant of the dye removal from the solution by smectite was determined using pseudo-first-order and pseudo-second-order equations.

The Lagergren[42] pseudo-first-order equation was used to fit the experimental results. The linear form of the Lagergren equation is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where k_1 (1/min) is the first-order rate constant; q_t ($mg \cdot g^{-1}$) is the amount of dye adsorbed at time t (min); and q_e ($mg \cdot g^{-1}$) is the equilibrium sorption capacity. The adsorption kinetic parameters from Figure 4 are included in Table 7.

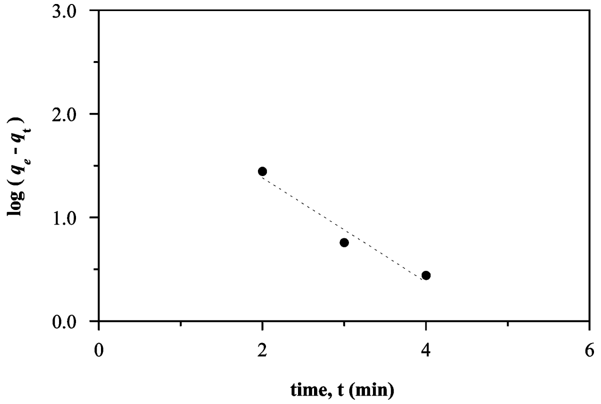

Figure 4. Pseudo-first-order adsorption kinetics.

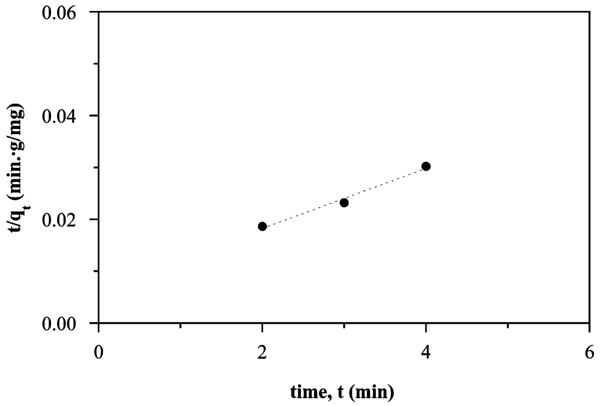

Figure 5. Pseudo-second-order adsorption kinetics.

Table 7. Adsorption Kinetic Parameters of Methylene Blue on Clay

pseudo-first-order			pseudo-second-order			
k_1	q_e		k_2	q_e		h
1/min	$mg \cdot g^{-1}$	R^2	$g \cdot mg^{-1} \cdot min^{-1}$	$mg \cdot g^{-1}$	R^2	$mg \cdot g^{-1} \cdot min^{-1}$
1.16	244.8	0.96	0.0050	172.8	0.98	149.7

The adsorption data were also analyzed in terms of a pseudo-second-order mechanism.[43,44] The linear form of the equation is

$$t/q_t = 1/k_2 q_e^{\,2} + (1/q_e)t \tag{6}$$

where q_e ($mg \cdot g^{-1}$) is the equilibrium sorption capacity and k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the rate constant of the pseudo-second-order adsorption.

If the initial adsorption rate is[45]

$$h = k_2 q_e^{\,2} \tag{7}$$

then eq 6 becomes

$$t/q_t = 1/h + (1/q_e)t \tag{8}$$

The adsorption kinetic parameters from Figure 5 are listed in Table 7.

From these results, the equilibrium sorption capacity and correlation coefficient for the second-order model are more reasonable when compared with the experimental results than that of the first-order model. Further, there was a minor deviation between the expected and the observed q_e values. It can be said that the sorption process may involve more than one step, calling upon the transfer by a diffusion layer, or an interface of diffusion, and the intraparticle diffusion.

Conclusion

The study of the adsorption of a pure organic dye, Methylene Blue, on Na-ghassoulite was undertaken in the static mode at 27 °C and atmospheric pressure. This clay showed great elimination capacity compared to other materials. The adsorbed quantity in the equilibrium reached 135 $mg \cdot g^{-1}$. The kinetic study revealed that approximately 5 min of agitation is sufficient to reach a complete equilibrium for the MB/Na-ghassoulite system. This study showed also that the equilibrium of adsorption of the MB/Na-ghassoulite system is suitably described by the Langmuir and Freundlich models. The process of adsorption is relatively fast and was best described by the pseudo-second-order rate model. These results generally showed that Na-ghassoulite could be considered as a potential adsorbent for MB removal from aqueous solutions.

Literature Cited

(1) Sidat, M.; Kasan, H. C.; Bux, F. Laboratory-Scale Investigation of Biological Phosphate Removal from Municipal Wastewater. *Water SA* **1999**, *25*, 459−462.
(2) Pagga, U.; Taeger, T. Development of a Method for Adsorption of Dyestuffs on Activated Sludge. *Water Res.* **1994**, *28*, 1051−1057.
(3) Reife, A. *Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: New York, 1993; Vol. 8, pp 753−784.
(4) Shenai, V. A. Non-Ecofriendly Textile Chemicals and their Probable Substitutes−An Overview. *Indian J. Fibre Text. Res.* **2001**, *26*, 50−54.
(5) Greene, J. C.; Baughman, G. J. Effects of 46 Dyes on Population Growth of Freshwater Green Alga Selenastrum Capricornutum. *Text. Chem. Color.* **1996**, *28*, 23−30.
(6) Coia-Ahlman, S.; Groff, K. A. Textile Wastes. *Res. J. Water Pollut. Control Fed.* **1990**, *62*, 473−478.
(7) Majewska-Nowak, K.; Kowalska, I.; Kabsch-Korbutowicz, M. Ultrafiltration of Aqueous Solutions Containing a Mixture of Dye and Surfactant. *Desalination* **2006**, *198*, 149−157.
(8) Saquib, M.; Muneer, M. TiO_2-Mediated Photocatalytic Degradation of a Triphenylmethane Dye (Gentian Violet), in Aqueous Suspensions. *Dyes Pigm.* **2003**, *56*, 37−49.
(9) Hachem, C.; Bocquillon, F.; Zahraa, O.; Bouchy, M. Decolourization of Textile Industry Wastewater by the Photocatalytic Degradation Process. *Dyes Pigm.* **2001**, *49*, 117−125.
(10) Abu-El-Sha'r, W. Y.; Gharaibeh, S. H.; Mahmoud, S. Removal of Dyes from Aqueous Solutions using Low-Cost Sorbents Made of Solid Residues from Olive-Mill Wastes (JEFT) and Solid Residues from Refined Jordanian Oil Shale. *Environ. Geol.* **2000**, *39*, 1090−1094.
(11) Allen, S. J.; McKay, G.; Khader, K. Y. H. Multi-Component Sorption Isotherms of Basic-Dyes onto Peat. *Environ. Pollut.* **1988**, *52*, 39−53.
(12) Wu, J. N.; Eiteman, M. A.; Law, S. E. Evaluation of Membrane Filtration and Ozonation Processes for Treatment of Reactive-Dye Wastewater. *J. Environ. Eng.-ASCE* **1998**, *124*, 272−277.
(13) Yu-Li, Y. R.; Thomas, A. Color Removal from Dye Wastewaters by Adsorption using Powdered Activated Carbon: Mass Transfer Studies. *J. Chem. Technol. Biotechnol.* **1995**, *63*, 48−54.
(14) Belkevich, P. I.; Kovzun, A. A.; Sobol, M. I.; Chistova, L. R. Organophilic Peat-Sorbent for Removing Oils and Petroleum-Products from Wastewaters. *J. Appl. Chem. USSR* **1980**, *53*, 1796−1799.
(15) Tahiri, S.; Messaoudi, A.; Albizane, A.; Azzi, M.; Bouhria, M.; Younssi, S. A.; Bennazha, J.; Mabrour, J. Removal of Dyes from Aqueous Solutions by Adsorption on Chrome-Tanned Solid Wastes Generated in the Leather Industry. *Water Qual. Res. J. Can.* **2003**, *38*, 393−411.
(16) McKay, G.; Ramprasad, G.; Mowli, F. P. Equilibrium Studies for the Adsorption of Dyestuffs from Aqueous Solutions by Low-Cost Materials. *Water, Air, Soil Pollut.* **1986**, *29*, 273−283.
(17) Ramakrishna, K. R.; Viraraghavan, T. Dye Removal using Low Cost Adsorbents. *Water Sci. Technol.* **1997**, *36*, 189−196.
(18) Ghosh, D.; Bhattacharyya, K. G. Adsorption of Methylene Blue on Kaolinite. *Appl. Clay Sci.* **2002**, *20*, 295−300.
(19) Rytwo, G.; Nir, S.; Margulies, L. A Model for Adsorption of Divalent Organic Cations to Montmorillonite. *J. Colloid Interface Sci.* **1996**, *181*, 551−560.

(20) Rytwo, G.; Tropp, D.; Serban, C. Adsorption of Diquat, Paraquat and Methyl Green on Sepiolite: Experimental Results and Model Calculations. *Appl. Clay Sci.* **2002**, *20*, 273−282.

(21) Gemeay, A. H. Adsorption Characteristics and the Kinetics of the Cation Exchange of Rhodamine-6G with Na^+-Montmorillonite. *J. Colloid Interface Sci.* **2002**, *251*, 235−241.

(22) Bergmann, K.; O'Konski, C. T. A Spectroscopic Study of Methylene Blue Monomer, Dimer, and Complexes with Montmorillonite. *J. Phys. Chem.* **1963**, *67*, 2169−2177.

(23) Yariv, S.; Lurie, D. Metachromasy in Clay Minerals. 1. Sorption of Methylene Blue by Montmorillonite. *Isr. J. Chem.* **1971**, *9*, 537−541.

(24) Cenens, J.; Schoonheydt, R. A. Visible Spectroscopy of Methylene-Blue on Hectorite, Laponite-b, and Barasym in Aqueous Suspension. *Clays Clay Miner.* **1988**, *36*, 214−224.

(25) Neumann, M. G.; Gessner, F.; Schmitt, C. C.; Satori, R. Influence of the Layer Charge and Clay Particle Size on the Interactions between the Cationic Dye Methylene Blue and Clays in an Aqueous Suspension. *J. Colloid Interface Sci.* **2002**, *255*, 254−259.

(26) Bujdak, J.; Komadel, P. Interaction of Methylene Blue with Reduced Charge Montmorillonite. *J. Phys. Chem. B* **1997**, *101*, 9065−9068.

(27) Elmchaouri, A.; Mahboub, R. Effects of Preadsorption of Organic Amine on Al-PILCs Structures. *Coll. Surf. A* **2005**, *259*, 135−141.

(28) Faust, G.; Hataway, J. C.; Millot, J. A Study of Stevensite and Allied Minerals. *Am. Miner.* **1959**, *44*, 342−370.

(29) Benhammou, A.; Yaacoubi, A.; Nibou, L.; Tanouti, B. Adsorption of Metal Ions onto Moroccan Stevensite: Kinetic and Isotherm Studies. *J. Colloid Interface Sci.* **2005**, *282*, 320−326.

(30) Kaoua, F.; Gaid, A.; Aitamar, H.; Tazairt, A. Cinétique d'Adsorption du Bleu de Méthylène sur Différents Types d'Argile Kaolinitique. *Bull. Soc. Chim. Fr.* **1987**, *4*, 581−588.

(31) Juang, R.-S.; Wu, F.-C.; Tseng, R.-L. Mechanism of Adsorption of Dyes and Phenols from Water using Activated Carbons Prepared from Plum Kernels. *J. Colloid Interface Sci.* **2000**, *227*, 437−444.

(32) Bagane, M.; Guiza, S. Elimination d'un Colorant des Effluents de l'Industrie Textile pas Adsorption. *Ann. Chim. Sci. Mater.* **2000**, *25*, 615−625.

(33) Rytwo, G.; Nir, S.; Crespin, M.; Margulies, L. Adsorption and Interactions of Methyl Green with Montmorillonite and Sepiolite. *J. Colloid Interface Sci.* **2000**, *222*, 12−19.

(34) Hang, P. T. Methylene Blue Absorption by Clay Minerals−Determination of Surface Areas and Cation Exchange Capacities. *Clays Clay Miner.* **1970**, *18*, 203−210.

(35) Graham, V. A.; Bilanski, W. K.; Menzies, D. R. Adsorption Grain Drying using Bentonite. *Trans. ASAE* **1983**, *26*, 1512−1515.

(36) Delville, A.; Sokolowski, S. Adsorption of Vapor at a Solid Interface−A Molecular-Model of Clay Wetting. *J. Phys. Chem.* **1993**, *97*, 6261−6271.

(37) Langmuir, I. The Constitution and Fundamental Properties of Solids and Liquids. *J. Am. Chem. Soc.* **1916**, *38*, 2221−2295.

(38) Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Condition. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 212−217.

(39) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: London, 1965.

(40) Freundlich, H. M. F. Over the Adsorption in Solution. *Z. Phys. Chem.* **1906**, *57*, 385−471.

(41) Gessner, F.; Schmitt, C. C.; Neumann, M. G. Time-Dependent Spectrophotometric Study of the Interaction of Basic-Dyes with Clays. 1. Methylene-Blue and Neutral Red on Montmorillonite and Hectorite. *Langmuir* **1994**, *10*, 3749−3753.

(42) Lagergen, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe. Kungliga Vetenskapsakademiens. *Handlingar* **1898**, *24*, 1−39.

(43) Deo, N.; Ali, M. Dye Adsorption by a New Low-Cost Material: Congored-1. *Indian J. Environ. Prot.* **1993**, *13*, 496−508.

(44) Ho, Y. S.; McKay, G. Sorption of Dye from Aqueous Solution by Peat. *Chem. Eng. J.* **1998**, *70*, 115−124.

(45) Gundogan, R.; Acemioglu, B.; Alma, M. H. Copper (II) Adsorption from Aqueous Solution by Herbaceous Peat. *J. Colloid Interface Sci.* **2004**, *269*, 303−309.

Received for review January 4, 2007. Accepted May 18, 2007. This work was supported by the CNRST-Morocco and the Spanish Agency of International Cooperation-*AECI* (A/2825/05 and A/6525/06). S.A.K. acknowledges the financial support from the Spanish Ministry of Education and Science through the Ramon-y-Cajal program.

JE700008G