Maghnia 산 Montmorillonite 수용액으로부터 양이온 염료의 제거 비교연구

A. Elaziouti* and N. Laouedj[†]

LCPCE Laboratory, Faculty of sciences, Department of industrial Chemistry,
University of the Science and the technology of Oran (USTO M.B). BP 1505 El M'naouar 31000 Oran, Algeria
[†]DR. Moulay Tahar University, Saida, Algeria
(접수 2010. 3. 29; 수정 2010. 3. 30; 게재확정 2010. 4. 5)

Comparison Study on the Removal of Cationic Dyes from Aqueous Suspension of Maghnia Montmorillonite

A. Elaziouti* and N. Laouedj[†]

LCPCE Laboratory, Faculty of sciences, Department of industrial Chemistry,
University of the Science and the technology of Oran (USTO M.B). BP 1505 El M'naouar 31000 Oran, Algeria
*E-mail: abdelkader923@yahoo.fr
[†]DR. Moulay Tahar University, Saida, Algeria. E-mail: nlaouedj@yahoo.fr
(Received March 29, 2010; Revised March 30, 2010; Accepted April 5, 2010)

요약. 대상 수용액으로부터 상업용 염료인 메틸렌 블루(MB)와 말라카이트 그린 옥살레이트(MG)의 제거를 위한 소듐-교환된 점토 입자의 흡착능을 다양한 실험조건에서 조사하였다. 용액의 pH, 교반 시간, 흡착물 농도, 흡착제 투여량 등의 효과를 조사하였다. pH 7, 298 K 조건에서 0.03 그람 점토를 사용한 경우 수용액으로부터 최대 > 90%의 염료가 제거되었다. 흡착과정은 빨랐으며 5분 내에 평형에 도달하였다. 사용된 염료들의 흡착반응에 대해 반응속도론 실험에서 유사 2차반응이 관찰되었고 실험 데이터와 잘 일치하였다. 흡착평형은 높은 회귀계수 $R^2 > 0.98$로 Langmuir 와 Dubini-Radushkevich (D-R) 등온에 따랐다. 이 D-R 모델로부터 평균자유에너지 E_a 는 MB와 MG 염료에 대해 각기 3.779와 2.564가 이었으며, 이것은 물리적 흡착과정에 해당된다.

주제어: 소듐-교환 점토, 염료, 흡착, 등온, Langmuir, Freundlich, D-R

ABSTRACT. The ability of sodium-exchanged clay particles as an adsorbent for the removal of commercial dyes, Methylene blue (MB) and Malachite green oxalate (MG) from aqueous solutions has been investigated under various experimental conditions. The effect of the experimental parameters, such as pH solution, agitation time, adsorbate concentration and adsorbent dose were examined. Maximum adsorption of dyes, i.e. >90% has been achieved in aqueous solutions using 0.03 g of clay at a pH of 7 and 298 K for both dyes. The adsorption process was a fast and the equilibrium was obtained within the first 5 min. For the adsorption of both MB and MG dyes, the pseudo-second-order reaction kinetics provides the best correlation of the experimental data. The adsorption equilibrium results follow Langmuir and Dubini-Radushkevich (D-R) isotherms with high regression coefficients $R^2 > 0.98$. The mean free energies E_a of adsorption from D-R model were 3.779 and 2.564 kj/mol for MB and MG respectively, which corresponds to a physisorption process.

Keywords: Sodium-exchanged clay, Dye, Adsorption, Isotherm, Langmuir, Freundlich, D-R

INTRODUCTION

Clay minerals, the most available, low cost and chemically active surface minerals world, are of great interest, practically because of their extensive uses in many scientific areas such as soil science (stoppage for fertilisers,[1] photostabilizers of pesticides[2]), industrial technology (heterogenrous catalysis),[3] colloidal science (decontamination of water,[4] pharmaceutical and paint industries[5]) and photochemistry (guide for photo-redox reactions).[6]

The adsorption of cationic dyes in aqueous solutions of smectite-type clay is studied. This clay is a dioctahedral smectite with isomorphic substitutions of Al^{+3} by Mg^{+2} with structural formula unit:

$$(Si_8)^{IV} (Al_{4-x} Mg_x)^{VI} O_{20} (OH)_4 \text{ where } x = 0.5 - 0.9.$$
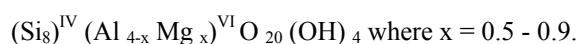
However for Maghnia montmorillonite, part of the negative charge around 15 - 50% is due to tetrahedral substitutions of Si^{+4} by Al^{+3}. This clay has an appreciable content of iron.

The interest of clay minerals for wastewater treatment in recent decade owing to their catalytic properties and high capacity in the removal pollutants too stable and resistant for conventional methods such as the oxydo-reduction and the exchanging resins of ions,[7] coagulation/flocculation,[8] membrane separation,[9] adsorption,[10] the biological methods,[11] and more recently the advanced processes of oxidation.[12]

The adsorption of cationic dyes is not exclusively due to the ionic exchange mechanism but other interactions, such a hydrophobic effect between guest molecules on the clay surface[13] and/or H-bonding[14] can contribute to the adsorption of organic dye on clay surface, favouring the dye agglomeration.

In this work, Maghnia montmorillonite is used as an adsorbent for removal of cationic dyes, Methylene blue and Malachite green oxalate, from aqueous solutions onto clay is investigated. The effect of the optical properties of dyes in aqueous solutions and adsorbed onto montmorillonite was assessed in terms of the absorption bands maxima as a function of pH. The equilibrium and kinetics adsorption of dyes onto clay were studied. The experimental data were evaluated by applying the pseudo-first- and second-order. The Langmuir, Freundlich and Dubini-Radushkevich (D-R) isotherm models were used to the isotherm data for their applicability.

MATERIALS AND METHODS

A thiazin group cation, Methylene blue (MB) (MW = 319,5 g.mol^{-1}, λ_{max} = 665 nm, ε = 95000 cm^{-1} $mole^{-1} dm^3$) and triphenylemethane dye, Malachite green oxalate (MW = 507. 51 g.mol^{-1}, λ_{max} = 617 nm, ε = 42000 cm^{-1} $mole^{-1} dm^3$), from Across product for microbiological analysis and were used without any further purification. Molecular structures of Methylene blue and Malachite green oxalate dyes were shown in *Figure* 1.

Aqueous dye solution stock was prepared by dissolving accurately weighed neat dye in distilled water to the concentration of 1 g/L. Experimental solutions were obtained by successive dilutions.

Natural clay was supplied by the Ceramics Society of Maghnia (west of Algeria). The sodium form of clay with a particle size < 0.2 μm was prepared in order to obtain good clay colloidal dispersions, as follows: clay was saturated

with Na^+ by repeated exchange with NaCl (1 M) aqueous solution. The < 0.2 particle size fraction was separated by centrifugation and it was washed several times with distilled water until free Cl^- was not detected in the suspension ($AgNO_3$ test). The < 0.2 fraction was collected by centrifugation and freeze dried at 60 °C for 24 h and is crushed. The material resulting from different treatments will be indicated by clay-Na.

Adsorption experiments were carried out as a single-stage batch test using a magnetically stirrer. A suspension containing 0.03 g of adsorbent sample was mixed with a 100 mL aqueous solution of dye at a known initial concentration and initial pH in a flask at constant temperature of 298 K. The initial pH values of the solutions were previous adjusted with 0.1 M HCl or NaOH using pH meter. Aliquot of the solution were withdrawn at a predetermined time intervals and were centrifuged at 4000 rpm for 10 min to remove any adsorbent particles. Dye concentrations in the supernatant solutions were subsequently estimated by measuring adsorbance at maximum wavelengths of dyes. The adsorption tests were continued until the equilibrium concentration was reached. The experiments were done by varying the initial pH from 3 to 13), amount of adsorbent doses from 0.07 to 0.7 g/L and concentration of dyes solutions from 20 to 200 mg/L at different time intervals.

The data obtained from the adsorption experiments were then used to calculate the adsorption capacity, Q_e (mg/g), of the adsorbent by a mass-balance relationship, which represents the amount of adsorbed dye per the amount of dry adsorbent Eq. (1):

$$Q \text{ (mg/g)} = \{(C_o - C_e) V\}/m \qquad (1)$$
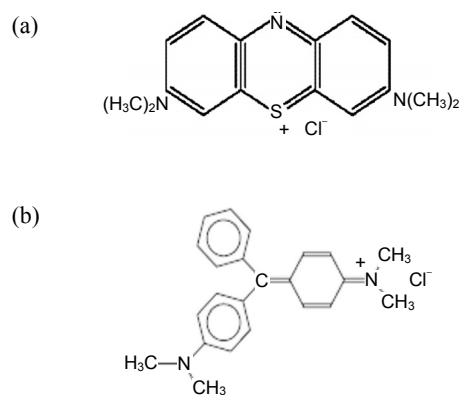
where C_o and C_e are the initial and equilibrium solution

Fig. **1.** Molecular structures of basic dyes: (a) Methylene blue (MB); (b) Malachite green oxalates (MG).

A. Elaziouti and N. Laouedj

Table 1. XRF analysis of the of the clay-Na sample.

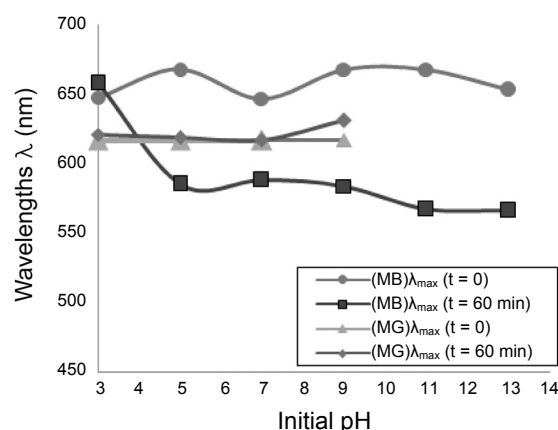| Element	Percentage by weight/unit
SiO_2	60.75
Al_2O_3	24.15
Fe_2O_3	2.51
CaO	1.56
MgO	2.54
Na_2O	3.63
K_2O	0.65
SiO_2/Al_2O_3	2.52
LIO	5.21

LOI: Loss on ignition

Fig. 2. The position of absorption bands maxima of dyes in aqueous solution and adsorbed onto clay-Na as a function of pH for [MB] = [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L, T = 298 K and contact time = 60 min.

concentrations (mg/L) respectively. V is volume of the solution (L), and m is the weight of the dry adsorbent used (g).

The removal rate A (%) of adsorbed dye was calculated based on following equation Eq. (2):

$$A(\%) = \{(C_o - C_e)\ 100\}/C_o \qquad (2)$$

The initial pH of the dye aqueous solution was recorded using (WTN: WISSENSCHAFLLICH TECHNISECHE WERKSTÄTTEN; weilehein Allemagne pH-330) digital pH-meter X-ray fluorescence was performed on a spectrometer of mark (Oxford). The sample is powder tiny room and prepared (pearl borated) is subjected to a source of X-radiation of fluorescence characteristic of its chemical composition.

Vis-absorption spectra of the dye in aqueous solution and adsorbed on incinerated sludge were obtained by Model: UV − 2401 (PC) SHIMADZU − corporation spectrometer in the range 350 - 800 nm, using 1 cm optical pathway cells.

RESULTS AND DISCUSSION

Table 1 displays the results of chemical composition in the clay-Na sample. The major elements of the clay-Na, expressed in terms of oxide, are primarily of silica, and alumina with appreciable iron content. The CaO and Na_2O (K_2O) reflect the contents of interlayer cationic in clay. The other oxides present in traces amounts such. In the perfect montmorillonite, the total theoretical content of SiO_2 and Al_2O_3 is 92% [15] and the content ratio of SiO_2 to Al_2O_3 is 2.6. In the Maghnia clay, the total content of SiO_2 and Al_2O_3 is 84.90% and the corresponding ratio of SiO_2 to Al_2O_3 is 2.52, so this type of clay belongs to the Na-montmorillonite category. The cation capacity of exchange and total specific surface of the clay-Na sample were estimated by the methylene blue (MB) method[16] are of 101.72 meq/100 gr of

clay-Na and 673.93 m^2/g respectively.

Figure 2 illustrates the evolution of absorption bands maxima of dyes in aqueous solution and adsorbed onto clay-Na at various pH values. The location of the absorption bans maxima of dyes are collected in *Table* 1.

The visible spectra of dyes in aqueous solution show that MB exhibits a main band at 668 nm assigned to the absorption of monomers and associated with a shoulder attributed to the 0 - 1 vibronic transition of monomers MB^+ at about 605 nm. However, MG shows two absorption bands in the visible region. The intense absorption band at 617 nm. The second band is in the shorter-wavelength part of the spectrum at 425 nm and is significantly weaker. The main band is attributed to the absorption of cations monomers (MG^+), whereas the second band is assigned to the protonated cations ($MG^{2+}H$).

The MB monomers have nearly constant absorption bands and absorbance intensities over the pH values in the range of pH between 3 and 13, while the shoulder is most sensitive to the pH solution. The absorbance of the vibronic shoulder at about 605 nm increases and shifts slightly to 624 nm (pH 7), 621 nm (pH 11), and 610 nm (pH 13), whereas no change is observed in 605 nm-shoulder at pH 3, 5 and 9. The increase and the bathochromic shift in 605 nm-shoulder are attributed to the partially self-association of MB monomers as cationic dimmers in face-to-face arrangement to minimize their hydrophobic interaction with water.[17]

For MG dye, the pH has no effect on the absorption band of the both forms of MG dye (MG^+ and $MG^{2+}H$), thus affirming their high stability over the pH range of 3 - 9. In addition, as the pH values increase from 3 to 9, the absorbance intensities of MG^+ decrease, while those of $MG^{2+}H$ show a dis-

crepancy. At high alkaline medium (pH > 9) the colorless carbinol base is formed. Such an effect was observed for the similar malachite green,[18] methyl green[19] and crystal violet.[20]

On the other hand, the behavior of the bands maxima of MB adsorbed onto clay-Na with the pH is characterized by a hyoschromic shift of the main absorption of MB^+ with respect to those in aqueous solutions. The maxima appear at 588 nm (pH 5), 584 nm (pH 7), 567 nm (pH 11) and 566 nm (pH 13). In the most case, this change consists of a substitution of the main absorption bands, which correspond to the absorption of monomers, MB^+, by new absorption bands placed at shorter wavelengths, the so-called methachromatic effect. The methachromasy observed in several clay/dye systems been attributed to different phenomena:

(i) an intermolecular interaction between the electronatic π-system of the dye with the electron lone-pairs of the oxygen atoms at the clay surface
(ii) the self-association of dye molecules when they are adsorbed on the clay surface.

The π-interaction is proposed for clays with partial tetrahedral substitution of Si^{+4} by Al^{+3}. Since Clay-Na has this type of substitution, methachromatic effect has to be related to the π-interaction.[21]

However, the main band of MB^+ at pH 3, gradually shifts from 648 nm (in aqueous solution) to longer wavelengths, almost reaching 658 nm (in clay-Na suspension) and the relative intensity of vibronic shoulder (around 605 nm) increases. These results are consistent with internally adsorbed MB^+ cations and dimerisation, shifting the monomer-dimer equilibrium, when the MB molecules are adsorbed on both in external and in the internal surfaces of the clay-Na.
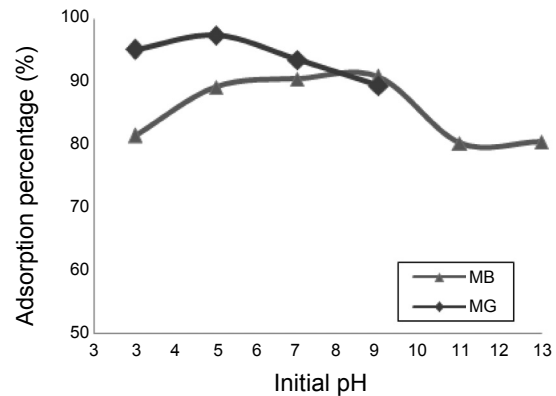

Fig. 3. Adsorption percentage of dyes onto clay-Na as a function of pH [MB] = [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L, T = 298 K and contact time of 60 min.

The results (*Table* 1) show the slight stability of the main absorption maxima of both forms (MG^+ and $MG^{2+}H$) of MG dye in clay-Na suspension under pH values in the range of 3 - 7. However, the absorption maximum of monomers shifted to 631 nm at pH 9 to longer wavelengths with respect to that in aqueous solution. The shift did not exceed 10 nm in the range of pH between 3 and 7, but is significantly higher at pH 9, being 14 nm.

Shift to higher wavelengths of ≈ 10 nm are always observed for dye monomers adsorbed at the clay surface. The observed shift can be attributed to the change in the environmental polarity/acidity of negatively-charged clay surface with respect to water surrounding, suggesting that the adsorption process is instantaneous.[22]

In addition, this change is accompanied by the appearance of new band at 596 nm placed in shorter wavelengths assigned to an influence on π-orbital. Such influence might

Table 2. The position absorption bands and adsorption percentage of dyes in aqueous solution and adsorbed onto clay-Na as a function of pH for [MB] = [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L , T = 298 K and contact time = 60 min.

	MB						MG				
	In aqueous solution		Adsorbed on clay-Na			Percentage Adsorption (%)	In aqueous solution		Adsorbed on clay-Na		Percentage adsorption (%)
Initial pH	Species (nm)		Species (nm)				Species (nm)		Species (nm)		
	MB^+	$(MB^+)_2$	MB^+	$(MB^+)_2$	$(MB^+)_n$		MG^+	$MG^{2+}H$	MG^+	$MG^{2+}H$	
3	648	-	658	608	658	81.47	617	424	621	426	95.15
5	668	624	-	-	585	89.19	617	425	619	-	97.52
7	647	-	-	-	588	90.53	617	424	617	426	93.56
9	668	-	-	-	584	90.81	617	423	631 / 596	-	89.46
11	668	621	-	-	567	80.23	Col.	Col.	Col.	Col.	-
13	653	610	-	-	566	80.46	Col.	Col.	Col.	Col.	-

MB^+: monomer cation, $(MB^+)_2$: dimer including 0-1 vibronic transition of the monomer and $(MB^+)_n$: agglomerates, n > 3.
MG^+: monomer cation and $MG^{2+}H$: protonated cation.
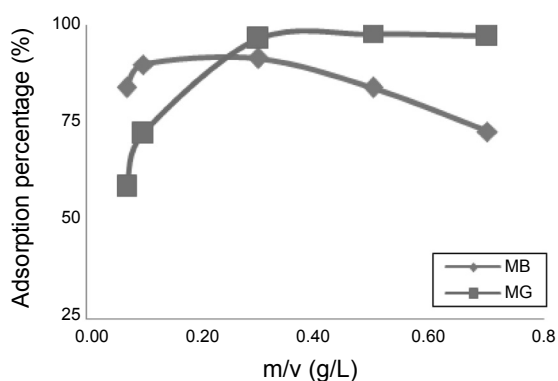Col.: colorless

Fig. 4. Adsorption percentage of dyes onto clay-Na onto clay-Na as a function of adsorbent dose on for [MB] = [MG] = 50 mg/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.
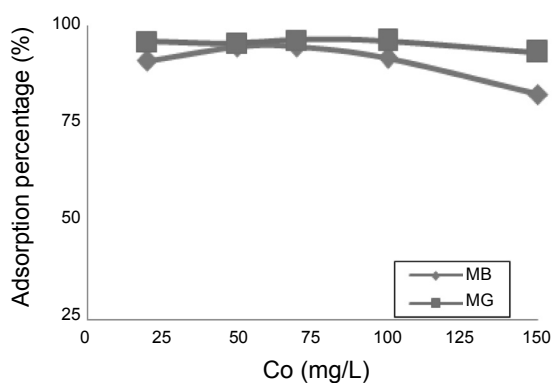

Fig. 5. Adsorption percentage of dyes onto clay-Na as a function of the initial concentration for [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.

be caused by an adjacent platelet, indication flocculation or by the formation of dimers on the surface of the clay-Na.[23,24]

The effects of initial pH solution on the adsorption rate of dyes onto clay-Na studied over a range of pH values of 3 to 13. The pH significantly affected the adsorption capacities of both dyes. As shown in *Figure* 3, for MB, the dye adsorption increases from 81.47% to 90. 81% with an increase in pH from 3 to 7 and then decreases to 80. 46% at pH = 13, whereas, for MG, the dye adsorption remains almost constant in the range of pH between 3 and 7, and then decreases to 89.46 % at pH 13. The maximum dye adsorption of MB (90.81%) and MG (93.55%) are achieved at pH 7. For this reason, for both dyes, the pH 7 is selected for subsequent experiments.

The effect of adsorbent dose on the adsorption percentage of dyes is conducted over a range of adsorbent doses of 0.07 to 0.7 g/L. As elucidated in *Figure* 4, the percentage of dyes adsorbed increases from 53.55 to 98.28% in MB and from 85.55 to 93.09 % in MG when the adsorbent dose increases from 0.07 to 0.3 g/L for both byes. The adsorption percentage of dyes adsorbed decreases from 93.09 to 73.91% in MG, while it remains nearly constant in MB with the same adsorbent doses. Increase in adsorption with the sorbent dose can be assigned to increased surface are and the availability of more adsorption sites. In the range of adsorbent doses between 0.3 and 0.7 g/L, the adsorption of MB is constant, whereas that of MG decreases. This may be attributed to overlapping of adsorption sites as a result of overcrowding of adsorbent.[25] The adsorbent dose of 0.3 g/L for both dyes was used in all other parameter experiments.

Figure 5 illustrates the effect of initial dye concentration

Table 3. The adsorption percentages and the amounts of adsorbed dyes onto clay-Na as function of adsorbent doses and initial concentrations for [MB] = [MG] = 20 - 200 mg/L, [Clay-Na] = 0.07 - 0.7 g/L , pH = 7 (MB and MG), T = 298 K and contact time of 60 min.

Experimental parameters		MB			MG		
		C_e (mg/L)	Q_e (mg/g)	Adsorption percentage (%)	C_e (mg/L)	Q_e (mg/g)	Adsorption percentage (%)
Adsorbent dose [Clay-Na] (g/L)	0.07	20.45	340.58	59.55	2.89	244.39	85.54
	0.10	13.80	361.97	73.50	1.69	183.08	91.54
	0.30	1.38	160.77	98.29	1.38	62.07	93.10
	0.50	0.25	99.36	99.63	2.92	34.16	85.39
	0.70	0.52	70.48	98.97	5.22	21.12	73.91
Initial concentration [Dye] (mg/L)	20	1.37	95.44	97.81	1.43	185.72	92.86
	50	1.33	228.90	97.46	1.77	482.32	96.46
	70	1.38	162.06	98.29	2.46	675.42	96.49
	100	1.42	228.60	97.97	6.42	935.81	93.58
	150	5.02	316.61	94.98	23.95	1260.53	84.04
	200	18.72	437.61	87.52	24.69	1753.06	87.65

R^2: Regression coefficient

on the percentage of dyes. The percentages of dyes adsorbed are basically unaffected by the dye concentration in the range of 20 to 50 mg/L, and fluctuated between 97.89 and 98.29% in MB and between 98.43 and 97.81 % in MG. However, when dye concentration increases from 50 to 150 mg/L, the percentages of dyes adsorbed decrease from 98.29 to 87.52% in MG and from 97.81 to 84.04 % in MG. Decrease in adsorption with initial concentration of dyes in due to the dyes agglomeration and the reduction of the thermal mobility of the adsorbed aggregates. So, for both dyes, the initial dye
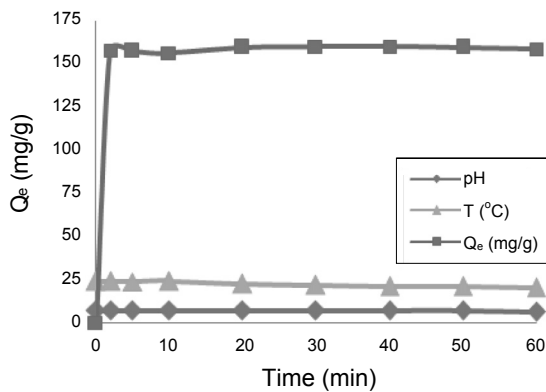

Fig. 6. Adsorption kinetic of MG onto clay-Na for [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 and 298 k.
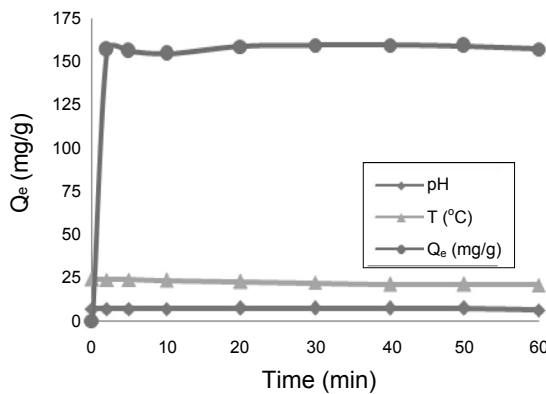

Fig. 7. Adsorption kinetic of MB onto clay-Na for [MB] = 50 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 and 298 K.

concentration of 50 mg/L was chosen for the other experiments.

The adsorption kinetics of dyes is measured in the range of 0 to 60 min by varying the equilibrium time between adsorbate and adsorbent. The amount of dyes adsorbed, temperature and initial pH solution at equilibrium as a function of contact time are illustrated in *Figures* 6 and 7. The results show that the equilibrium time required for the dyes adsorption onto clay-Na is almost 5 min for both dyes. These results also indicate that the temperature decreases with the amount of adsorbed MB, whereas the pH solution remain practically constant, which can be explained by an endothermic adsorption as a consequence of an exchange phenomenon between organic cations and clay-Na surface.[26] However the pH solution and the temperature are unaffected by the amount of adsorbed MG, which deduce the phenomenon of physisorption.[27] The kinetic adsorption data illustrated in *Figures* 5 and 7 were treated with a pseudo-first order and pseudo-second order model.

The pseudo-first order equation of Lagergren[28] is generally expressed as follows Eq. (3):

$$dQ_t/dt = k_1(Q_e - Q_t) \qquad (3)$$

where Q_e and Q_t are the amount of malachite green adsorbed per unit weight of adsorbent at equilibrium and at any time t (mg/g) respectively and K_1 is the rate constant for adsorption of dye (1/min). At given boundary conditions for t = 0, $Q_t = 0$, the equation Eq. (3) can be integrated to give Eq. (4):

$$\log_{10} (Q_e - Q_t) = \log_{10} Q_e - (K_1/2.303) \, t \qquad (4)$$

The values of k_1 were calculated from the slopes of the respective linear plots of log $(Q_e - Q_t)$ *versus* t (*Figure* 8). The regression coefficients, R^2, (given in *Table* 4) for the pseudo-first-order model did not exceed the values of 0.36 for both dyes respectively. The calculated Q_e values obtained from pseudo-first-order kinetic model were much different compared with experimental Q_{exp} values. These results su-

Table 4. Kinetic parameters of dyes adsorbed onto clay-Na for [MB] = [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG) and T = 298 K.

	Experimental results		Pseudo-first order model				Pseudo-second order model		
System	Q_{max} (mg/g)		Q_e (mg/g)	K_1 (min^{-1})	R^2 (%)		Q_e (mg/g)	K_2 (g/mg.min)	R^2 (%)
MB/Clay-Na	163.810		6.622	0.055	0.355		166.667	0.001	0.999
MG/Clay-Na	163.011		1.919	0.055	0.36		166.667	0.601	0.999

R^2: Regression coefficient

ggest that the adsorption processes of MB as well as MG do not follow the pseudo-first-order adsorption rate equation of Lagergren.

The sorption kinetics following pseudo-second order model given by Ho[29] is represented in the form Eq. (5):

$$dQ/dt = K_2 (Q_e - Q)^2 \qquad (5)$$

where Q and Q_e represent the amount of dye adsorbed (mg/g) at any time t; K_2 is the rate of sorption (g/mg.min) and Q_e the amount of dye adsorbed onto clay-Na at equilibrium (mg/g). Separating Eq. (6), gives:

$$dQ/(Q_e - Q)^2 = K_2 dt \qquad (6)$$

Integrating Eq. (5) with respect to the boundary conditions Q = 0 at t = 0 and Q = Q at t = t, the linearised form of pseudo second order expression can be obtained as Eq. (7):

$$1/(Q_e - Q) = 1/Q_e + K_2 t \qquad (7)$$

Equation (7) can be further linearised to Eq. (8) :

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \qquad (8)$$

The straight lines for all initial concentrations of the plots of t/Q_t *versus* t (*Figure* 8 and *Table* 4) with extremely high regression coefficients (0.999) for the pseudo-second-order kinetic model compared to those for the pseudo-first-order strongly suggest that all the adsorption systems are a pseudo-second-order model, based on the statement that the rate-limiting step may be chemisorptions involving valency forces through sharing or exchange of electrons between the hydrophilic edge sites of clay-Na and polar dye ions.[30] The measured Q_e values obtained from pseudo-second-order kinetic model were close to the experimental Q_{exp} data.

Figure 9 displays the results of the adsorption isotherms of dyes. The adsorption of both dyes forms a typical Langmuir-type isotherm according to Giles classification system.[31] The maximum adsorption capacities of dyes were 437.61 and 420.18 mg/g for MB and MG respectively. It indicates that the adsorption seems to favor the dye MB slightly than MG. This behavior of preferential adsorption can be explained in point of view of structures and molecular weight of the dyes (MB = 319.5 g/mole and MG = 507.51 g/mole). The MB with one weaker size and molecular weight will compete with faster for the actives sites than MG.

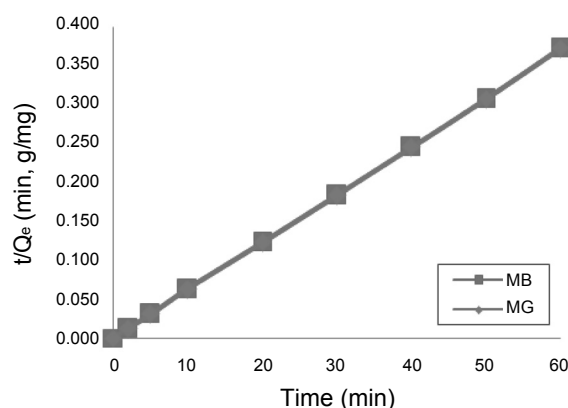Langmuir[32] and Freundlich[33] and Dubini-Radushkevich[34]

Fig. 8. Pseudo-second order plots of the kinetics of dyes onto clay-Na for [MB] = [MG] = 50 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.
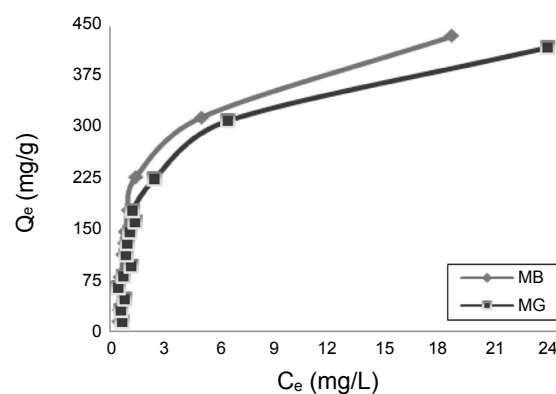

Fig. 9. Adsorption isotherm of dyes onto clay-Na for [MB] = [MG] = 5 - 150 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.

(D-R) isotherms were applied to assess the performance of the adsorption process of MB and MG dyes onto clay-Na.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogenious sites within the adsorbent and has found successful application in many adsorption processes of monolayer adsorption. The linear form of the Langmuir isotherm equation is represented by the following equation Eq. (9):

$$C_e/Q_e = 1/(K_L Q_{max}) + C_e/Q_{max} \qquad (9)$$

where Q_{max} (mg/g) is the maximum amount of the dye per unit weight of clay-Na to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, and K_L is the Langmuir constant related to the free energy of adsorption (L/g). The plots of C_e/Q_e *versus* C_e for the adsorption of MB and MG onto clay-Na (*Figure* 10) give a straight line of slope of $1/Q_{max}$ and intercept $1/Q_{max}K_L$.
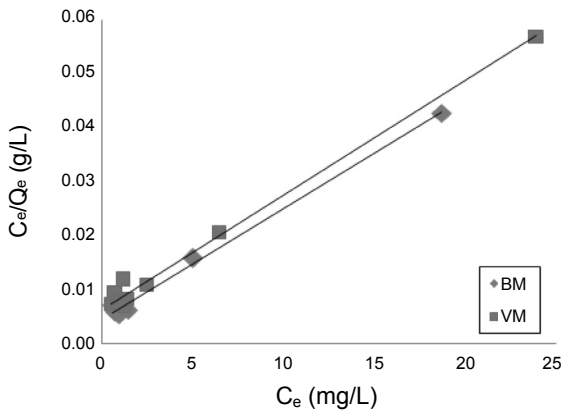
Fig. 10. Langmuir isotherm of dyes onto clay-Na for for [MB] = [MG] = 5 - 150 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.
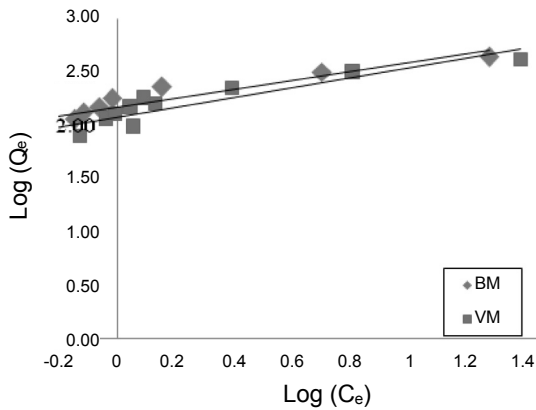

Fig. 11. Freundlich isotherm of dyes onto clay-Na for for [MB] = [MG] = 5 - 150 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.
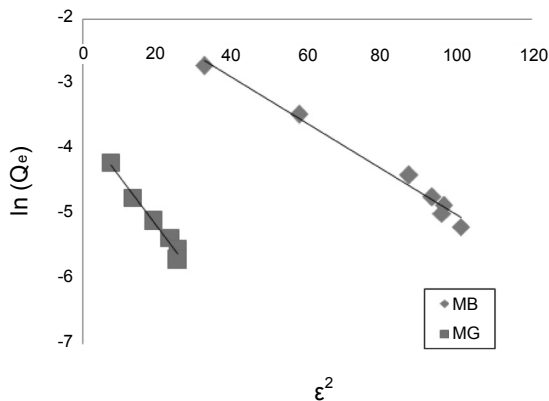

Fig. 12. D-R isotherm of dyes onto clay-Na for for [MB] = [MG] = 5 - 150 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.

The essential features of the Langmuir isotherm[35] can be expressed by means of K_R, a dimensionless constant referred to as separation factor or equilibrium parameter which is calculated by relationship Eq. (10):

$$K_R = 1/(1 + K_L C_o) \qquad (10)$$

where K_L is the Langmuir constant (L/mg) and C_o is the highest initial dye concentration (mg/L). The value of K_R indicates the type of the isotherm to be either unfavorable ($K_R > 1$), linear ($K_R = 1$), irreversible ($K_R = 0$) or favorable ($0 < K_R < 1$).

The Freundlich isotherm is an empiric equation employed to describe heterogeneous systems. The logarithmic form of the Freundlich equation Eq. (11) is:

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \qquad (11)$$

where K_{Fe} and n are Freundlich adsorption isotherm constants (L/mg), being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The values of Freundlich constants (K_F and n) were calculated from the plots (*Figure* 11) of $\ln Q_e$ against $\ln C_e$.

The Dubini-Radushkevich (D-R) isotherm is more general than the Langmuir isotherm because it does not assume a homogenous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of dye. The linear D-R isotherm can be represented in the form Eq. (12):

$$\ln Q_e = \ln Q_m - K_{DR} \, \varepsilon^2 \qquad (12)$$

where K_{DR} is related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kj^2), Q_m is the theoretical saturation capacity (mg/g), and ε is the Polanyi potential, which is defined by Eq. (13):

$$\varepsilon = RT \ln (C_o/C_e) \qquad (13)$$

where R is the gas constant (j/mol.k) and T is the absolute temperature (K). Hence the D-R plots (*Figure* 12) $\ln Q_e$ against ε^2 indicates a straight line with a regression coefficient (R^2) of > 0.98. The values of K_{DR} and Q_m evaluated from the slopes and intercepts of these plots are listed in *Table* 5.

The constant K_R gives an idea about the mean free energy of adsorption (E_a) when one mole of the ion is transferred to the surface of the adsorbent from the infinity in the solu-

A. Elaziouti and N. Laouedj

***Table* 5.** Isotherm parameters of dyes adsorbed onto clay-Na for [MB] = [MG] = 5 - 70 mg/L, [Clay-Na] = 0.3 g/L, pH = 7 (MB and MG), T = 298 K and contact time of 60 min.

Experimental results		Langmuir model $C_e/Q_e = 1/(K_L Q_{max}) + C_e/Q_{max}$				Freundlich model $Ln(Q_e) = Ln(K_F) + 1/n)Ln(C_e)$			Dubini-Radushkevich model $lnQ_e = lnX_m - K_{DR} \varepsilon^2$			
System	$Q_{exp.}$ (mg/g)	Q_{max} (mg/g)	K_L (L/g)	K_R	R^2 (%)	K_F (L/g)	1/n	R^2 (%)	Q_m (mg/g)	K_{DR} (mol^2/kj^2)	Ea (kj/mol)	R^2 (%)
MB/Clay-Na	437.612	500	0.500	0.013	0.994	147.908	0.422	0.856	4.388	0.035	3.779	0.985
MG/Clay-Na	420.176	500	0.333	0.019	0.991	119.949	0.467	0.855	38.939	0.076	2.564	0.982

R^2: Regression coefficient

tion and it can be computed using the following relationship[35] Eq. (14):

$$Ea = (-2K_{DR})^{-1/2} \qquad (14)$$

The mean energy provides information about adsorption mechanism is physical adsorption (0 < Ea < 8 kj/mol) or chemisorptions[36] (20 < Ea < 40 kj/mol).

Parameters of Langmuir, Freundlich and D-R plots of dyes adsorption onto clay-Na were shown in *Table* 5. The Langmuir monolayer capacity Q_{max} was 500 mg/g for both dyes. The high values of regression coefficients, R^2, (0.994 and 0.991 for MB and MG respectively), suggesting that the adsorption of MB as well as MG onto clay-Na closely follow a Langmuir isotherm. The high fit to the Langmuir model for both dyes suggests that the adsorption is limited with monolayer coverage. The values of R_L obtained were 0.013 and 0.019 for MB and MG respectively. As the K_R values lie between 0 and 1, the on-going adsorption process is favorable.

The numerical value of the apparent free energies E_a from D-R model resulted as 3.779 and 2.564 kj/mol for MB and MG respectively, indicates that the adsorption process is physisorption.

CONCLUSION

In the present study, Maghnia clay deposits was selected as a local, cheaper and readily available adsorbent for the removal of Methylene blue and Malachite green oxalate dyes from the aqueous solutions. Adsorption of the dyes was investigated under various experimental conditions by batch technique. The optimal pH for favorable adsorption of MB and MG dyes was 7. The percentages of dyes adsorbed increased then reached maximum values as the sorbent dose was increased, while the ratios of dyes adsorbed decreased as the initial concentration was increased. The maximum adsorption of both dyes (> 90%) in aqueous solutions were achieved within 60 min by using 0.03 g of clay-Na. For the adsorption of both MB and MG dyes, chemical reaction seems significant in the rate-controlling step and the pseudo-second-order chemical reaction kinetics provide the best correlation for the experimental data .The isothermal data fitted the Langmuir and D-R models. The numerical value of the mean free energies E_a from D-R model (3.779 and 2.564 kj/mol for MB and MG respectively), corresponds to physisorption process.

REFFERENCES

1. Then, B. K. G. Adam. Higle. London, 1974.
2. Margulies, L.; Rozen, H.; Cohen, E. *Nature.* **1985**, *315*, 658.
3. Dale Ortego, J.; Kowalska, M.; Coke, D. L. *Chemosphere.* 22, 1991; pp 769-798.
4. Srinivasan, K. R.; Fogler, H. S. *Clays minerals.* **1990a**, *38*, 277.
5. Murray, H. H. *Overview. Clay minerals application. Appl. Clay. Sci.* **1991**, *5*, 379.
6. Rabek, J. F., Ed.; CRC Press: Florida, Vols. I and III, 1990.
7. Dusart, O.; Serpaud, B. *La tribune de l'eau.* **1991**, *44*, 554; pp 15-22.
8. Linsheng, Z.; Dobias, B. *Water Treatment.* **1992**, *7*, 221-232.
9. Ciardelli, G.; Corsi, L.; Marucci, M. *Resour. Conserv. Recy.* **2000**, *31*, 189-197.
10. Paprowicz, J.; Slodezyk, S. *Env. Tech. Let. 9* 1988; pp 271-280.
11. Milano, J. C.; Loste-Berdot, P.; Vernet, J. L. *Environ. Techn.* **1994**, *16*, 329-341.
12. YENER, J.; KOPAC, T.; DOGU, Dogu, T. *Journal Mortland M. M. adv. Agr.* 1970; pp 22-75.
13. Schoonheydt, R. A. *Mineral surfaces.* D. J. Vanghen and R. A. D Pattrick, Eds.; Chpman-hall: London, 303, 1995.
14. Meifang, H.; Beiyan, M.; Fangbai, L. *et al. Geology-Geochemistry* **2003**, *30*(1), 70-73.
15. Pavan, P. C.; Crepaldi, E. L.; Valim, J. B. *Journal of Colloid and Interface Science* **2000**, *229*, 346-352.
16. Bergman, K.; O'Konski, C. T. *J. phys. Chem.* **1963**, *67*, 2169.
17. Rytwo, G.; Nir, S.; Crespin, M.;. Margulies, L. *Journal of Col-*

loid and Interface Science **2000**, *222*, 12-19.

18. Yariv, S. *Personal Communication* 1998.

19. Keusch, P. *Crystal Violet - a pH Indicator* 2009.

20. Yariv, S. *Int. Rev. Phys. Chem.* **1992**, *11*, 345.

21. Coine, A. P. P.; Neumann, M. G.; Gessner, F. *Journal of Colloid and Interface Science* **1998**, *198*, 106-112.

22. Yariv, S.; Ghosh, D. K.; Heple, L. G. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 1201.

23. Dobrovska, C.; Hepler, L. G.; Ghosh, D. K.; Yariv, S. J. *Thermal Ana.* **1991**, *37*, 1347.

24. Namasivayam, C.; Prabba, D.; Kumutha, M. *Bioresour. Technol.* **1998**, *48*, 79-81.

25. Bouabdesselam, H. *Asian Journal of Chemistry*. Vol. 17, No. 4, **2005**; pp 2289-2290.

26. Bouabdesselam, H.; Meddah, S.; Bouzidi, Y.; Bourg, D. *Asian Journal of Chemistry*. Vol.17, No 4, **2005**; pp 2291-2299.

27. Lagergren, S. *Kungl. Sv. Vetensk. Handl.* **1898**, *24*, 1-39.

28. Ho, Y. S.; Mckay, G. A. *Resources, Conservation and Recycling* Vol. 25, No. 3, March 1999; pp 171-193.

29. Ho, Y. S.; Mckay, G. *Process biochem.* **1999**, *34*, 451-565.

30. Giles, C. H.; Mac Ewan, T. H.; Nakhwa S. N.; Smith, D. J. *Chem. Soc.* **1960**, 3973.

31. Langmuir, I. *J. Phys. Chem.* **1918**, *40*, 1.

32. Freundlich, H. F. M. *J. Phys. Chem.* **1906**, *57*, 385-470.

33. Dubinin, M. M.; Radushkevich, L. V. 55. *Physical Chemestry Section, USSR* **1947**; pp 331-333.

34. Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 212-223.

35. Hobson, J. P. *J. Phys. Chem.* **1969**, *73*, 2720.

36. Helferrich, F. McGraw Hill, New York, NY, 1962.