



HAL
open science

Removal of cationic dye from the aqueous solutions by using the natural clay of Maghnia (Algeria)

Aissa Hadj Said, Marie-Hélène Manero, El-Habib Belarbi

► To cite this version:

Aissa Hadj Said, Marie-Hélène Manero, El-Habib Belarbi. Removal of cationic dye from the aqueous solutions by using the natural clay of Maghnia (Algeria). *Desalination and Water Treatment*, 2014, 52 (34-36), pp.6673-6683. 10.1080/19443994.2013.819147 . hal-02023319

HAL Id: hal-02023319

<https://hal.science/hal-02023319>

Submitted on 18 Feb 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.




Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/21830>

Official URL: <https://doi.org/10.1080/19443994.2013.819147>

To cite this version:

Hadj Said, Aissa and Manero, Marie-Hélène  and Belarbi, El-Habib *Removal of cationic dye from the aqueous solutions by using the natural clay of Maghnia (Algeria)*. (2014) *Desalination and Water Treatment*, 52 (34-36). 6673-6683. ISSN 1944-3994

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Removal of cationic dye from the aqueous solutions by using the natural clay of Maghnia (Algeria)

Aissa Hadj Said^{a,*}, Marie H el ene Manero^b, El-Habib Belarbi^c

^a Faculty of Nature and Life Sciences, Laboratory of Agro-Biotechnology and Nutrition in Semi-arid Areas, Ibn Khaldoun University, BP 78 Zaaroura 14000, Tiaret, Algeria
Tel. +213 46 41 58 87; Fax: +213 46 4158 85; email: hsaissa25@yahoo.fr

^b Laboratory of Chemical Engineering, UMR CNRS 5503, Toulouse University, Toulouse Cedex, France

^c Faculty of Technology and Matter Sciences, Laboratory of Synthesis and Catalysis, Ibn Khaldoun University,

ABSTRACT

The results obtained in this study showed that more than 80% of methylene blue (MB) was eliminated in the first five minutes with a neutral pH at 20°C and with the variable initial concentrations of MB between 5 and 30 mg/l in the presence of 1 g/l of clay. The clay of Maghnia flocculates in the presence of the MB in solution regardless of the strength of the pH of the medium. The optimal elimination of both MB (99%) and clay (98%) has been reached when mixing 120 mg/l of MB with 0.4–0.5 g/l of clay (FMC or SMC). The same result was obtained when mixing 20 mg/l of MB with 0.16–0.2 g/l of clay (FMC or SMC). Adding a suspension from the clay of Maghnia to the wastewater textile industry has proven effective. Second-order kinetic model represents well, this elimination with a coefficient of correlation R^2 ranging between 0.9991 and 1.0. Freundlich, Temkin, and Dubinin–Radushkevich models showed that the temperature between 10 and 40°C does not have a great effect on this elimination. Thermodynamic parameters ΔG° , ΔH° and ΔS° indicated that the process is spontaneous with a weak energy.

Keywords: Clay of Maghnia; Cationic dye; Wastewater; Coagulation; Flocculation; Kinetics; Isotherms

1. Introduction

The dyes are largely used in many industries such as the textiles, paper industry, etc. In the effluents of those industries, great proportions of dyes are present; their concentration is estimated between 10 and 20% [1]. Generally, the synthetic dyes have a complex aromatic molecular structure containing hydrocarbons

such as benzene, naphthalene, anthracene, toluene and xylene. More than 10,000 chemical dyes are currently present on the market; they can be classified in three categories: the anionic, the cationic and the non-ionic ones [2]. The world production is estimated to be approximately 7×10^5 tons per annum [3,4].

Water colouration is a visible form of pollution; even with small quantities of dye (10–50 mg/l), this can cause the reduction of light penetration and the solubility of gases in water and disturbing the

*Corresponding author.

photosynthetic and microbiological activities of aquatic environment [5].

Methylene blue (MB) was used in many studies like standard dye to study its elimination from the aqueous media [6–10]. It is a cationic dye which gives a very intense colour in solution even at very weak concentrations [4]. The MB is used in several applications such as the coating and the colouring of paper, hair, cotton and wool; it is also used as an indicator of oxidation-reduction and as a disinfectant, besides its many other medical usages [10].

The decontamination of any effluent containing the dyes is essential before its rejection to the natural environment. Several physico-chemical techniques of treatment were developed to eliminate the dyes from water in particular: coagulation, flocculation, chemical oxidation, separation by membranes, electrochemistry and techniques of adsorption [6,11].

Various research works are undertaken to study the elimination of the dyes by using several types of adsorbent materials, in particular clays and sludge [5,6,11–15]. There is a very strong link between surfaces of clay minerals and the molecules of the cationic dyes. The latter are easily adsorbed in contact with clay in suspension [16].

The reuse of treated wastewater in the industry and/or in agriculture is a way recommended for the countries with weak hydrous resources. The traditional process, coupling a physico-chemical and biological one, is not very effective to treat the effluents of textile industry charged with synthetic dyes that are slightly biodegradable. This work is a contribution to test the local adsorbent materials that are readily available and are inexpensive such as the natural bentonite of Maghnia to treat water polluted with a dye. It is on this ground that we have undertaken this study to find the possibilities of eliminating the methylene blue from water by using two types of clays of Maghnia: the filtered one (*FMC: Filtered Maghnia Clay*) and the sedimented one (*SMC: Sedimented Maghnia Clay*). We determined the influence of the time of contact, the initial concentration of dye and clay, the temperature and the pH on this elimination. Then, we evaluated the various parameters related to the best conditions of the treatment: elimination effectiveness, application of certain models of isotherms of adsorption and determination of thermodynamic constants.

2. Experimental

2.1. Materials

The natural bentonites are clay minerals that contain primarily montmorillonite, which belongs to

the group of the smectites of type 2:1; formed by the superposition of three layers: an octahedral layer sandwiched between two tetrahedral layers. In water, clays remain in suspension in the form of small particles having an average diameter of approximately 2 μm with a lamellate structure (succession of layers) [17].

The material used is the natural clay of Maghnia (Algeria), supplied by ENOF company of bentonites. This clay was dry sifted through the 80 μm sieve; the fraction obtained was noted *FMC*. One part of this clay was used directly in the tests; the other part was sedimented to recover the argillaceous fraction constituted by the particles less than 2 μm in diameter. For this purpose, 20 g of clay *FMC* was put in suspension by agitation for 2 h in one liter of distilled water, followed by a 24 h rest in a test-tube. The top 400 ml of this suspension was siphoned off and centrifuged [18]. The recovered base was dried, grinded and filtered through the 80 μm sieve. The obtained clay was noted *SMC*. The clay of Maghnia belongs to montmorillonites and its principal characteristics are presented in Table 1 [19].

The FTIR spectra of exchanged clay of Maghnia were studied by Bouras [19] and Bouras et al. [20], and the functional groups were identified.

The analyses were carried out on samples of the two types of clay, *FMC* and *SMC*, at the laboratory of chemical engineering of Toulouse (France) for the determination of specific area by the adsorption of nitrogen by BET method and the density using the Metromeritics pycnometer Accupyc 1330 as well as the granulometry by dry sifting of natural clay on a series of sieves between 150 and 80 μm .

2.2. Dye

The dye used in the tests is the methylene blue (CI 52015) of molar mass 373.9 g/mol and formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot \text{H}_2\text{O}$. It was supplied by Merck. Oz et al. reported that the reduced form of BM has a pK_a equal to 5.8 [21]. Its molecular structure is shown in Fig. 1.

2.3. Elimination of the methylene blue

Mixtures of 50% (v:v) MB and clay were prepared with a concentration of MB varying from 5 to 30 mg/l and a concentration of clay (*FMC* or *SMC*) varying from 0.1 to 1 g/l. This was done at a constant agitation of 120 rpm and a varying temperature between 10 and 40 °C at the pH of the mixture, which is close to neutral.

Samples were taken, during the testing period, to evaluate the residual MB in the mixture until the saturation of clay, which allows to determine the

Table 1
Chemical analyses in % weight of the natural clay of Maghnia [19]

Oxide	%
Na ₂ O	0.5
SiO ₂	69.4
K ₂ O	0.8
Al ₂ O ₃	14.7
TiO ₂	0.2
FeO ₃	1.2
As	0.05
L.O.I ^a	11
CaO	03
MgO	1.1

^aLoss on the ignition at 900°C.

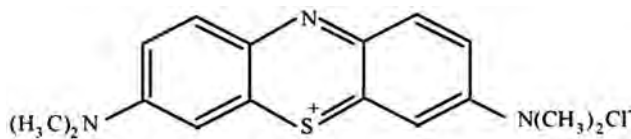


Fig. 1. Molecular structure of the methylene blue.

contact time. Samples were immediately centrifuged at 4,000 rpm for 5 min. Spectrophotometric measurement (using Pharmacia Biotech spectrophotometer) of the supernatant optical density at 20°C and 665 nm (wavelength of maximum absorption), allows to determine the MB residual concentration. At time t , Eq. (1) allows to calculate the eliminated quantity of MB " q (mg/g)", which is the difference between the initial concentration " C_0 (mg/l)" and residual concentration " C (mg/l)" of MB at time t , with respect to the concentration of clay in the mixture " W_a (g/l)". The effectiveness of MB elimination " R (%)" was determined by Eq. (2).

$$q = \frac{C_0 - C}{W_a} \quad (1)$$

$$R(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

3. Results and discussions

3.1. Granulometry BET surface area and density measurements

More than 80% of the particles of the natural clay of Maghnia have a size less than 100 μm in diameter and more than 90% have a size less than 80 μm in

diameter. Average specific areas and the densities were found to be, respectively, 40.35 m^2/g , 2.44 g/cm^3 for FMC and 40.51 m^2/g , 2.49 g/cm^3 for SMC.

It is noted that the average values of specific surfaces and densities of montmorillonites, in general, vary, respectively, between 31 and 61 m^2/g [11] and between 2 and 3 g/cm^3 [22].

3.2. Kinetics of equilibrium

Fig. 2 represents the influence of the initial concentration C_0 of MB on the variations of the MB quantity eliminated with FMC as a function of time. It should be noted that, in all the cases, elimination was fast. The time of contact necessary to reach equilibrium was established during the first five minutes. At 20°C in a neutral pH when the concentration C_0 increased from 5 to 30 mg/l and with the same quantity of clay 1 g/l, the quantities of MB eliminated increased from 4.1 to 26.6 mg/g for FMC and from 4.2 to 26.9 mg/g for SMC. This corresponds to the effectiveness of the elimination increasing from 82 to 88% for FMC and 84 to 89% for SMC.

A study on the use of ashes of the mud filtered through a 75 μm -size sieve in the adsorption of the MB showed that they have a capacity of adsorption of 80% for 10 min and that they have a specific surface varying between 2.1 and 2.9 m^2/g and a density of 2.74 g/cm^3 [13].

3.3. Influence of the clay concentration

The influence of the clay concentration W_a on the variations of the effectiveness of elimination of the MB by FMC as a function of time is shown in Fig. 3. With the initial concentration 20 mg/l of MB and under the same conditions of temperature and pH, when the concentration W_a of the clay increased from 0.1 to 1 g/l, the effectiveness of elimination of the MB remained practically the same and equals 88% for FMC and 90% for SMC.

The two types of clays (FMC and SMC), which have practically the same behaviour in the elimination of the MB indicate that an important proportion from the argillaceous particles of less than 2 μm in diameter is present in the natural clay of Maghnia. Indeed, the company ENOF of bentonites indicates that approximately 54% of the particles of this clay have a diameter less than 2 μm [23]. In practice, it would be interesting to use this clay after a simple sifting instead of sedimentation in order to recover the small argillaceous particles.

Fig. 4 shows the variations of the quantity of the MB eliminated according to the clay concentration

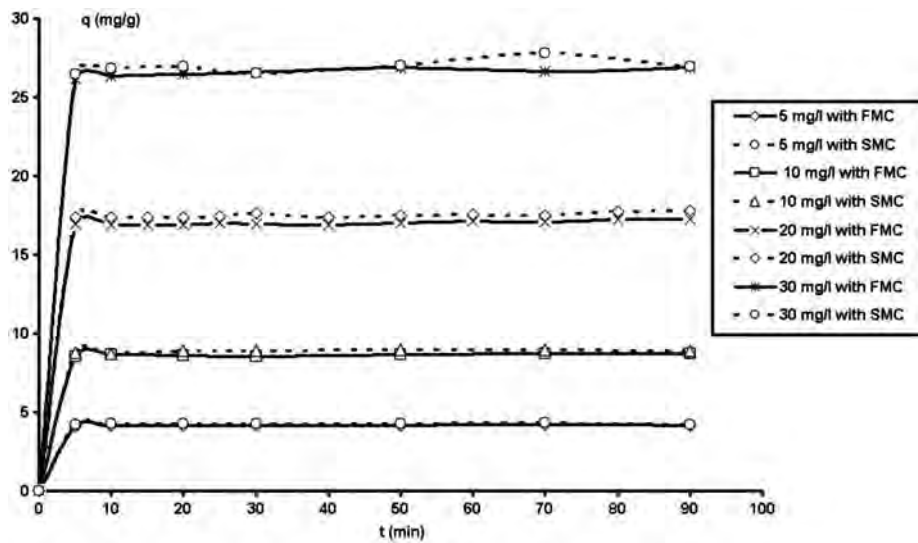


Fig. 2. Effect of the initial concentration of MB on the kinetics of elimination with FMC and SMC at $W_a=1$ g/l; pH=7 and $T=20^\circ\text{C}$.

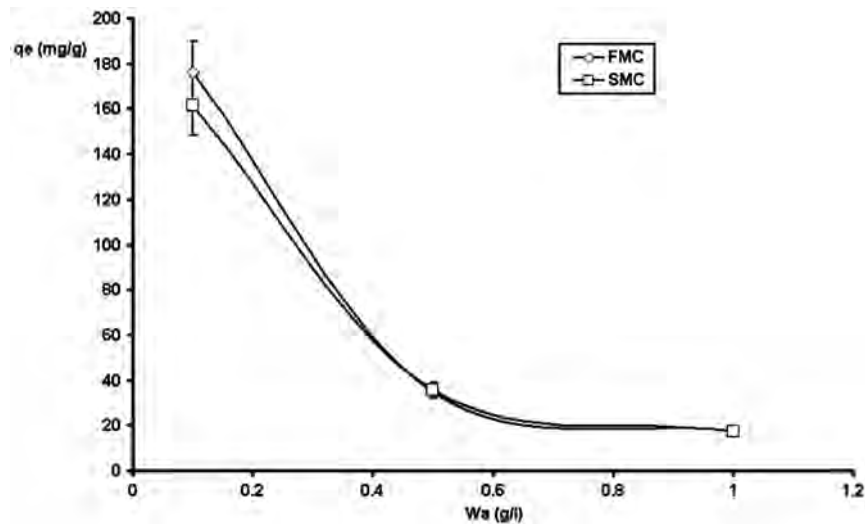


Fig. 3. Effect of the clay concentration on the effectiveness of MB elimination with $C_0=20$ mg/l; pH=7 and $T=20^\circ\text{C}$.

FMC and SMC. At 20°C and neutral pH, when C_0 of MB was 20 mg/l, the eliminated quantity of dye decreased quickly when W_a of clay increased. This could be due to the fact that the number of argillaceous particles in suspension becomes much more important compared to the number of cations of the MB in solution. It would, therefore, be interesting to find out if there is an optimal elimination of the MB.

In water, the clay suspension is stable; the particles remain regularly distributed in the liquid. This stability is due to the mutual repulsion of the particles, generally negatively charged. In the presence of

an electrolyte, the clay suspension can flocculate [24]. So, in the presence of the MB in solution, the clay suspensions (FMC and SMC) flocculate at the ambient temperature ($20\text{--}22^\circ\text{C}$) and neutral pH (pH of the mixture). When C_0 of MB was 120 mg/l, the optimal quantity of clay in suspension to treat the polluted water was 0.4–0.5 g/l and the average quantity of eliminated MB became equal to 270 mg/g for the two types of clay. At C_0 of MB 20 mg/l, the optimal quantity of clay in suspension to treat the polluted water was 0.16–0.2 g/l and the average quantity of eliminated MB became equal to 110 mg/g for the two types

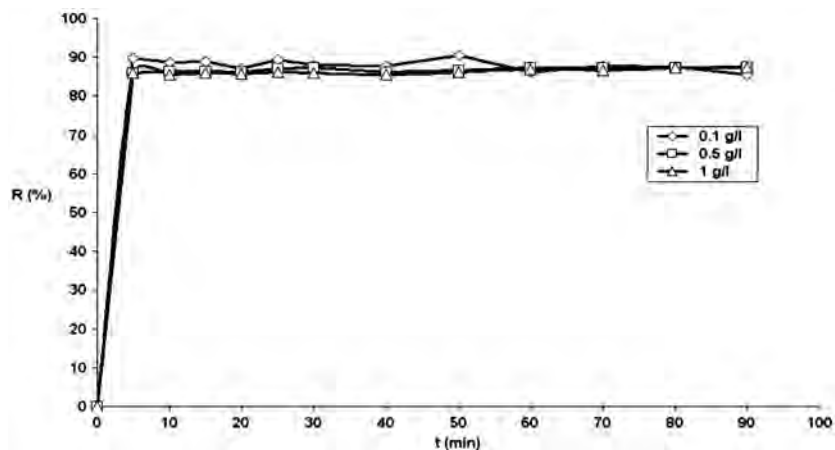


Fig. 4. Effect of the clay concentration on the quantity of eliminated MB with $C_0 = 20 \text{ mg/l}$; $\text{pH} = 7$ and $T = 20^\circ\text{C}$.

of clay. At the optima, water becomes clear and the optimal effectiveness of MB elimination is higher than 99%. The turbidity of the supernatant does not exceed 1.5 NTU representing an effectiveness of clay elimination of more than 98%. The tests of flocculation were carried out at the laboratory of the chemical engineering (UMR 5503 of CNRS) of Toulouse (France), using a jar test (Bioblock Scientific Flocculator 11198) with six positions (initial agitation with 180 rpm for 2 min and then with 20 rpm for twenty minutes. After a rest of 15 min, a sample of the supernatant was taken to determine the residual concentration in MB).

Most of the clays are negatively charged and form with the exchangeable ions, a double electrostatic layer [25]. Indeed, the increase in dye concentration at the interface of the clay is due to the electrostatic forces between the negative charges of clay particles in suspension and the positive charges of the cations released by the MB in solution [26]. This can explain

why at the optimum, when there is neutralization between the charges, the particles of clay and the cations of the MB flocculate then precipitate. It would be, therefore, interesting to use the clay of Maghnia in suspension to a concentration that can be determined by the use of jar test to purify the water polluted with a cationic dye. In fact, treating the wastewater of a textile industry (using cationic dyes in their manufacturing process) with suspension of Maghnia's clay has proven to be effective at laboratory level as can be seen in Figs. 5 and 6.

A comparison of MB efficiency removal of some other low-cost adsorbent materials under certain experimental conditions is listed in Table 2. It is seen that when the added clay was optimized, our results were the highest (99%) but when the added clay was not optimized our results (88.7%) were quite similar to the clay of Brazil (91.9%) but higher than clay of Turkey (58.2%) and activated sludge (61.3%). The



Fig. 5. Industrial wastewater before treatment.



Fig. 6. Industrial wastewater treated by the clay of Maghnia.

Table 2

Comparison of the MB removal efficiency of some low-cost adsorbent materials

Adsorbent	C_0 (mg/l)	W_a (g/l)	S_a (m ² /g)	T (°C)	pH	q (mg/g)	R (%)	Refs.
Clay (Algeria)	120	0.4–0.5	40.35	20–22	7	270	99 ^a	this work
Clay (Algeria)	20	0.16–0.2	40.35	20–22	7	110	99 ^a	this work
Clay (Algeria)	30	1	40.35	20	7	26.6	88.7 ^b	this work
Clay (Brazil)	600	2	62	35	6	275.64	91.9	[15]
Clay (Turkey)	100	1	30	20	5.65	58.2	58.2	[8]
Activated sludge	100	1	/	20	7	61.3	61.3	[5]

Note: ^aOptimized added clay. ^bNot optimized added clay.

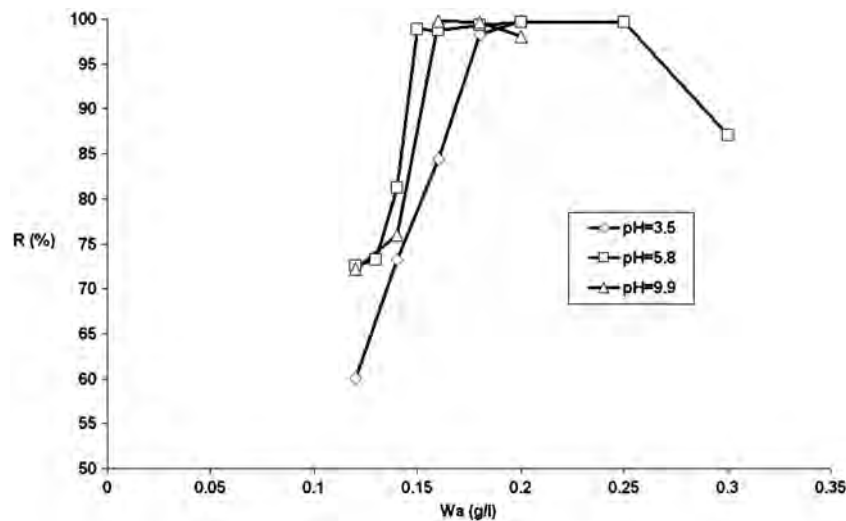


Fig. 7. Effect of the pH on the effectiveness R according to W_a of the FMC with $C_0=20$ mg/l of MB and ambient temperature.

natural clay of Maghnia could be employed as a low-cost adsorbent and could be considered as an alternative to the commercial one for the removal of colour.

3.4. Effect of the pH

At the ambient temperature and 20 mg/l of MB, Fig. 7 represents the effect of the pH (adjusted by addition of NaOH or HCl 0.1N) on the effectiveness of elimination, R , according to the concentration W_a of the FMC. The optimum of elimination of the MB can be reached, regardless to the pH of the medium. With the pH 5.8 and 9.9, the effectiveness of elimination was practically the same, while it was weaker with pH 3.5.

The pH is an important parameter in a process of coagulation–flocculation, beyond pH 6, its influence becomes weak because the concentration in ions H^+ is practically void; therefore, its competition with the

cations released by the dye is limited [5]. The maximum elimination of all the dyes is observed in an alkaline medium [27].

3.5. Effect of the temperature

In Fig. 8, the quantity of the eliminated MB q_e in contact with 1 g/l of FMC; according to the equilibrium concentration C_e of MB, after saturation of FMC (time of contact 90 min.), at the pH of the mixture and at different temperature (between 10 and 40 °C); allows to notice that the temperature does not influence this elimination.

It is interesting to find the model which represents the obtained experimental values. The models of isotherms used are:

The model of Freundlich in its linear form [5], Eq. (3):

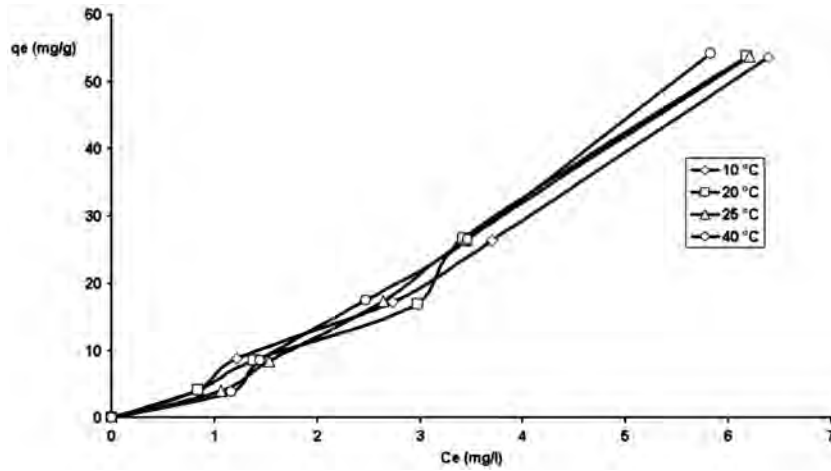


Fig. 8. Effect of the temperature on the elimination of the MB by 1 g/l of FMC at neutral pH.

$$\ln(q_e) = \frac{1}{n} \times \ln(C_e) + \ln(k_f) \quad (3)$$

where k_f and n are the constants of Freundlich. n depends on the nature of the pair adsorbate-adsorbent; there is a good adsorption when $1 < n < 10$.

The model of Temkin [28] written in its linear form, Eq. (4):

$$q_e = A + B \times \ln(C_e) \quad (4)$$

where $A = (R \times T)/b_t \times \ln(a_t)$ and $B = (R \times T)/b_t$ are constants of Temkin; with $R = 8.314 \text{ J/mol K}$ and T are, respectively, the constant of perfect gases and the temperature in Kelvin.

The model of Dubinin-Radushkevich (DR.) [29], Eq. (5):

$$\ln(q_e) = \ln(q_m) - \beta \times \varepsilon^2 \quad (5)$$

where q_m is the maximum quantity adsorbed in mol/g, β constant in mol^2/kJ^2 bound to the free energy, and $\varepsilon = R \times T \times \ln(1 + \frac{1}{C_e})$. q_e and C_e are expressed in mol/g and mol/l. The Eq. 6 makes it possible to calculate the free energy E of the process of elimination in kJ/mol:

$$E = -(2\beta)^{-0.5} \quad (6)$$

The values of E ranging between 8 and 16 kJ/mol indicate an ionic exchange process. If E is lower than 8 kJ/mol, the process of fixation of physical type is due to the weak van der Waals forces.

The computed values of the constants of Freundlich, Temkin and Dubinin-Radushkevich are shown in Table 3, with their coefficients of correlation R^2 .

The value of n is in all cases lower than one. This indicates the existence of electrostatic interactions between the MB molecules and the surface of the clay; that is responsible for the rapid fixation. The calculation of the value of b_t shows that the energy required is weak and that the variation with the temperature is negligible and its value remains about 0.1 kJ/mol. The values of the free energy E vary between 7.67 and 7.04 kJ/mol indicating a physical process of fixation in the limit between the ionic exchange and the one due to the weak van der Waals forces.

3.6. Kinetics modelling

Several authors [5,8,9,12,23,30] applied the following kinetic models to explain the mechanism of adsorption of their materials:

The kinetic model of the pseudo-first order, whose mechanism corresponds to adsorption preceded by diffusion through a boundary layer, is represented by the equation of Largegren in its linear form, Eq. (7):

$$\log(q_{e1} - q) = \log(q_{e1}) - \frac{k_1 \times t}{2.303} \quad (7)$$

where k_1 is the pseudo-first-order rate constant in min^{-1} ; q_{e1} and q in mg/g are, respectively, the maximum quantities adsorbed at the equilibrium and at the time t .

The kinetic model of the pseudo-second order of Ho and Mc Kay is represented in its linear form by Eq. (8):

Table 3
Freundlich, Temkin and Dubinin–Radushkevich parameters at different temperatures

Model	Parameters	10°C	20°C	25°C	40°C
Freundlich	n	0.84	0.80	0.69	0.65
	k_f	5.72	5.27	4.09	3.92
	R^2	0.9848	0.9862	0.9904	0.9690
Temkin	A	3.54	2.34	-2.70	-3.78
	B	22.05	22.95	27.35	29.30
	b_f (kJ/mol)	0.107	0.106	0.091	0.089
	R^2	0.8613	0.8377	0.9155	0.9264
Dubinin–Radushkevich	q_m (mol/g)	0.044	0.061	0.289	0.425
	β (mol ² /kJ ²)	0.0087	0.0085	0.0101	0.0096
	$-E$ (kJ/mol)	7.58	7.67	7.04	7.22
	R^2	0.9866	0.9830	0.9867	0.9604

Table 4
Parameters of kinetic models for the elimination of the MB by FMC

C_0 (mg/l)	Pseudo-first order			Pseudo-second order			Intra-particles diffusion		
	k_1 (min ⁻¹)	q_{e1} (mg/g)	R^2	k_2 (g/mg.min)	q_{e2} (mg/g)	R^2	k_i (g/mg.min ^{0.5})	I (mg/g)	R^2
5	0.002	4.18	0.041	nd ^a	4.18	0.9995	0.008	4.11	0.2945
10	0.024	8.73	0.4765	0.405	8.73	0.9999	0.019	8.51	0.436
20	0.016	17.24	0.5798	0.154	17.24	0.9999	0.048	16.73	0.6985
30	0.030	26.95	0.4208	0.151	26.95	1	0.094	26.04	0.8376

^and: not determined.

$$\frac{t}{q} = \frac{1}{k_2 \times q_{e2}^2} + \frac{t}{q_{e2}} \quad (8)$$

where k_2 and q_{e2} are, respectively, the pseudo-second-order rate constant of the adsorption in g/mg.min and the maximum quantity adsorbed in mg/g.

The kinetic model of intra-particle diffusion by Weber and Morris represented by Eq. (9), corresponds to a mechanism of adsorption that is being held in four stages:

- The diffusion of the molecules of the solution towards the surface of the adsorbent;
- The diffusion through a boundary layer on the surface of the adsorbent;
- The diffusion of inter-particles from outside towards the interior of the pores of the adsorbent;
- The adsorption on the active sites by reactions of the ionic exchange types, complexations and/or chelations.

$$q = k_i \times t^{0.5} + I \quad (9)$$

where k_i and I are, respectively, the constant of speed of diffusion intra-particles in mg/g.min^{0.5} and the quantity adsorbed under the effect the thickness of the boundary layer in mg/g.

Table 4 shows the values obtained of the various constants of the kinetic models applied to the experimental values of the elimination of the MB by 1 g/l of FMC, with neutral pH at a temperature of 20°C. The obtained coefficients of correlation R^2 show that only the kinetic model of the pseudo-second order gives a good representation of our experimental results. Fig. 9 shows the application of the second-order kinetic model on the elimination of the MB by FMC.

The pseudo-second-order kinetic model represents, with a small deviation, the results obtained on the adsorption of the MB by the activated sludge by micro-organisms, resulting from the cleaning water treatment of transport station in Adana in Turkey [5]. It also represents well, the adsorption of the MB on the montmorillonite of the north-east of Brazil [15] and the adsorption of the acid dyes used in the industry of the textile on bentonite of Maghnia and

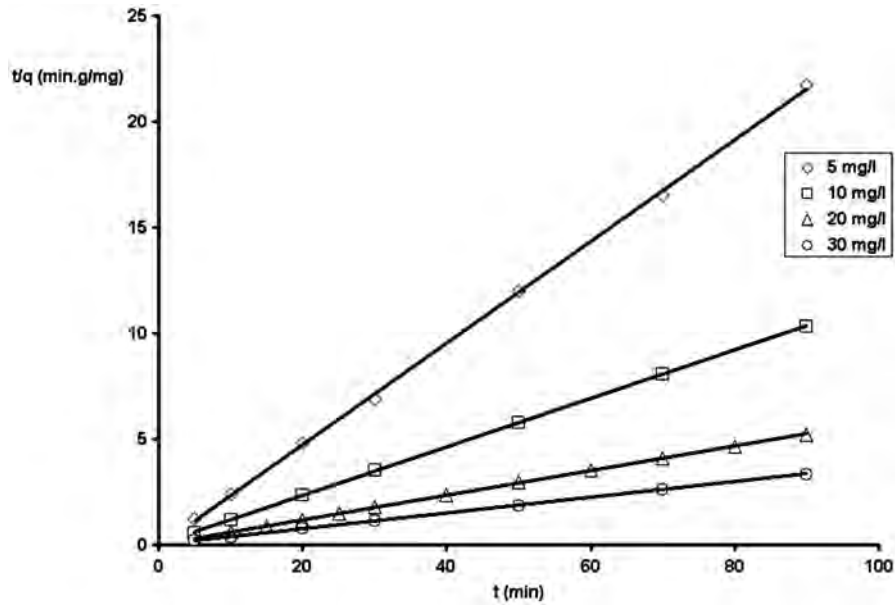


Fig. 9. Application of the kinetic model of the second order to the elimination of the MB by 1 g/l FMC at 20°C and neutral pH.

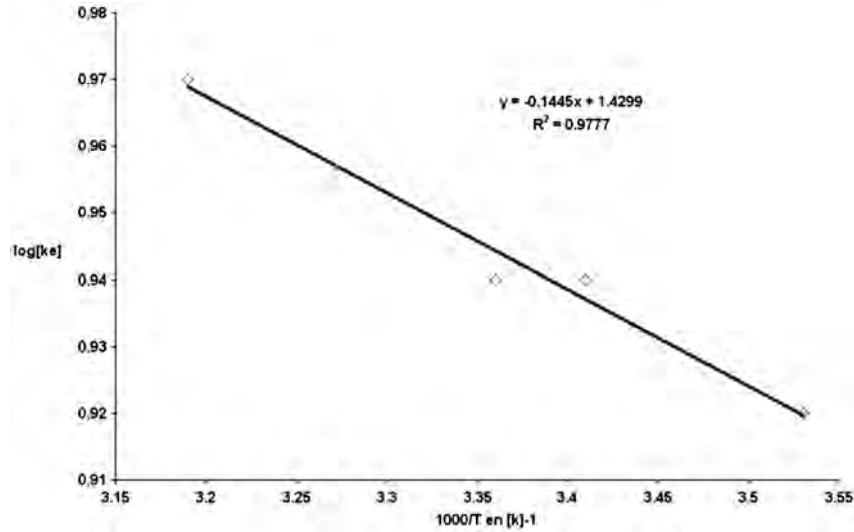


Fig. 10. Effect of the temperature on the elimination of the MB by 1 g/l FMC suspension at neutral pH.

the kaolin [23], and the adsorption of cationic dyes on kaolin [30].

3.7. Thermodynamic study

Eqs. (10) and (11) [12] were used to determine thermodynamic constants of MB elimination by 1 g/l FMC suspension, varying the temperature between 10 and 40°C at neutral pH.

$$\log(k_e) = \frac{\Delta S^0}{2.303 \times R} - \frac{\Delta H^0}{2.303 \times R \times T} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T \times \Delta S^\circ \quad (11)$$

where $k_e = \frac{q_e}{C_e}$ is the equilibrium constant, R is the perfect gas constant and T is the absolute temperature. ΔH° , ΔS° and ΔG° are, respectively, the standard enthalpy, the entropy and the free enthalpy of adsorption.

Table 5
Thermodynamic parameters of MB fixation on FMC

T (°C)	k_e (l/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
10	8.39	-4.84	-	-
20	8.67	-5.11	-	-
25	8.66	-5.24	2.8	0.027
40	9.29	-5.65	-	-

The representation in Fig. 10 of the variation of the $\log(k_e)$ vs. $\frac{1}{T}$, allows us to determine the various thermodynamic constants, as showed in Table 5.

Generally, the ΔG° value of a physical process of adsorption varies between -20 and 0 kJ/mol, while during chemisorption it varies between -80 and -400 kJ/mol [15]. Between 10 and 40°C, the values of ΔG° are negative indicating that the process of MB adsorption on the clay of Maghnia is spontaneous and of physical type. This confirms the result obtained by the calculation of the free energy E .

The enthalpy ΔH° is positive but very weak; confirming that the energy brought is negligible. The entropy ΔS° is positive and also weak indicating a small increase of the disorder in the solid-liquid interface compared to the liquid phase. Thus, the weak effect of the temperature (10-40°C) on the elimination of the MB by the clay of Maghnia is confirmed.

4. Conclusion

At 20°C in a MB-clay mixture at neutral pH and initial concentrations between 5 and 30 mg/l of MB, the elimination of MB is fast in the first five minutes and corresponds to more than 80%. The two types of natural clay of Maghnia FMC and SMC seem to have the same behaviour in eliminating the MB indicating the presence of an important proportion in argillaceous particles of less than 2 µm in diameter.

The clay of Maghnia flocculates in the presence of the MB solution because of the neutralization of the electrostatic forces between the negative charges of clay particles in suspension and the positive charges of the cations released by the MB in solution. Regardless to the pH of the medium, the optimum elimination of the MB can be reached by using a jar test to determine the optimal quantity of clay in suspension. At the optima, the effectiveness of MB elimination is more than 99% and clay is eliminated with an average of 98%. The clay of Maghnia seems to be a good and available low-cost material to treat by flocculation, the water polluted by cationic dyes. At laboratory level, adding Maghnia's clay suspension to the wastewater of a textile industry has proven effective. The second-

order kinetic model represents well this elimination with a coefficient of correlation R^2 ranging between 0.9991 and 1.0. The influence of the temperature between 10 and 40°C on this elimination is negligible and the calculated thermodynamic parameters indicate that the process is spontaneous with a negligible energy brought into play.

References

- [1] W. Somasiri, W. Ruan, L. Xiufen, C. Jian, Decolourization of textile wastewater containing acid dyes in UASB reactor system under mixed anaerobic granular sludge, *Electron. J. Environ. Agric. Food Chem.* 5 (2006) 1224-1234.
- [2] R. Gong, X. Zhang, H. Liu, Y. Sun, B. Liu, Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel, *Bioresour. Technol.* 98 (2007) 1319-1323.
- [3] J.W. Lee, S.P. Choi, R. Thiruvenkatachari, W.G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, *Dyes Pigm.* 69 (2006) 196-203.
- [4] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, *Bioresour. Technol.* 97 (2006) 512-521.
- [5] O. Gulnaz, A. Kaya, F. Matyar, B. Arikan, Sorption of basic dyes from aqueous solution by activated sludge, *J. Hazard. Mater.* 108 (2004) 183-188.
- [6] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, *J. Hazard. Mater.* 121 (2005) 247-250.
- [7] S. Karaca, A. Gürses, R. Bayrak, Investigation of applicability of the various adsorption models of methylene blue adsorption onto lignite/water interface, *Energy Convers. Manage.* 46 (2005) 33-46.
- [8] A. Gürses, E. Dogar, M. Yalcin, M. Acikyildiz, R. Bayrak, S. Karaca, The adsorption kinetics of the cationic dye, methylene blue, onto clay, *J. Hazard. Mater.* 131 (2006) 217-228.
- [9] N. Yeddou, A. Bensmaili, Equilibrium and kinetic modelling of methylene blue biosorption by pretreated dead streptomyces rimosus: Effect of temperature, *Chem. Eng. J.* 119 (2006) 121-125.
- [10] N. Zaghbani, A. Hafiane, M. Dhahbi, Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration, *Sep. Purif. Technol.* 55 (2007) 117-124.
- [11] C.H. Weng, Y.F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, *J. Hazard. Mater.* 144 (2007) 355-362.
- [12] Z. Boubarka, A. Khenifi, N. Benderdouche, Z. Derriche, Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite, *J. Hazard. Mater.* 133 (2006) 154-161.
- [13] C.H. Weng, Y.F. Pan, Adsorption characteristics of methylene blue from aqueous solution by sludge ash, *Colloids Surf. A* 274 (2006) 154-162.
- [14] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, *J. Hazard. Mater.* 135 (2006) 264-273.
- [15] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, *J. Colloid Interface Sci.* 332 (2009) 46-53.
- [16] M.G. Neumann, F. Gessner, C.C. Schmitt, R. Sartori, 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.* 255 (2002) 254-259.
- [17] T. Shichi, K. Takagi, Clay minerals as photochemical reaction fields, *J. Photochem. Photobiol. C* 1 (2000) 113-130.

- [18] H. Belarbi, A. Haouzi, J.C. Giuntini, J.V. Zanchetta, J. Niezette, J. Vanderschueren, Interpretation of orientation polarization in homoionic dry montmorillonite, *Clay Miner.* 32 (1997) 13–20.
- [19] O. Bouras, Propriétés adsorbantes d'argiles pontées organophiles: synthèse et caractérisation, PhD study, University of Limoges, France, 2003.
- [20] O. Bouras, J.-C. Bollinger, M. Baudu, H. Khalaf, Adsorption of diuron and its degradation products from aqueous solution by surfactant-modified pillared clays, *Appl. Clay Sci.* 37 (2007) 240–250.
- [21] M. Oz, D.-E. Lorke, M. Hasan, G.-A. Petroianu, Cellular and molecular actions of methylene blue in the nervous system, *Med. Res. Rev.* 31 (2011) 93–117.
- [22] H. Sakamoto, M. Shibata, H. Owada, M. Kaneko, Y. Kuno, H. Asano, Development of an analytical technique for the detection of alteration minerals formed in bentonite by reaction with alkaline solutions, *Phys. Chem. Earth* 32 (2007) 311–319.
- [23] B. Benguella, A. Yacouta-Nour, Elimination des colorants acides en solution aqueuse par la bentonite et le kaolin [Removal of acid dyes by bentonite and kaolin in aqueous solution], *C. R. Chimie.* 12 (2009) 762–771.
- [24] R. Morel, *Les sols cultivés [Cultivated soils]*, Tec&Doc Lavoisier, Paris, 1989.
- [25] D. Hillel, *L'eau et le sol [Water and soil]*, 2nd ed., Pedasup Academia, Louvain-La-Neuve, 1988.
- [26] J. Bujdak, Effect of the layer charge of clay minerals on optical properties of organic dyes, A review, *Appl. Clay Sci.* 34 (2006) 58–73.
- [27] R. Sanghi, B. Bhattacharya, A. Dixit, V. Singh, Ipomoea dasyperma seed gum: An effective natural coagulant for the decolorization of textile dye solutions, *J. Environ. Manage.* 81 (2006) 36–41.
- [28] R. Han, Y. Wang, P. Han, J. Shi, J. Yang, Y. Lu, Removal of methylene blue from aqueous solution by chaff in batch mode, *J. Hazard. Mater.* 137 (2006) 550–557.
- [29] Z. Bekçi, Y. Seki, M.K. Yurdakoç, Equilibrium studies for trimethoprim adsorption on montmorillonite KSF, *J. Hazard. Mater.* 133 (2006) 233–242.
- [30] B.K. Nandi, A. Goswami, M.K. Purkait, Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies, *Appl. Clay Sci.* 42 (2009) 583–590.