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Removal of Cationic Dye Methylene Blue onto Moroccan Clay

By Ghizlane Mourchid, Ibtissam Maghri, Mohamed Elkouali, Abdelkbir Kenz, Mohamed Talbi & Aicha Amougay

Bharathier University, Coimbatore

Abstract - This study reports the adsorption of Methylene Blue dye, a cationic dye used in dyeing cotton, wood and silk, on the crude and purified clay from Morocco. The adsorption experiments demonstrated that adsorption equilibrium is established after 20 minutes. Various experimental parameters were analyzed: adsorbent mass, initial dye concentration, adsorbent particle size. The experimental results showed that adsorption of Methylene Blue onto Moroccan Clay are related to the mass of the adsorbent and the initial dye concentration. The adsorption capacity was determined using the Langmuir and Freundlich isotherms. The adsorption kinetics of Methylene Blue was studied using the equations of the Firstorder and Second order reactions. The kinetics of adsorption of Methylene Blue dye onto Moroccan Clay can be described by a Second-order model. Results showed that the Moroccan clay can be considered as a good adsorbent for the removal of Methylene Blue and treatment of industrial wastewater.

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Removal of Cationic Dye Methylene Blue onto Moroccan Clay

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I. Introduction

Problems of water pollution that we know come from all human activities, domestic, industrial and agricultural. The national and international scientific research focuses its activities in the field of the environment, to the development of technical, economic and easy to implement. Among these techniques, there is adsorption on activated carbon. This treatment was effective but in most cases very costly. The researches are then directed to methods of treatment using natural materials because of their availability and their low cost. For this, several studies have been devoted to the search for new materials that can replace the activated carbon. Many kinds of adsorbents have been developed for various applications [1–9]. All these considerations led our research team to examine the last few years, the problem of development of techniques for removal of dyes and adsorption of new natural materials less expensive due to their abundance.

Clays with considerable economic interest, they can be one of the most important industrial materials, they are important in geology, agriculture, construction and environmental applications, in addition to their interest in clarifying oils, currently, they are increasingly used in various fields: there are clays for liquid fertilizer suspension, nano composites and plastic clays for adsorption of waste [10].

II. Methods

a) Clay origin

Our clay, the purpose of this study, denoted (AR), comes from the city Safi the region Douar Oueld Brahim Ben Dehmane, located about 35 km from the region El yousofia in Morocco .

b) Preparation of Clay

The experimental protocol used for the preparation of samples is illustrated in the following chart: The crude sample in the form of blocks is crushed and ground, the homogeneous powder obtained was washed with distilled water. After filtration, the residue was dried in an oven for 48 hours at 70°C. Finally, it is ground and sieved to a particle size between 40 and 100 microns

c) Optimization of adsorption of methylene blue on Clay

In order to optimize the conditions of adsorption of methylene blue on clay, we studied the effect of a number of factors may be involved in the process of this phenomenon: Effect of adsorbent dose, Effect of concentration and Effect of particle size of Moroccan clay

d) Adsorption Isotherms Modeling

i. Langmuir model

The second most commonly used model [11] is that of Langmuir. Initial assumptions are that the solid adsorbent has a limited adsorption capacity (q_m), all the active sites are identical, they can only complexing solute molecule (monolayer adsorption) and that there is no interaction between the adsorbed molecules.

$$\frac{1}{q_e} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L.C_e.q_m}\right) \quad (LangmuirI) \tag{1}$$

Author α σ ρ ω ¥ : Faculty of sciences Ben M'sik, BP: 7955, 20702 Casablanca, Morocco. E-mails : ghizlanemourchid@gmail.com, maghri.ibtissam@gmail.com, m.elkouali@gmail.com, a.kenz@voila.fr, maarifcentre@yahoo.fr

Author § : Faculty of sciences Ain chock, route eljadida, Casablanca, Morocco. E-mail : a.amougay@gmail.com

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L.q_m}\right) + \left(\frac{C_e}{q_m}\right) \quad (LangmuirII) \quad (2)$$

When q_e and q_m are expressed in $mg.g^{-1}$ and C_e $mg.L^{-1}$, the constant K_L is expressed in $L.mg^{-1}$. Some authors define the ratio R_L as a unitless quantity indicating whether more favorable adsorption tends to zero as R_L (R_L 0) and much worse than RL tends towards a to 1(R_L 1) [12].

$$R_L = \frac{1}{1 + K_L.C_0} \quad (3)$$

ii. *Freundlich model*

The simple model and empirical Freundlich is the most commonly used. We consider that it applies to many cases, especially in the case of multilayer adsorption with possible interactions between the adsorbed molecules [13,14].

$$q_e = K_F.C_e^n \quad (4)$$

The most common form exploited is the plot in logarithmic scale variations q_e according to C_e:

$$\log q_e = \log K_F + n \log C_e \quad (5)$$

Another possible use of the results by the Freundlich isotherm plot is in logarithmic scale changes in the distribution coefficient K_d based q_e:

$$\log K_d = \left(\frac{1}{n}\right)\log k_F + \left[\frac{(n-1)}{n}\right](\log q_e) \quad (6)$$

K_F is a constant which relates to the adsorption capacity. This is often expressed as $mg.L^{-1}$ and qe as $mg.g^{-1}$ unit K_F mg $(1\text{-}n).Ln.g^{-1}$. Consistent with the relationship between K_F and the maximum capacity of adsorption (q_m) is:

$$K_F = \frac{q_m}{C_0^n} \quad (7)$$

The constant n (dimensionless) gives an indication of the intensity of adsorption. It is generally accepted [15] that low values of n (0.1 <n <0.5) are characteristics of a good adsorption, whereas higher values indicate a moderate adsorption (0.5 <n <1) or low (n> 1).

e) Adsorption Kinetics modeling

i. *first order Model*

The first order model is usually expressed by [16]:

$$\frac{dq(t)}{dt} = k_1(q_e - q(t)) \quad (8)$$

This equation (1) becomes after integration, as follows [17,18]:

$$\ln(q_e - q(t)) = \ln q_e - k_1.t \quad (9)$$

ii. *Second order model*

It is an equation that is often used in the representation of adsorption kinetics. It is in the form [19]:

$$\frac{dq(t)}{dt} = k_2(q_e - q(t))^2 \quad (10)$$

This equation (3) becomes after integration, as follows [19]:

$$\frac{1}{q\ (t)} = \frac{1}{k_2.q_e^2.t} + \frac{1}{q_e} \quad (11)$$

III. Results And Discussions

a) Adsorbate Concentration Effect

The figure 1 shows the adsorption kinetics of methylene blue onto clay at different initial concentrations. We notify a decrease in the residual concentration. After sixty minutes, it reaches a constant value whatever the initial concentration; this shows that the equilibrium time is independent of the initial concentration of the dye.

b) Effect of Adsorbent Dose

The adsorption kinetics of methylene blue with three different masses of adsorbents is shown in figure 2. From these results, the biosorption is important for a mass of $0.4g.L^{-1}$ of adsorbent.

c) Adsorbent Particle Size Effect

In this study we used different size fractions. The adsorption kinetics of methylene blue is shown in Figure 3. The adsorption capacity is better for a size range <40μm for clay because the adsorption depends on the external surface of the adsorbent material increases with the fineness of its particles.

d) Modeling Adsorption Isotherms

i. *Langmuir and freundlich isotherms*

The experimental isotherms of adsorption equilibrium and maximum adsorption capacity have been validated in detail by the Langmuir model (Table 1) and Freundlich model (Table 2). The isotherms obtained were L-type according to the classification of Giles [20],

which promotes a monolayer adsorption and the interaction between the adsorbate and the adsorbent is important.

The results show that the maximum adsorption capacity (q_m) obtained from Langmuir model decreases with increasing the concentration value of the Methylene Blue (C_0). The adsorption of methylene blue onto clay is favorable (R_L tends to 0).

The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of Methylene Blue is not strongly adsorbed inside the pores because of its size. The adsorption of methylene blue onto clay is good (0,1< n <0,5).

ii. *First and second order models*

First and second order equation accounting both with theoric and experimental point of view was used to describe the adsorption kinetics of Methylene Blue onto Clay

The calculated q_e values are lower than the experimental value. The values of k_1, qe and regression coefficients provided in Table 3, demonstrate that methylene blue adsorption by Clay are not first-order.

The correlation coefficients (R^2) for these plots are superior (in most cases > 0.9) (Figure 3). The experimental q_e values were compared to q_e values determined by second order rate kinetic models. The q_e values calculated from the pseudo second order kinetic model exhibit excellent agreement with the experimental qe values (Figure 3). Thus, the sorption process is pseudo-second order. The pseudo-second order model is based on the assumption that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent. This provides the best correlation of the data.

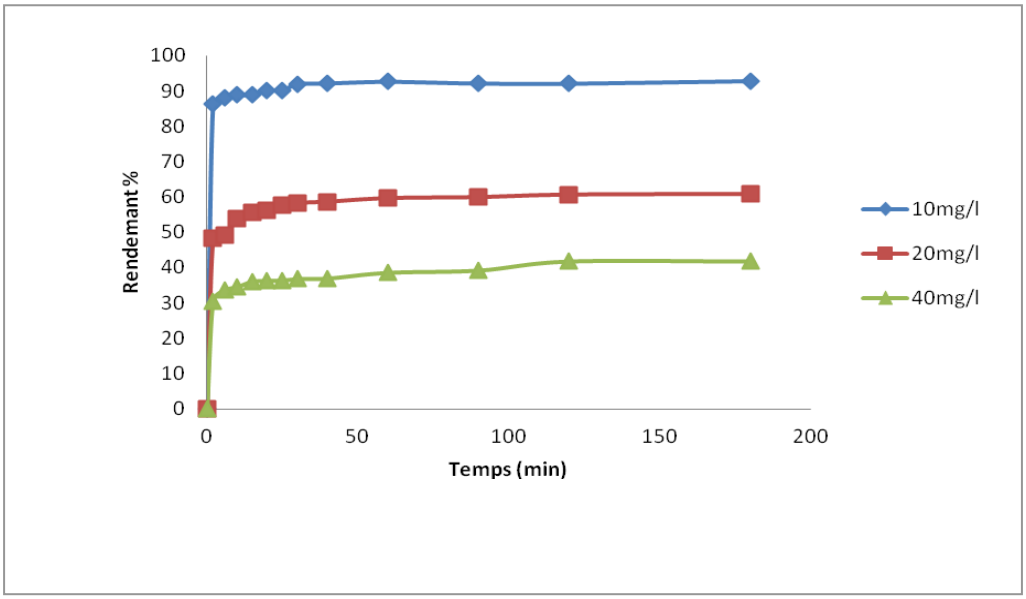

Figure 1 : Effect of Methylene Blue concentration, pH = 6,8; g <0,056 mm; adsorbent dosage 4 $g.L^{-1}$; ambient temperature

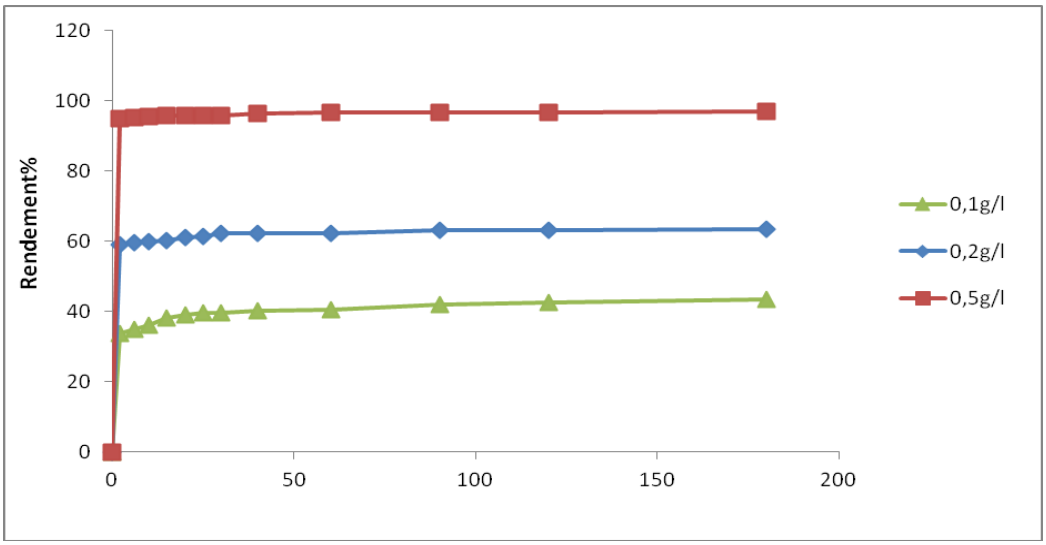

Figure 2 : Effect of adsorbent dose, pH = 6,8; initial concentration 10 mg.l^{-1}; G <0,056 mm; ambient temperature

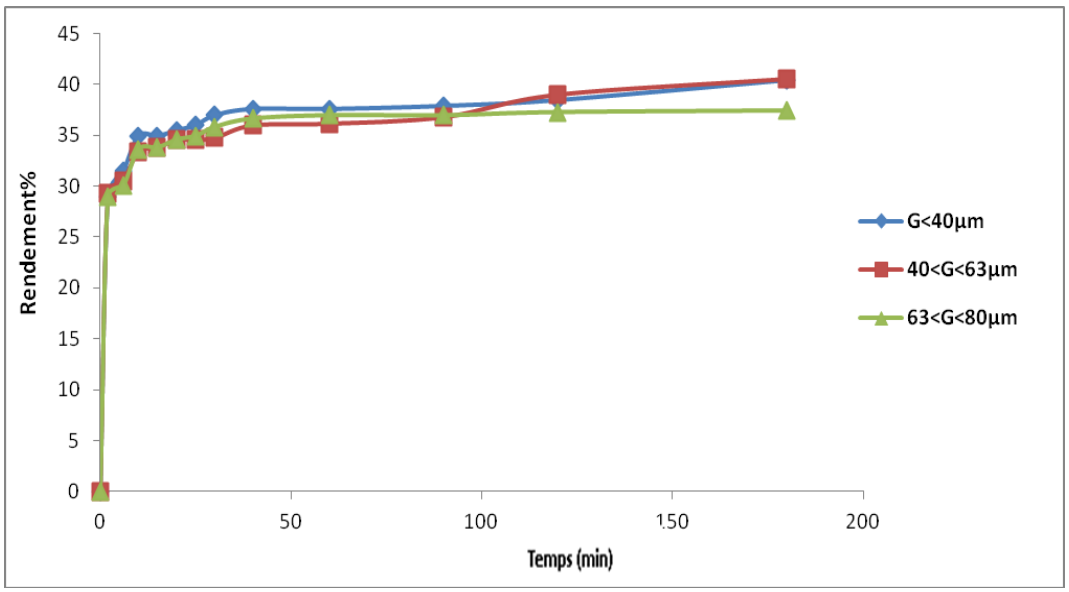

Figure 3 : Effect of adsorbent particle size, pH = 6,8; initial concentration 10 mg.L^{-1}; adsorbent dosage 4 g.L^{-1}; ambient temperature

Table 1 : Parameters of Langmuir adsorption of Methylene Blue onto Moroccan Clay

Langmuir 1 isotherm					
Experience	K_L (L.mg^{-1})	q_m (mg.g^{-1})	R^2	R_L	$\overline{R_{L\,i}} = \sum_{j=1}^{5} R_{L_{ij}}$
Exp1:10mg^{-1}	1,1367	71,9425	0,9436	0,0285	0,034
				0,0215	
				0,0917	
				0,0145	
				0,0124	
Exp2: 20mg^{-1}	0,6182	73,5294	0,9709	0,0512	0,034
				0,0389	

				0,0313	
				0,0273	
				0,0226	
Exp3: 40mg^{-1}	0,8861	71,4286	0,9615	0,0363	0,024
				0,0274	
				0,0221	
				0,0185	
				0,0158	
Langmuir 2 isotherm					
Exp1: 10mg^{-1}	1,433	71,9425	0,9973	0,0227	0,015
				0,0172	
				0,0138	
				0,0115	
				0,0099	
Exp2: 20mg^{-1}	1,2752	71,9425	0,9969	0,0255	0,017
				0,0192	
				0,0154	
				0,0129	
				0,0111	
Exp3: 40mg^{-1}	1,6023	70,922	0,9985	0,0204	0,014
				0,0154	
				0,0123	
				0,0103	
				0,0084	
Langmuir 3 isotherm					
Exp1: 10mg^{-1}	0,8578	71,949	0,9142	0,0374	0,025
				0,0283	
				0,0227	
				0,0191	
				0,0164	
Exp2: 20mg^{-1}	1,6526	73,566	0,9539	0,0197	0,013
				0,0149	
				0,0119	
				0,0098	
				0,0085	
Exp3: 40mg^{-1}	1,1534	71,523	0,9457	0,0281	0,019
				0,0212	
				0,0171	
				0,0142	
				0,0122	
Langmuir 4 isotherm					
Exp1: 10mg^{-1}	0,7842	72,6535	0,9142	0,0408	0,027
				0,0309	
				0,0249	
				0,0208	
				0,0179	
Exp2: 20mg^{-1}	1,7325	73,566	0,9539	0,0189	0,015
				0,0142	
				0,0114	
				0,0095	
				0,0082	
Exp3: 40mg^{-1}	1,2196	48,3642	0,9457	0,0266	0,019
				0,0201	
				0,0172	
				0,0135	
				0,0116	

Langmuir 5 isotherm					
Exp1: 10mg^{-1}	0,8256	72,2226	0,9142	0,0388 0,0294 0,0237 0,0198 0,017	0,026
Exp2: 20mg^{-1}	0,599	73,6527	0,9539	0,0527 0,0401 0,0323 0,02701 0,0233	0,035
Exp3: 1:40mg^{-1}	0,8472	71,6831	0,9457	0,0379 0,0286 0,023 0,0193 0,0166	0,025

Table 2 : Parameters of Freundlich adsorption of Methylene Blue onto Moroccan Clay

Freundlich isotherm				
Experience	K_F(mg$^{(1-n)}$L^{n}g^{-1})	n	R^2	q_m(mg.g^{-1})
Exp1: 10mg^{-1}	5,29	0,1251	0,9983	8,1 8,4 8,63 8,83 9
Exp2: 20mg^{-1}	5,13	0,1475	0,9912	8,47 8,84 9,14 9,38 9,6
Exp3: 40mg^{-1}	5,31	0,1205	0,9887	8 8,28 8,5 8,7 8,86

Table 3 : Parameters of First and Second order model of Methylene Blue adsorption onto Moroccan Clay

C_0 (mg.l^{-1})	10	20	40	20	20	20
m_s (g)	0,02	0,02	0,02	0,01	0,02	0,05
Q_e (mg.g^{-1}) Experimental 1st Order	46,4195	60,852	83,5285	86,64	63,329	38,7706
Q_e (mg.g^{-1}) theoric 1st Order	13,72	46,47	90,86	50	20,39	4,98
K_1	0,387	0,3911	0,3722	0,2621	0,3494	0,3573
R^2	0,7686	0,9153	0,5459	0,8659	0,8134	0,6692
Q_e (mg.g^{-1}) experimental 2nd Order	42,01	46,23	60,98	67,02	162,17	37,65

Q_e ($mg.g^{-1}$) theoric 2nd Order	43,29	48,78	62,11	67,11	162,28	37,88
K_2	-5,34	-1,05	-0,86	-0,74	-1,48	-13,94
R^2	0,8801	0,8316	0,8912	0,9283	0,9705	0,9605

IV. Conclusion

This work demonstrates that natural clay from Yousofia can be used as a metal ion adsorbent for treating water/wastewater contaminated with methylene blue.

The removal of methylene blue by adsorption onto clay was found to be rapid at the initial period of contact time and then slows down with increasing reaction time. The application of adsorption models allowed us to conclude that: The kinetic study of the phenomenon of adsorption follows the model of second order, because the correlation coefficient R^2 (2nd order) is higher than the correlation coefficient R^2 (1st Order). We can conclude that this is a Chimisorption. On average R_L is constant and close to 0. This shows that the adsorption is more favorable. We can say therefore that the clay can be considered as a good adsorbent for the removal of Methylene blue in aqueous solution. We have a good adsorption because for the different concentrations, we note that ($0.1 < n < 0.5$). This study showed that the clay could be used as an adsorbent to remove Methylene Blue dye from aqueous solution.

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