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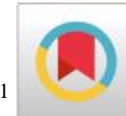
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A STUDY OF THE REMOVE CATIONIC AND ANIONIC DYES IN AQUEOUS SOLUTION BY A NEW NATURAL CLAY

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Abstract:

The objective of this work is to study the possibility of eliminating both dyes Methylene Blue (MB) and Congo Red (CR) by adsorption on natural clay of the region of Agadir and determine the different reaction parameters effect on the proceeds. Orientation tests have been carried out in distilled water solutions. The results of the kinetics of adsorption showed that optimal contact time is 60 min; it corresponds to a maximum removal rate of MB and CR respectively of the order of 99% and 75%. Increased adsorbent ratio (0,1 à 2 g / l) improves the removal efficiency of the CR especially dyes for an initial concentration of 10 mg/l. NaNO₃ salt and pH of the medium greatly influence the CR of retention. Whatever the reaction parameter tested; it appears that the clay has a good efficiency for the retention of two dyes.

Keywords: Methylene Blue; Congo Red; Adsorption; Clay Agadir; Reaction Parameters

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1. Introduction

The majeure source of the water pollution is industrialization, because with technology development several chemical products are manufactured, such as pesticides, detergents, heavy metals, dyes, and other toxic substances, and represents a real danger to the environment [1]. The dyes that are of interest in particular, have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded [2]. So it is necessary to limit as much as possible these pollutants by setting up a processing mean adapted as discoloration unit.

There are several physical, chemical and biological methods for treating and discolor polluted effluent such as coagulation and flocculation, biodegradation, membrane filtration, chemical oxidation, ion exchange, electrochemical methods and adsorption ... [3]. The technique of adsorption is the most favorable method for the removal of dyes and has become an analytical method of choice, very effective and simple in use. Several solid materials called adsorbent (clays, zeolites, and activated carbon ...) can be used in water treatment. Activated carbon is the most widely used adsorbent because of its great capacity for adsorption of organic materials. However, this adsorbent is difficult to regenerate cost. The search for other effective and less costly adsorbent

is therefore interesting. In this context, the use of clay as adsorbent is of great interest because of its efficiency, its accessible cost and abundance.

In this work, we study of the adsorption of methylene blue dye and Congo Red on a clay of the Agadir region, which is a natural adsorbent and available. [4] The study also examine different operational parameters may influencing the dye adsorption kinetics, such as the adsorbent's weight, the initial dye concentration, pH, temperature, ionic strength, and also the validation of the various models isotherms.

2. Materials and Methods

2.1. Dyes and Adsorbent Use

The clay (of the Agadir region) used was ground in a mortar and sieved in order to obtain fine particles. Both dyes used in this study, Methylene Blue (cationic dye) and Congo Red (anionic dye), taken as model of organic pollutants are used without any prior purification. The solutions are prepared by dissolving the quantities of the dye in distilled water. Their chemical structures are shown in Figure 1 and their characteristics are summarized in Table 1.

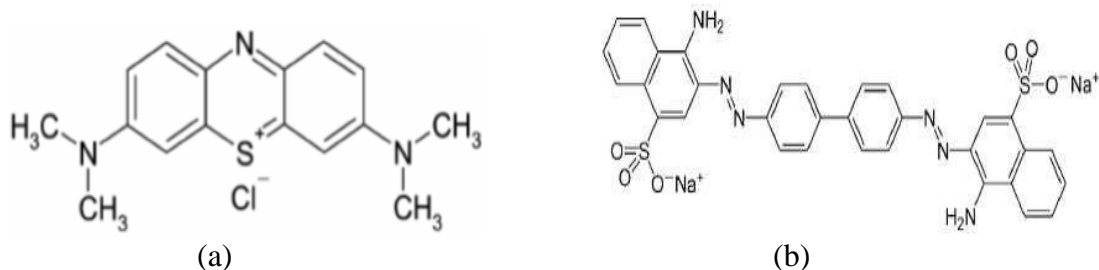


Figure 1: Chemical structures of methylene blue (a) and Congo Red (b).

Table 1: Physico-chemical of Methylene Blue and Congo red [31]

Name	Methylene blue	Congo red
Family	Basic dyes	direct dyes
Brute formula	C ₁₆ H ₁₈ N ₃ SCl	C ₃₂ H ₂₂ N ₆ Na ₂ O ₆ S ₂
Solubility in water	40 g·L ⁻¹ at 20 °C	25 g·L ⁻¹ at 20 °C
Molecular weight (g / mol)	320	696.65
λ _{max} (nm)	662	498

2.2. Analytical Methods

Stock solutions of MB and CR 10 ppm were prepared in distilled water. Solutions to be used in the analysis were obtained by serial dilutions to desired concentrations ranging from 1 to 10 for adsorption tests. After contact between solutions and of a defined mass clay, the samples were filtered through 0.45μm HA type Millipore membrane. Analyzes are carried out on a UV / Visible (JASCO V-630) driven by a computer. The maximum wavelengths of the MB and CR are obtained by a spectral scanning between 400 and 800 nm are respectively 662 nm and 498 nm. The adsorbed amount and the retention rate are calculated using the following formulas:

$$Q_{ads} = (C_0 - C_{eq}) / R$$

$$\text{Removal Efficiency (\%)} = (C_0 - C) / C_0 \times 100$$

Where:

C₀: Initial concentration at t = 0 (mg/l).

C_{eq}: Concentration at equilibrium (mg/l).

R: The clay mass solution by volume unit (g/l).

3. Results and Discussions

3.1. Characterization of Local Clay

3.1.1. Infrared Spectroscopy

Chemical analysis of the clay by the infrared spectra (500-4000cm⁻¹) is shown in Figure 2. The spectrum showed broad bands and superposed in the region 3200-3600 cm⁻¹, which are due to the elongation of O-H bonds. The band at 1590cm⁻¹ corresponds to the vibration of the groups C = C of the carboxylic groups. The peaks observed at 1370cm⁻¹ reflect vibrations of symmetrical or asymmetrical valence of the carboxylic groups of pectin's [5]. The band at 1020 cm⁻¹ could be due to the vibration of COC or -OH and polysaccharides [6]. The adsorption bands of which the wave number is less than 800cm⁻¹ can be attributed to nitrogen bioligands [7].

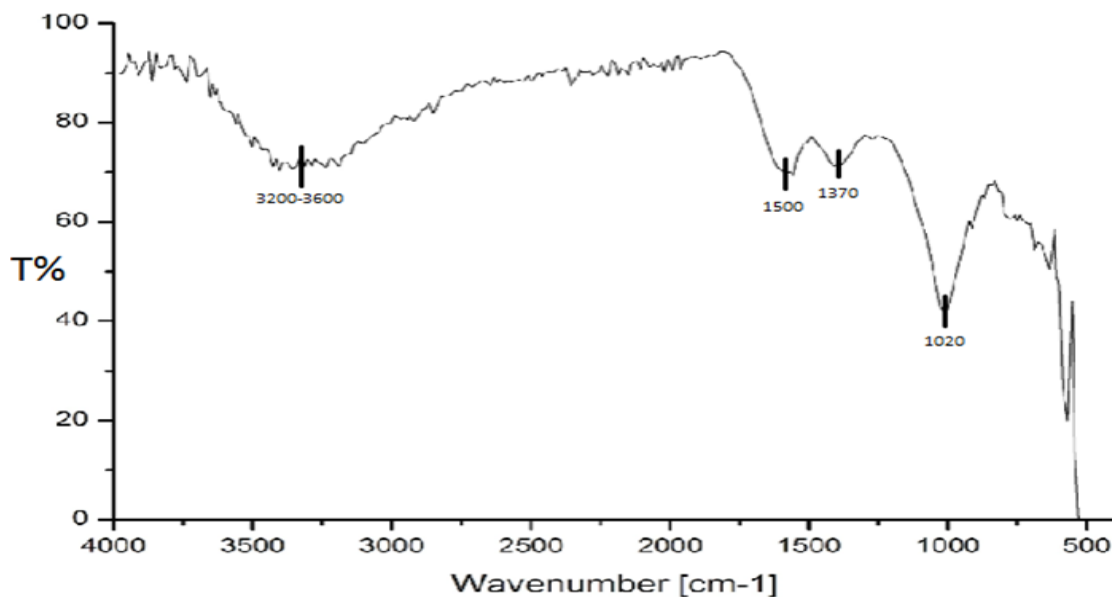


Figure 2: Spectrum Infrared of powder Clay

3.1.2. Scanning Electron Microscopy

Microscopic observation allows visualizing the morphology of the ground material. Figure shows that the ground material is formed of agglomerates of small particles and also indicates the presence of grains and small pieces of material in its structure [8].

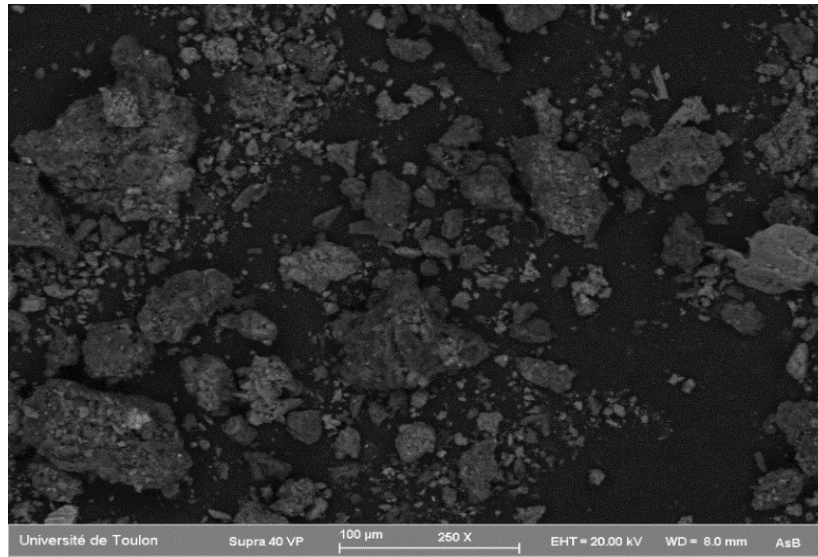


Figure 3: Scanning electron microscopy of the powder Clay.

3.1.3. Point of Zero Charge (pH_{PZC})

The point of zero charge (PZC) of our clay was determined by the method of solid addition, as described by Vieira et al. [9]. Nine vials containing solutions of pH between 2 and 10 (pH₀) and 0.10 g of adsorbent were stirred for 24 hours at room temperature and the final pH was measured. The difference between the initial pH and the final pH ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_f$) was plotted against the initial pH (pH₀) and the intersection of the curve with the axis that passes through the zero ($\Delta\text{pH} = 0$) gives $\text{pH}_{\text{PZC}} = 7.9$.

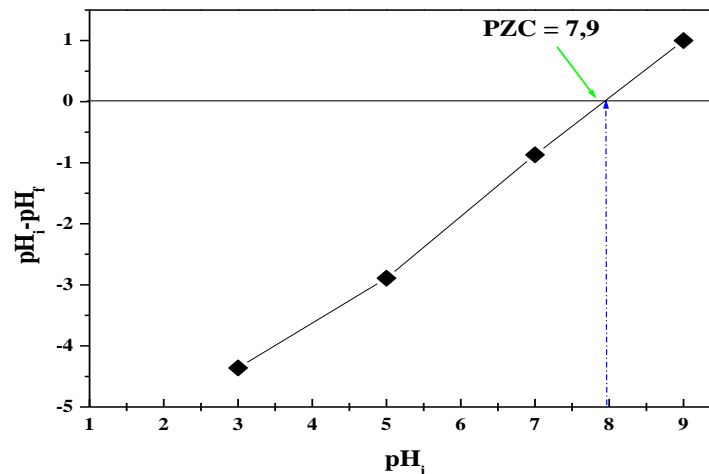


Figure 4: Point of zero charge for clay.

3.2. Adsorption Study

3.2.1. Effect of Contact Time

The effect of contact time on the rate of elimination of the CR and MB was studied over a range of 0 to 120 min, and the variation of the adsorption capacity, for an initial concentration of 10 mg

/ L, and a different adsorbent mass, is shown in Figure 5. The results obtained show that the removal rate increases quickly at first, until a time of 60 min, and then remains almost constant. We consider the adsorption of the MB and CR on clay is a quick process, since we obtain an equilibrium time of around 60 minutes. In the rest of our study, we will set a contact time to 60 min. The increase in removal rate for the first 30 min could be due to external mass transfer that is rapid. Then, a slow increase in amount adsorbed is observed. This means that the transfer of internal mass of the adsorbent control the process.

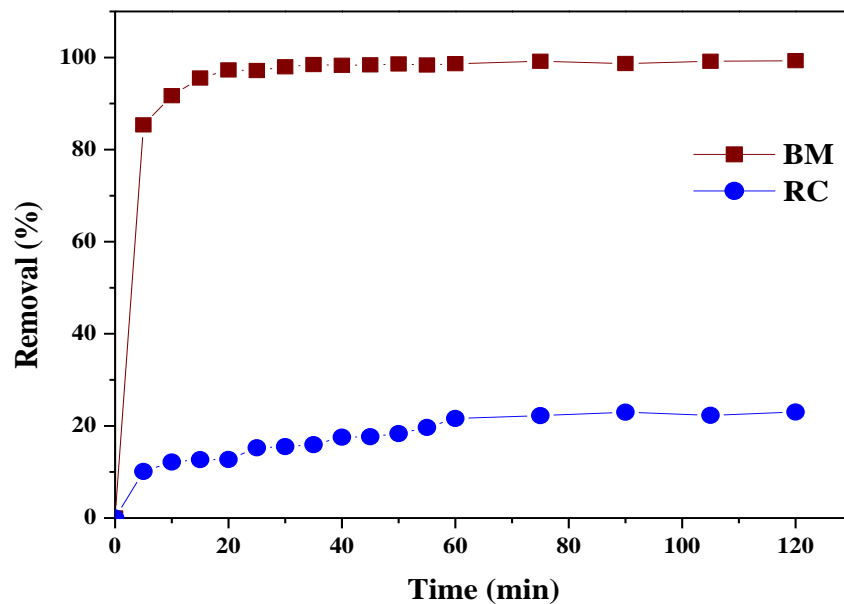


Figure 5: Effect of contact time on the adsorption of CR and MB by the clay. (C0 = 10 mg/l, pHi (MB) = 5.4, pHi (CR) = 6.2, R = 0.5 g/l, V = 500 ml, T = 22 ° C).

3.2.2. Effect of the Ratio R

The aim of this part of study is to determine the minimum ratio R which would result in a maximum removal rate of MB and CR dyes. It is performed by varying the mass of the support while maintaining the constant volume solution (500 ml). The stirring time is 60 min at a ambient temperature. Figure 6 shows that the removal rate increases with the addition of adsorbent until R = 0.5 g/l and R = 2.5g/L, respectively for MB and CR. For a ratio higher than those values, the adsorbed amount of the dyes remains constant. This behavior can be attributed to the increases of the number of adsorption sites, with the amount of adsorbent until the ration reach the values cited and the number of sites becomes stable [10,11]. This compartment can be explained by:

- i) As long as the amount of adsorbent added to the polluted solution is low, the dye ion can easily access the adsorption sites. The addition of adsorbent can increase the number of adsorption sites but the dye ions have more difficulty in approaching these sites due to congestion;
- ii) A large quantity of adsorbent creates particle agglomerations, resulting in a reduction in total adsorptive surface and, consequently, a decrease in the amount eliminated by the adsorbent mass.

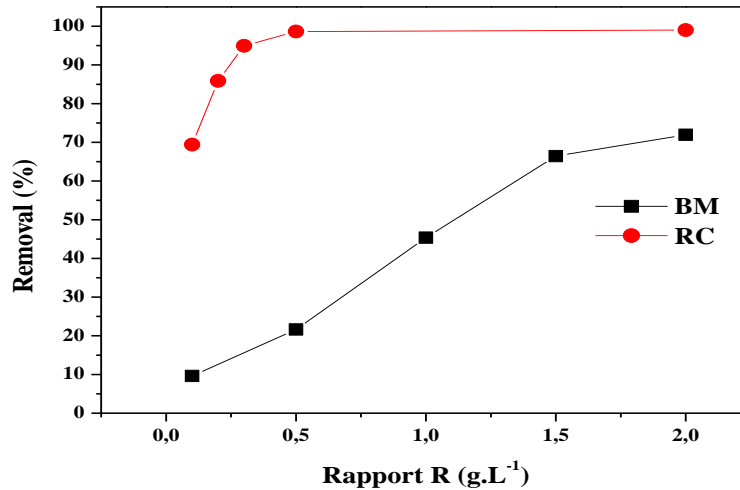


Figure 6: Effect of ration R (m / V) on the adsorption of MB ($C_0 = 10 \text{ mg/l}$; $\text{pHi (MB)} = 5.4$; $\text{pHi (CR)} = 6.2$; $V = 500 \text{ ml}$; $t = 60 \text{ min}$).

3.2.3. Dye Effect Concentration

The effect of the concentration of colorant has been studied in the range 5-100 mg L⁻¹. The evolution of the rate of elimination is shown in Figure 7. The results show that the removal rate slightly decreases with increasing concentration of WB. We also note that there is a slow saturation of the support for higher concentrations. Results obtained for CR showed a fast adsorption until 40 minutes when adsorption becomes slower. This phenomenon is probably due to the resistance to mass transfer within the clay particles. To high concentrations, the gap becomes tight and the adsorbed fraction is small.

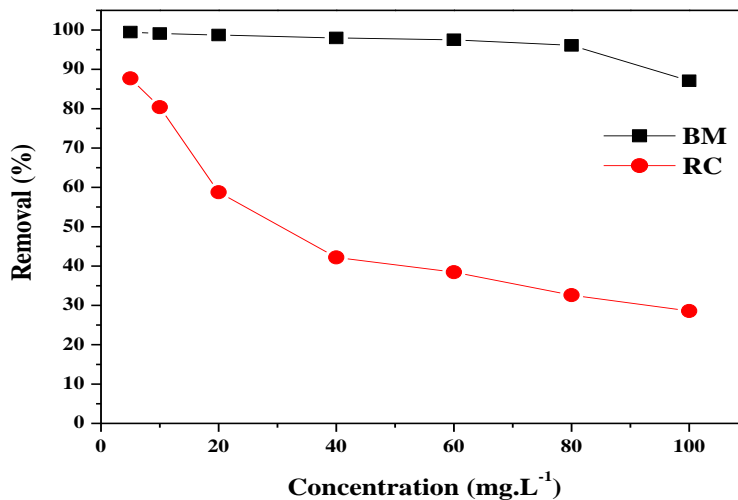


Figure 7: Influence of initial concentration on MB and CR adsorption. ($m = 1 \text{ g}$; $V = 500 \text{ ml}$; $\text{pHi} = 6.2$; $t = 60 \text{ min}$).

3.2.4. Effect of pH on the Adsorption of MB and CR

pH is an important factor in any study of adsorption, as it can influence both the adsorbent and the adsorbate structure and the adsorption mechanism. We studied the MB dye adsorption efficiency

by varying the initial pH of solution from 3 to 9 using a solution of nitric acid HNO₃ (0.1 N) or NaOH (0.1 N) according to the desired pH. The results are presented in Figure 8. The MB dye removal percentage is constant as a function of pH. For the CR dye, in the range of pH than 4, the solution changes color from red to dark blue and in the analysis of UV-visible spectrophotometer dye characteristic band CR it changes from 498 to 540nm. That is why the pH study with this dye was carried out at pH between 5 and 9. The results show that the basic medium is earlier favorable than the acid medium to the adsorption of CR on clay. The maximum adsorption is obtained at pH around 9.

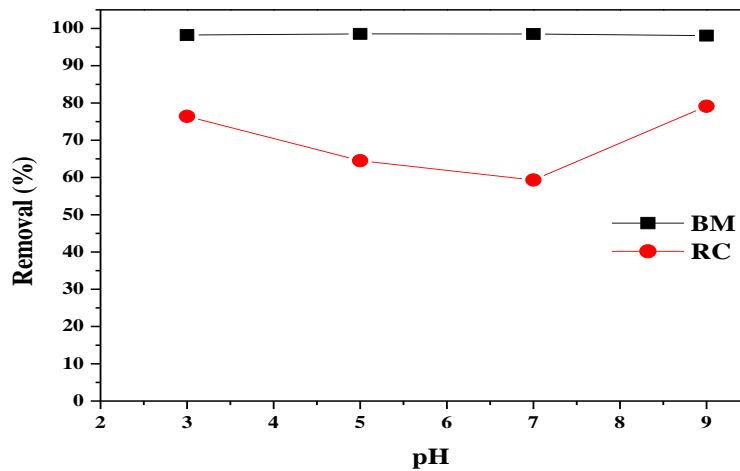


Figure 8: Influence of pH on the adsorption of CR on Clay. (m (MB) = 1g; m (OR) = 0.25 g; V = 500 ml; C₀ = 10 mg/l; t = 60min)

3.2.5. Effect of Ionic Strength NaNO₃

It is known that textile wastewater contains, in varying concentrations, organic and inorganic ions, such as nitrates, chlorides, sulfates, carbonates and hydrogencarbonates, etc. [12]. So, in order to better understand the influence of these ions, experiments were conducted on mixtures containing at different concentrations of NaNO₃ (10⁻¹M, 10⁻²M, 10⁻³M, 10⁻⁴M). The concentration of MB and CR was sited to 10mg / L, with 0.25 g of clay. The residual concentrations were analyzed after 60 minutes of reaction (Figure 9).

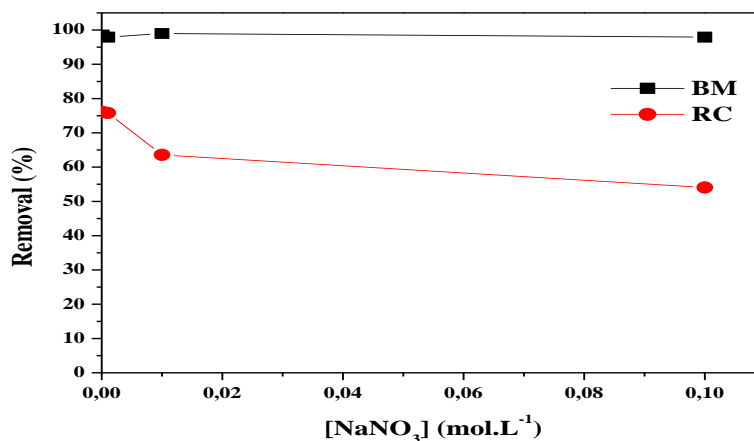


Figure 9: Influence of ionic strength on the adsorption of MB and CR on Clay. (PHi (MB) = 5.4, pHi (CR) = 6.2, V = 500ml; C = 10 mg/l; t = 60min)

The results show that the addition of NaNO_3 10^{-4} to 10^{-1} M did not practically no effect on the adsorption of cationic dye (Methylene Blue). In the case of anionic dye (Congo Red), this adsorption is inhibited, The percentage of elimination is in the range from 58% to 76.8. This inhibition in the case of adsorption of CR is mainly due to a competition between nitrate ions and the anionic dye.

3.2.6. Effect of Temperature

The influence of temperature was studied by varying the temperature of 30 to 60 ° C. The results in Figure 10 show that for both dyes, the amount removed is slightly increased with the temperature. This, indicate that the reaction is endothermic. The elevation of temperature promotes the mobility of dye ions and produces a swelling effect of the internal structure of the clay. It will also allow dye molecules to penetrate further [13,14].

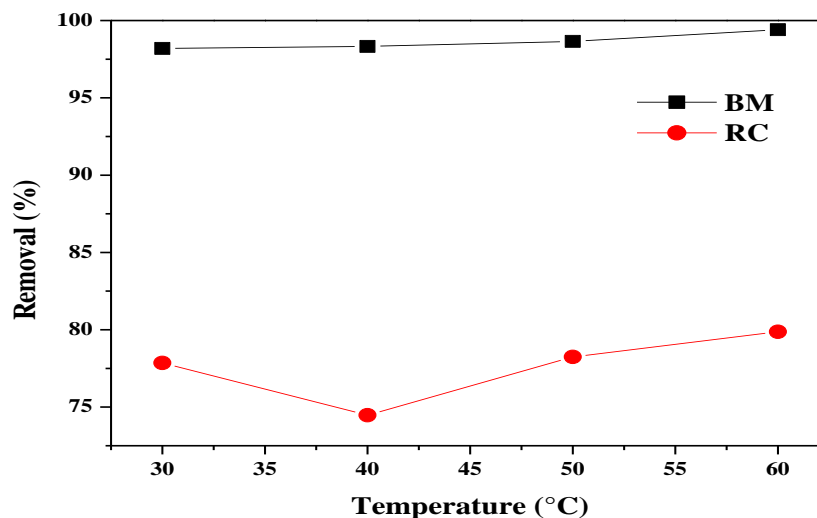


Figure 10: Influence of temperature on the adsorption of MB and CR (m (MB) = 0.25 g; m (OR) = 1g; V = 500 ml; pHi (MB) = 5.4; pHi = 9; C_0 = 10 mg/l; t = 60min).

3.2.7. Adsorption Isotherms

The adsorption isotherms are often used for the determination of maximum capacities for setting pollutants and for the identification of the adsorption-type. The results obtained, fitted according to the models of Langmuir and Freundlich, have enabled us to calculate the maximum adsorption capacity and the adsorption isotherms constant from the graphical representation of $Q_{ads} = f(C_e)$. Where Q_{ads} and C_e are respectively the amount of dye adsorbed per gram of adsorbent and the equilibrium concentration of this dye. Figure 11 shows the obtained adsorption isotherms. The curves show that as the initial concentration of dye increases, the adsorbed amount increases.

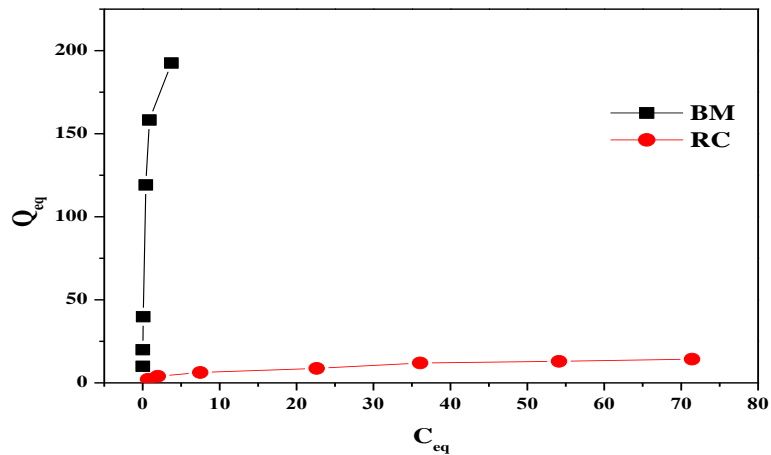


Figure 11: adsorption isotherm MB and CR.

For modeling data obtained we use the linear form of the Langmuir isotherm gives by the following equation:

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}K_L C_e}$$

Where C_e ($mg L^{-1}$) is the concentration at equilibrium, Q_e ($mg.g^{-1}$) is the amount adsorbed at equilibrium, Q_{max} ($mg.g^{-1}$) is the maximum quantity adsorbed and K_L ($L.mg^{-1}$) is the Langmuir isotherm constant. Two lines are obtained by plotting $1 / Q_e$ as a function of $1 / C_e$ in the concentration range studied of the two dyes (Figure 12).

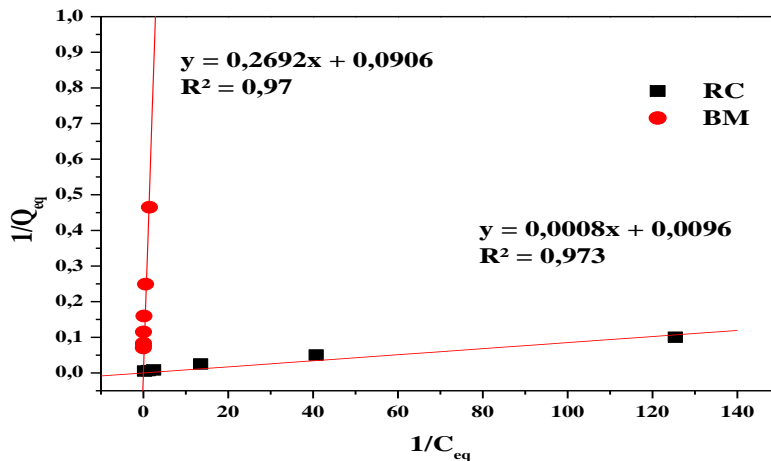


Figure 12: Modeling of Langmuir MB and CR adsorption.

In the case of Freundlich model, the linear form is given by the following equation:

$$\ln Q_e = \ln K_f + 1/n_f \ln C_e$$

$1/n$ is the intensity of adsorption and K_f (mg/g) is the Freundlich isotherm constant. Figure 13 gives the logarithm representation of (Q_e) versus $\ln(C_e)$ for the MB and CR. The value of $1 / n$ gives an indication of the validity of the adsorption of the adsorbent-adsorbate system. A value of $1 / n$ between 0 and 1 indicates a favorable adsorption [15]. The linear representations allowed us

to determine the equilibrium parameters and values of the constants for both models Langmuir and Freundlich given in Table 2.

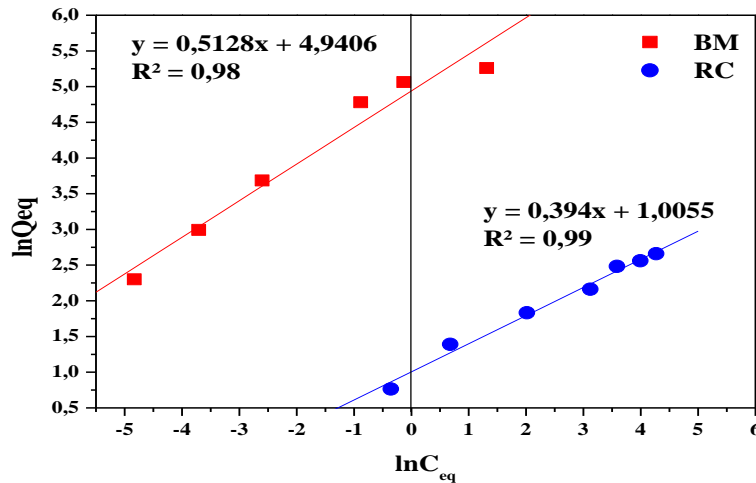


Figure 13: Modeling according Freundlich CR and MB.

Table 2: Langmuir and Freundlich Isotherm parameters.

Isothermes	Isotherme de Langmuir				Isotherme de Freundlich		
	Parameters	K_L (mg.g ⁻¹)	Q_m (L.mg ⁻¹)	R^2	R_L	n	K_F
MB	0.083	104.16	0.97	0.54	1.894	139.85	0.96
CR	2.969	11.03	0,97	0.032	2.538	2.73	0,99

The values of correlation’s coefficients (R^2), which are very close to 1, indicate that the adsorption process of MB and CR dyes on clay are described by both models Langmuir and Freundlich models. The adsorption of MB on the clay is unfavorable since the separation factor R_L is greater than 1 ($R_L > 1$), while the adsorption of CR on the clay is favorable since this factor is between 0 and 1 ($0 < R_L < 1$) [16].

4. Conclusions

This study focuses on the adsorption of methylene blue dye (cationic) and Congo Red (anionic) on the local clay Agadir region. The experimental results of adsorption of MB and CR on clay have shown that:

- Methylene blue (10 mg/l) adsorbs easily on the support within 60 minute contact time which corresponds to 99% removal. This gives it a very high affinity for the support.
- Congo Red (10mg/l) adsorbs less well on this medium with also 60minute contact time corresponding to 75% adsorption. This gives it a low affinity for the support.
- The adsorption capacity decreases with the increase of the initial concentration of the dyes.
- The effects of salts and pH had no effect on the MB but influenced the adsorption capacity of the CR.
- The study of the influence of temperature showed that the adsorption is endothermic.
- The modeling of adsorption isotherms is in good agreement with the model of Langmuir and Freundlich for each of the studied dyes.

- The adsorption of MB on the clay is unfavorable since the RL separation factor is greater than 1 ($RL > 1$).
- CR adsorption on the clay is favorable since the RL separation factor is between 0 and 1 ($0 < RL < 1$).

After this study, we can judge that the clay is a good adsorbent running low costs and has a great capacity to eliminate MB and CR from aqueous solutions.

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