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Removal of blue levafix dye from aqueous solution by clays

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Abstract

Dyes have become one of the main sources of severe water pollution as a result of the rapid development of the textile industries. It is reported that there are over than 100.000 commercially available dyes with a production of over $7x10^5$ metric tons per year. In order to eliminate Blue Levafix dye from aqueous solution, batch adsorption studies were carried out using natural clay (Bentonite of Nador-Morocco), and commercial clays (Montmorillonite and Kaolin). Adsorption experiments were conducted under various conditions: initial dye concentration, amount of clay, contact time, solid-liquid ratio, and organic matter concentration. Adsorption process fitted the first order kinetic. All isotherms were described by the Freundlich equation with a good regression factor (>0.9). The Freundlich parameters K_f permit to classify different adsorbents in ascending order Bentonite < Montmorillonite < Kaolin. The sorption of Blue Levafix dye on clays is favored with the presence of organic matter, in acid media and for solid liquid ratio 1 for bentonite and montmorillonite and 2 for kaolin.

Keywords: Adsorption, clay, dye, isotherm, organic matter.

1. Introduction

Textile manufacturing is considered as one of the biggest industrial producers of wastewater due to the high consumption of water in dyeing and finishing operations. Dyes constitute an important class of organic pollutants, which are mainly used in these industries [1-3]. It was estimated that around 100.000 tons of dyes are used per year and 5-50% of the dyes are released into waterways from textile factory. In comparison with other processes for the treatment of wastewater, the adsorption process allows flexibility in terms of both design and operation and produces pollutant-free effluents that are suitable for reuse. Also, as the adsorption is sometimes reversible, the sorbent can be regenerated, there by resulting in significant cost savings. The sorbents used in this study are clays because they are thought to act as a filter of pollutants and they present many advantages such as their abundance in nature, high surface areas, ion exchange ability and low cost [4-6].

The aim of the present work is to remove Levafix Blue dye from textile waste water by adsorption onto clays supports. In our study, we have used one natural clay originating from Nador region/Morocco and tow commercial clays (montmorillonite and kaolin). The influences of parameters like initial dye concentration, amount of clay, contact time, solid-liquid ratio, solution pH, and organic matter concentration have been investigated. Langmuir and Freundlich isotherm models were used to fit the equilibrium data. The kinetics of adsorption was also studied.

2. Materials and methods

2.1. Dye solution

Levafix Blue dye **LB** is an azo dye, widely used in the textile industry. It was purchased from DyStar (Levafix Blue CA). The chemical structure of commercial Levafix Blue CA reactive dyes is not disclosed.

The stock solution of the dye was prepared by diluting 100mg of LB in 1L of double distilled water. The experimental solutions of desired concentration were prepared by diluting the stock solution with double distilled water.

2.2. Mineral sorbents

The natural clay used in this study is a Bentonite of Nador, Morocco **B-N.** It is white clay with by location of the spots of iron oxide. This mineral was ground in order to obtain very fine particles (diameter < 2nm), and it was used without any preliminary purification.

In addition, two commercial clays have been used, as model adsorbents, were potassium Montmorillonite (**K-M)** and Kaolin (**Ka).** Both were purchased from Fluka Chemistry AG and they were used as received.

2.2. Adsorbent characterization

A series of analyses was undertaken to characterize the studied clays. Chemical analysis by X-ray fluorescence was engaged to determine chemical components of **B-N**, wavelength-dispersive X-ray-fluorescence spectrometer used is AXIOS-P analytical. XRD measurements were conducted using a Philips X-Ray diffractometer employing nickel filtered CuKά radiation. The IR spectra were performed using a spectrophotometer Perkin Elmer 2000, on a range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}. Specific Surface Area (SSA) and pore diameter were measured by N_2 adsorption isotherm at 78K using the Brunauer-Emett-Teller (BET) method. Cation Exchange Capacity (CEC) determination was conducted according to the "Metson" method of Exchange by ammonium acetate percolation (1 $mol.L^{-1}$, pH 7).

2.3. Adsorption studies

Adsorption experiments were carried out in a batch equilibration technique [7] using aqueous solution of LB dye with clays under various conditions to observe the effect of many parameters (initial dye concentration, humic acid amount, shaking time, solid-liquid ratio and pH). Solution pH has been measured by a pH-meter GLX. Temperature of each solution was also noted. Preliminary studies have shown that water clays washing have no effect on the adsorption capacity. All experiments were run in triplicate.

After shaking at known time, the suspensions have been centrifuged at 9500rpm for 15min. Dye concentration was measured using a spectrophotometer UV (Selecta UV-2005). Analysis was realized at wavelength corresponding to the maximum adsorption of dye (λmax = 613 nm).

Amount of dye adsorbed is deducted by the difference between C_0 and C_e, where $\mathbf{C_0}$ is the initial concentration of (LB) dye, Ce is the concentration of LB dye at equilibrium.

Adsorption isotherms were obtained by plotting the amount of adsorbed dye (Cads = mmol/kg clay, Ce (mM)).

3. Results and discussion

3.1. Characterization of clays

The chemical analysis of studied clays is given in Table 1. It shows the preponderance of silica followed by alumina for the three studied clays. SSA of (**B-N)** was found to be 66 (m²/g), and its CEC (100 meq/100g) is more important than those found for (**K-M)** and (**Ka**) (see table 2).

Table 1: Chemical composition of studied clays

Clays	SiO_2 (%)	MgO (%)	CaO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Others (%)
B-N	60.17	5.69	4.13	3.44	15.13	11.44
K-M [7]	71.42	1.414	0.207	2.992	14.362	9.605
Ka[7]	45.41	0.211	0.052	0.652	35.066	18.609

Table 2: Cationic exchange capacity (CEC) and SSA of studied clays

Clay	Ka	B-N	K-M
CEC (meq/100g)	6.1	100	60.72
SSA (m²/g)	23.5	66	166

The examination of **B-N** XRD pattern (figure 1) reveals the principal presence of Montmorillonite, characterized by an intense peak at (d =4,45Å; 2θ=19.92°) and a series of peaks with varying intensities. **Ka** XRD pattern shows the presence of a characteristic intense peak of kaolin (001) d=7.15. **K-M** XRD pattern is relatively poor in rays compared to kaolin one. Both **Ka** and **K-M** XRD patterns are constituted by a sharp 001 reflection which means that the number of water layers between the sheets is constant [8].

The **B-N** IR-spectrum reveals a double wide and thin band located respectively at 3624 and 3626.2 cm^{-1} corresponding to the stretching of O-H linkage of the octahedral layer, a band centered at 1635.7 cm^{-1} represents the H_2O molecules deformation, an intense band at 1033,4 cm^{-1} of the Si-O stretching bonds, a band at 916.5 cm^{-1} allocated to Al-Al-OH deformation, a band situated at 524cm^{-1} due to the Si-O-Al deformation linkage and, finally, a fine and broad band centered at 467cm^{-1} attributed to the Si-O-Mg deformation. However, the **K-M** IR spectrum shows a double band located at 3420-3640 cm^{-1} characteristic of the H_2O molecules vibrations, an intense band centered at 1130cm^{-1} attributed to the Si-O linkage, and a double band at 480 and 510 cm^{-1} corresponding to the Si-O-Si binding (Figure 2).

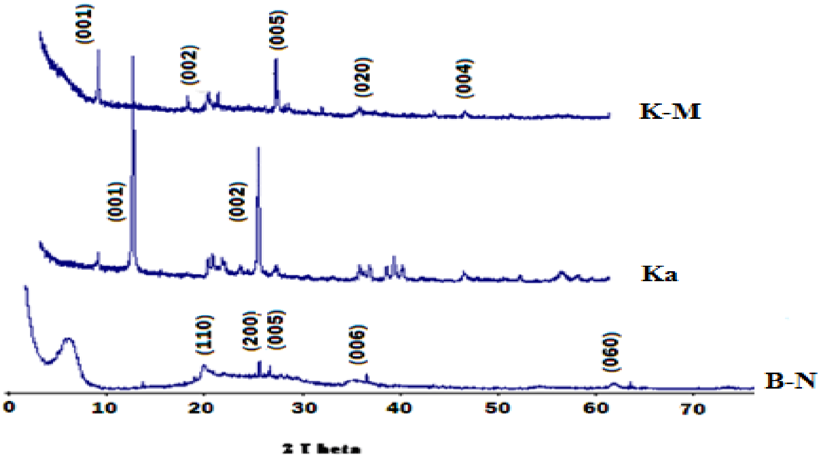

Figure 1: XRD patterns of studied clays

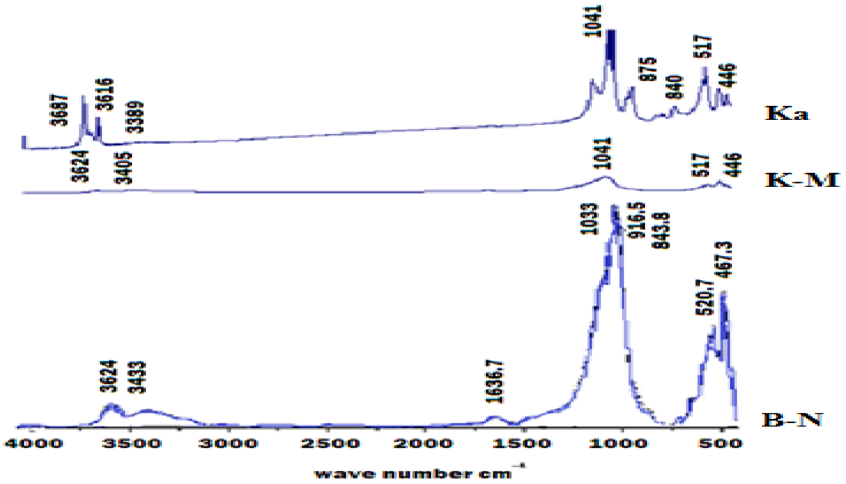

Figure 2: Infrared spectrums of studied clays

The **Ka** IR spectrum displays characteristic bands located at 3687, 3616 and 3589 cm^{-1} corresponding to the octahedral OH vibration. It also shows a dual band at 875 and 840 cm^{-1} with the same intensity, corresponding to the Al-OH-Mg link. There is also the presence of an intense band between 900 and 1200 cm^{-1} centered at 1041 cm^{-1} corresponding to the Si-O stretching vibrations. Bands located to 517 and 446 cm^{-1} are also observed, they are respectively attributed to Si-O-Al and Si-O-Mg deformations (Figure 2).

3.2. Study of the adsorption of LB onto clay surfaces

3.2.1. Contact time effect

In order to determine the optimal time for **LB** adsorption onto some selected clay surfaces, equilibrium concentrations were measured at definite time. The results of this study are illustrated by figure 3. They show that adsorption equilibrium was reached at 50min, 90min and 4 hours, respectively for **B-N**, **K-M** and **Ka**. The adsorption capacity of clays increased rapidly during the 25 first minutes and became slower until equilibrium, then, a stationary phase was observed. The first increase was due to the occupation of the free sites of clays external surfaces by dye molecules. This quick adsorption and the long contact time between dye and adsorbent generated a *saturation* of clays surface [4; 9].

3.1.1 Initial pH effect:

pH is a parameter that determines both solid surface and molecular states in which the compound present in the solution is located. This study is illustrated by figure 4.

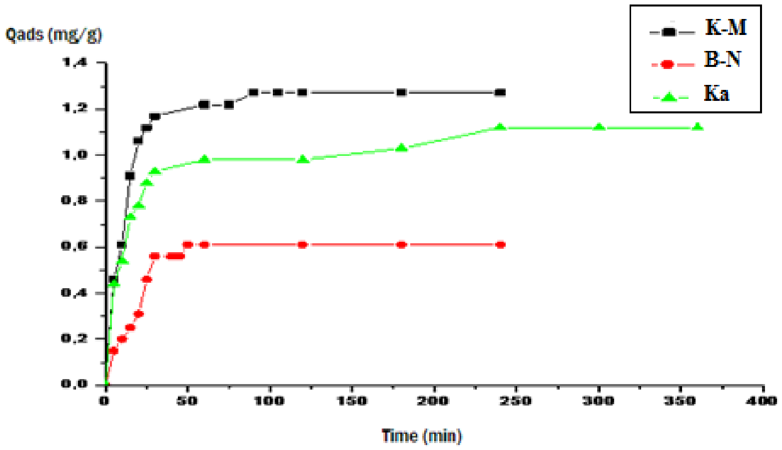

Figure 3: Effect of contact time on adsorption of LB onto clays

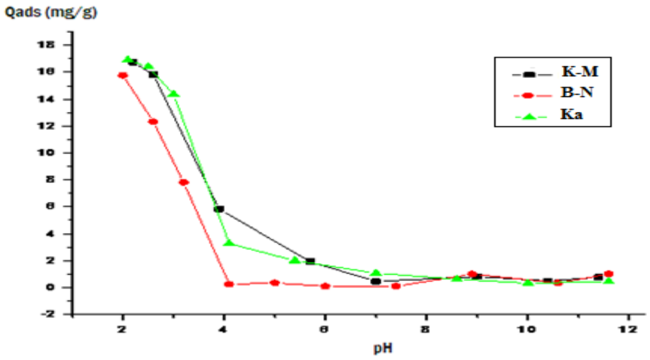

Figure 4: Effect of pH on adsorption of LB onto clays supports

The curves show that the adsorbed quantities are most important for especially acidic pH values below pH 3 (Figure 4). At higher pH, adsorption decreases when pH increases. But, at basic pH, despite the presence of OH^- ions, we see that adsorption capacity is greater than that found at pH between 7 and 10. These results were explained by the fact that in the acidic medium; the positive charge dominates the surface of the adsorbent. Thus, an electrostatic attraction exists between positive charges of H^+ deposited on clay surface and the negative charges of the dye. These results have been shown by other authors [10; 11].

3.1.2 Solid-liquid ratio effect:

The variation of adsorption capacity depending on the solid-liquid ratio is represented in figure 5. It shows that the evolution of **B-N** and **K-M** adsorption follows the same form with an increase to a ratio of solid liquid 1 followed by a deprivation of adsorption beyond this value. For **Ka**, the adsorption maximum is reached at a ratio of 2. These results indicate that the suspended particles dispersion is changed depending on the solid-liquid ratio. The increase of the ratio allows increasing the free surface area of clay and subsequently the amount adsorbed. It reached a mass where there is an aggregation phenomenon of clay particles together, thereby lowering the total surface of molecules adsorption [5].

3.1.3 Organic matter effect

The influence of organic matter on the adsorption has been investigated. Humic acid is an important compound of soil and water which can interact with organic and mineral products. Humic acid has an important adsorption capacity due to its functional groups. This study shows that the adsorption capacity is positively correlated with the increase of the organic matter content (Figure 6). This can be explained by enhance of adsorption surface area which provides a greater number of active sites for adsorption [4].

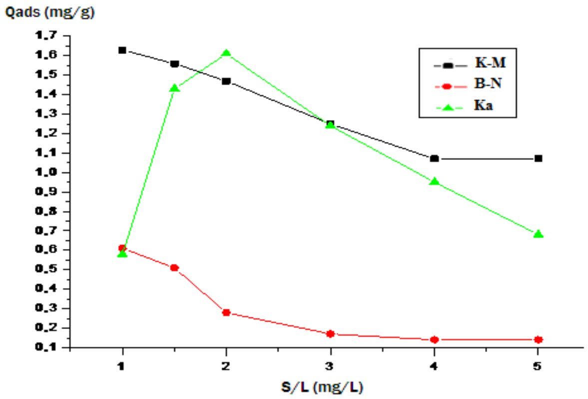

Figure 5: Effect of solid-liquid ratio on adsorption of LB onto clays

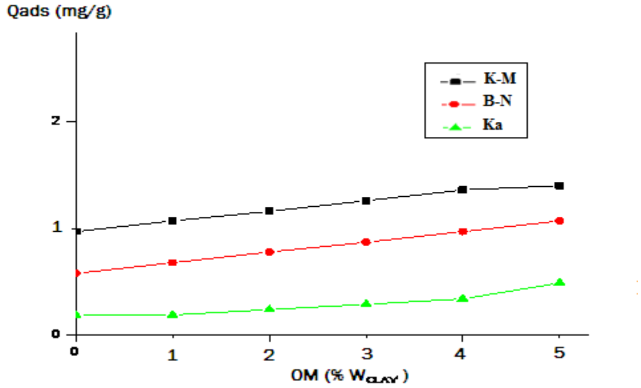

Figure 6: Effect of Organic matter on adsorption of LB onto clays

3.3. Adsorption kinetics

Kinetic study of adsorption process provides information about adsorption mechanism and transfer mode of liquid phase solutes to the solid phase. The literature reports a number of kinetic adsorption models depending on the nature and complexity of the adsorbent [4; 5; 9]. In this work, the study of the adsorption kinetics experiment will focus on models based on the composition of the medium, including the pseudo-first and pseudo-second order kinetic models. The rate constant of the pseudo-first order adsorption is inferred from the pattern established by Lagergren [12; 13]:

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t) \qquad (1)$$

q_e is the amount of dye at equilibrium per gram of adsorbent, t is the contact time (min), k_1 is the adsorption rate constant of pseudo-first order. The linear form of the equation (1) is:

$$\log\frac{dq_e}{q_t} = \log q_e - \frac{k_1 t}{2{,}303} \qquad (2)$$

The pseudo-second order kinetic model allows the characterization of the kinetics of adsorption taking into account both the case of a rapid fixation of solutes on the most responsive sites and slow attachment on low energy sites.

The equation of this model is written as follows [14]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

The integration of equation (3) gives:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \qquad (4)$$

q_e is the dye amount at equilibrium per gram of adsorbent. t is the contact time (min), k_2 is the rate constant of pseudo-second order adsorption.

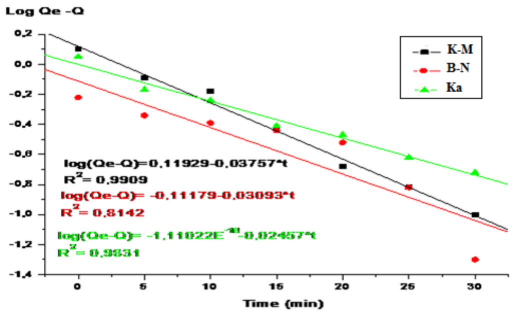

Figure 7: Pseudo-first order model for adsorption of LB onto clays

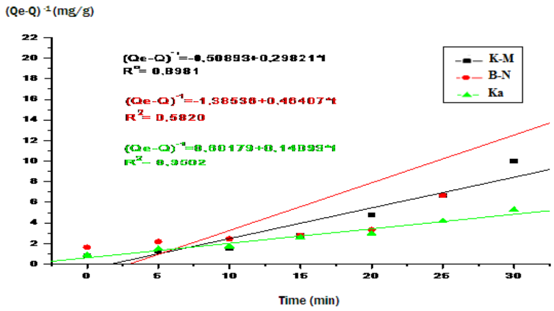

Figure 8: Pseudo-second order model for adsorption of LB onto clays

Correlation coefficients (R²) of both pseudo-first and pseudo-second order kinetic are summarized in table 3. They show that the adsorption of LB onto all clays follows the pseudo-first order kinetics. We can therefore assume that in this case the adsorption is reversible and the sorption rate at time t is proportional to the difference between the quantity adsorbed at equilibrium and the amount adsorbed at this time.

Table 3: Pseudo-first order and Pseudo-second order kinetic parameters of the three Clays

Clays	**Pseudo-first order model**			**Pseudo-second order model**		
	K_1 (min $^{-1}$)	Qe $_{exp}$ (mg/g)	R²	K_2 (min -1)	Qe (mg/g)	R²
K-M	0.087	1.32	0.9909	0.2982	-1.97	0.8981
B-N	0.071	0.77	0.8142	0.4641	-0.72	0.5820
Ka	0.057	1	0.9831	0.1409	1.66	0.9562

3.4. Adsorption isotherms

Adsorption isotherms play an important role in the determination of the maximum adsorption capacity and the identification of the type of adsorption to occur. Several models of adsorption isotherms have been developed by various researchers. The most mathematical equations used are Langmuir and Freundlich isotherms [4; 5; 8].

The Langmuir isotherm assumes that the sorbent is uniform and all adsorption sites have homogeneous energy. It is based on the assumption that the number of adsorption sites on the surface is limited and that a site can adsorbs only a single molecule. In this case, adsorption process is reversible, with formation of monolayer and without interaction between the adsorbed molecules [15].

The Langmuir isotherm is represented by the following equation [15]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}\,k_L} - \frac{C_e}{Q_{max}} \qquad (5)$$

C_e is the solution concentration at equilibrium (mg/L), Q_e is the adsorption capacity at equilibrium (mg/g), Q_{max} is the maximum adsorption capacity (mg/g), and k_L is the Langmuir adsorption constant (L/mg).

The Freundlich isotherm is an empirical equation used to describe the heterogeneous systems. It describes the reversible adsorption and is not limited to monolayer formation [8; 15].

The linear form of the expression of Freundlich is written as follows:

$$\text{Ln}\, Q_e = \log k_L + \frac{1}{n}\,\text{Ln}\, C_e \qquad (6)$$

Q_e is the adsorption capacity at equilibrium (mg/g), k_F is the Freundlich adsoption constant (L/g) which indicates the sorption capacity of the adsorbent, n^{-1} is the intensity factor, expressing the slope of the adsorption isotherm. The plots of C_e/Q_e versus C_e and LnQ_e versus LnC_e are respectively shown in figures 9 and 10. The table 4 includes correlation factors (R²), Langmuir and Freundlich models parameters.

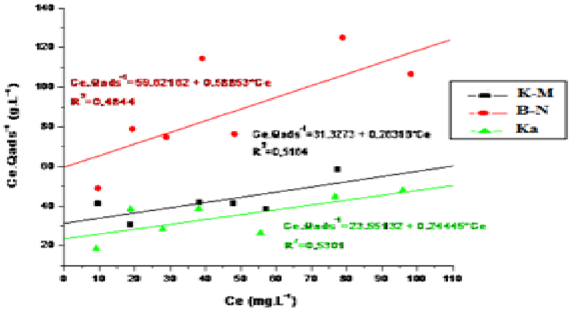

Figure 9: Langmuir isotherms for adsorption of LB on clays

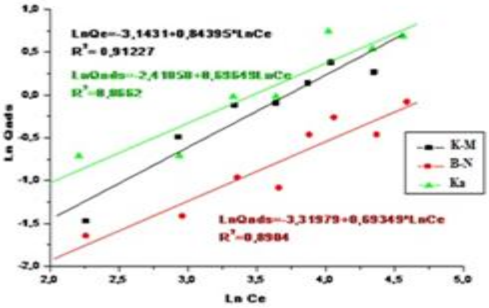

Figure 10: Freundlich isotherms for adsorption of LB onto clays

Correlation coefficients (R²) values, listed in table 4, allowed deducting that the adsorption of LB on clays has a good correlation with the Freundlich model. It means that adsorption process toke place with formation of multilayer and interaction between adsorbed molecules. The n value less than 1 indicates that adsorption is favorable. In this case, the sorption capacity increases with creation of new adsorption sites [16].

Table 4: Freundlich and Langmuir models parameters

Clays	**Freundlich model**			**Langmuir model**		
	K_F (L/g)	1/n	**R^2**	K_L (L/g)	Q_{max} (mg/g)	**R^2**
K-M	0.043	0.84395	**0.91223**	8.40	3.80	**0.5164**
B-N	0.036	0.69349	**0.8904**	9.87	1.70	**0.4844**
Ka	0.089	0.69649	**0.8662**	10.38	4.09	**0.5301**

Conclusion

This investigation indicates that clays could be considered as potential low-cost adsorbents for dye removal from aqueous solution. The adsorption process was found to be of first order kinetic for the three clays studied. The adsorption capacity of all adsorbents increases significantly in acidic medium and with the presence of organic matter. All adsorption isotherms were described by the Freundlich formalism with a good regression factor (>0.9). This brings to mind that formation of hydrogen linkage or van der waals forces could better explain the adsorption mechanism. The Freundlich parameters permitted to classify different sorbents in ascending order **B-N < K-M < Ka**.

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