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## Adsorption of Rhodamine B and methylene blue in solution using an Algerian iron oxide.

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### ABSTRACT

In this work, the removal of Methylene Blue and Rhodamine B, which are two cationic dyes, has been studied by adsorption using natural iron oxide (NIO). The characterization of this adsorbent revealed that NIO has a mixed elemental composition and consists mostly of iron oxide ( $\alpha\text{-Fe}_2\text{O}_3$ ). To describe the equilibrium isotherms for the both dyes, the Langmuir and Freundlich adsorption models were applied, the results showed that the Langmuir model agreed very well with experimental data ( $R^2 > 0.99$ ). The decolorization efficiency for different initial dye concentrations were evaluated by the pseudo first-order and second-order models, the data agreed very well with the pseudo second-order kinetic model. The adsorption rate was strongly influenced by the pH of medium and the doses of NIO. In fact, the capacity of adsorption was increased largely with decreasing solution pH.

**Keywords:** Adsorption, water, methylene blue, rhodamine B, natural iron oxide.

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## INTRODUCTION

Dyes can give various products beautiful colors, and therefore they are widely used in many fields such as textiles, paper, plastic, food, painting, and medicine [1]. Dyeing industry wastewater is one of the major environmental problems, because they consume dissolved oxygen and their color inhibits sunlight penetration into the stream and reduces photosynthetic action [2-3]. Moreover, most of them are carcinogenic and mutagenic and they can seriously harm human health [4]. Dyes have a synthetic origin and complex aromatic molecular structures which make them stable to biological degradation. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating dye wastewater. Hence, investigations have been conducted on physicochemical methods of removing color from textile effluents [5]. These studies include chemical oxidation [6], membrane filtration [7-8], coagulation [9], flocculation [10], photochemical destruction [11-12] and adsorption techniques [13-15]

The adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. In these techniques, adsorption has been found to be an efficient process to remove dye [16]. Activated carbon [17] and natural adsorbents such as banana and orange peel [18], apple pomace and wheat straw [19], waste mud and wood materials [20], palm kernel fiber [21], have been extensively used as adsorbents.

In this study, the natural iron oxide (NIO) whose we have utilized as an adsorbent, was provided from the iron deposits from Chaabet El-Ballout which is located in the North-East Algerian.

The aim of this work is to study the adsorption of two dyes Methylene blue and Rhodamine B into the natural iron oxide. The Langmuir and Freundlich equations were used to fit the equilibrium data. The adsorption rates were determined quantitatively and those obtained using the pseudo first and pseudo second order models. The effects of initial concentration and pH were investigated.

## MATERIALS AND METHODS

### Materials

Rhodamine B and methylene blue were purchased from MERCK (98%) and Reidel-de Haën (99%) respectively. The formula, molecular weight and maximum wavelength of light absorbed by RhB and MB were  $C_{28}H_{31}N_2O_3Cl$ ,  $C_{16}H_{18}ClN_3S$ ,  $479.02 \text{ g.mol}^{-1}$ ,  $385.19 \text{ g.mol}^{-1}$  and  $552 \text{ nm}$  and  $664 \text{ nm}$ , respectively. NaOH from Carlo Erba Reagenti (98%). HCl from Merck (37%). The natural iron oxide (NIO) was washed several times with distilled water and dried at  $45 \text{ }^\circ\text{C}$ .

### Batch adsorption experiments

Batch adsorption experiments were carried out at temperature ( $20^\circ\text{C}$ ). The stock solution of RhB and MB ( $10^{-3} \text{ mol.L}^{-1}$ ) was prepared from a set of ultrapure water (Millipure) and suitably diluted to the required initial concentrations ( $8.10^{-6}$ -  $4.10^{-5} \text{ mol.L}^{-1}$ ). The experiments were carried out in reactor with double envelope with about 7 cm in diameter, containing 100 ml of synthetic dye solution. The reactor was placed on a magnetic stirring plate for 120 minutes. The reaction temperature was kept at  $20 \pm 1 \text{ }^\circ\text{C}$  by cycling water. The particles of iron oxide were removed after adsorption by filtration through cellulose acetate (Millipore  $0.45 \text{ }\mu\text{m}$ ). The concentration of MB and RhB were monitored by measuring the absorbance at  $\lambda_{\text{max}}=664 \text{ nm}$  and  $\lambda_{\text{max}}=552 \text{ nm}$  respectively, using a UNICAM HELIOS  $\alpha$  UV-visible spectrophotometer. The indicated absorbance is proportional to the Beer-Lambert law in the range of studied dyes concentrations. The percentage removal of dye and the amount adsorbed at moment  $t$  ( $q_t$ ) and at equilibrium ( $q_e$ ) were calculated from:

$$\% \text{ of removal} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (1)$$

$$q_t = \frac{C_0 - C_t}{m} \cdot v \quad (2)$$

$$q_e = \frac{C_0 - C_e}{m} \cdot v \quad (3)$$

Where  $C_t$  is the dye concentration at time  $t$ ,  $C_0$  and  $C_e$  are the initial and the equilibrium concentration respectively in ( $\text{mol.L}^{-1}$ ),  $m$  is the amount of NIO ( $\text{g.L}^{-1}$ ) and  $v$  the volume of dye's solution (L).

### Characterization of iron oxide

In order to determine the crystal phase composition of natural iron oxide sample, X-ray diffraction (XRD) measurement was carried out using a spectrometer D8 Advance Bruker NXS, operating at 40 kV and 30 mA, using a  $\text{Cu K}\alpha$  monochromatic radiation ( $\lambda = 0.15418 \text{ nm}$ ). The total surface area and total pore volume of natural iron oxide sample were measured by the Brunauer–Emmett–Teller (BET) method in which the  $\text{N}_2$  adsorption at 77 K was applied and (Quantachrome) Sorptometer was used. The natural iron oxide was analyzed by X-ray Fluorescence using CUBIX- PANALYTICAL (Ex PHILIPS) equipment to determine the chemical composition of NIO fractions.

## RESULTS AND DISCUSSION

### Properties of iron oxide

The XRD patterns of natural iron oxide (NIO) confirmed that the sample has 9 characteristic peaks of hematite. The results of BET show that the NIO had the surface area equal to  $79.015 \text{ m}^2.\text{g}^{-1}$  and total pore volume  $0.0892 \text{ cm}^3 \text{ g}^{-1}$  (Detailed analysis has been already published in our previous study [22]).

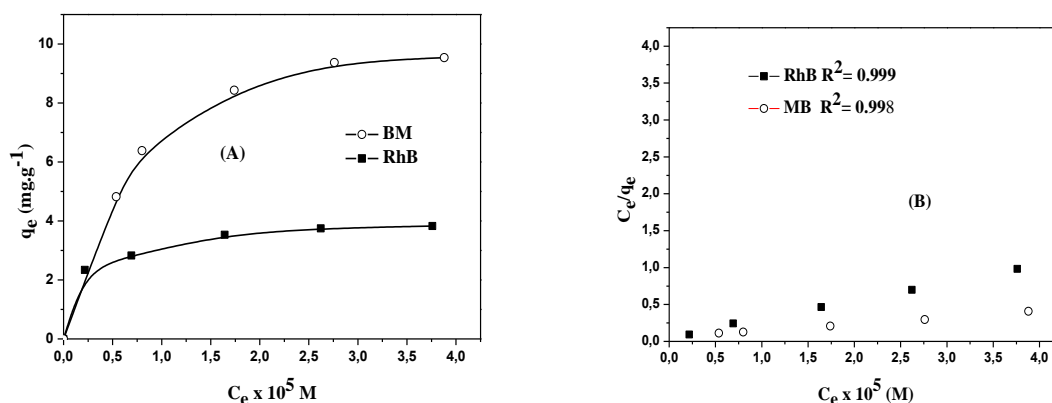
### 3.2. Adsorption isotherm experiments

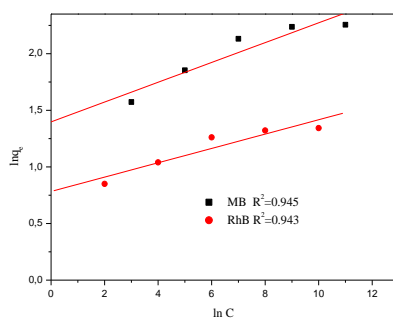
Studies on the adsorption isotherm are a prerequisite to understand the adsorbate-adsorbent interaction. Figure 1, shows the adsorption isotherms of NIO for methylene blue and rhodamine B. It was found that the adsorption capacity of the NIO for two dyes increased with the increase of their equilibrium concentration, until maximum values were obtained. In order to investigate the adsorption model, Langmuir and Freundlich adsorption isotherms were used to fit the adsorption curves. The Langmuir isotherm model assumes monolayer adsorption on a surface with a finite number of identical sites that all the sites are energetically equivalent and there is no interaction between the adsorbed molecules [23-24]. The Freundlich isotherm assumes a heterogeneous surface with non-uniform distribution of the heat of adsorption over the surface and a multilayer adsorption can be formed. The Langmuir and Freundlich isotherms may be expressed as Eqs (4) and (5) respectively [25-26].

$$\frac{C_e}{q_e} = \frac{1}{k_L \cdot q_m} + \frac{C_e}{q_m} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Where  $q_e$  is the amount of dye adsorbed per gram of iron oxide ( $\text{mg.g}^{-1}$ );  $C_e$  denotes the equilibrium concentration of dye in solution ( $\text{mol.L}^{-1}$ );  $k_L$  represents the Langmuir constant ( $\text{mol.L}^{-1}$ ) that relates to the affinity of binding sites and  $q_m$  the theoretical saturation capacity of the monolayer ( $\text{mol.l}^{-1}$ ).  $K_f$  and  $n$  are the Freundlich constants.





**Figure 1. Adsorption isotherm of methylene blue and rhodamine B on the surface of NIO. (a); obtained by plotting the equilibrium concentration ( $C_e$ ) vs the adsorbed amounts of RhB ( $Q_e$ ). (b) Langmuir plots (c) Freundlich plots of methylene blue and rhodamine B.**

**Table 1: The constants of Langmuir and Freundlich for methylene blue and rhodamine B adsorption**

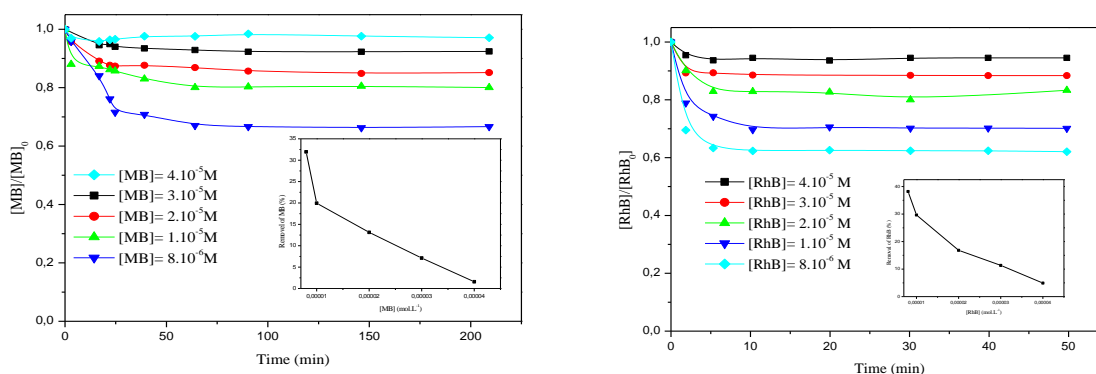
Dye	Langmuir			Freundlich		
	$R^2$	$q_{max}(mg.g^{-1})$	$K_L(L.mg^{-1})$	$K_f(mg.g (mg.L^{-1})^n)$	$n$	$R^2$
MB	0.998	11.28	1.56	6.477	2.93	0.967
RhB	0.999	4.05	4.41	3.098	5.44	0.991

Table 1, lists the values of  $q_m$  and  $K_L$ , as determined from the slope and intercept of the linear plots of  $C_e/q_e$  versus  $C_e$ , and the values of  $K_f$  and  $n$ , as determined from the slope and intercept of the linear plot of  $\ln q_e$  versus  $\ln C_e$ . The resulting correlation coefficients listed in Table 1 reveal that the data were fitted better by the Langmuir equation than by the Freundlich equation for MB and RhB. Fitting of the Langmuir isotherm indicates monolayer coverage of these two adsorbents on the surface of NIO during adsorption. The maximum monolayer copper uptake ( $q_m$ ) was found to be  $4.05 \text{ mg.g}^{-1}$  for RhB and  $11 \text{ mg.g}^{-1}$  for MB.

Adsorption kinetics of RhB and MB

Effect of the initial concentration of dyes

Figure 2 (a) and (b) represent the effect of initial concentration of methylene blue and rhodamine B on the adsorption kinetics. It can be seen that the adsorption efficiency decreased with the increase of the initial dye concentration (the initial concentration of dye increased from  $8.10^{-6} \text{ mol.L}^{-1}$  to  $4.10^{-5} \text{ mol.L}^{-1}$ ). The results reported in the inserted figure showed that the adsorption removal decreased from 33% to 2% and from 38 to 5% for MB and RhB respectively.



**Figure 2. Effect of initial dye concentration; a: MB, b: RhB, on dye removal.**

In order to investigate the mechanism of adsorption, the pseudo first-order and the pseudo second-order adsorption models were used to test dynamical experimental data. The first-order rate expression of Lagergren [27] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

Where  $q_e$  and  $q_t$  are the amounts of dye adsorbed on adsorbent at equilibrium and at time  $t$ , respectively and  $k_1$  is the rate constant of first order adsorption. The slopes and intercepts of plots of  $\ln(q_e - q)$  vs.  $t$  were used to determine the first-order rate constant  $k_1$ . In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [27]. The second-order kinetic model [28] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \quad (7)$$

Where  $k_2$  is the rate constant of second-order adsorption. The slopes and intercepts of plots of  $t/q_t$  vs.  $t$  were used to calculate the second-order rate constant  $k_2$  and  $q_e$ . It is more likely to predict the behavior over the whole range of adsorption and is in agreement with the chemisorption mechanism being the rate-controlling step [27-28]. Table 2 lists the results of rate constant studies for different initial dye concentrations by the pseudo first-order and second-order models.

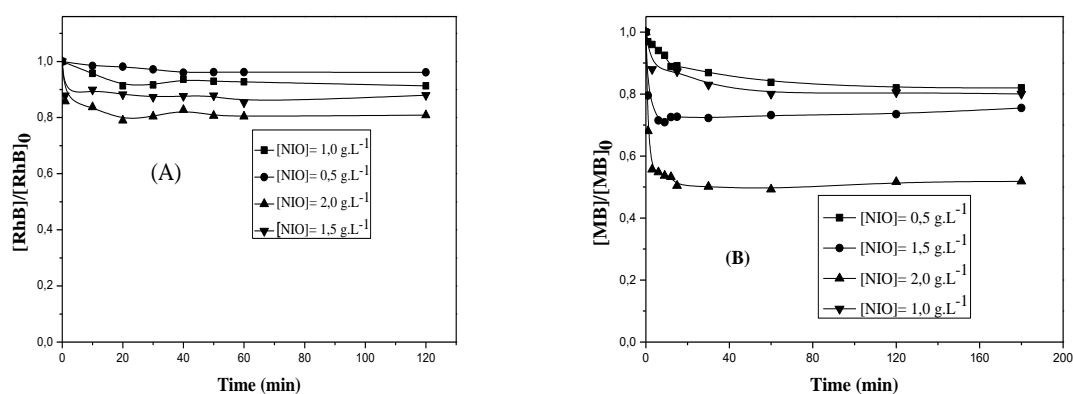
**Table 2: First-order kinetic model and the second-order model adsorption kinetic parameters for MB and RhB onto NIO.**

Initial concentration of dye	First-order kinetic model			Second-order kinetic model		
	$Q_e$	$k_1$	$R^2$	$k_2$	$Q_e$	$R^2$
[MB]= $4.10^{-5}$				$2.93 \times 10^5$	$7.96 \times 10^{-7}$	0.964
[MB]= $3.10^{-5}$	$10^{-6}$	$9.41 \times 10^{-3}$	0.81	$5.29 \times 10^4$	$3.89 \times 10^{-6}$	0.998
[MB]= $2.10^{-5}$	$1.125 \times 10^{-6}$	$1.1 \times 10^{-2}$	0.85	$5.34 \times 10^4$	$2.5 \times 10^{-6}$	0.999
[MB]= $1.10^{-5}$	$8.38 \times 10^{-6}$	$5.09 \times 10^{-4}$	0.67	$8.96 \times 10^4$	$1.48 \times 10^{-6}$	0.999
[MB]= $8.10^{-6}$	$6.77 \times 10^{-6}$	$7.99 \times 10^{-4}$	0.68	$4.89 \times 10^4$	$1.55 \times 10^{-6}$	0.997
[RhB]= $4.10^{-5}$	$4.781 \times 10^{-7}$	$5.975 \times 10^{-2}$	0.74	$7.73 \times 10^5$	$2.24 \times 10^{-6}$	0.998
[RhB]= $3.10^{-5}$	$7.615 \times 10^{-7}$	$5.992 \times 10^{-2}$	0.74	$8.83 \times 10^5$	$3.62 \times 10^{-6}$	0.998
[RhB]= $2.10^{-5}$	$2.86 \times 10^{-6}$	$5.538 \times 10^{-2}$	0.98	$2.39 \times 10^5$	$3.45 \times 10^{-6}$	0.999
[RhB]= $1.10^{-5}$	$5.53 \times 10^{-6}$	$1.01 \times 10^{-3}$	0.91	$6.14 \times 10^5$	$3.73 \times 10^{-6}$	0.999
[RhB]= $8.10^{-6}$	$1.072 \times 10^{-6}$	$1.92 \times 10^{-2}$	0.51	$4.67 \times 10^5$	$2.41 \times 10^{-6}$	0.998

The correlation coefficient  $R^2$  for the pseudo second order adsorption model has extreme high value. These suggest that the pseudo second-order adsorption mechanism is predominant and that the overall rate of the dye adsorption process appears to be controlled by the chemisorptions process [29].

#### Effect of initial concentration of NIO

To check the influence of the adsorbent dose on the adsorption kinetics and the percentage of elimination of RhB and BM, we conducted a series of experiments, maintaining the concentration of dyes constant ( $[BM] = 10^{-5}$  M,  $[RhB] = 4 \times 10^{-5}$  M), the temperature is 20 °C and the adsorbent dose varies between 0.5 and 2.0  $g \cdot L^{-1}$ . The obtained results are shown in figure 3.



**Figure 3. Effect of NIO doses on the kinetic of adsorption of (A) RhB, (B) MB.**

From fig.3 A and B, it is found that the percentage of adsorption of the two dyes increases with the increase of the adsorbent dose's, it is equal to 18 %, 20 %, 27 % and 50 % for MB and 4 %, 7 %, 15 % and 20 % for RhB, when iron oxide doses are equal to 0.5 g.L<sup>-1</sup>, 1.0 g.L<sup>-1</sup>, 1.5 g.L<sup>-1</sup> and 2.0 g.L<sup>-1</sup> respectively.

#### Effect of pH on adsorption of RhB and MB onto NIO

The effect of pH value on the adsorption of dye onto NIO was determined with a pH range of 2–11 for RhB and from 2 to 6 for MB, which was adjusted by titrating diluted NaOH or HClO<sub>4</sub> before reaction. In fact, the maximum absorbance of methylene blue decreases at basic pH that is why monitoring the effect of pH on the MB percentage adsorption on the surface of the oxide of iron has been only studied at pH acid. Figure 4 shows the performance of NIO adsorbent in adsorbing MB and RhB at different solution pH values.

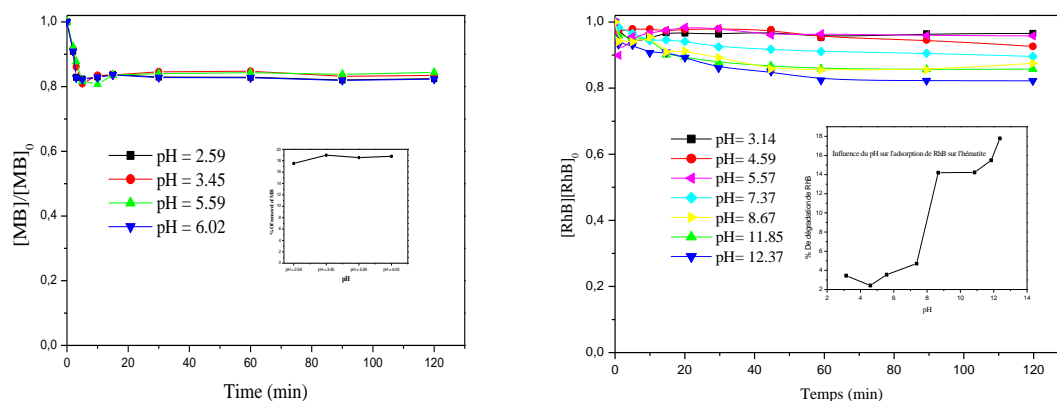


Figure 4. The effect of pH value on the adsorption of MB and RhB by NIO at 20 °C.

From fig.4, we can see that, contrasting to MB, the adsorption capacity of the RhB is affected very highly by the pH. Since the structure of RhB and MB at different pH are the same, the NIO is positively charged at pH below 8.3 (the pzc of NIO) and negatively when the pH is higher than 8.3. It is why, the percentage of adsorption of the two dyes is low in acidic medium (pH<8.3). However, from pH equal to 8.3 (the pzc NIO), the percentage adsorption of Rhodamine B is significantly increased, because of the existence of the electrostatic attraction between the negatively charged surface of NIO and positively charged dye.

#### CONCLUSION

Adsorption experiments showed that the uptake capacity on the NIO for MB and RhB were 11 and 4.05 mg.g<sup>-1</sup> respectively, the adsorption capacity of RhB and MB onto NIO increased when the initial concentration of both dyes decreasing. The Langmuir equation fitted the sorption isotherm well. The basic pH found to be most favorable for the adsorption of RhB

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