Kinetics of Congo red Dye Adsorption onto Marble Powder Sorbents

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ABSTRACT: The aim of this present work is evaluation of the effect of marble powder, which is an industrial discharge, in the adsorption of "Congo Red" dye, used in traditional industries of textile.

The effect of various experimental factors; adsorbent dose, contact time (equilibrium is established after 90 minutes), dye concentration and pH media, were studied by using the batch technique.

The isotherms of adsorption data were analyzed by various adsorption isotherm models such as Langmuir and Freundlich. The dye Congo Red adsorption by marble powder made have excellent performance related to the adsorption potential.

KEYWORDS: Adsorption isotherm, Marble powder, Congo Red.

I. INTRODUCTION

Azo dyes are the most important and most used for coloring in the textile industries, endanger human health due to either toxic or mutagenic and carcinogenic effects [1] .They are very stable because of their aromatic structures, are difficult to degrade.

They can cause environmental pollution problems by the formation of hazardous aromatic amines through metabolic processes in plants and animals. They can cause carcinogenic and mutagenic effect to animals, even at low concentrations [2] .The azo dye can also cause coloration of the surface of the water, which would block the penetration of sunlight and lower oxygen levels in the water.

Moreover, the azo dyes are difficult to deteriorate owing to their complexity aromatic and their molecular structure which is stable [3].

Congo red (sodium salt of benzidinediazo bis-1-naphthylamine-4-sulfonic acid) is an azo dye and the first synthetic anionic dye of azo dyes, which is synthesized by coupling of the tetra benzidine with two molecules napthionique acid [4].

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This dye can cause allergic reactions [5] .Congo Red Treatment in wastewater is difficult because the dye is generally present as sodium salt which gives it very good solubility in water. Through their chemical structures, dyes resist fading when exposed to light, in water and in contact with many chemicals product, they are difficult to be discolored when they are released into the aquatic environment.

Many processing techniques including biological treatment, coagulation, flotation, oxidation, ozonation and nanofiltration are used for the removal of dyes in wastewater [6-8].

Adsorption is recognized as one of the most efficient methods for removing dyes from aqueous solutions. In recent years, compounds such as the nanoporous silica, hematite, γ-Fe_2O_3 / SiO_2, $CuFe_2O_3$, mesoporous TiO_2, bentonite, activated carbon ... were used to eliminate the azo dyes [9-11].

II. MATERIALS AND METHODS

II-1 Adsorbate

Concentrations of dyes were determined by finding out the absorbance characteristic wavelength using UV spectrophotometer (Jasco). A standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (l_{max}) was determined from this plot. The l_{max} for CR are found to be 497 nm. Calibration curves were plotted between absorbance and concentration of the dye solution.
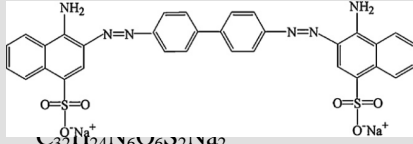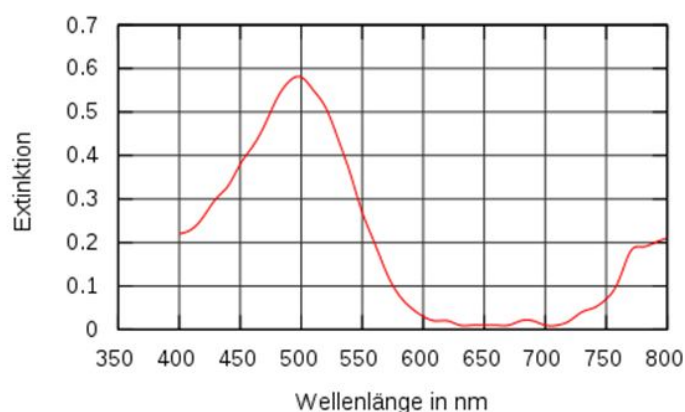

Figure 1: Absorption Spectrum Red Congo dye

The adsorbent used is the Congo Red. Table 1 represents a descriptive card of this dye (CR).

Table 1	structure and characteristics of Direct Yellow 50 dye
Name	Congo Red
Chemical structure	
Molecular formula	$C_{32}H_{24}N_6O_6S_2Na_2$
Other name	Sodium salt of benzidine diazo bis-1-naphthylamine-4-sulfonic acid
Molecular weight (g/mol)	696.67
Maximum absorbance wavelength λ_{max}(nm)	497

II-2 Adsorbent

Marble powder (MP) used in this work was provided in powder form by the "Company Marble Great Northern". This adsorbent was used without any prior treatment.

II-3 Experimental procedure

The MP was tested for the adsorption of CR from aqueous solutions at room temperature conducted by mixing various amount of MP for RC dye removal in glass erlenmeyer flacks containing 250 ml of a dye solution at various pH using digital heating controlled magnetique stirrer (Stuart). Dye solutions were prepared using ultrapure water (MILLIPORE, direct-Q, UV3 with Pump) to prevent and minimize the possible interferences. The effect of several variable of MP dose (1-9 g/l), pH (2-10), contact time (0-120 min) and initial dye concentration (5-50 mg/l) were studied.

At the end of the adsorption experiment the dye concentration was determined, 4 ml of suspension was taken and then centrifuged for 10 min at a speed of 4000 rpm and the supernatant was immediately dosed by UV spectrophotometer (Jasco V530).

The pH of the solution is adjusted by addition of a minor amount of HCl or NaOH (0, 1 M). At the end of the experiments of adsorption, the concentration of dye was given by measuring the absorbance of the solution with $\lambda = 497$ nm using a UV-visible spectrophotometer. All the experiments were carried out in double and the median values are presented.

The amount of equilibrium adsorption Q_e (mg/g) was calculated using the formula:

$$Q_e = \frac{C_0 - C_e}{W} V$$

Where C_0 and C_e (mg/L) are the liquid concentrations of dye initially and at equilibrium, V is the volume of the solution (L) and W is the mass of dye adsorbent (g).

The dye removal percentage can be calculated as follows:

$$\% \text{ of dye removal} = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of dye in solution.

III.RESULTS AND DISCUSSION

III.1. Study of effect of various parameters on the adsorption of the Congo Red

A-Influence time of contact on the adsorption of the Congo Red

The study of the kinetics of elimination of the Congo Red by Marble powder MP in aqueous solution is shown in Figure 2. The analysis of the temporal evolution of the percentage of CR adsorbed per gram of MP, for a given concentration (from 5 to 50 mg/l), shows that it increases rapidly during the first 10 minutes and then reached equilibrium around a stationary maximum value. The increase observed during the first ten minutes is probably due to the abundance of active sites on the surface of the adsorbent. According to the curve of Figure 2 the contact time required to reach equilibrium conditions was 90 min.
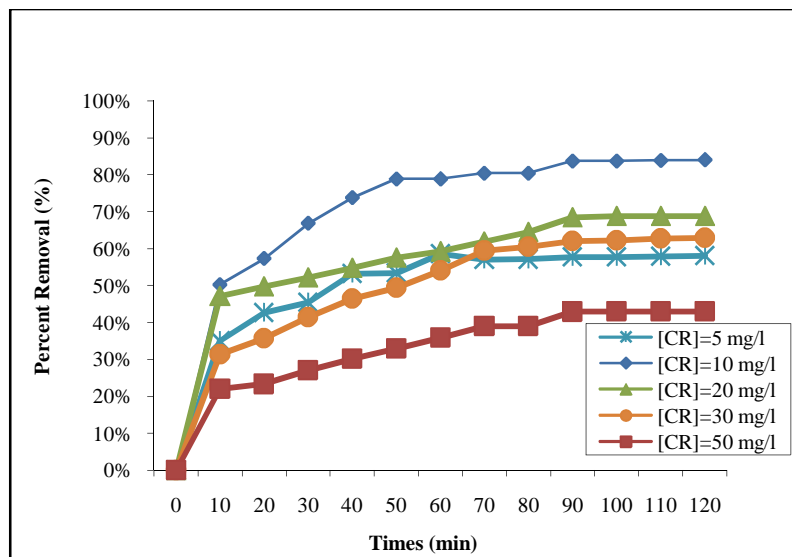

Figure 2: Influence time of contact on the kinetics of adsorption of the CR on MP

B-Influence amount of adsorbent

The study's results of the mass's effect of the adsorbent on the rate of reduction are represented in Figure 3.

The results show that for a dye concentration of 30 mg/l and for a contact time of 90 minutes, an increase of the mass of marble from 1 g to 8 g increases the percentage of removed dye (R%) in solution from 14% to 62%.

The increase in the percentage of removed dye (R%) in solution is due to the increase in the number of active sites of the MP.
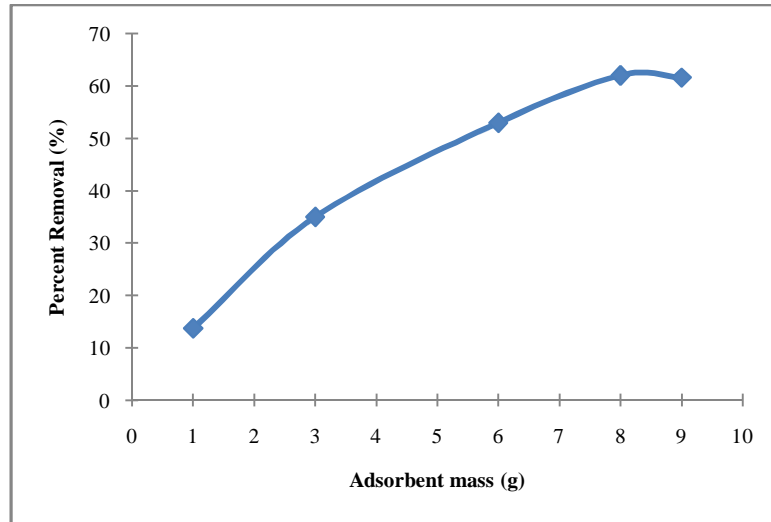
International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 2, February 2015

Figure 3 : Effect of adsorbent amounts on dye removal CR

C-Effect of initial dye concentration on adsorption of the dye by marble powder

Figure 4 show the analysis of the percentage of removed dye CR (%R) by MP. The results shows that %R increases from 58% to 84% when the dye concentration change from 5 mg/l to 10 mg/l, beyond this value the %R is halved (84% to 43%) for a dye concentration of 10 mg/l to 50 mg/l, this could be interpreted by an increase of competitive molecules by increasing the initial dye concentration.

The results of the decrease in the abatement rate by increasing the concentration of the dye, are similar to those found on the adsorption of Congo Red on the activated carbon prepared from coir pith, where the percentage of elimination dye equilibrium decreased from 66.5% to 30.5% when the concentration of dye increases. It appears that the removal of dyes depends on their concentrations. [12].
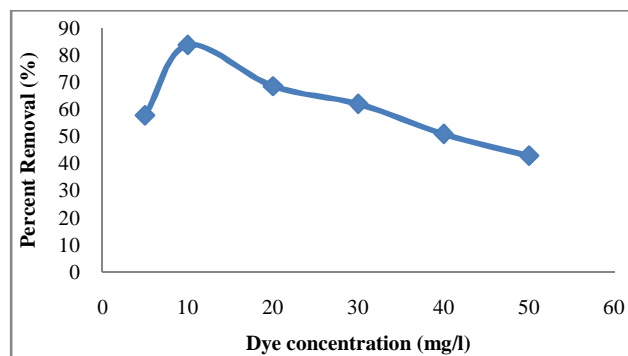

Figure 4: Effect of initial dye concentration on adsorption of the dye by the marble powder

D-Effect of the pH on the holding capacity of the Direct Yellow 50 dye

The Congo Red is an example of diazo dye, the initial pH influences the molecular structure of Congo Red dye in the aqueous solution [13]. In this research, the pH of the solution is maintained between 2.5 and 10.5. The percentage of the reduction rate of the dye by the marble powder at equilibrium for a dye concentration of 10 mg/l and a weight of the marble powder 8 g/l at different pH values is shown in Figure 5. It is found that the rate of reduction has not changed significantly in the pH range of 6.5 to 9.5, while the rate of reduction at pH 10.5 was relatively low. Similar results were obtained for the adsorption of Congo red on Bentonite Ca^{2+} [14].

International Journal of Innovative Research in Science, Engineering and Technology

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The initial pH of the dye solution affects the chemistry of the dye molecule and the adsorbent. The pH is also known to affect the structural stability of Congo Red and therefore its color intensity.

The variation of the color intensity by changing the pH can be due to structural changes in the dye molecule.

Over 80% of Congo Red abatement rate is observed in the pH range from 2.5 to 9.5. Similar results were observed for adsorption of Congo red on montmorillonite [15] and bentonite [11]. This is due to the chemical structure and behavior of Congo Red and marble powder under the conditions studied.

In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye ($D-SO_3Na$) are dissociated and converted to anionic ions:

$$D - SO_3Na \xrightarrow{H_2O} D - SO_3^- + Na^+$$
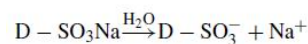
At initial pH, less than 8.3, a high electrostatic attraction exist between the positively charged surface of the adsorbent and the anionic dye. When the pH increases, the number of negatively charged sites increases and the number of positively charged sites decreases.

At initial pH above 8.3, the significant adsorption has taken place. In this pH range, the surface of the adsorbent is negatively charged. Thus, the electrostatic repulsion between the surface of the marble powder and the dye anion causes a little reduction of the elimination of the dye from the solution.

The Congo Red is a dipolar molecule ($H_3N + -R-SO_3^-$) at low pH [16]. Pigorsch et al. [17] have suggested the presence of two tautomers protonated species of Congo Red zwitterion, the ammonium form, where the protons are attached to the amino nitrogen and the azonium form, where the protons are attached to the azo nitrogen.

⊠

Many N-site functions are present in the Congo Red and some of the nitrogen atoms form bonds with hydrogen atom accepting protons from the solution and some are protonated to form cationic species [18].

Thus, the cationic dye is adsorbed by the powder of marble, probably by the cation exchange mechanism, replacing the Na^+.

A study was made by Acemoglu [19] , on the adsorption of Congo Red by fly ash, said that the interaction between Congo Red and fly ash occurs between the active sites of fly ash and SO_3^- and N-N- groups of Congo Red.

Fu and Viraraghavan [20] have suggested that both primary amines ($-NH_2$) fixed on both naphthalene rings on both extremity of the Congo Red molecule can be protonated ($-NH_3$) at initial pH 6 and may have a strong basicity, which may result the attraction between the protonated amine ($-NH_3$) and the negatively charged surface of the adsorbent. They also proposed that the electrostatic attraction is the main mechanism, while other mechanisms may also be involved in the adsorption of Congo Red.
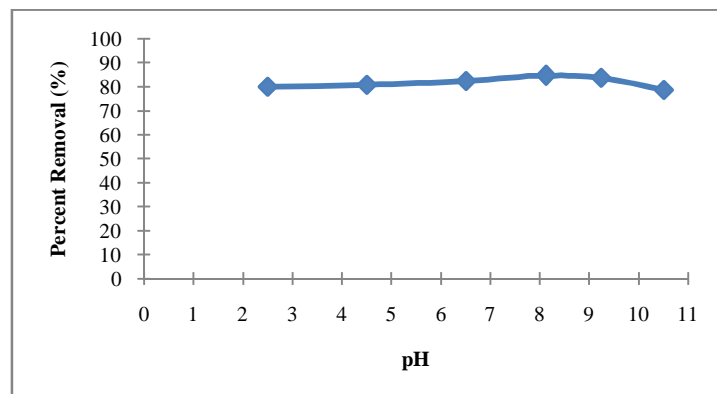

Figure 5 : Influence pH on the capacity of adsorption of the Direct Yalow 50

III.2. Adsorption kinetics

The model of the kinetics of first order is adapted the most for the weakest concentrations of aqueous solution. This model is presented by the relation of Lagergren [21], based on the adsorbed quantity, is the first equation speed established to describe the kinetics of adsorption in a liquid/solid system. This model of pseudo-first-order is represented by the following relation [22]:

Where qt: quantity of adsorbate adsorbed at t $\ln(q_e - q_t) = lnq_e - K_1 t$ lsorbed at equilibrium (mg.g^{-1});

k1: constant speed of adsorption of the pseudo model - first order (min^{-1}), T: time (min).

Evolution of ln (q$_e$-q$_t$) according to time, presented in our work. If the Lagergren relation is checked, while carrying ln(q$_e$-q$_t$) according to time, we must obtain a line of slope - K$_{ads}$. This indicates that the kinetics of adsorption of the CR on MP does not correspond to the kinetics of the pseudo-first order.

The reaction speed of pseudo-second-order depends on the quantity adsorbed on the surface on the adsorbent and the quantity adsorbed at equilibrium. The model of pseudo-second-order can, being represented in the following form [23]:

Where k$_2$: constant speed of adsorption of the mod $\dfrac{t}{q_t} = \dfrac{1}{K_2 q_e^2} + \dfrac{t}{q_e}$ order (g.mg-1.min^{-1}).

If this equation is checked, by tracing t/q$_t$ according to t, we must obtain a line of slope 1/q$_e$ and ordinate in the beginning equal to 1/ (K$_2$ q$_e^2$).

The modeling of the kinetics of adsorption of CR on adsorbent MP by the model of pseudo-second order is presented on Figure 6. These results are obtained with constant operating condition: with 20°C (agitation = 600 tpm and [MP] = 2 g/l).
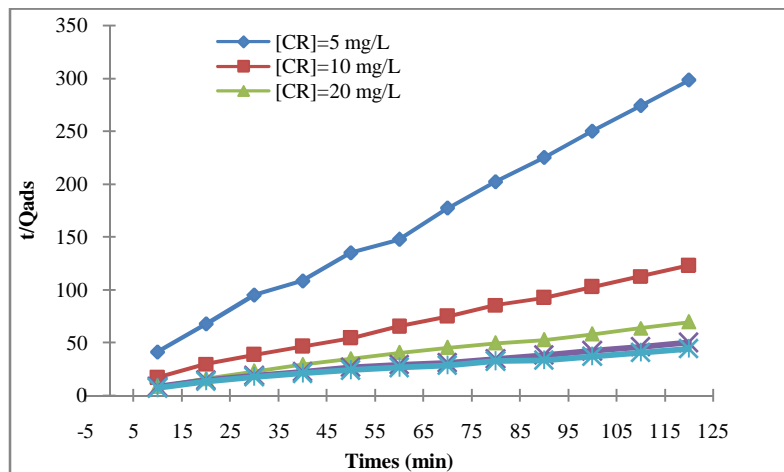

Figure 6 : Model of the pseudo-second-order for the adsorption of the DY50 on adsorbe MP

The corresponding parameters were gathered in the Table 2 which also presents the coefficients of correlation. These calculated coefficients are more about the unit for the kinetic model of pseudo second-order. That indicates that this last model described well the experimental results of the adsorption of the CR on the adsorbent.

C$_o$ (CR) (mg.L^{-1})	Q$_{exp}$ (mg.g^{-1})	Kinetics of the 2nd order		
		K$_2$ (g.mg^1.min^{-1})	Q$_{cal}$ (mg.g^{-1})	R^2
[CR]=5	0,4	0,277	0,434	0,997
[CR]=10	0,97	0,096	1,062	0,998
[CR]=20	1,71	0,043	1,886	0,992
[CR]=30	2,36	0,016	2,840	0,991
[CR]=50	2,7	0,012	3,267	0,984

Table 2 : Parameters characterizing the kinetics of adsorption of Congo Red on the marble powder.

III.3. Isotherms of adsorption

The last step is adsorption isotherms which study to model the curve, or more precisely to report it by a mathematical equation of the entire curve. Traditional models of Langmuir and Freundlich will be used for their simplicity of implementation.

The Langmuir model [24] is based on the following assumptions:
- Forming a single layer of adsorbate on the surface of the adsorbent.
- The existence of the defined sites of adsorption.
- The surface is uniform without interaction between the adsorbed molecules.

The Langmuir equation can be written as follows:

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \left(\frac{1}{KQ_{max}}\right)\frac{1}{Cr}$$

Where Q is the adsorption capacity in mmole or mg of solute per gram of adsorbent (mmol/g) or (mg/g), Q_{max} is the maximum adsorption capacity (mmol/g) or (mg/g), C_r is the concentration of residual solute (mmol/l) or (mg/l) and K is the equilibrium constant to the torque solute adsorption/adsorbent (l/mmol) or (l/mg).

The Freundlich model [25], is based on an empirical equation that reflects a variation of energy with the adsorbed amount. This distribution of interaction energies can be explained by heterogeneity of adsorption sites. Differently to the Langmuir model, the Freundlich equation does not provide an upper limit for the adsorption which restricts its application to dilute media. However, this model admits the existence of interactions between adsorbed molecules [38]. It is of the following form:

$$Ln\left(\frac{Ca}{m}\right) = LnK + \left(\frac{1}{n}\right)Ln\ Cr$$

Where m is the mass of the adsorbent (mg/l), C_a is the concentration of solute adsorbed (mmol / l) or (mg/l), K and n are the equilibrium constant to the torque solute adsorption/adsorbent and C_a/m is the adsorption capacity per unit mass of adsorbent (mmol/g) or (mg/g).

To study the adsorption isotherm of the dye at 25°C, a volume of one liter of distilled, water containing the red dye, at a concentration 30 g/l and the initial pH is brought into contact with different masses of MP. The stirring speed is set at 600 rpm. To determine the instantaneous concentration of the dye with time, the sample is centrifuged for 10 min at 4000 rpm, and the supernatant was immediately measured by a UV spectrophotometer.

To measure the adsorption isotherms of the red dye in the marble powder at 25 °C, the duration of contacting solution-adsorbent was set to 90 min, at which time it is ensured that there is no significant variation concentration of the dye in equilibrium.
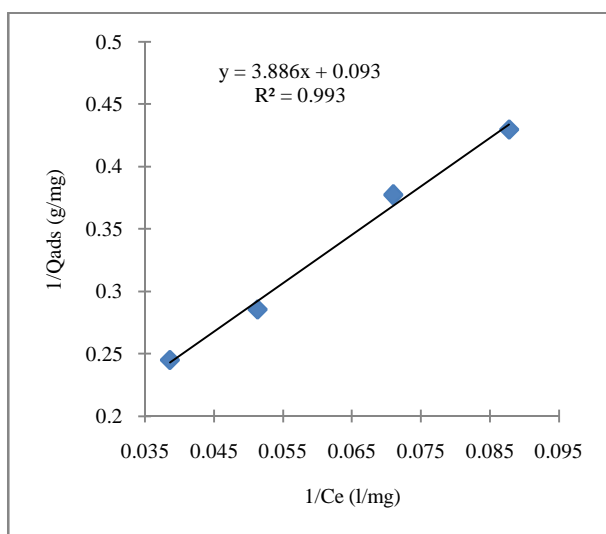

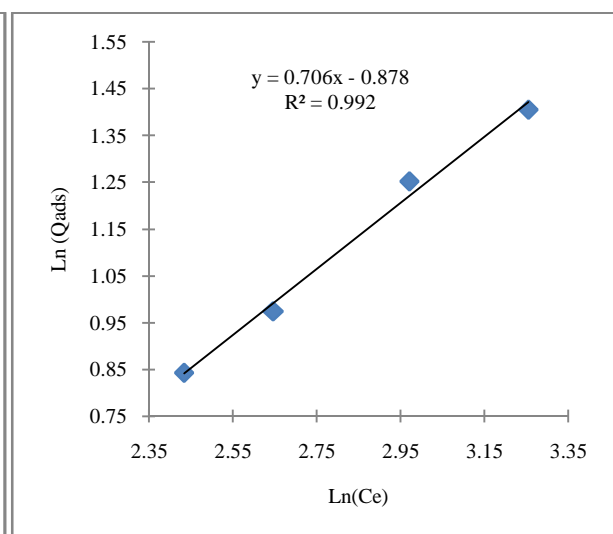**Figure 7:** Isotherm of Langmuir

Figure 8: Isotherm of Freundlich

The estimated parameters of the isotherms of adsorption of Langmuir and Freundlich, for the adsorption of Congo Red dye, by using adsorbent (MP), are gathered in Table 3.

Parameters	(mg/g)	K	K_f	n_f	R^2
Langmuir	10,75	0,024			0,993
Freundlich			0,42	1,42	0,992

Table 3 : The estimated parameters of the isotherms of adsorption of Langmuir and Freundlich

IV.CONCLUSION

Marble powder has shown its effectiveness in removal of the dye in aqueous solution. The adsorption is highly dependent on various parameters such as the mass of adsorbent, contact time, pH and initial concentration of the dye. The reduction rate of the Congo Red has increased with the increase of the mass of the adsorbent. On the contrary, the rate of reduction decreased with increasing concentration of the dye. While the change in pH has little influence on the adsorption of CR dye.

The kinetics of dye adsorption on the marble powder is not fast, the equilibrium is reached after 90 min. The dye adsorption isotherms by the marble powder following the model of Langmuir and Freundlich.

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