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Agadir Clay Materials as a New Adsorbent to Remove Cationic and Anionic Dyes from Aqueous Solutions

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Abstract

This study investigated the potential use of clay minerals originated from barrage situated in Agadir (Morocco), as a low-cost, natural, eco-friendly and alternative adsorbent for removal of Methylene Blue (MB) and Congo Red (CR), respectively a basic and an acid dye, from aqueous solution within a batch process. The adsorbent was characterized by X-ray diffraction, BET surface area, scanning electron microscopy (SEM) and dispersive energy of spectroscopy (EDS). The effects of various experimental parameters were examined such as contact time, initial dye concentration, adsorbent concentration, solution pH, and temperature. In order to determine the best-fit-isotherm, the experimental data were analyzed by the Freundlich and Langmuir equations. The adsorption equilibrium was well described by the Langmuir isotherm model with maximum adsorption capacity of $125\text{mg}\cdot\text{g}^{-1}$ for MB and $91\text{mg}\cdot\text{g}^{-1}$ for CR, at room temperature. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order models. The pH heavily affects the adsorption capacity, the removal percentage reached 99.22% for MB at $\text{pH}=10$, and 98.97% for CR at $\text{pH}=2$. The values of activation parameters such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also determined. However, the results pointed to the effectiveness of this Agadir Clay (AC) as an interesting alternative material with respect to more costly adsorbent used, for removing basic and acid dyes from aqueous solutions.

Keywords: Methylene Blue, Congo Red, Agadir Clay, Adsorption, Low-cost adsorbent.

Introduction

Controlling pollution is the main concern of society today. Large amounts of dyes are annually produced and used in textile, cosmetics, paper, rubber, plastics, leather, pharmaceutical, food and other industries. Today over 100,000 commercially available dyes exist, and more than 7×10^5 tons are produced annually, with a considerable fraction being discharged directly in aqueous effluent [1]. Dyes, which usually have a synthetic origin, are generally characterized by complex aromatic molecular structures which afford physicochemical, thermal, and optical stability [2].

The extensive use of dyes often poses pollution problems in the form of colored wastewater discharged into environmental water bodies. Most of the dyes are toxic and carcinogenic compounds; they are also recalcitrant and thus stable in the receiving environment, posing a serious threat to human and environmental health [3]. Not only do they harm the aesthetic nature of the environment, they are commonly toxic to aquatic life [4], by diminishing the transparency of the water, dyes modify the

penetration of solar radiation, and affecting the aquatic life and food web [5]. Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical, and commercial importance [6, 7].

Various physical, chemical and biological methods, including coagulation/flocculation, ozonation, membrane filtration and liquid-liquid extraction have been widely used for the treatment of dye-bearing wastewater. The advantages and disadvantages of every removal technique have been extensively reviewed [8, 9]. Adsorption of various dyes from aqueous solution has proven to be an excellent way to treat effluent also a cost effective technique. Adsorption is a very effective separation technique in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances, and the use of clays as alternative adsorbents has been receiving attention for the removal of dyes from wastewater in recent years [10, 11]. They have advantages over commercially available adsorbents in terms of low-cost, abundant availability, high adsorption properties, non-toxicity and large potential

for ion exchange, resulting from a net negative charge on the structure of the minerals. Utilization of clays could bring massive economic and environmental benefits to wastewater industries.

The main purpose of this study is to evaluate the adsorption capacity of locally available clay materials originated from barrage situated in Agadir (AC), to remove Methylene Blue (MB) and Congo Red (CR) from aqueous solutions. MB and CR are, respectively, basic and acid dye molecules and therefore release negative and positive charged colored moieties in aqueous solution, allowing the assessment of any preferential surface interaction. The chemical structures of these dyes are shown in figure 1(a) and (b). The effects of main parameters, i.e., solution pH, mass of adsorbent, dye concentration, contact time, and solution temperature, were studied. The kinetics, isothermics and thermodynamics parameters of adsorption were also evaluated.

Materials and methods

Adsorbent

The untreated clay used in this work is crushed then sifted in order to get fractions $<80 \mu\text{m}$. Afterwards, the support is rinsed many times with demineralized water, of $\text{pH} = 6.6$ and of conductivity $= 1.2 \mu\text{S}$. After every rinse, the clay is put in a sedimentation test, and during one hour of decantation, we recover the two thirds of supernatant volume. Finally, it is placed in an oven between 100°C and 110°C during 24 h, before being subjected to different adsorptions.

Adsorbates

Methylene Blue (MB), [cationic dye, chemical formula $= \text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$, molecular mass $= 373.90 \text{ g mol}^{-1}$, $\lambda_{\text{max}} = 665 \text{ nm}$]. Congo Red (CR), [anionic dye, chemical formula $= \text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$, molecular mass $= 696.7 \text{ g mol}^{-1}$, $\lambda_{\text{max}} = 497 \text{ nm}$], were obtained from Sigma-Aldrich

and used without further purification. The chemical structures of these dyes are shown in figure 1(a) and (b).

Experimental protocol

The ability of our clay mineral AC to adsorb MB and CR was tested at different conditions (Table 1) using a series of batch tests. The adsorption experiments were carried out to investigate the effect of pH, adsorbent dose, initial dye concentration, contact time and temperature on the adsorption of MB and CR on AC. The experiments were carried out in 200 ml conical flasks by mixing a pre-weighed amount of adsorbent with 100 ml of dye solution and the solution was agitated at 350 rpm on a stirrer, at natural pH of the dye solution (Table 1), at constant temperature (20°C) and with $R=1 \text{ g/l}$. All samples were filtered (through a $0.45 \mu\text{m}$ Millipore) prior to analysis using disposable syringes in order to minimize interference of the particles fines with the analysis. Afterwards, the filtrate was immediately dosed by spectrophotometer type JASCO V-630 at λ_{max} . (MB $\lambda_{\text{max}} = 665 \text{ nm}$; CR $\lambda_{\text{max}} = 497 \text{ nm}$). The percentage removal of dye and amount of dye adsorbed on adsorbents (Q) was calculated by Eq. (1) and (2), respectively:

$$Q = (C_0 - C_e)/R \quad (1)$$

$$\% \text{ removal} = (C_0 - C_e).100/C_e \quad (2)$$

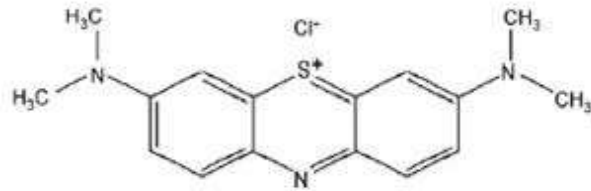
With:

Q: Quantity of dye adsorbed per gram of adsorbent (mg/g).

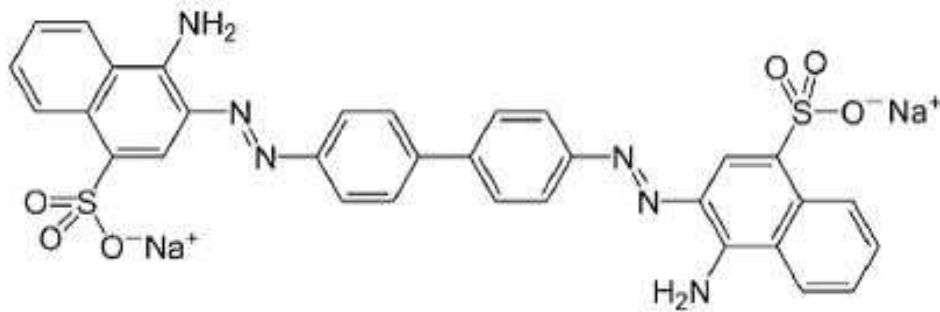
C_0 : Initial concentration (mg/l).

C_e : Equilibrium concentration (mg/l).

R: Mass of adsorbent per liter of aqueous solution (g/l).



(a)



(b)

Figure 1: Chemical structures of (a) Methylene Blue (MB) and (b) Congo Red (CR)**Table 1. Experimental conditions**

Experiment	Conditions					
	Solution pH	AC dose (g/l)	Concentration (mg/l)	Temperature (°C)	Mixing Time (min)	Volume (ml)
Effect of contact time	pH _{natural} =5.9 (MB) pH _{natural} =6.2 (CR)	1	100	20	180	500
Effect of solution pH	2-10	1	100	20	120 for MB 180 for CR	100
Effect of sorbent dose	pH _{natural} =5.9 (MB) pH _{natural} =6.2 (CR)	0,2-3	100	20	120 for MB 180 for CR	100
Effect of temperature	pH _{natural} =5.9 (MB) pH _{natural} =6.2 (CR)	1	100	20-60	120 for MB 180 for CR	100
Effect of initial dye concentration	pH _{natural} =5.9 (MB) pH _{natural} =6.2 (CR)	1	20-200	20	120 for MB 180 for CR	100

Characterization of the adsorbent

The clay was characterized by diffraction of X-rays (XRD), using the diffract meter XPERT-PRO type PW3064, with copper anticathode. The spectrum of XRD shows that the untreated clay contains a large amount of the Kaolinite and Illite followed by Quartz and Calcite (Figure 2).

The specific surface area was measured using the Brunauer–Emmet–Teller (BET) method. Result was obtained by nitrogen (N₂) adsorption-desorption isotherms at (77K) using an automated gas sorption system (Micromeritics, QUANTACHROME instrument). It is equal to 53.47 m²/g.

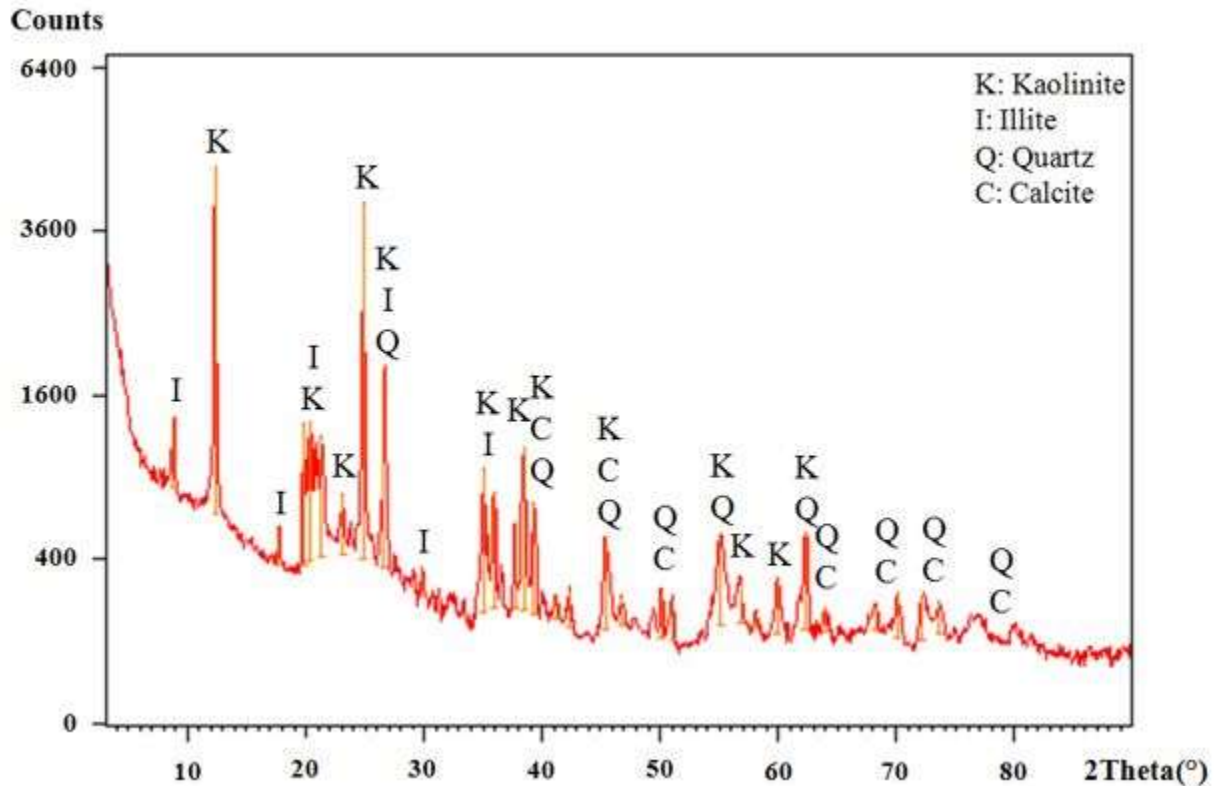


Figure 2: X-rays diffraction of the AC

The surface morphology of the clay was observed by Scanning Electron Microscopy (SEM, using ZEISS ULTRA PLUS) with a coupled Energy Dispersive Spectroscopy (EDS), at 5 kV, after gold coating (Figure 3). The SEM of this figure shows the scattering of flaky shaped particles with consistent

distribution of deep and apparent micropores that formed noticeable cage-like cavities. These cavities provide suitable binding sites for dyes molecules. On the basis of this fact, it can be concluded that AC presents an adequate morphology for MB and CR adsorption.

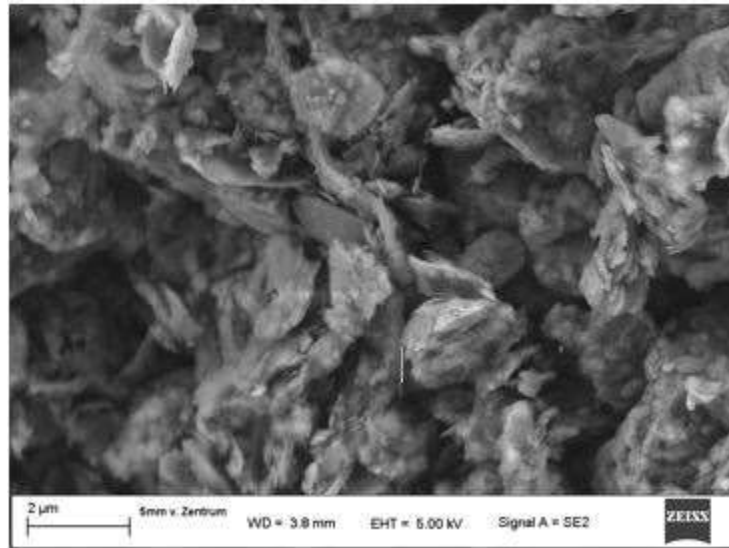


Figure 3: SEM micrograph of the AC particles

The clay is also characterized by the utilization of dispersive energy of spectroscopy (EDS, type X'Pert Pro, PANALYTICAL) (Figure 4). The elements that

constitute the clay are given in atomic and mass percentage in table 2.

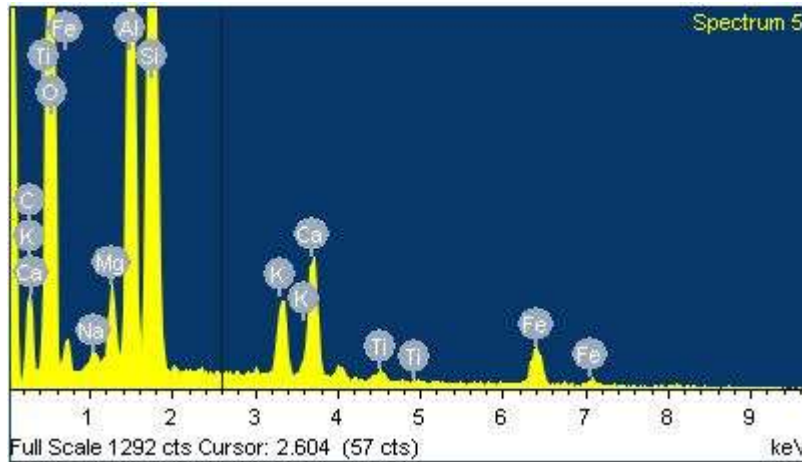


Figure 4: Dispersive energy spectrum of AC spectroscopie (EDS)

Table 2: Atomic and mass percentage of the clay constituents

Elements	O	C	Na	Mg	Al	Si	K	Ca	Ti	Fe
% Atomic	67.71	3.27	0.26	1.03	7.20	14.82	1.36	2.29	0.26	1.79
% Mass	53.58	1.94	0.30	1.24	9.61	20.59	2.63	4.53	0.62	4.94

The point of zero charge (PZC) of our clay was determined by the solid addition method, as described by Vieira et al. [12]. Nine vials containing solutions of pH in the range of 2–10 (pH₀) and 0.10 g of AC were shaken for 24 h at room temperature and the final pH was measured. The difference between

the initial and final pH ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_f$) was plotted against the initial pH (pH₀) and the point where $\Delta\text{pH} = 0$ was taken as the point of zero charge. As shown in figure 5, the pH_{PZC} of AC was determined to be 5.6.

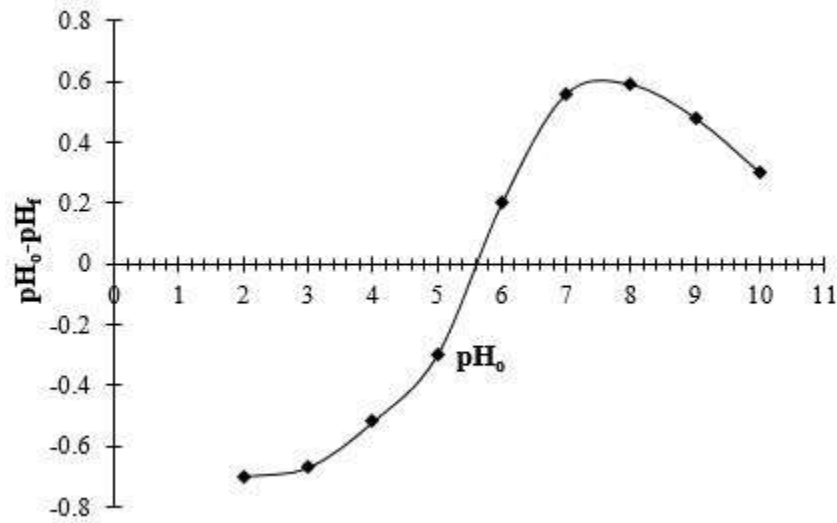


Figure 5: Point of zero charge of AC

Results and discussion

Effect of contact time

The adsorption of both dyes was studied as a function of contact time in order to determine the required time for maximum adsorption. The plots for MB and CR (100 mg/l) are shown in figure 6. The kinetic study indicates that the adsorption equilibrium state is reached after a contact time of 30 min for MB with Q=78.39 mg/g and 120 min for CR with Q=61.19 mg/g, since no change in the adsorbed amount is detected afterward. The plots also indicate that the adsorption is initially fast for MB and slower for CR with increasing contact time; this probably is due to rapid and slow diffusion of dye molecules into the

macro- and micropores of the adsorbent. Adsorption processes in liquid–solid interfaces are frequently affected by boundary layer diffusion, or external mass transfer, the nature of the dye and intraparticle diffusion [13]. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of dye on the adsorbent surface [14, 15]. To be sure that the equilibrium state is reached for higher concentrations, a contact time of 2h and 3h were applied in the adsorption experiments respectively for MB and CR.

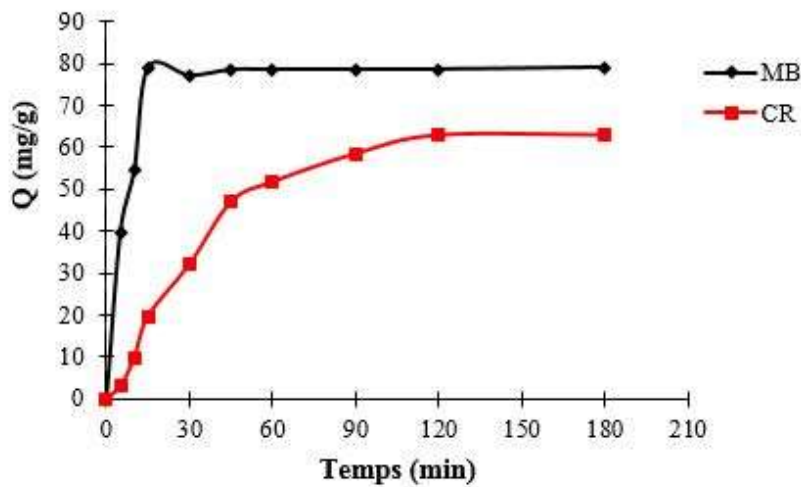


Figure 6: Effect of contact time on the adsorption of MB and CR

Adsorption kinetics

The kinetics of adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. Two kinetic models were applied to the adsorption kinetic data in order to investigate the behavior of adsorption process of dyes onto our clay. These models are the pseudo-first-order and pseudo-second order models.

Pseudo-first-order kinetic model

The pseudo-first order equation of Lagergren [16] is given by:

$$dq_t/dt = K_1(q_e - q_t) \tag{3}$$

Where q_t and q_e are the amounts of dye adsorbed (mg/g) at time t and equilibrium, respectively, and k_1 is the pseudo-first order rate constant for the adsorption process (1/min).

Pseudo-second-order kinetic model

The pseudo-second order chemisorption kinetic rate equation is expressed as [17]:

$$dq_t/dt = K_2(q_e - q_t)^2 \tag{4}$$

Where k_2 is the equilibrium rate constant of pseudo-second order equation (g/mg.min).

The straight line plots of $\ln(q_e - q_t)$ against time were tested to obtain the pseudo-first adsorption rate constant (Figure 7a). The pseudo-second order constants were determined by plotting t / q_t against t (Figure 7b). The kinetic constants, correlation coefficients and the predicted and experimental q_e values are given in table 3. The results showed that the adsorption system of MB followed the pseudo second order model, with R^2 value of 0.999 and the calculate q_e value from the model is also in good agreement with the experimental value. Concerning the CR, the process follows pseudo-first-order kinetics, with R^2 value of 0.926 and the calculated q_e value obtained from this model give reasonable value since it is good compared with experimental q_e value.

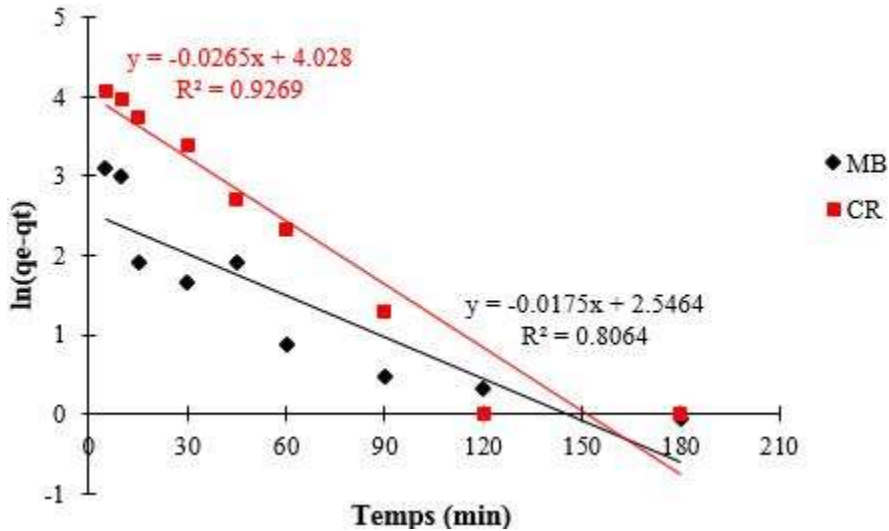


Figure 7 a: Pseudo-first-order kinetic plots for MB and CR adsorption onto AC

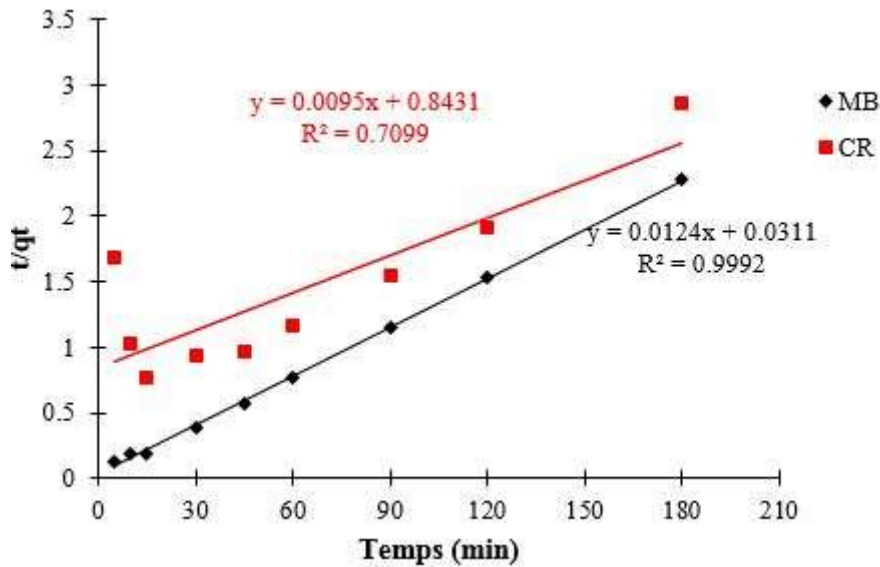


Figure 7 b: Pseudo-second-order kinetic plots for MB and CR adsorption onto AC

Table 3: Kinetic parameters for the adsorption of MB and CR onto Agadir Clay

Adsorbates	Pseudo-first-order			Pseudo-second-order		
	$K_1(\text{min}^{-1})$	$q_e(\text{mg/g})$	R^2	$K_2(\text{g/mg}\cdot\text{min})$	$q_e(\text{mg/g})$	R^2
MB	0,017	12,75	0,806	$4,645.10^{-3}$	83,33	0,999
CR	0,026	56,14	0,926	$9,608.10^{-5}$	111,11	0,709

Effect of sorbent dose

Adsorbent dose is an important parameter influencing adsorption processes since it determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of adsorbent dose on removal of MB and CR (100 mg/l) were studied in range of 0.2–3.0 g/l. Figure 8 showed that the % removal of

dye increased from 19.75% to 80.83% for MB and 2.84% to 60.95% for CR, as adsorbent dose increased from 0.2 to 1 g/l. Such a trend is attributed to an increase in the adsorptive surface area and the availability of more binding sites [18]. Further increase in adsorbent dose, did not show significant increase in % removal of dye, therefore, 1 g/l adsorbent dose was chosen for all experiments.

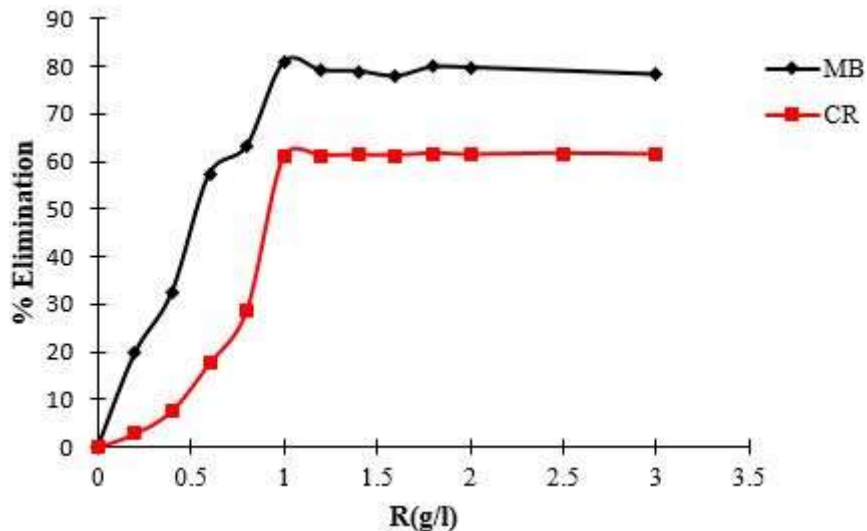


Figure 8: Effect of adsorbent dose on adsorption of MB and CR

Effect of solution pH

Generally pH is considered to be an important parameter which controls the adsorption at water-adsorbent interfaces. The effects of initial pH on adsorption percentages of dyes were researched over a range of pH values from 2 to 10 (Figure 9). The initial pH values were adjusted by adding 0.1M of HCl or NaOH. As can be seen in figure 9, the highest adsorption capacity was 99.22% for MB at pH=10, and 98.97% for CR at pH=2. The pH_{PZC} of AC was determined to be 5.6, at a solution $pH > 5.6$ the AC surface is negatively charged and at $pH < 5.6$ the surface becomes positively charged.

As the pH of the system decrease ($pH < 5.6$), there is a significant increase in electrostatic attractions between negative charges of anionic dye (CR) and positive charges of clay sites, thereby increasing dye

adsorption [19], i.e. the adsorption of CR^- moieties is favorable. However, reduced adsorption of MB (cationic dye) reflects the compete of excess H^+ ions with dye cations for the adsorption sites

As the pH of the system increases ($pH > 5.6$), the number of negatively charged sites raises and the number of positively charged sites declines. A low adsorption capacity can be attributed to ionic repulsion between the clay surface and the anionic dye molecules of CR. Besides this, an abundance of OH^- ions in basic solution creates a competitive environment with anionic ions of CR for the adsorption sites causing a decrease of adsorption [20, 21]. In contrast, it was causing better MB cations adsorption through the electrostatic attraction phenomenon, i.e. the adsorption of MB^+ moieties is favorable.

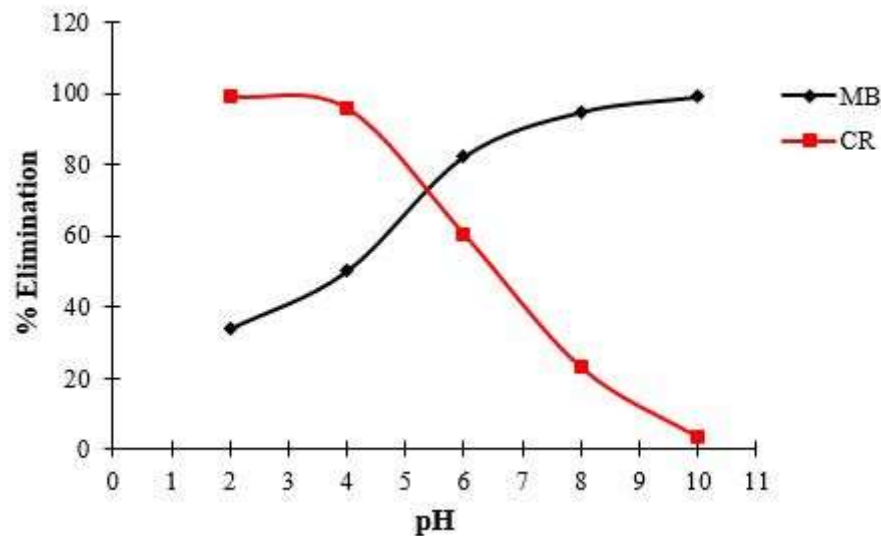


Figure 9: Influence of pH on the adsorption of MB and CR

Influence of initial dye concentration

The influences of dye concentration on adsorption percentages of dyes were estimated. As shown in figure 10, when the dye concentration was increased from 20 to 200 mg/l, the percentages of dyes sorbed decreased from 98.08 to 64.42 % for MB and from 88.85 to 51.50 % for CR. This is probably due to the limitation of adsorption sites on the clay mineral surface [21, 22]. The reduction of removal percentage of every dye with the increase of its initial concentration can be explained as follows: because the mass of AC is constant for all concentrations, the dye molecules must compete for sites onto which they can adsorb. In fact, when the dye concentration

is higher, the ratio of the adsorbate molecules to AC is greater, and therefore the percentage of pollutant removed is lower. Nevertheless, the experimental adsorption capacity of days at the selected conditions increased from 19.46 to 128.37mg MB/g AC, and from 17.77 to 103.01mg CR/g AC when the concentration of dye was increased from 20 to 200 mg/l. This can be explained by the enhancement of mass transfer rates due to a higher dye gradient concentration, subsequently causing the uptake of more adsorbate molecules and thereby increasing the mass ratio of dye to AC (i.e. adsorption capacity)

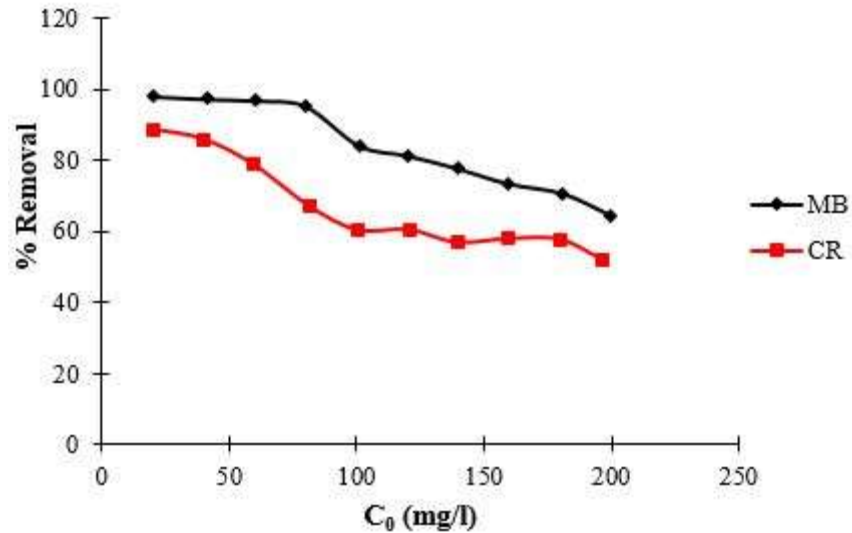


Figure 10: Influence of dye concentration on adsorption of MB and CR

Adsorption isotherm

The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state [23]. It is expressed by relating the amount of adsorbate taken up per gram of adsorbent, Q_e ($\text{mg}\cdot\text{g}^{-1}$), to the equilibrium solution concentration, C_e ($\text{mg}\cdot\text{l}^{-1}$), at a fixed temperature (25°C) and at different concentrations of dyes solution (20, 40, 60, 80, 100, 120, 140, 160, 180 and 200mg/l), (Figure 11). Monolayer saturation is attained for both dyes, but the MB uptake is higher than that of CR.

The adsorption capacity and other parameters were evaluated using Langmuir and Freundlich isotherm models. The Langmuir isotherms are based upon an assumption of monolayer adsorption onto surface of adsorbent containing a finite number of adsorption sites of uniform energies of adsorption. It can be written as follows [24]:

$$Q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (5)$$

The linearized form of Eq. (5) can be written as Eq.

$$C_e/q_e = 1/bQ_m + C_e/Q_m \quad (6):$$

$$C_e/Q_e = 1/K_L \cdot Q_m + C_e/Q_m \quad (6)$$

Where Q_e is the adsorption density (mg/g) of MB and CR at equilibrium, C_e is the equilibrium concentration (mg/l) of MB and CR in solution, Q_m is the monolayer adsorption capacity (mg/g) and K_L is the Langmuir constant ($1/\text{mg}$) related to the free energy of adsorption. The values of Q_m and K_L were calculated from the slopes ($1/Q_m$) and intercepts ($1/K_L Q_m$) of the linear plots of $1/q_e$ vs. $1/C_e$ (Figure 12) and are given in table 4. The maximum monolayer adsorption capacity of AC-MB and AC-CR systems was found to be 125 mg/g and 91 mg/g , respectively. The higher values of correlation coefficients (0.994 for MB and 0.977 for CR) indicate the applicability of Langmuir isotherm. The favorability of MB and CR adsorption onto AC was further analyzed using a dimensionless parameter ($R_L = 1 / (1 + K_L C_i)$) derived from the Langmuir equation where C_i is the initial concentration of the target dye under adsorption. The adsorption process can be defined as irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavorable ($R_L > 1$) in terms of R_L [25]. The calculated values of R_L for adsorption of MB and CR fall between 0 and 1 (Table 4); therefore, the adsorption process of these two dyes onto AC were favorable.

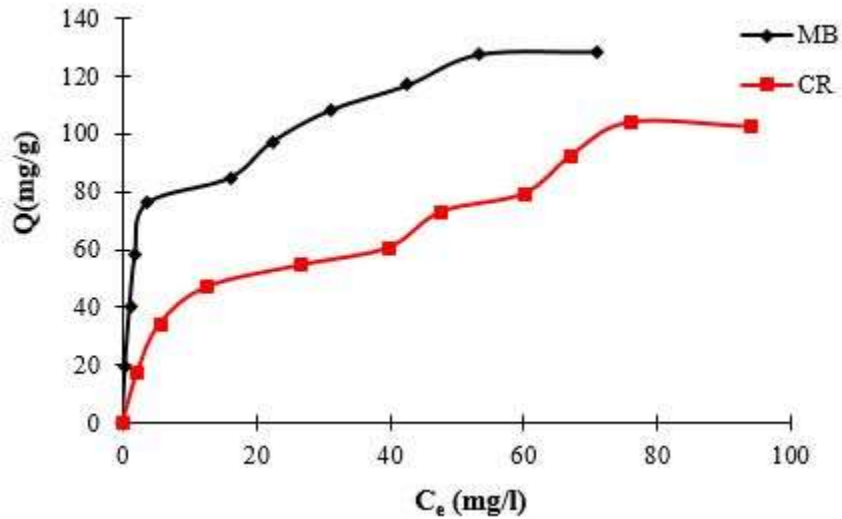


Figure 11: Adsorption isotherm of MB and CR

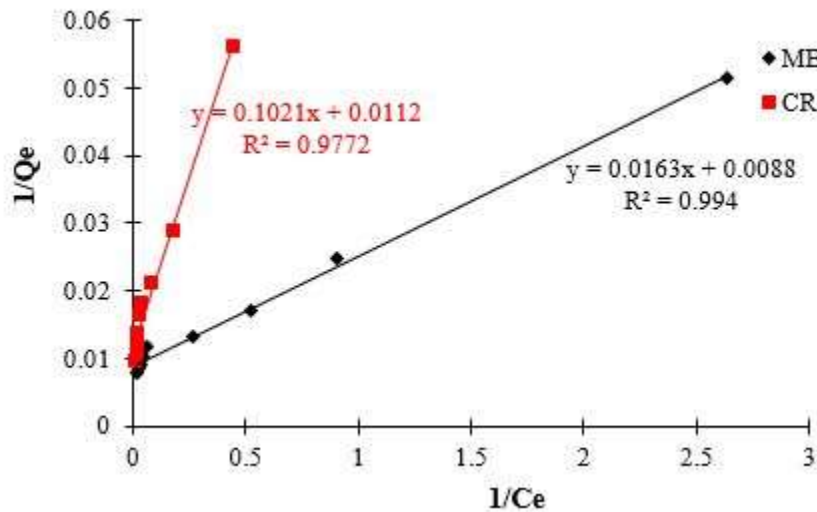


Figure 12: Langmuir isotherm linear plots for the adsorption of MB and CR

The Freundlich isotherm assumes that adsorption process occurs on heterogeneous surfaces and the capacity of adsorption is related to the concentration of MB and CR at the equilibrium. The Freundlich equation is expressed as follows [26]:

$$Q_e = K_f \cdot C_e^{1/n} \quad (7)$$

Logarithmic form of Eq. (7) can be written as Eq. (8):

$$\ln Q_e = \ln K_f + (1/n) \cdot \ln C_e \quad (8)$$

Where K_f and n are Freundlich constants related to adsorption capacity [$\text{mg g}^{-1}(\text{mg l}^{-1})^{-1/n}$] and adsorption

intensity of adsorbents, respectively. The values of the K_f and n were calculated from the intercepts ($\ln K_f$) and slopes ($1/n$) of the plots $\ln q_e$ vs. $\ln C_e$ (Figure 13) and are presented in Table 4. The values of regression correlation coefficients for all the four adsorption systems are closer to unity indicated the data were also fitted well in Freundlich isotherm model. The value $1/n$ gives an indication on the validity of the adsorption of adsorbent-adsorbate system. A value $1/n$ between 0 and 1 that indicates a favorable adsorption [27]. In addition to that, this also indicates that the adsorption capacity increases, and further, adsorption sites appear. When $1/n > 1$, the adsorption is not favorable, the adsorption connections become weak and the adsorption

capacity decreases. The values of $1/n$ were less than one (Table 4) revealed favorable adsorption conditions. The correlation coefficients values (0.911

for MB and 0,966 for CR) are lower than Langmuir values. Therefore, adsorption onto AC does not follow Freundlich isotherm closely for the two days.

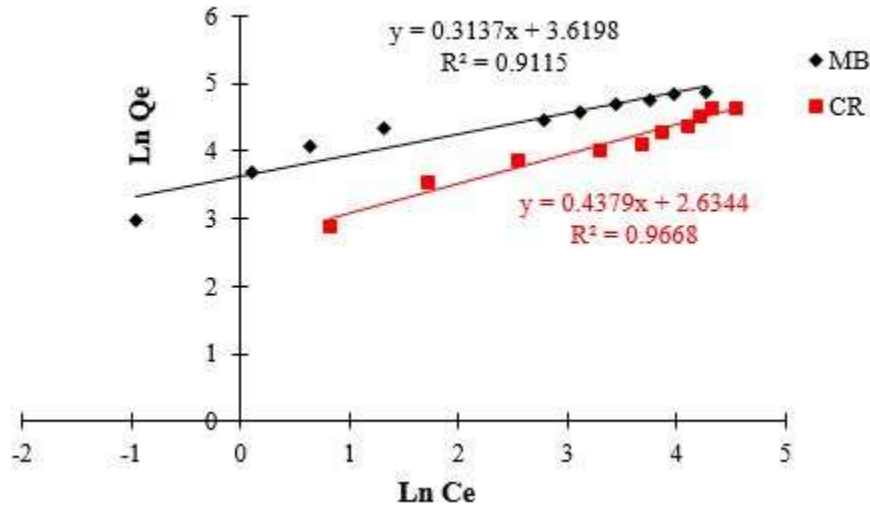


Fig. 13: Plot of linearized Freundlich isotherm for the adsorption of MB and CR

Table 4: Langmuir and Freundlich Isotherm parameters

Dye	Langmuir parameters				Freundlich parameters		
	Q_m	K_L	R^2	R_L	K_F	$1/n$	R^2
MB	125	0,5	0,994	$9,937 \cdot 10^{-3} \leq R_L \leq 0,091$	37,3	0,313	0,911
CR	91	0,107	0,977	$0,045 \leq R_L \leq 0,317$	13,929	0,437	0,966

Thermodynamic studies

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution [28]. In addition, changing the temperature alters the equilibrium capacity of the adsorbent for a particular adsorbate [28]. A study of the temperature

dependence of the adsorption processes therefore gives valuable information about the enthalpy and entropy changes accompanying adsorption [29]. Figure 14 shows the effect of temperature on the adsorption of MB and CR on AC, initially at 100 mg.l^{-1} , in the range of $20\text{--}60^\circ\text{C}$ ($293\text{--}333\text{K}$). The increase of solution temperature from 20 to 60°C causes increase of the equilibrium removal percentage of MB from 79.13 to 92.69% and decrease from 61.03 to 50.44% for CR.

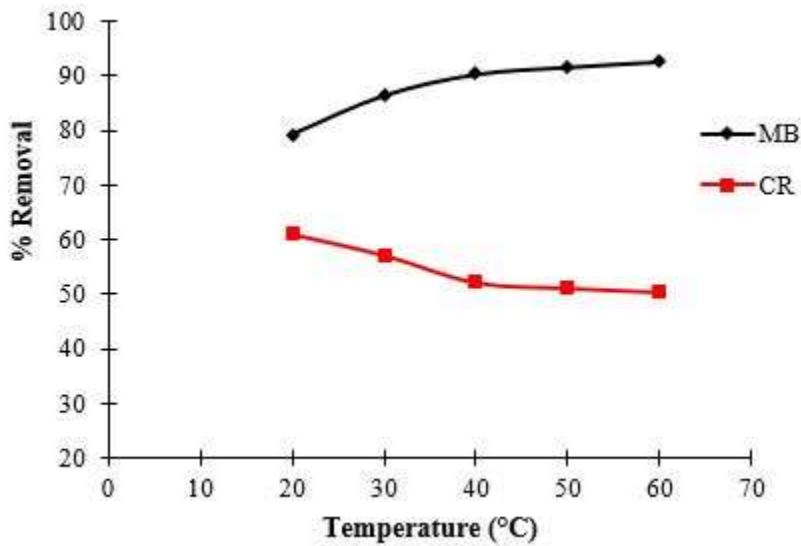


Fig. 14: Plot Effect of temperature on the adsorption of MB and CR

Thermodynamic reaction of adsorption process can be determined via thermodynamic parameters, such as the changes in the standard free energy (ΔG°), the enthalpy (ΔH°) and entropy (ΔS°) associated with the adsorption process, using the following relation:

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \quad (9)$$

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

Taking advantages of Eqs. (9) and (10), the van't Hoff equation can be written as:

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (11)$$

Where K_c is the equilibrium constant, which is the ratio of the equilibrium concentration of the dye ions on adsorbent to the equilibrium concentration of the dye ions in solution. R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the adsorption temperature in Kelvin. Values of ΔG° (kJ mol^{-1}) at

different temperatures were evaluated from Eq. (10), lot of $\ln K_c$ versus $1/T$ should give a linear line, where values of ΔH° (kJ mol^{-1}) and ΔS° ($\text{J mol}^{-1} \text{ K}^{-1}$) can be calculated from the slope and intercept of van't Hoff plots (Figure 15). The values of the thermodynamic parameters for the adsorption of MB and CR onto the clay are respectively collected in Table 5, the values of ΔG° for all tested temperatures were calculated to be negative, which suggests that the adsorption of MB and CR onto AC is spontaneous. Values of ΔG° between -20 and 0 kJ/mol indicate a physical adsorption process [30]. The adsorption process is endothermic for MB ($\Delta H^\circ > 0$) and exothermic for CR ($\Delta H^\circ < 0$). The positive value of ΔS° of MB indicates an increase in disorder of solid-liquid interface of material during adsorption of dye [31, 32]. Conversely, the negative values ΔS° of CR suggest a decrease in randomness at their solid/solution interface and no significant changes occur in the internal structure of the adsorbents through the adsorption.

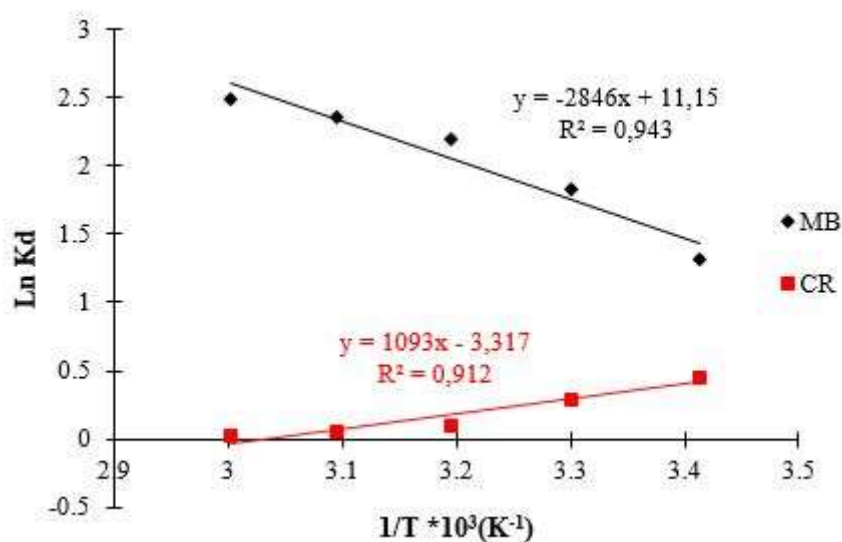


Fig. 15: Plot of $\ln K_L$ versus T^{-1} : estimation of thermodynamic parameters for the adsorption of MB and CR

Table 5: Thermodynamic parameters of MB and CR

Dye	ΔG° (kJ mol ⁻¹)					ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
	20°C	30°C	40°C	50°C	60°C		
MB	-1,316	-1,822	-2,199	-2,357	-2,493	23,650.10 ³	92,656
CR	-0,455	-0,296	-0,093	-0,052	-0,023	-9,082.10 ³	-27,564

Conclusion

This natural clay mineral (AC) is highly effective as low-cost adsorbent for the removal of MB and CR dyes from aqueous solutions. In batch studies, the adsorption was exceedingly dependent on various operating parameters, like: contact time, pH, initial dye concentration, amount of adsorbent and temperature. The adsorption equilibrium was attained within times of 30 min for MB and 120 min for CR. The kinetics of the adsorption was found to follow the pseudo second order model for the basic dye and pseudo-first-order for the acid dye. The equilibrium data fitted well in the Langmuir isotherm equation and the maximal uptakes were 125mg.g⁻¹ for MB and 91mg.g⁻¹ for CR, at room temperature. The increase in mass adsorbent leads to increase in dye adsorption due to increase in number of adsorption sites, R=1 g/l was chosen for all experiments. The reduction of removal percentage with the increase of the initial dye concentration from 20 to 200 mg/l is due to the limitation of adsorption sites on the clay mineral

surface. The pH strongly affects the adsorption process, the adsorption capacity reached 99.22% for MB at pH=10, and 98.97% for CR at pH=2, that is justified by the point of zero charge (pH_{PZC}). Thermodynamic studies showed that, at the experimental conditions, adsorption of these adsorbates were spontaneous, endothermic for the cationic dye (MB) and exothermic for the anionic dye (CR).

Finally, this clay seems to be an excellent alternative, as it is an abundant adsorbent available at low cost.

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