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## Cationic Dye Adsorption onto various natural adsorbents: A comparison study

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### ABSTRACT

The present study investigated the adsorption behavior of methylene Blue dye from aqueous solution onto activated carbon, bentonite, kaolin, animal charcoal and wood charcoal. To assess the adsorptive effectiveness of these natural adsorbents and their comparative adsorption capacities, initial dye concentration and contact time, the effect of adsorbent dosage and solution pH were studied. Activated carbon and Bentonite were top ranking and exhibit outstanding adsorption capacities followed by kaolin and animal charcoal with similar behavior but less effective. Finally, wood charcoal showed the poorest adsorption capacity. Generally, Langmuir adsorption isotherm model has the best fit compared to Freundlich model. The study of adsorption kinetics was well described by the pseudo-second order model.

**Keywords:** methylene blue, adsorption, activated carbon, bentonite, kaolin, animal charcoal.

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## INTRODUCTION

Currently, several industries such as textile, plastic, paper, food and cosmetic used dyes to provide color to their products. However, these dyes are always left in industrial waste and discharged generally to the water body [1-4]. Once they are released into the environment, they are greatly visible even in very low concentration ( $< 1$  mg/L) [5-10]. Several dyes may be toxic to some aquatic life due to the presence of aromatics and metals (aquatic plants, microorganisms, fish...) [11,12]. It can also cause damage to human beings such as the brain, respiratory diseases and central nervous system [13]. The remove of dyestuffs from effluents is of great importance. There are numerous methods to remove dye contaminants from waters, such as chemical oxidation, coagulation, membrane separation and electrochemical process. As for environmental purpose, adsorption techniques are widely used to remove chemical contaminants from waters, particularly those that are unaffected by conventional biological wastewater treatments [14,15]. Adsorption has been found to be insensitive to toxic pollutants and ease of operation and does not produce harmful substances [1]. In the present study, we used five commercial adsorbents, i.e., activated carbon, animal charcoal, wood charcoal, kaolin and bentonite to remove methylene Blue (MB) dye used as the test compound. The influence of different factors that affect adsorption efficiency such as initial concentration, contact time, solution pH and the adsorbent amount was achieved. Results allowed us to compare the adsorption capacity of these adsorbents and, therefore, evaluate their effectiveness to remove MB from aqueous solution.

## MATERIALS AND METHODS

### *Chemicals and Materials*

Methylene blue (Molecular formula:  $C_{16}H_{18}ClN_3S$ ) was purchased from Aldrich company and used without purification. The adsorbents used were all commercial. Activated carbon powder (CAS: 7440-44-0) and bentonite powder (CAS: 1302-78-9) were purchased from (Biochem chemopharma) company. Wood charcoal was purchased from (BAMSCO-Hospithera, Bruxelles). Kaolin was purchased from Labosi (reference number: A4828401). Animal charcoal was marketed by Prolabo (containing 15 % ashes).

### *Adsorption procedure*

Batch adsorption experiments were carried out to study MB adsorption. Experiments were accomplished using a shaker at room temperature and at a constant speed. For almost all tests (contact time effect, solution pH effect and kinetics study), 50 mL of MB solution ( $100$  mg  $L^{-1}$ ) were placed into a 250 mL conical flasks with a 20 mg of activated carbon, 15 mg of bentonite, 80 mg of animal charcoal, 60 mg of kaolin and 1.5 g of wood charcoal. The equilibrium time (30 minutes) was determined after agitating the flasks for predetermined time intervals. Samples were withdrawn from flasks and separated from the solution by centrifugation (REMI R-8C) at 2660 rpm for 10 minutes. To investigate the MB initial concentration effect, the study was performed on activated carbon adsorbent. For that, we kept constant a dose of (20 mg/50 mL) of activated carbon, and then we varied MB initial concentration in the range from 10 to 100 mg/L. For adsorbents dosage effect, we used 50 mL of MB solution ( $100$  mg  $L^{-1}$ ) and varied the adsorbents amounts. The adsorbent quantity ranged between (5-40 mg) for both bentonite/activated carbon, (60-200 mg) for both animal charcoal/kaolin and (1.5-5.5 g) for wood charcoal. Based on this study and from economical point view, experiments were carried out using the minimum adsorbent mass (mentioned below) that allow a dye adsorption. To obtain adsorption isotherms, dye solutions of different mass concentrations were stirred with the same amounts of adsorbents used previously until equilibrium was reached. For all tests, the equilibrium dye concentration was determined using a calibration curve prepared at MB maximum absorption wavelength (660 nm) by means of a JENWAY 6505 UV-Visible spectrophotometer. The adsorbed dye amount at equilibrium,  $q_e$  (mg/g) was evaluated using the following equation (a):  $q_e = (C_0 - C_e) \frac{V}{W} \dots (a)$

Where  $C_0$  and  $C_e$  are the initial and equilibrium dye concentrations ( $mg.L^{-1}$ ) respectively,  $V$  (L) is the volume of the solution and  $W$  (g) is the adsorbent mass. The dye removal percentage (R %) was calculated using the following equation (b) :  $R \% = \frac{C_0 - C_e}{C_0} 100 \dots (b)$

Where  $C_0$  and  $C_e$  are the initial and equilibrium dye concentrations respectively. [16].

RESULTS AND DISCUSSION

Factors affecting MB adsorption

MB initial concentration effect

This study was particularly achieved using activated carbon vis-à-vis its known excellent adsorption capacity [17].

Table 1: Initial dye concentration effect on MB removal percentage (R %)

C <sub>0</sub> (mg/L)	10	20	40	60	80	100
R %	98.9	98.5	98.2	95.1	80.8	51.6

It results from the above that, when the MB concentration increased from 10 mg/L to 100 mg/L, the MB removal percentage decreased from 96.9% to 51.6%. This is mainly due to the saturation of the available sites on the adsorbent surface [18]. For all tests, the adopted initial MB concentration was 100 mg/L.

Contact time effect

The influence of contact time on the amount of MB adsorbed per unit mass (mg/g) of various adsorbents is presented in figure 1. It clearly appears that dye removal was rapid at the initial stage of contact (t < 5 minutes) due to the abundant availability of active sites on the external surface, so the dye was quickly adsorbed. Then gradually decreased with time until equilibrium was reached. The slower rate was due to dye diffusion into the adsorbent interior because the external surface had been completely occupied by dye molecules. The equilibrium stage corresponds to a total adsorbent saturation with dye molecules. From Table 2, the time required for equilibrium establishment related to the five adsorbents materials was relatively short and less than 30 minutes. Therefore, 30 minutes was fixed as the agitation time for all materials. Moreover, q<sub>m</sub> (mg/g) values showed important MB adsorption on the surfaces of bentonite and activated carbon, against kaolin and animal charcoal, both with similar but fewer adsorption capacities. Wood charcoal revealed the poorest adsorption capacity.

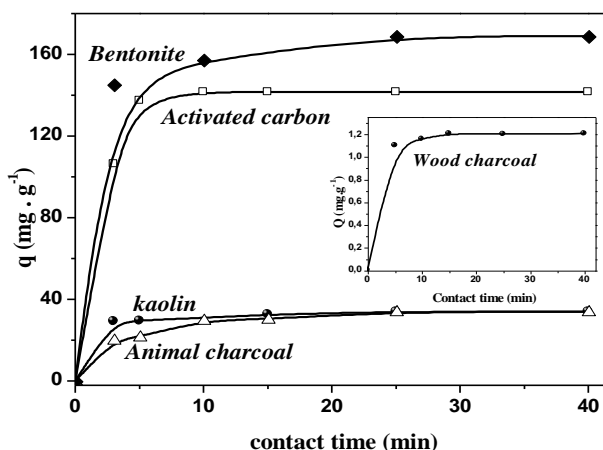


Figure 1: Time contact effect on MB adsorption capacity q (mg/g) on various natural materials.

Table 2: q<sub>m</sub> (mg/g) of natural materials in MB removal and their corresponding contact time

Adsorbents	q <sub>m</sub> (mg/g)	Contact time (min)
Bentonite	169	25
Activated carbon	141.67	10
Kaolin	34.07	25
Animal charcoal	34.06	25
Wood charcoal	1.2	15

**Solution pH effect**

pH is an important factor in any adsorption study; it can affect both the structure of the adsorbent and adsorbate as well as the adsorption mechanism. The effect of solution pH was studied at acidic, neutral and basic medium (pH = 2.4, pH = 7 and pH = 9.7). The Addition of 0.1 M HCl or 0.1NaOH was used to adjust the solution pH. Experiments were described in the adsorption procedure. The amounts of MB adsorbed in (mg/g) were calculated and listed in table 3.

**Table 3: Adsorption capacities  $Q_m$  (mg/g) according to the solution pH**

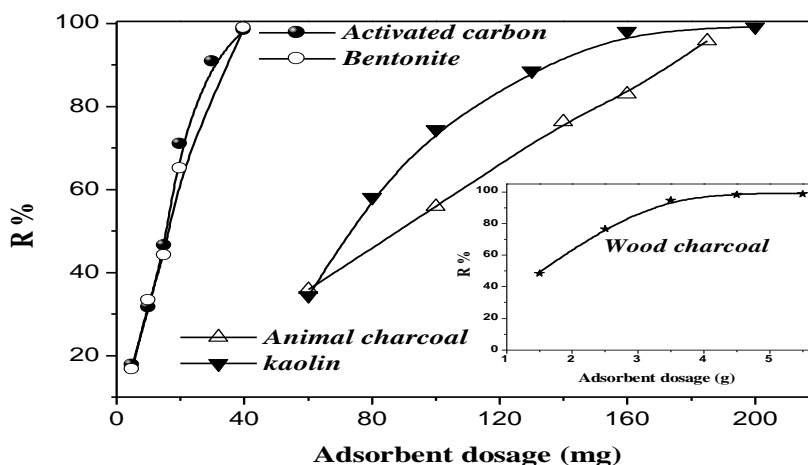
Adsorbents	q (mg/g)		
	pH = 2.4	pH = 7	pH = 9.7
Activated carbon	138	162	175.5
Bentonite	116.4	118.2	188.6
Animal charcoal	34.5	38.5	42
Kaolin	35.16	42.6	43.33
Wood charcoal	0.86	1.33	1.42

Whatever the adsorbent, it was observed that MB uptake was the lowest at acidic pH (pH = 2.4) and the greatest at basic pH (pH = 9.7). At lower pH, a high concentration of protons is provided and thus the adsorbent surface becomes positively charged. MB adsorption can be attributed to its amine groups that are ionizable by quaternization with the  $H^+$  ions present at this pH. However, the repulsion between positively charged molecules of the cationic dye and positively charged adsorption sites decreases the dye adsorption capacity on the adsorbent surface. A relatively higher adsorption was obtained at pH = 7, it is probably due to the increasing electrostatic attraction between positively charged dye and negatively charged adsorption sites. At higher pH (pH = 9.7), the adsorbent surface becomes more negatively charged and therefore the dye tendency to be adsorbed increases. Based on the above, the basic medium is the most favorable medium to give the best adsorption results. The adsorption capacity comparison for the three pH is of the following order:

- Basic pH: bentonite  $\approx$  activated carbon > kaolin  $\approx$  animal charcoal >>> wood charcoal
- Neutral pH: activated carbon  $\approx$  bentonite > kaolin  $\approx$  animal charcoal >>> wood charcoal
- Acidic pH: activated carbon  $\approx$  bentonite > kaolin  $\approx$  animal charcoal >>> wood charcoal

Whatever the pH, the ranking in term of adsorption capacity remains the same. Thus, pH has absolutely no influence on the classification of adsorption ability. Generally, activated carbon with the highest adsorption capacities is top ranking, followed by bentonite adsorbent with a closest adsorption capacities values. Kaolin and animal charcoal have similar adsorption abilities but smaller than the first two adsorbents. The final ranking is the wood charcoal showing the lowermost adsorption capacities.

**Adsorbent dosage effect**



**Figure 2: Adsorbent amount effect in MB removal**

The purpose of this study was to investigate the adsorbent dosage effect on MB adsorption. Firstly, we plotted the MB adsorbed quantities expressed as R% (dye removal percentage) versus adsorbent dosage. Results are illustrated in figure 2.

Generally, the MB removal percentage increases with adsorbent mass increasing. We even noticed an almost complete dye disappearance. This result is visual to the naked eye because MB blue color becomes transparent. The mass range used for both bentonite and activated carbon was too low (5 mg - 40 mg). The amount of 40 mg was largely enough to get an almost complete dye removal (98 %). For both kaolin and animal charcoal materials, MB elimination required a larger adsorbent mass without exceeding 200 mg. An almost complete dye removal was obtained using 200 mg of kaolin and 185 mg of animal charcoal. Oppositely, MB elimination required high masses when using wood charcoal. The amount of 5.5 g of this latter was used to get an almost dye removal (98 %), which is huge compared to the others adsorbents. These results are supported by the fact that *the quantity of adsorption sites at the adsorbent surface will increase by increasing the adsorbent amount*. From economical point view, the study of the adsorbent mass effect is of great importance and gives an idea about the minimum amount of adsorbent to use for the ability of a dye adsorption to be adsorbed. For all experiments, the choice of the adsorbents amounts was based on this study.

**Applicability of various adsorption isotherm models on MB adsorption**

Adsorption isotherm is important to explain how an adsorbent interacts with the adsorbate and give an idea about adsorption capacity. To describe MB adsorption isotherm, a number of isotherm models are presented in the literature [19] and the most widely used are Langmuir and Freundlich models.

**Langmuir adsorption isotherm model to MB adsorption**

Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent. It had been used successfully for many adsorption processes of monolayer adsorption [20]. Langmuir isotherm is expressed by equation (1).

$$Q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Where;  $q_e$  ( $\text{mg.g}^{-1}$ ) is the amount of MB adsorbed at equilibrium time,  $C_e$  ( $\text{mg.L}^{-1}$ ) is the equilibrium dye concentration in solution,  $q_m$  ( $\text{mg.g}^{-1}$ ) is the maximum adsorption capacity,  $K_L$  ( $\text{L.mg}^{-1}$ ) is the Langmuir constant. The linearized form of Langmuir isotherm can be written by equation (2).

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (2)$$

From equation (2), the slope and intercept of the plot  $1/q_e$  versus  $1/C_e$  (figure 3) give  $K_L$  and  $q_m$  respectively. Another parameter of Langmuir isotherm can be expressed in terms of  $R_L$ , given by equation (3).

$R_L = \frac{1}{1 + K_L C_0}$  ... (3) Where  $C_0$  ( $\text{mg.l}^{-1}$ ) is the initial dye concentration.  $R_L$  indicates the type of isotherm to be reversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavorable ( $R_L > 1$ ) [21].

**Freundlich adsorption isotherm model to MB adsorption**

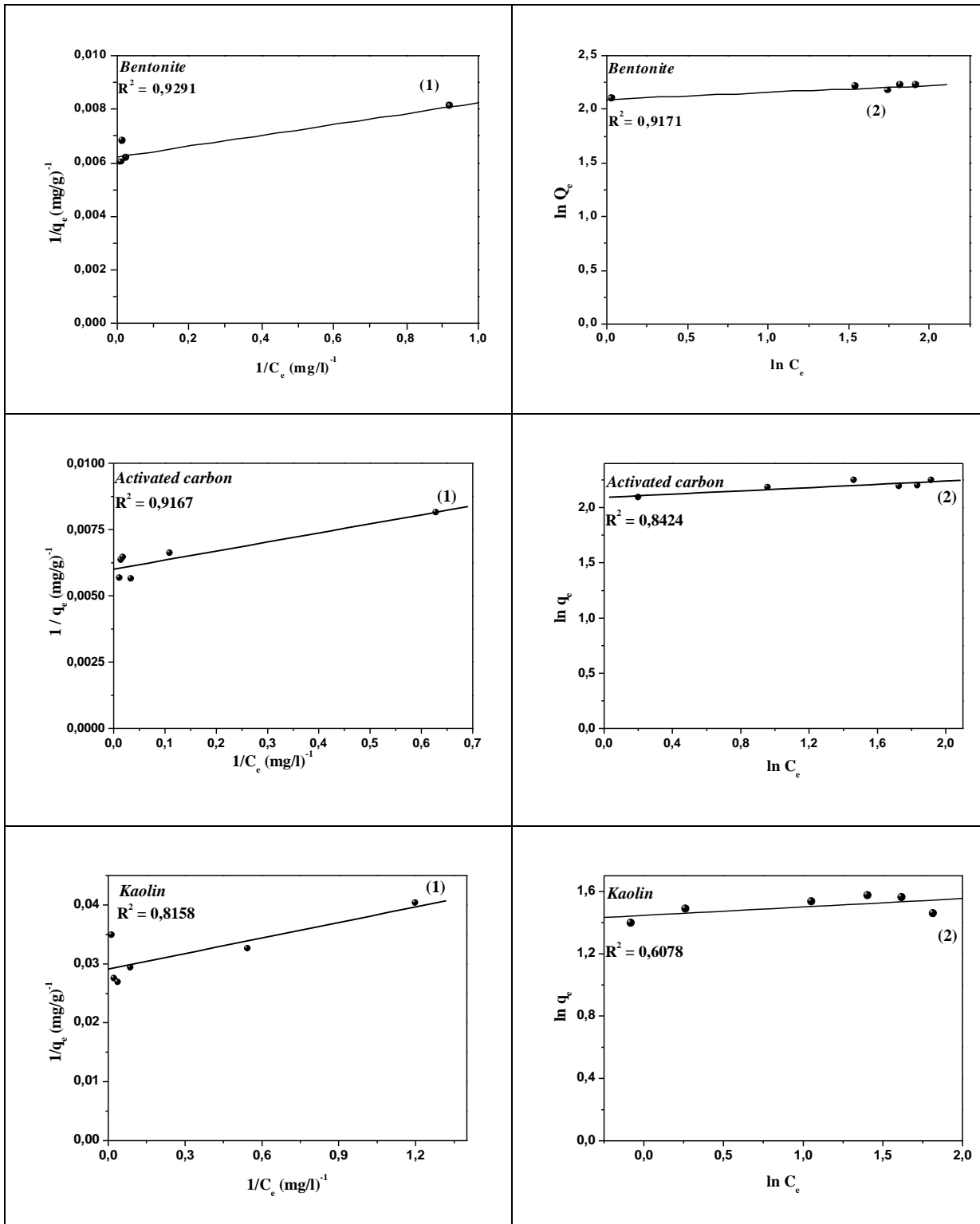
The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different adsorption energies [22]. The non-linear Freundlich isotherm is expressed by equation (4).

$q_e = K_F C_e^{1/n}$  ... (4) Where  $q_e$  ( $\text{mg.g}^{-1}$ ) is the amount of MB adsorbed at equilibrium time,  $C_e$  ( $\text{mg.L}^{-1}$ ) is the equilibrium dye concentration in solution,  $K_F$  ( $(\text{mg.g}^{-1}) (\text{L.mg}^{-1})^{1/n}$ ) is the Freundlich constant related to the capacity of the adsorbent and  $1/n$  is the heterogeneity factor of adsorption. The linearized form of Freundlich can be written by equation (5).

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

Within the same figure 3, we presented the plot  $\ln q_e$  versus  $\ln C_e$  of equation (5). The parameters  $K_F$  and  $1/n$  are determined from the intercept and slope respectively.  $1/n$  values indicate the type of isotherm to be irreversible ( $1/n = 0$ ), favorable ( $0 < 1/n < 1$ ), unfavorable ( $1/n > 1$ ) [23].

Table 4 listed the most important constants related to Langmuir and Freundlich isotherm models used for MB adsorption onto different adsorbents.



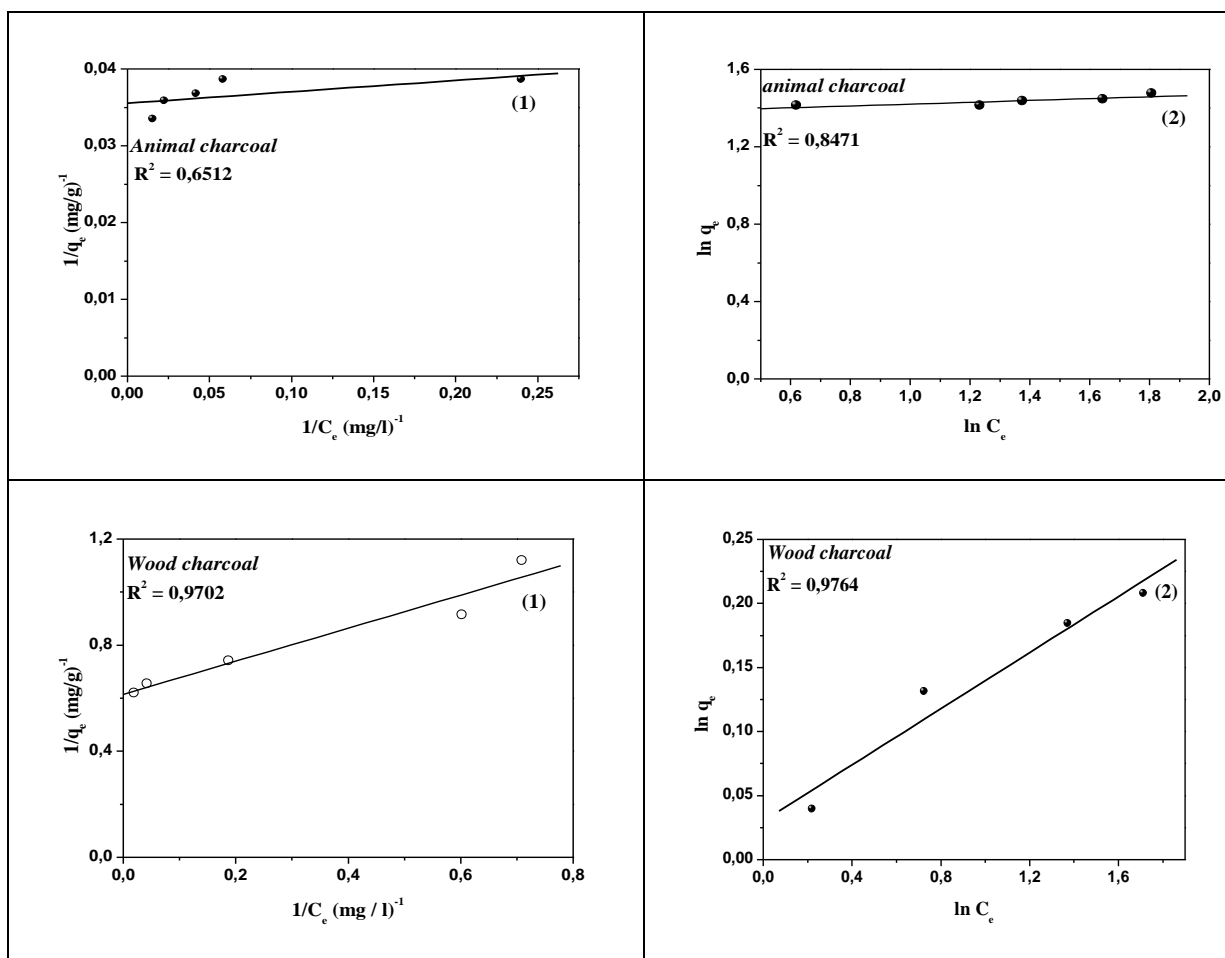


Figure 3: Adsorption isotherm model to MB adsorption (1) Langmuir, (2) Freundlich

Table 4: Langmuir and Freundlich constants for MB adsorption on various adsorbents

Adsorbents	Langmuir Constants				Freundlich Constants		
	$q_m$ (mg.g <sup>-1</sup> )	$K_L$ (L.mg <sup>-1</sup> )	$R_L$	$R^2$	$n$	$k_F$	$R^2$
Activated carbon	166.66	1.76	0.0056	0.916	0.074	123.714	0.842
Bentonite	161.29	3.0244	0.0033	0.929	0.064	123.282	0.917
Kaolin	34.340	3.316	0.0030	0.815	0.053	27.919	0.607
Animal charcoal	28.145	2.378	0.0041	0.651	0.047	23.599	0.847
Wood charcoal	1.628	0.98	0.010	0.970	0.109	1.0717	0.976

Generally, the correlation coefficient  $R^2$  gives an idea about the best model that can be chosen to give the best fit. Referring to  $R^2$ , generally, Langmuir model described better MB adsorption onto various adsorbents except animal charcoal, which is better described by Freundlich model. The maximum adsorption capacity  $q_m$  decreased from 166.66 mg/g to 1.628 mg/g following the same adsorbents' ranking described previously; in other words, better adsorption corresponds to the activated carbon and bentonite adsorbents against animal charcoal and kaolin with less adsorption capacities. The poorest adsorption corresponds to the wood charcoal.  $R_L$  values were less than one, which indicates a favorable adsorption.  $1/n$  values ranged between zero and one indicating also a favorable adsorption onto the adsorbents.

#### MB adsorption Kinetic study

The kinetic study is required to optimize different operation condition for dyes adsorption. The kinetics of MB onto the commercial materials was analyzed using Lagergren pseudo-first order model and Lagergren pseudo-second order model.

**Application of Lagergren pseudo-first order model on MB adsorption**

The pseudo-first order model may describe the adsorption kinetic. The linearized integral form of this model generally known and expressed as [24]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

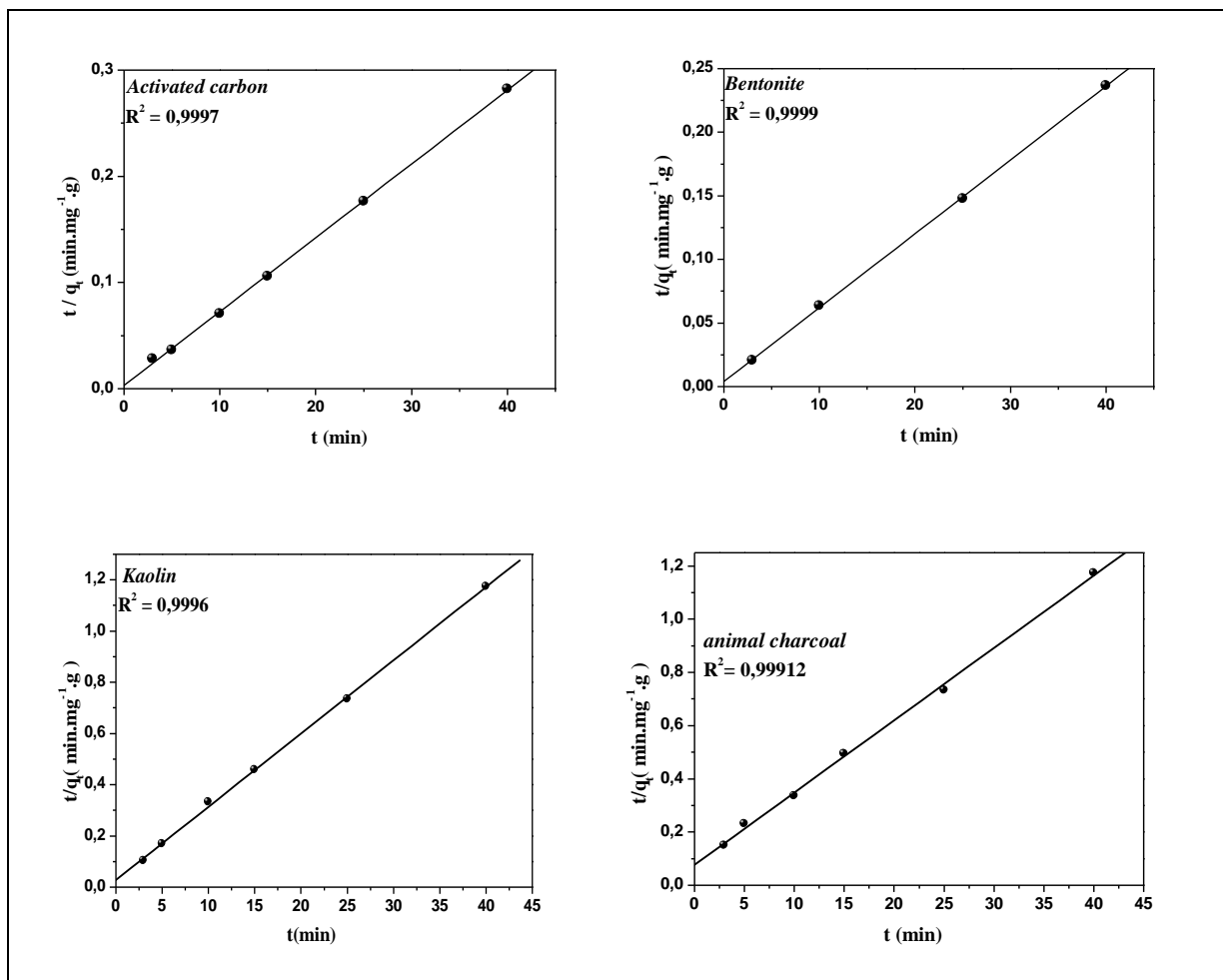
Where  $q_e$  and  $q_t$  ( $\text{mg.g}^{-1}$ ) are the adsorption capacities at equilibrium and time  $t$  respectively,  $k_1$  is the pseudo-first order rate constant ( $\text{min}^{-1}$ ) and  $t$  is the contact time (min). A plot of  $\log(q_e - q_t)$  versus time gives a linear line from which  $k_1$  and  $q_e$  values were determined from the slope and the intercept respectively. This kinetic presented relatively poor fit of the experimental data. For this reason, we just presented the results in table 5. The best fit of the kinetic data to the equation 6 reveals that the external mass transfer through a boundary layer is the rate of limiting step.

**Application of Lagergren pseudo-second order model on MB adsorption**

The pseudo-second order model may also describe the adsorption kinetic. The differential equation of this model is known and expressed as [25]:  $\frac{dq_t}{dt} = K_2(q_e - q_t)^2$  (7)

Where;  $k_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) is the second-order rate constant. The linearized integral form of this model is expressed as:  $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$  (8)

$K_2$  and  $q_e$  were calculated from the intercept and slope of the plot  $t/q_t$  versus  $t$  (figure 4) according to equation (8). The best fit of kinetic data to the equation 8 indicates that the forming of adsorbent-adsorbate interaction on the adsorbent external surface is the rate of limiting step. Results are listed in table 5.





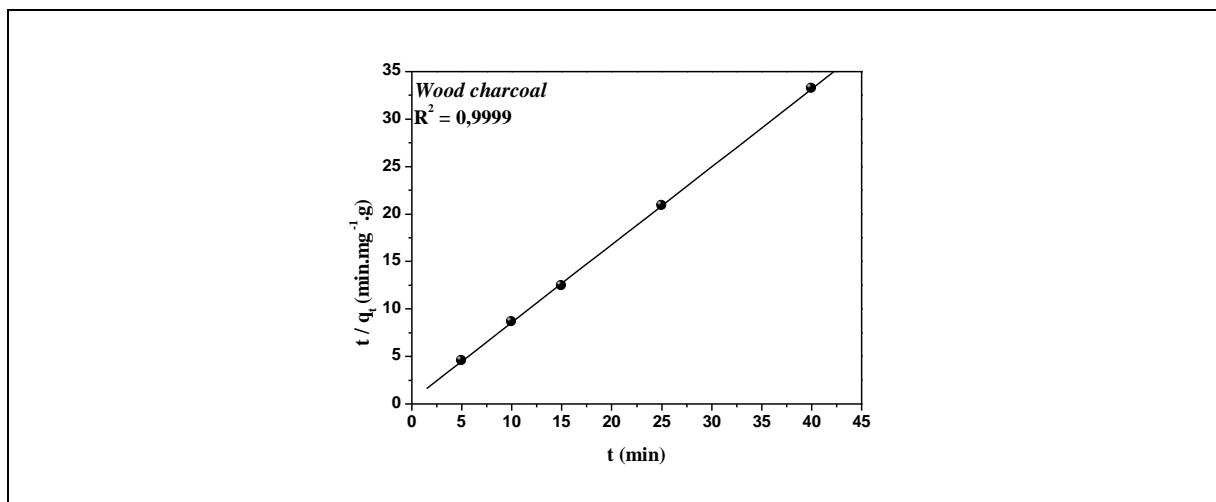


Figure 4: Kinetics plot of MB adsorption onto the adsorbents according to the pseudo-second order model.

Table 5: Results of kinetics parameters for MB adsorption

	$q_{e \text{ exp}}$ (mg/g)	pseudo-first order kinetics				pseudo-second order kinetics			
		$q_{\text{theo}}$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$\Delta q$	$q_{\text{theo}}$ (mg/g)	$K_2$ ( $\text{g.mg}^{-1}$ $\text{min}^{-1}$ )	$R^2$	$\Delta q$
Bentonite	169,03	101,331	0,548	0,883	67,69	172,117	$8,48 \cdot 10^{-3}$	0,999	3,08
Activated carbon	141,67	171,616	1,579	0,871	29,94	143,884	$1,54 \cdot 10^{-2}$	0,999	2,21
Kaolin	34,068	16,434	0,40	0,875	17,63	34,9406	$2,97 \cdot 10^{-2}$	0,999	0,87
Animal charcoal	34,06	26,154	0,336	0,856	7,91	36,778	$9,7 \cdot 10^{-3}$	0,999	2,71
Wood charcoal	1,2038	0,544	0,45	0,752	0,65	1,2195	1,794	0,999	0,01

The best-fit model was chosen based on the values of linear regression correlation  $R^2$ . Besides the values of  $R^2$ , the applicability of the kinetic model was also verified through  $\Delta q$ , which is the difference between experimental ( $q_{\text{exp}}$ ) and theoretical ( $q_{\text{theo}}$ ) values of MB adsorbed amounts at equilibrium. The lower values of  $\Delta q$  and the higher values of  $R^2$  indicate undoubtedly that MB adsorption onto the various adsorbents is well described by the pseudo-second order kinetic.

### CONCLUSION

This study was conducted using non-treated commercial adsorbents in the removal of MB dye from aqueous solution. To evaluate the adsorption capacity, initial dye concentration, contact time, the effect of adsorbent dosage and solution pH were investigated in a batch mode. Adsorption equilibrium was reached in 30 minutes. The kinetics data conform to the pseudo-second order model demonstrating an agreement with a chemisorption mechanism. The adsorption ability was affected by the solution pH, it was mostly favored in basic medium. However, the adsorbents' ranking was hardly affected by the solution pH. Activated carbon and bentonite were the best adsorbents showing outstanding adsorption capacities. Animal charcoal and kaolin behaved as moderate adsorbents whereas wood charcoal presented the poorest adsorption capacities. Generally, adsorption isotherm followed Langmuir model for almost all the adsorbents except animal charcoal, which is better described by Freundlich model. From the above results, it appears that activated carbon and bentonite were the effective adsorbents for MB dye removal from effluents.

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