Adsorption Kinetics and Modeling of Methylene Blue Dye onto Corn Cobs: Comparative Analysis of Static and Dynamic Systems

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ABSTRACT

The purpose of this work was to study the removal of methylene blue (MB) from aqueous solutions by adsorption on corn cobs in static and dynamic modes. This agricultural by-product was first characterized and then a series of experiments was conducted to highlight the effect of different operating conditions on the adsorption capacity. Batch experiments revealed that adsorption of MB on corn cobs is affected by too acidic medium. Equilibrium data were represented well by a Langmuir isotherm equation with maximum adsorption capacity of 40 mg/g. RL values obtained at different dye concentration indicate that the sorption of MB on corn cobs is favorable. The second-order kinetic model describes perfectly adsorption kinetic data and adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. The effectiveness of corn cobs biomass in the removal of methylene blue (MB) dye from its aqueous solution was tested by a fixed-bed column adsorption study. The results of dynamic mode were then modelled using Thomas and Yoon-Nelson equations. The results demonstrated that corn cobs are suitable for removal of MB from water using batch as well as fixed bed sorption system.

INTRODUCTION

Organic synthetic dyes are widely used in textile industry. The affinity of dyes for textiles depends on their chemical structures and the nature of fibers employed. The presence of dyes in the effluents is a major concern due to their effect on health and environment [1]. Thus, these pollutants must be removed from wastewaters by appropriate treatments before their evacuation. Various techniques have been employed for the removal of dyes from water. The conventional methods are coagulation and flocculation, oxidation, membrane filtration and adsorption [2-6]. Biological treatment is generally incapable of obtaining satisfactory colour elimination because of the low biodegradability of organic dyes. At the industrial scale, physical/chemical methods can be combined with biodegradation process to remove pollution due to dyes [7]. Other physico-chemical treatments such as electrocoagulation, ozonation and reversed osmosis are currently used. All these methods are sensibly different in terms of colour removal efficiency, operation and cost [8,9]. Adsorption is known as an effective process for the removal of hazardous pollutants from wastewater. It can be carried out in batch systems with powdered adsorbents or in continuous flow in packed bed column [10]. The adsorption of dyes in aqueous solutions on different solid materials, active coal in particular, has been the subject of several works [11-15]. The search for alternative and effective cheap adsorbents, especially derived from locally available natural by-products and waste materials, has nowadays become a main research focus.

In our previous work, we tested two industrial residues from a thermal station, fly and bottom ash, and two plant materials, palm bark and sugarcane bagasse, as adsorbents for the removal of organic dyes [16,17]. This work is in the same context, it consists to study the discoloration of water using a natural agricultural by-product, namely the corn cob which is very abundant in Morocco. This material has been the subject of several studies: Sanchez et al. [18] have studied the lactic acid production by alkaline hydrothermal conversion of corn cobs. Gil Tortosa et al. [19] have developed an economic process for preparation of xylose and derivatives from corn cobs. This agricultural by-product was also used to remove heavy metal ions from the aqueous solutions [20].

The main objectives of this study were to: (i) evaluate the feasibility of removing MB dye from aqueous solution by adsorption onto corn cobs in static and dynamic modes; (ii) investigate the effect on adsorption process of various operational conditions, including adsorbent mass, pH, contact time, initial concentration of dye and agitation speed; and (iii) describe the adsorption process using mathematical models and discuss the adsorption mechanism of MB onto adsorbent.

MATERIALS AND METHODS

Adsorbate

Methylene blue (C.I. 52015; 373.9 g/mol; λ_{max} = 664 nm), a cationic dye, was chosen in this study as adsorbate because of its known strong adsorption onto solids, and its recognized usefulness in characterizing adsorptive material. The solutions at the desired concentration were prepared with distilled water. Figure 1 shows the chemical structure of MB dye.

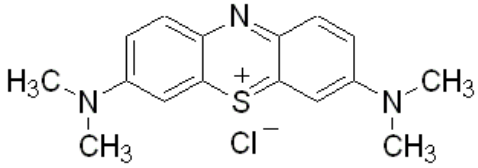

Figure 1: Chemical structure of methylene blue

Adsorbent

Corn cobs were recovered from a farm located in the region of El Jadida (Morocco). These agricultural by-products were cut into 1 cm. They were dried in ambient air and then in an oven at 60°C for 24 hours. The material thus obtained was ground, using a laboratory mill type POLYMIX, to obtain particle size less than 2 mm. Before using, the material was dried for 24 hours at 105°C and then stored in plastic bags. The morphology of the corn cobs was examined by a scanning electron microscope type XL30 ESEM equipped with an EDAX system. Figure 2 illustrates the morphological structure of the studied adsorbent. It is clear that corn cobs are porous material, their morphology can facilitate the retention of adsorbate due to their irregular surfaces. So, it can be concluded that they present an adequate morphological profile to retain dyes. In fact, the cavities of the fibrous materials tested in this work can allow the diffusion of the solutes through its macroporous structure.

Elemental analysis of corn cobs, performed using an elemental analyzer CHNS EA 1110 Thermo Fisher, shows that elements detected can be classified according to their percentage content in the following order: Carbon (42.7%) > Hydrogen (6.3%) > Nitrogen (0.4%). It must also be noticed that sulfur was not detected in any of the products assayed. On the other hand, chemical analysis of corn cobs, conducted under the standards of American Society for Testing and Materials (ASTM), shows the following composition: cellulose (65%), hemicellulose (13%) and lignin (17%). In fact, this composition can vary from cultivar to cultivar, the nature of soil, fertilizer to be used, and climatic conditions.

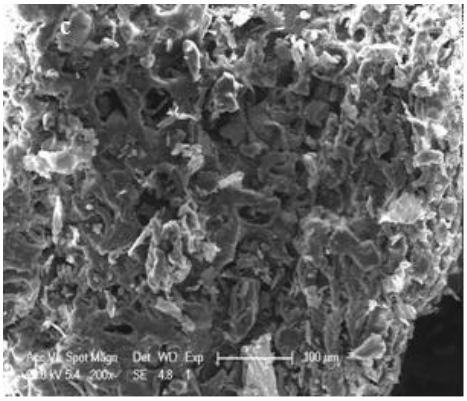

Figure 2: Scanning electron micrograph of corn cobs

Adsorption experiments

First, adsorption of MB dye on corn cobs was studied in static mode. Experiments were carried out, at room temperature, under different operating conditions. The effects of adsorbent mass, pH, contact time, initial concentration of dye and agitation speed were evaluated. At the end of the equilibrium period, the supernatant was subsequently analyzed at 664 nm for residual concentration of methylene blue using a spectrophotometer (Shimadzu 3600 UV/Visible). Appropriate dilution was processed, some time, to ensure that the concentration of the solution was within the range of the standard curve. The amount of methylene blue adsorbed Q_e (mg/g), was obtained as follows:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad \text{(Eq.1)}$$

where C_0 and C_e (mg/L) are the initial and final concentrations of solute in solution, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent used.

The pseudo-first-order and the pseudo-second-order models were used to evaluate the adsorption kinetics. The Langmuir and Freundlich isotherms were selected in this study to model adsorption equilibrium and the characteristic parameters for each isotherm were determined.

Secondly, adsorption of MB on corn cobs was performed at room temperature in dynamic mode by the use of a Pyrex column of 1.4 cm internal diameter, 47 cm in height and a total volume of 72.3 cm^3. Glass reservoirs were used for storing the raw solution, the treated water and the solution overflowing from the column. Initial concentration of MB and adsorbent mass (bed height) were chosen as parameters and their effects on dye removal efficiency were monitored.

RESULTS AND DISCUSSION

Adsorption In Static Mode

Effect of adsorbent mass

Adsorption tests were carried out with different adsorbent dosages (ranging from 0.05 to 2.4 g) in erlenmeyer flasks containing 100 mL of the MB solution at 25 mg/L. The resulting mixture was then stirred (500 rpm) for 2 hours. The supernatants obtained were analyzed to determine the residual concentration of the dye based on the weight of added adsorbent. The results of the experiments with varying adsorbent mass, presented in Figure 3, show that the residual concentration of the adsorbate decreases by increasing the adsorbent mass. This can be explained by the increase of the number of available adsorption sites which promotes the discoloration phenomenon [21]. Maximum removal percentage was observed with corn cobs dosage of about 0.2 g. This optimal weight has been taken into consideration to conduct the experiments presented hereinafter.

Effect of pH

The pH is an important factor in any adsorption study, because it can influence both the adsorbent and adsorbate structure and the adsorption mechanism. In order to investigate the effect of pH on the MB removal by corn cobs, experiments were carried out, at pH values ranging from 2 to 12, by stirring 0.2 g of adsorbent in 100 mL of MB solution at 25 mg/L. Values of pH were adjusted using HCl (0.1N) or NaOH (0.1N) depending on the pH desired. Obtained results presented in Figure 4 show that the adsorption of the dye (MB) is influenced by too acidic medium. This is mainly due to the presence of an excess of H^+ ions which compete with the cationic dye for the active sites. In the further experiments, all tests were conducted at normal pH of MB solution (without correction, pH = 6.4) to avoid possible negative effect of this parameter.

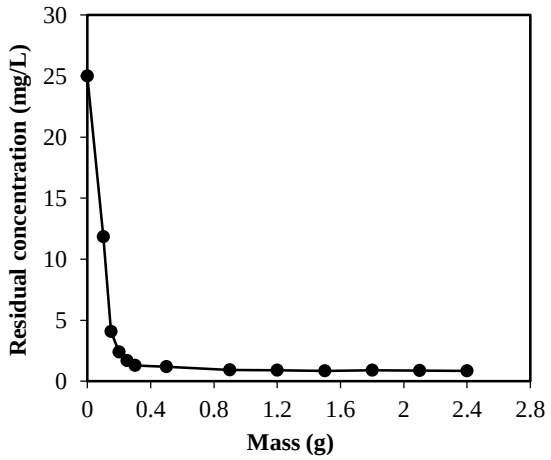

Figure 3: Residual concentration of MB as a function of corn cobs weight (C_0 = 25 mg/L; pH=6.4; 500 rpm; Contact time = 2h; V=100 mL; T = 25±2°C)

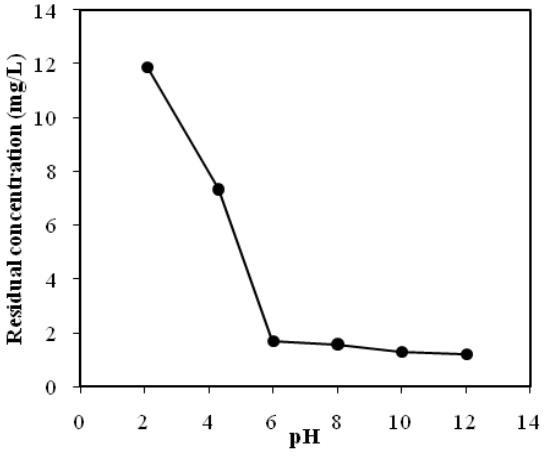

Figure 4: Residual concentration of MB as a function of pH (C_0 = 25 mg /L; Adsorbent = 0.2 g;V = 100 mL; Contact time = 2 h; 500 rpm; T = 25±2°C)

Effect of stirring speed

Stirring speed is among the operating parameters that can influences significantly adsorption process. It contributes to the distribution of the adsorbate into the adsorbent material and it should be considered in the determination of the maximum quantity adsorbed [22]. In this work, stirring speed was varied from 100 to 900 rpm to determine its effect on yield discoloration. As can be seen in Figure 5, residual concentration of MB decreases with increasing the stirring speed and becomes constant from 500 rpm.

Effect of contact time

The effect of contact time on the removal of methylene blue was evaluated in order to highlight the time necessary to achieve adsorption equilibrium. The experiments were conducted under the same operating conditions described above: 0.2 g of corn cobs were added to 100 mL of MB solution (25 mg/L, pH 6.4) and the mixture was stirred at 500 rpm. Samples for analysis were taken at regular time intervals for determining the residual concentration of the dye. The results obtained and illustrated in Figure 6 show that the adsorption process of MB presents generally two phases: an initial rapid phase where adsorption capacity sharply increased within the first 10 min due to the rapid surface adsorption and a second slow phase associated with the internal surface adsorption. Results obtained show that adsorption equilibrium can be reached after a contact time of about 30 min. After that, the adsorption percentage did not change with further increase in contact time because the amount of dye adsorbed reached a steady state with the amount of residual dye in the solution.

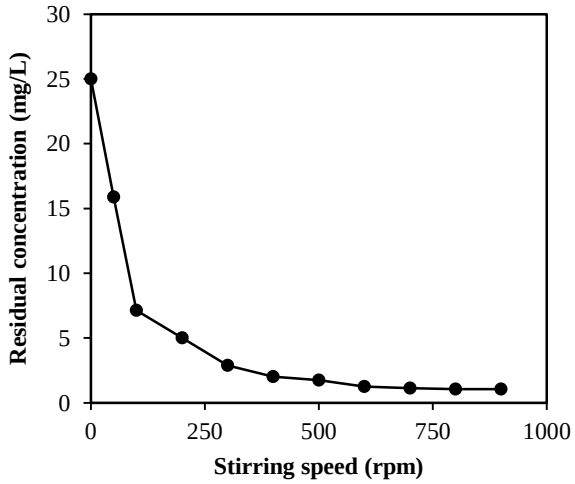

Figure 5: Residual concentration of MB as a function of stirring speed (C_0 = 25 mg/L; Adsorbent = 0.2 g; V = 100 mL; pH = 6.4; contact time = 2 h; T = 25± 2°C)

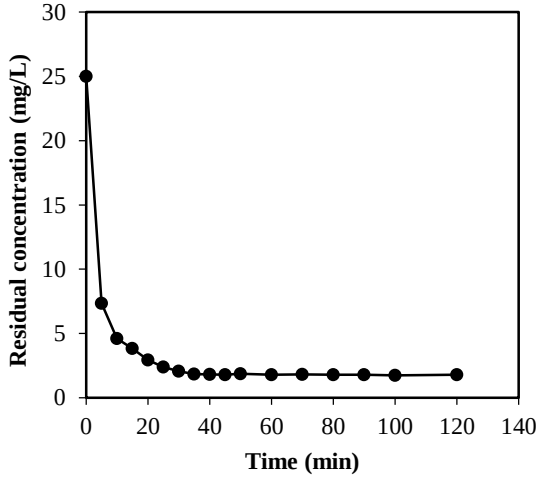

Figure 6: Residual concentration of MB as a function of time (C_0 = 25 mg/L; Adsorbent = 0.2 g; V = 100 mL; pH = 6.4; 500 rpm; T = 25±2°C)

Kinetic modelling

Adsorption kinetics data were modelled using *both* pseudo-first-order [23] and pseudo-second-order [24] models. The pseudo-first Lagergren equation is expressed as:

$$\frac{dQ_t}{dt} = K_1.(Q_e - Q_t) \qquad \text{(Eq. 2)}$$

where Q_t and Q_e are the amounts of MB adsorbed (in mg/g) at time t and at the equilibrium, respectively, and K_1 being the constant rate of pseudo-first-order adsorption process (1/min).

The integration of equation 2 gives:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1.t}{2{,}303} \qquad \text{(Eq. 3)}$$

Furthermore, the pseudo-second order equation is often used with success to describe the kinetics of the adsorption. Pseudo-second-order equation is expressed as:

$$\frac{dQ_t}{dt} = K_2.(Q_e - Q_t)^2 \qquad \text{(Eq. 4)}$$

where Q_e and Q_t have the same meaning as mentioned previously and K_2 is the rate constant for the pseudo-second-order kinetics. The integration of equation 4 gives:

$$\frac{t}{Q_t} = \left(\frac{1}{Q_e}\right).t + \frac{1}{K_2 Q_e^2} \qquad \text{(Eq. 5)}$$

Using the slopes and intercepts, different kinetic parameters i.e. equilibrium adsorption capacity ($Q_{e,cal}$) and correlation coefficient (R^2) values were calculated. The results of the kinetic study are shown in Figure 7. Parameters for both models, pseudo-first order and pseudo-second order, are summarized in Table 1.

Table 1. Pseudo-first-order and pseudo-second-order parameters for the adsorption of MB onto corn cobs

	Parameter	Value
Pseudo-first order	$Q_{e,exp}$ (mg/g)	9.13
	$Q_{e,cal}$ (mg/g)	0.84
	K_1 (min^{-1})	0.044
	R^2	0.70
Pseudo-second order	$Q_{e,exp}$ (mg/g)	9.13
	$Q_{e,cal}$ (mg/g)	10,63
	K_2 ($mg.g^{-1}.min^{-1}$)	0.02
	R^2	0.996

As can be seen, the second-order equation provided a better-fitting model than the first-order equation with a high correlation coefficient which is very close to the unit (R^2 = 0.9945). It was found that the pseudo-second-order rate model gave perfect fittings to the experimental data. The calculated Q_e values agree well with the experimental data.

The intra-particle diffusion model was also tested in this work in order to verify the influence of mass transfer resistance on the adsorption of MB dye on the adsorbent surface. The intra-particle diffusion model [25] is expressed as:

$$Q(t) = k_{int}\, t^{1/2} + C \qquad \text{(Eq. 6)}$$

where Q_t (mg/g) is the amount of MB dye sorbed at time t, C (mg/g) is the intercept and k_{int} ($mg/g.min^{0.5}$) is the intra-particle diffusion rate constant.

Obtained results (Figure 8) show that the linear plot of intra-particle diffusion model between the dye and corn cobs did not pass through the origin. So, the intra-particle diffusion is not the only *rate*-limiting *step*. There may be other *steps* involved in *control* of the *rate* of adsorption. On the other hand, we note that the curve Q vs. $t^{0.5}$ is divided into two parts with different slopes. This indicates that two intra-particle diffusion steps took place during the dye sorption process. The first straight part is allocated to the macro-pore diffusion while the second linear part is due to the diffusion in the micropores [26].

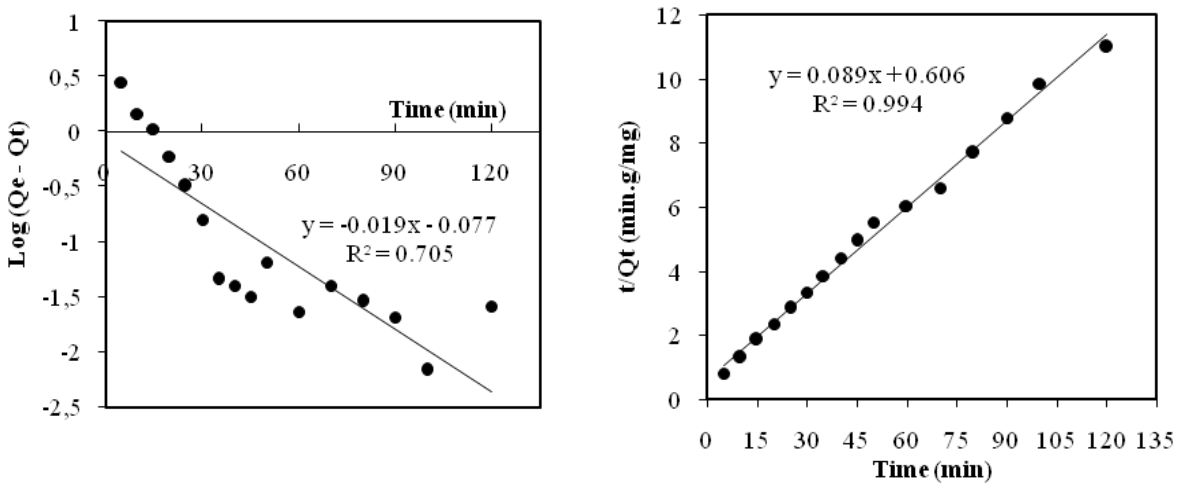

Figure 7: Pseudo-first-order and pseudo-second-order kinetic plots for MB adsorption onto corn cobs (C_0 = 25 mg/L; Adsorbent = 0.2 g; V = 100 mL; pH = 6.4; 500 rpm; T = 25±2°C)

Effect of initial dye concentration

The effect of the initial concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases [27]. The effect of the initial concentration is studied by adding 0.2 g of corn cobs to 100 mL of MB solutions at concentration range of 10 and 250 mg/L. The experiments were conducted at room temperature at normal pH of MB solution (pH 6.4) and at a stirring speed of 500 rpm for 2 h. Residual concentrations and amounts of adsorbate per unit mass of adsorbent were determined. The evolution of Q (mg/g) as a function of the initial concentration of the dye is shown in Figure 9. The results show that the amount of MB dye adsorbed increases with the increase of the initial concentration. This is due to the increase in the driving force of the concentration gradient. However, the amounts of MB adsorbed remains constant beyond a concentration of 180 mg/L. This is due to the saturation of active sites of corn cobs.

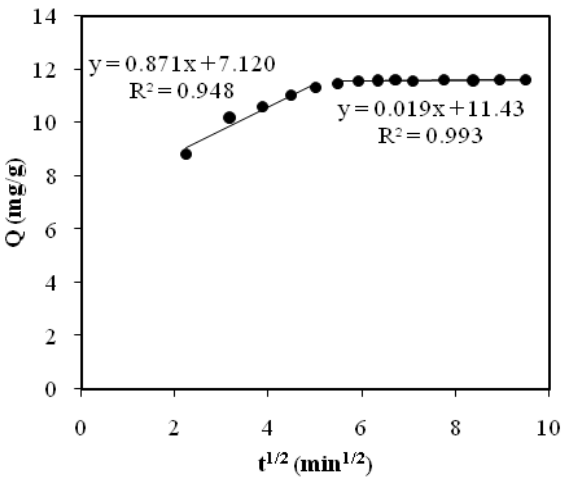

Figure 8: Linear plot of intra-particle diffusion model for the adsorption of MB dye on corn cobs

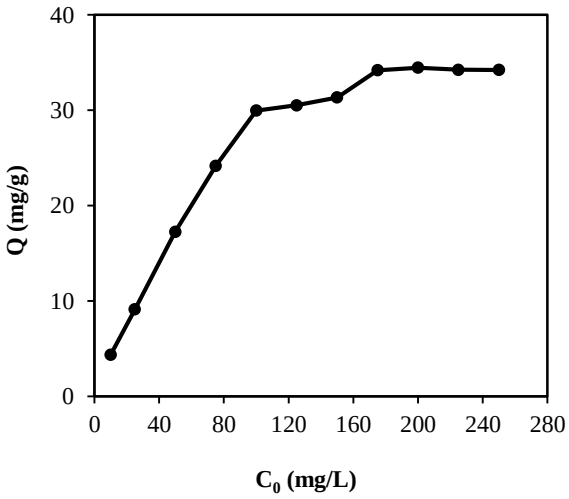

Figure 9: Effect of the initial concentration of MB dye on the discoloration (V =100 mL; Adsorbent = 0.2 g; pH = 6.4; Contact time = 2 h; 500 rpm; T = 24±2°C)

Adsorption isotherms

Adsorption isotherms were determined at ambient temperature and the experimental data obtained were modelled with the Langmuir (Eq. 7) and Freundlich (Eq. 8) isotherms equations [28,29].

$$\frac{1}{Q_e} = \frac{1}{K_L.Q_{max}.C_e} + \frac{1}{Q_{max}} \quad \text{(Eq. 7)}$$

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \quad \text{(Eq. 8)}$$

where Q_e is the adsorption capacity at equilibrium (mg/g), Q_m is the maximum adsorption capacity (mg/g), C_e is the residual concentration of adsorbate at equilibrium (mg/L), K_L is the Langmuir constant (L/mg), K_F is a constant indicative of the adsorption capacity of the adsorbent and n is an empirical constant related to the magnitude of the adsorption driving force.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [30]:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{(Eq. 9)}$$

There are four probabilities for the R_L value: favorable sorption ($0 < R_L < 1$); unfavorable sorption ($R_L > 1$); linear sorption ($R_L = 1$) and irreversible sorption ($R_L = 0$) [31].

The adsorption isotherms were studied by adding 0.2 g of corn cobs to MB solutions at different concentrations (ranging from 10 to 250 mg/L). After stirring at 500 rpm for 2 h, supernatants were analysed and residual concentrations were determined. After that, Langmuir and Freundlich isotherms were applied to model the equilibrium adsorption. The typical graphical representations of the linearised plots are shown in Figure 10.

The best fitted model was selected based on the determination coefficient (R^2). The R^2 of the Langmuir isotherm model was higher than that obtained using the Freundlich model. Thus, adsorption isotherms data fitted well to Langmuir isotherm model. This finding supports the assumption that MB is adsorbed as a homogeneous monolayer onto the adsorbents and has a free-energy change for all adsorption sites [32].

The Langmuir and Freundlich constants determined from the slopes and intercepts of the respective plot are summarized in Table 2. The maximum sorption capacity of methylene blue on corn cobs was 40 mg/g. For all concentrations, the R_L values were in the range of 0–1 at room temperature (results are not shown), indicating that the sorption of MB on corn cobs is favorable.

Table 2. Adsorption equilibrium parameters according to Langmuir and Freundlich models

Isotherm	Parameters	Value
Langmuir	Q_{max} (mg/g)	40
	K_L (L/mg)	0.111
	R^2	0.95
Freundlich	K_f	7.21
	n	2.994
	R^2	0.845

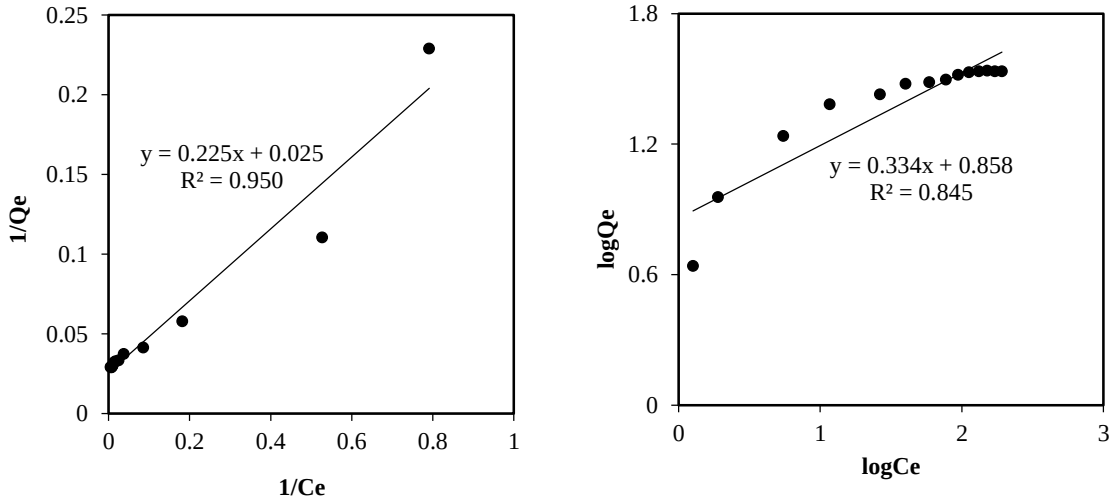

Figure 10: Langmuir and Freundlich isotherm plots for MB adsorption onto corn cobs (pH = 6.4; V = 100 mL; Adsorbent = 0.2 g; Contact time = 2 h; 500 rpm; T = 25±2°C)

DYNAMIC MODE

Effect of adsorbent mass on the breakthrough time

The kinetics of removal of methylene blue from aqueous solutions using the column method with a fixed bed of corn cobs has been examined. The adsorption capacities of fixed bed column with adsorbent mass 1.5 and 3 g were tested at a constant flow rate of 2.36 mL/min and 1.71 mL/min, respectively. The influent concentration of MB solution was 50 mg/L. Experimental results are presented as breakthrough curves which are plots of C/C_0 as a function of time (Figure 11). It is clear that breakthrough time increased with bed depth which is proportional to the mass of the adsorbent. This can be explained by more sites which were supplied for dye. The lower end of the curve is indicated by a zero concentration and the upper end is indicated by the influent concentration, indicating that C/C_0 ratio is equal to unity and the filter bed is fully saturated with the dye. During filtration, the bed becomes progressively saturated with MB dye from inlet to outlet, forming an adsorption front within the bed, which moves progressively over time. When the adsorption front reaches the bottom of the bed, the concentration of solution leaving the bed increases producing the characteristic breakthrough curve.

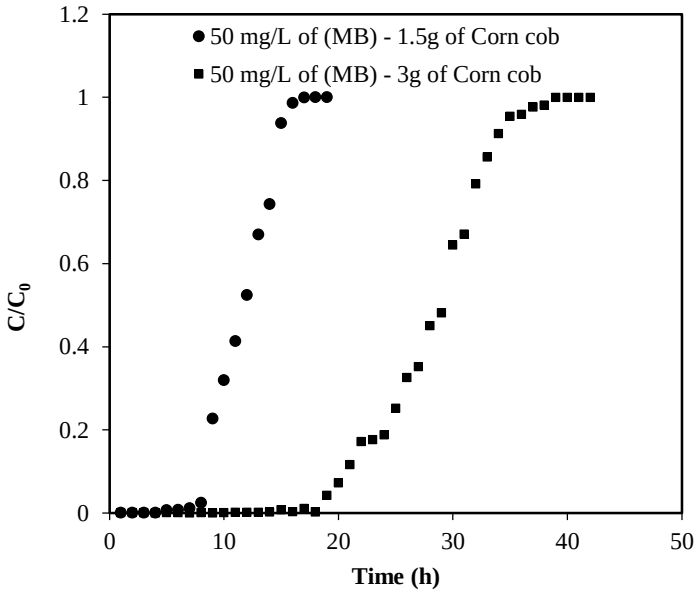

Figure 11: Effect of weight bed on breakthrough curve for MB adsorption on corn cobs (C_0 = 50 mg/L; bed weight = 1.5 and 3g; pH = 6.4; T = 25±2°C)

Effect of influent concentration on the breakthrough time

The effect of initial concentration of MB dye on breakthrough curves was studied at two different influent concentrations 50 mg/L and 75 mg/L using a bed weight of 3 g. From the Figure 12, it was observed that the

breakthrough time varied greatly with influent concentration. Obtained results show that the increase in the MB concentration from 50 to 75 mg/L decreased the breakthrough from 18 h to 7 h. This is due to the increase in the amount of the dye in contact with the material which promotes rapid saturation and to the improvement of the diffusion of MB dye in the pores of corn cobs. The reason is that the driving force for adsorption is the concentration difference between the dye on the adsorbent and the dye in the solution. These results are in agreement with those obtained by the use of other materials [33,34]. The mass of the sorbent forming the homogeneous fixed bed is proportional to the bed height. As the bed mass and height increased, the MB dye molecule has more time to contact with the biosorbent resulting in higher dye removal efficiency.

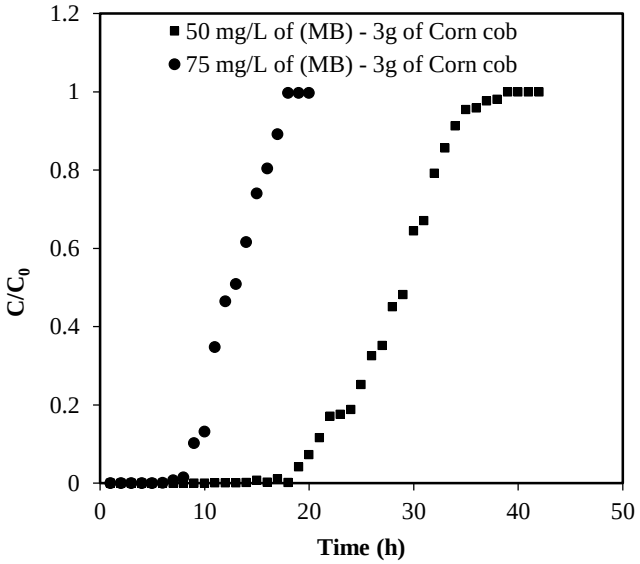

Figure 12: Effect of influent concentration on breakthrough curve for MB adsorption on corn cobs (C_0 = 50 and 75 mg/L; bed weight = 3 g; pH = 6.4; T = 25±2°C)

Modeling of breakthrough curves

In the literature, there are many mathematical models available to describe the adsorption through a fixed bed column. These models use the results of the breakthrough curves. Two models, Thomas and Yoon-Nelson, were applied in this work to treat the experimental data in the column.

Application of Thomas Model

The mathematical model of Thomas is widely used to describe column performance. It was used for the adsorption of organic compounds, inorganic and heavy metals. Thomas model is based on the assumption that the process follows Langmuir kinetics of adsorption-desorption with no axial dispersion. It describes that the rate driving force obeys the second order reversible reaction kinetics [35]. The expression of Thomas model is given by the following equation [36].

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{K_{Th}.q_0.m}{Q}-K_{Th}.C_0.t \qquad \text{(Eq. 10)}$$

where C_0 is the influent concentration of the adsorbate (mg/L), C is the effluent concentration at time t (mg/L), m is the amount of the adsorbent in the column (g), K_{Th} is the Thomas rate constant (L/mg.h), q_0 is the maximum solid-phase concentration of solute (mg/g), Q is the feed flow rate ($L.h^{-1}$), and t is the time relating to the concentration C at the outlet of the column (h). The value of C_0/C is the ratio of influent and outlet concentrations.

The curve $\ln[(C_0/C)-1]$ as a function of time is shown in Figure 13. This linear plot was employed to determine values of q_0 and K_{Th} from the intercept and slope of the plot. The application of the Thomas model in the case of corn cobs material and MB, allowed us to determine the characteristic parameters (Table 3). As can be seen, several conclusions can be drawn:

- The values of the Thomas rate constant K_{Th} decreased with increasing the weight or the height of the corn cobs bed. These results are similar to those obtained using different materials [37,38].

- The regression coefficients are very close to the unit; this indicates that the kinetic data are conforming to Thomas model.
- The maximum solid-phase concentration of dye q_0 (mg/g) is important. The results obtained highlight the performance of the filtration column and the feasibility of this process for decolorizing water.
- The well-fitting of the experimental data with the Thomas model indicate that the external and internal diffusion will not be the limiting step and no axial dispersion is present.

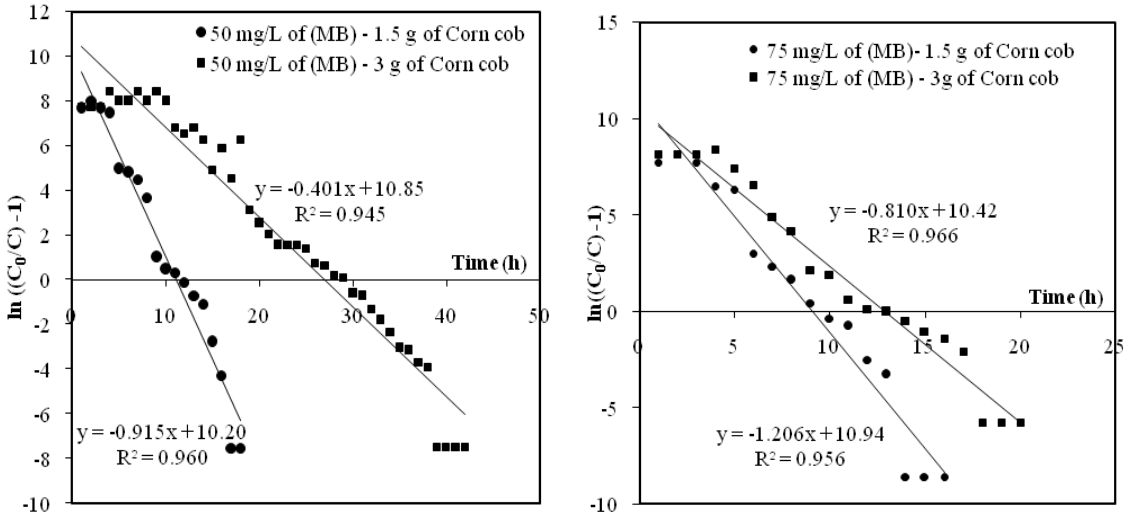

Figure 13: Linearized form of Thomas model for the adsorption of MB dye on corn cobs bed (C_0 = 50 and 75 mg/L; bed weight = 1.5 and 3 g; pH = 6.4; T = 25±2°C)

Application of Yoon-Nelson model

Yoon and Nelson [39] developed a model based on the hypothesis that the rate of decrease in the adsorption probability of adsorbate molecules is proportional to the breakthrough of adsorption on the adsorbent. The linear form of Yoon-Nelson model regarding a single-component system is expressed by the following equation:

$$\ln\left(\frac{C}{C_0 - C}\right) = K_{YN}.t - \tau.K_{YN} \qquad \text{(Eq. 11)}$$

where C_0 is the influent concentration of the adsorbate (mg/L), C is the effluent concentration at time t (mg/L), K_{YN} is the Yoon-Nelson constant (min^{-1}), τ is the time corresponding to the adsorption of 50% of adsorbate (min), and t is the time relating to the concentration C at the outlet of the column (min).

The linear plot of ln[C/(C_0-C)] against sampling time (t) was employed to determine values of τ and K_{YN} from the intercept and slope of the plot (Figure 14). The sorption bed should be completely saturated at t = 2 τ because 50 % breakthrough occurs at t = τ. Owing to the symmetrical nature of breakthrough curves due to the Yoon–Nelson model, the amount of solute being sorbed in the fixed bed is half of the total solute entering the sorption bed within 2 τ period. The value of the biosorption capacity q_{YN} is determined according to the following equation [39,40]:

$$q_{YN} = \frac{q_{total}}{m} = \frac{(1/2).C_0\left[\left(\frac{Q}{1000}\right).2\tau\right]}{m} = \frac{C_0.Q.\tau}{1000.m} \qquad \text{(Eq. 12)}$$

where C_0 (mg/L) and τ (min) have the same meaning as mentioned previously, m is the mass of the adsorbent (g), and Q is the feed flow rate (mL/min).

The values of K_{YN}, τ, q_{YN} and R^2 are listed in Table 3. These results show that, for the same bed weight, the rate velocity constant (K_{YN}) increases and the 50% breakthrough time τ decreased with increasing influent concentration C_0. However, with the bed height increasing for each C_0, the values of τ increased and the values of K_{YN} decreased. This is in agreement with other studies carried out using other materials [38]. On the other hand, the biosorption capacity q_{YN} determined according to the Yoon-Nelson model is important and it is of the order of 42.3–46.3 mg/g.

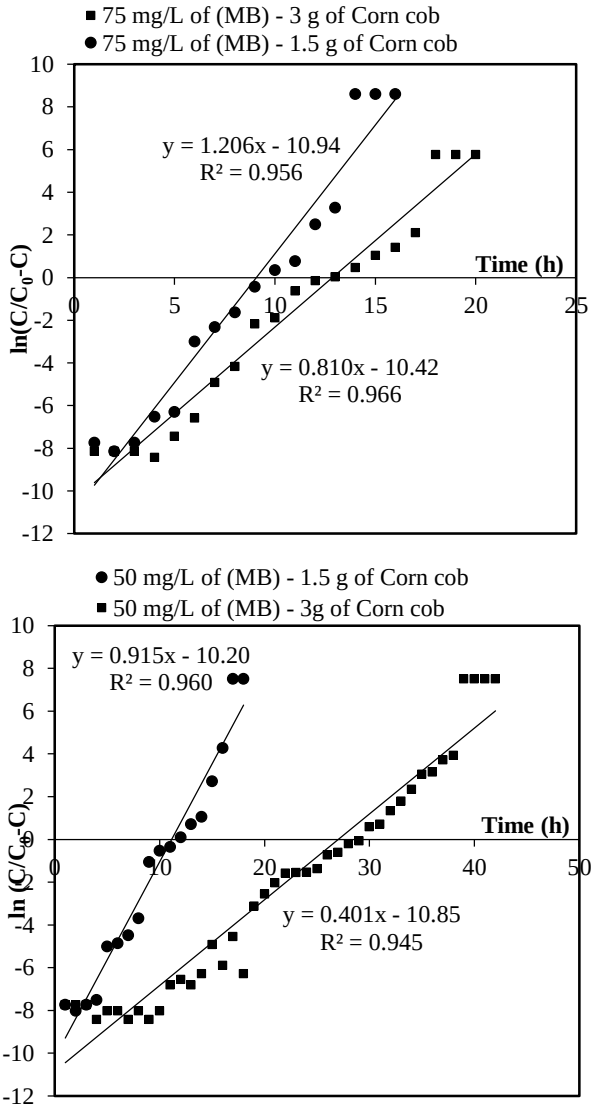

Figure 14: Linearized form of Yoon-Nelson model for the adsorption of MB dye on corn cobs bed (C_0 = 50 and 75 mg/L; bed weight = 1.5 and 3 g; pH = 6.4; T = 25±2°C)

Table 3. Characteristic parameters of Thomas and Yoon-Nelson models

Parameter	Thomas model		Yoon-Nelson model	
C_0 (mg/L)	50	75	50	75
Bed weight (g)	3	3	3	3
Bed length (cm)	3	3	3	3
R^2	0.946	0.966	0.960	0.956
Q (mL/min)	1.7±0.3	2.2±0.2	1.7±0.3	2.2±0.2
K_{Th} ($L.mg^{-1}.h^{-1}$)	0.00802	0.0108	-	-
q_0 (mg/g)	46.3±8.4	42.5±4.4	-	-
K_{YN} (h^{-1})	-	-	0.401	0.810
τ (h)	-	-	27.05	12.86
q_{YN} (mg/g)	-	-	46.3±8.3	42.4±4.4

CONCLUSIONS

The present study showed that corn cobs were an effective biosorbent for the removal of methylene blue from aqueous solution. Batch adsorption experiments were carried out as function of adsorbent mass, pH, stirring speed, contact time and initial concentration of dye. The results suggested that the adsorption of the MB dye is influenced by too acidic medium and that there is no need to change the initial pH of the MB solution (pH 6.4). The speed of agitation must be controlled because it contributes considerably to the distribution of the adsorbate into the

adsorbent material. The amount of MB dye adsorbed increases with the increase of the initial concentration. The kinetic study shows that the adsorption equilibrium can be reached after 30 min when 100 mL of MB solution at 25 mg/L is treated with 0.2 g of corn cobs. On the other hand, it was found that pseudo-second-order rate model and Langmuir isotherm model gave perfect fittings to the experimental data. The maximum sorption capacity of methylene blue on corn cobs was 40 mg/g and the R_L values indicate that the sorption of MB on corn cobs is favorable.

Regarding the dynamic mode, it can be concluded that both models of Thomas and Yoon-Nelson are appropriate for describing the adsorption of MB dye on corn cobs. In comparison to batch system, column adsorption capacity is relatively higher because of greater dye concentration gradient at the interface zone of dye solution and material bed.

Taking into consideration the above results, it can be concluded that corn cobs can be considered as low cost adsorbent for dye removal, eventually, in textile wastewater treatment processes. The results obtained in this study at laboratory scale confirm the technical and economic interests of the adsorption process using corn cobs which are agricultural by-products.

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