KINETIC AND EQUILIBRIUM STUDIES OF METHYLENE BLUE REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON TREATED SAWDUST

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The aim of this study is to use treated sawdust as an adsorbent for the removal of methylene blue (MB) dye. The adsorption equilibrium and kinetics of methylene blue dye on this adsorbent were then examined at 25 °C. The adsorption isotherm of the methylene blue on the treated adsorbent was determined and correlated with common isotherm equations. The sorption data were then correlated with the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm exhibited a better fit for the adsorption data than the Freundlich isotherm with maximum monolayer adsorption capacity of 236.16 mg g^{-1}. The kinetics of methylene blue adsorption on the treated adsorbent has also been studied by fitting the data in the Lagergren's first order, the Ho-McKay's pseudo second order, the Elovich and the Intraparticulate kinetic models. It was observed that the removal of methylene blue over the treated adsorbent undergoes the second order processes at all the concentrations of the dye. The kinetic parameters of this best-fit model were calculated and discussed.

Key words: sawdust; adsorbent; dye; kinetic models; adsorption isotherm

СТУДИЈА ЗА КИНЕТИКАТА И РАМНОТЕЖАТА ПРИ ОТСТРАНУВАЊЕ НА МЕТИЛЕНСКО СИНО ОД ВОДНИ РАСТВОРИ СО АТСОРПЦИЈА ВРЗ ОБРАБОТЕНИ СТРУГАНИЦИ

Проучувана е употребата на обработени струганици како атсорбент за отстранување на бојата од метиленско сино (МС). При 25 ºС се испитувани атсорпционата рамнотежа и кинетиката на преминувањето на бојата на метиленско сино врз споменатиот атсорбент. Атсорпционата изотерма на МС на обработениот атсорбент е определена и корелирана со вообичаени изотермни равенки. Потоа потадоци за сорпцијата се корелирани со Лангмјуровиот и Фројндлиховиот атсорпционен и изотермен модел. Подобра согласност за атсорпционите податоци покажува Лангмјуровата изотерма (отколку Фројндлиховата) со максимален едно-слоен атсорпционен капацитет од 236,16 mg g^{-1}. Кинетиката на атсорпцијата на МС врз обработениот атсор-бент е изучувана и преку интерполација на податоците од прв ред според Лажергрен, од псевдовтор ред според моделите на Хо-Меккеј, на Елович и внатрепартикуларниот кинетички модел. Покажано е дека от-странувањето на МС од обработениот атсорбент се одвива преку процеси од втор ред при сите концентрации на боја. Пресметани се и дискутирани се кинетичките параметри од методот кој дава најдобра интерполација.

Клучни зборови: струганици; атсорбент; боја; кинетички модел; атсорпциона изотерма

1. INTRODUCTION

Colored materials and dyes constitute the focus of many environmental concerns because of their non-biodegradable and polluting nature [1, 2]. Thus, prior to their discharge into receiving waters, there is a considerable need to treat colored effluents efficiently [3–5]. There are several physicochemical processes for removal and recovery of colored materials and dyes from effluents, out of which adsorption is one of the most effective one [6–8]. The important aspect of the adsorption process is easy regenerability and less operational cost. Adsorption techniques have proven

successful in removing colored organic species and the choice of the adsorbent is one of the key factors determining the effectiveness of any adsorption process. In recent years, activated carbon has been found as the most widely used adsorbent, as it possesses high capacity for the adsorption of organic materials [9–11]. However, due to the high cost of the activated carbon, the scope of many adsorption studies has been focused on deriving cheaper adsorbents from waste materials. Thus, cheap and effective adsorbents have been developed from various waste materials such as chitin and chitosan [12], peat [13], rice husk [14], clay [15], bottom ash and de-oiled soya [16–18], coal ash [19], crushed bricks [20], sugar beet pulp [21], tea waste [22], feathers [23, 24]. Gupta and his co-workers [25–29] have also made substantial contributions in this area. We have also investigated the use of the activated carbon derived from periwinkle shells in the adsorption of methylene blue dye in recent time [30].

Methylene blue (MB) dye had also been adsorbed using kaolinite and activated carbon produced from palm tree cobs [31, 32]. The removal of methylene blue from wastewater needs considerable attention. In this present study, treated sawdust has been utilized as an adsorbent for the removal of methylene blue from aqueous solutions. The sorption data have also been correlated with adsorption isotherms and kinetics of adsorption has been studied to determine the efficiency of adsorption process.

2. MATERIALS AND METHODS

2.1. Methylene blue

Methylene blue (MB) was obtained from BDH. It was used as an adsorbate and was not purified prior to use. Double distilled water was employed for preparing all the solutions and reagents. The chemical structure of the dye is shown in Appendix A.

2.2. Preparation and characterization of adsorbent

The sawdust (*Gmelina arbhoria*) used in this experiment was collected from a local sawmill and dried in sunlight until constant weight was maintained. It was ground to fine powder and sieved to

150 μm size. Sawdust contained water-soluble compounds like tannin, which gave brown color to the effluents during the treatment. The chemical treatment with formaldehyde led to polymerization of the compounds responsible for colorization. Sawdust (50 g) was washed repeatedly with distilled water and subsequently dried for 24 h at 233 K to washout the coloring materials. To improve the physical characteristics further, it was treated with 1% formaldehyde in the ratio of 1:4 (sawdust : formaldehyde, w/v) and 100 ml of 0.2 M H_2SO_4. It was heated with cover-over hotplate at 323 K for 6 h with occasional stirring. The product was cooled and washed several times with distilled water and finally dried at 333 K to eliminate all toxicity due to the presence of formaldehyde. The treated sawdust sample (10 mg) was ground with 200 mg of KBr (spectroscopic grade) in a mortar pressed into 10 mm diameter disks under 10 tonnes of pressure and high vacuum for 10 min. The FTIR spectra were obtained on a JASCO FTIR-3500 spectrometer. The analysis conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400 and 4000 cm^{-1}. The FTIR spectra of sawdust, treated sawdust and the sawdust after adsorption are shown in Fig. 1. The FTIR spectra of sawdust showed peaks at 3240, 3015, 1650, 1540, 1450, 1420 1250 and 1160 cm^{-1} which may be assigned to the OH group, aliphatic C–H group, unsaturated groups like alkene, amide, CH deformation, OH deformation, aromaticity and OH stretch, respectively. The intensity of the peaks were either minimized or shifted slightly in case of treated and adsorbed sawdust, respectively. These results are similar to the ones reported earlier [33].
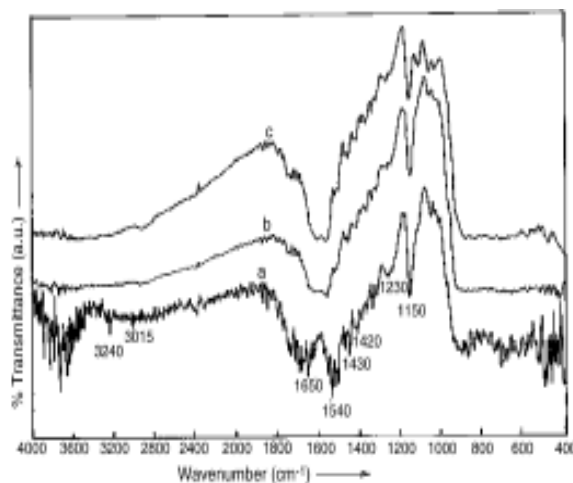

Fig. 1. FTIR spectra of (a) untreated sawdust, (b) treated sawdust and (c) treated sawdust after adsorption

2.3. Batch equilibrium studies

Adsorption isotherms were performed in a set of 43 Erlenmeyer flasks (250 ml) where solutions of dye (200 ml) with different initial concentrations (100–500 mg l^{-1}) were placed in these flasks. Equal mass of 0.2 g of particle size (150 μm) treated sawdust was added to dye solutions and kept in an isothermal shaker (25 ± 1°C) for 48 h to reach equilibrium of the solid-solution mixture. Similar procedure was followed for another set of the Erlenmeyer flask containing the same dye concentration without the adsorbent to be used as a blank. The pH was adjusted to 7 by adding either few drops of diluted hydrochloric acid or sodium hydroxide (0.1 mol l^{-1}). The flasks were then removed from the shaker and the final concentration of dye in the solution was analyzed. The concentration of methylene blue in the supernatant solution after and before adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan) at 668 nm. It was found that the supernatant from the treated sawdust did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.

The samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg g^{-1}), was calculated by

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg l^{-1}) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

2.4. Batch kinetic studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of dye were similarly measured. The amount of adsorption at time t, q_t (mg g^{-1}), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_o and C_t (mg l^{-1}) are the liquid-phase concentrations of dye at initial and any time t, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

2.5 Desorption and regeneration studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be adsorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If sulphuric acid or alkaline water desorps the dyes, then the adsorption is by ion exchange. If organic acids like acetic acid desorp the dyes, then the dye is attached to the adsorbent through chemisorption [34, 35].

3. RESULTS AND DISCUSSION

3.1. Effect of agitation time and concentration of dye on adsorption

A series of contact time experiments for the MB dye has been carried out at different initial concentrations (100–500 mg l^{-1}) and at temperature of 25 °C. Fig. 2 shows the contact time necessary for MB dye with initial concentrations of 100–200 mg l^{-1} to reach equilibrium in 6 h. For the initial concentration of 300 mg l^{-1} it took 8 h to reach equilibrium. However, for the MB dye with higher initial concentrations (400–500 mg l^{-1}), longer equilibrium time of 24 h is needed. As it can be seen from Fig. 2, the amount of the adsorbed dye onto the treated sawdust increases with time and, at some point of time, it reaches a constant value beyond which no more is removed from solution. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the treated sawdust. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions.

The adsorption capacity at equilibrium increases from 67.5 to 410.2 mg g^{-1} with an increase in the initial dye concentration from 100 to 500 mg l^{-1} (see Table 1). It is evident that the treated sawdust is efficient in adsorbing the MB dye from aqueous solution, the process attaining equilibrium gradually.

T a b l e 1

Comparison of the pseudo first- and second-order adsorption rate constants and calculated experimental q_e values for different initial dye concentrations

| Initial concentration (mgg^{-1})	$q_{e,exp}$ (mgg^{-1})	First order kinetic model				Second order kinetic model			
		k_1 (h^{-1})	$q_{e,,cal}$ (mgg^{-1})	R^2	SSE (%)	k_2 (g(mgh)$^{-1}$)	$q_{e,,cal}$ (mgg^{-1})	R^2	SSE (%)
100	67.5	0.637	76.02	0.87	3.81	0.0154	69.93	0.99	0.432
200	154.8	0.612	236.28	0.94	36.44	0.0084	156.25	0.99	0.648
300	232.5	0.595	326.36	0.77	41.98	0.0031	243.90	0.99	5.098
400	321.3	0.334	415.72	0.96	42.22	0.0021	335.42	0.99	6.315
500	410.2	0.327	524.71	0.96	51.21	0.0013	430.78	0.99	9.204
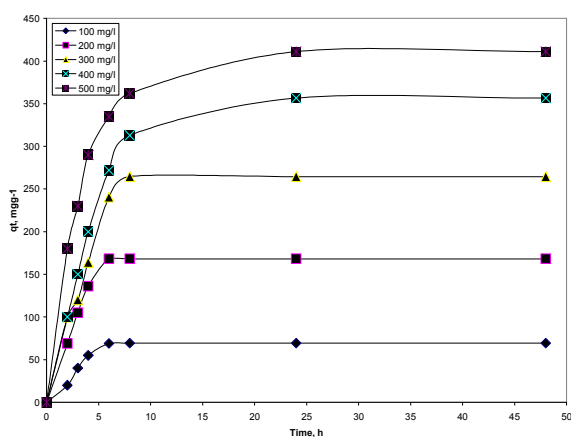
Fig. 2. The variation of adsorption capacity with adsorption time at various initial MB concentrations at 25 ^{0}C (pH 7, W = 0.2 g)

3.2. Adsorption kinetics

The pseudo first-order equation. The rate constant of adsorption is determined from the pseudo first-order equation given by Langergren and Svenska [36]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where q_e and q_t are the amounts of the MB adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 the rate constant adsorption (h^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t for different concentrations of the MB. The correlation coefficient values at high concentrations are higher than 0.70, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 1). This shows that the adsorption of the MB onto treated sawdust is not the first-order kinetics.

The pseudo second-order equation. The pseudo second-order equation based on equilibrium adsorption [37] is expressed as:

$$1/q_t = 1/k_2 q_e^2 + (1/q_t)\, t \qquad (4)$$

where k_2 (g/mg h) is the rate constant of the second-order adsorption. If the second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q versus t (Fig. 3) show a good agreement between experimental and calculated q_e values (Table 1).
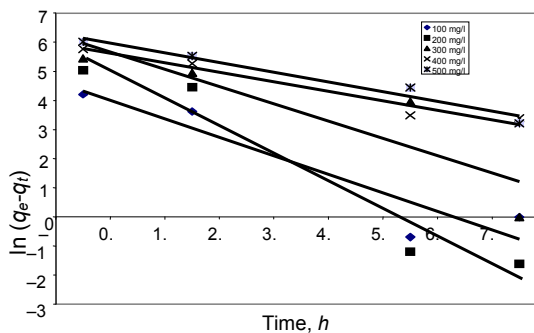

Fig. 3. Pseudo-first order kinetics for adsorption of the MB using treated sawdust at 25 ^{o}C

The correlation coefficients for the second-order kinetic model are greater than 0.9 indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of the MB on treated sawdust.
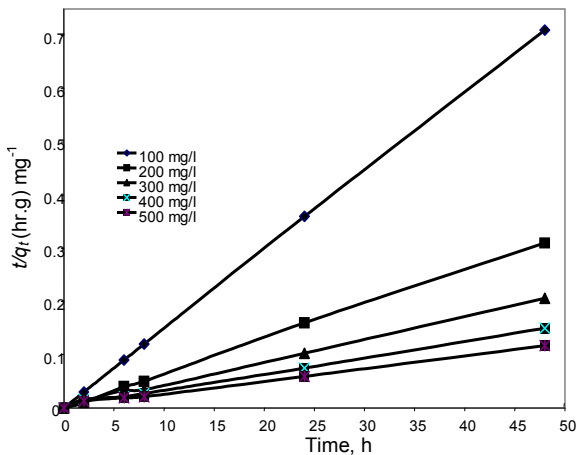
Fig. 4. Pseudo-second order kinetics for adsorption of the MB using treated sawdust at 25 °C.

The intraparticle diffusion model. The intraparticle diffusion model [38, 39] is expressed as

$$R = K_{id} (t)^a \qquad (6)$$

A linearised form of the equation is followed by

$$\log R = \log K_{id} + a \log (t) \qquad (7)$$

where: R is the percent of the MB adsorbed, t is the contact time (hr), "a" is the gradient of linear plots, K_{id} is the intraparticle diffusion rate constant (hr^{-1}), "a" depicts the adsorption mechanism. K_{id} is taken as a rate factor, i.e. percent of the MB adsorbed per unit time. If the mechanism of adsorption fits the intraparticle diffusion model, then a plot of $\log R$ against $\log t$ will yield a straight line with a slope "a" and an intercept of $\log K_{id}$. The intraparticle diffusion model for the adsorption of the MB by activated carbon produced from treated sawdust at 25°C is shown in Fig 6. The values of K_{id} were calculated from the slope of such plots and the R^2 values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of K_{id} illustrate an enhancement in the rate of adsorption; such high K_{id} values illustrate a better adsorption mechanism, which is related to an improved bounding between the MB and the adsorbent particles (Table 2). [40].

The Elovich equation. The Elovich equation based on equilibrium adsorption [38] is generally expressed as:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln (t) \qquad (5)$$

where: α is the initial adsorption rate (mg g^{-1} min^{-1}), β is the desorption constant (g·mg^{-1}) during any experiment. If the adsorption fits the Elovich model, a plot of q_t vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha\beta)$. The graph of the Elovich model for the adsorption of the MB by activated carbon produced from treated sawdust at 25 °C is shown in Fig 5.
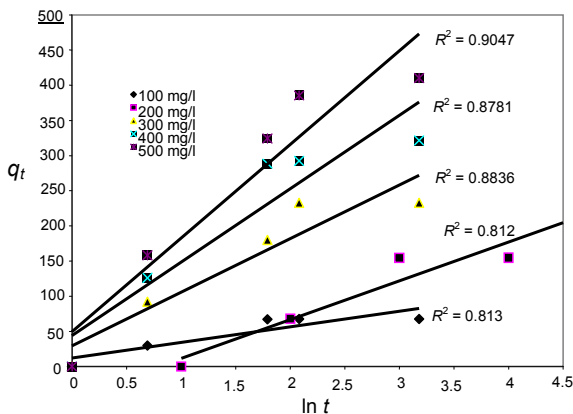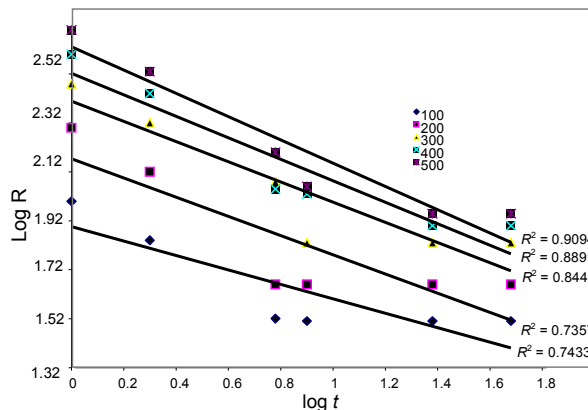

Fig. 5. The Elovich model for the adsorption of the MB using treated sawdust at 25 °C

Fig. 6. The intraparticulate diffusion model for the adsorption of the MB using treated sawdust at 25 °C

T a b l e   2

Comparison of the intraparticle and the Elovich kinetic model values for different initial dye concentrations

Initial concentration (mg l^{-1})	Intaparticle kinetic model			Elovich kinetic model		
	K_{id}	a	R^2	β	α	R^2
100	78.723	0.295	0.7433	203.50	0.1512	0.9324
200	149.000	0.393	0.7357	176.29	0.1175	0.7845
300	255.918	0.413	0.8448	155.90	0.0441	0.8336
400	333.426	0.440	0.8891	111.70	0.0436	0.8228
500	427.563	0.475	0.9094	106.50	0.0257	0.8557

3.3. Test of kinetic models

Besides the value of R^2, the applicability of the two kinetic models are verified through the sum of error squares (SSE, %). The adsorption kinetics of the MB on treated sawdust derived from treated sawdust was tested at different initial concentrations. The validity of each model was determined by the sum or error squares (SSE, %) given by:

$$\text{SSE}(\%) = \sqrt{\frac{\Sigma\left(q_e, \exp - q_e, cal\right)^2}{N}} \qquad (8)$$

where N is the number of data points. The higher is the value of R^2 and the lower is the value of SSE; the better the goodness of fit will be. Table 1 lists the calculated results. It was found that the adsorption of methylene blue on AC produced from treated sawdust can be best described by the second-order kinetic model. Similar phenomena processes have been observed in the adsorption of direct dyes on treated sawdust prepared from sawdust [41] and adsorption of Congo red dye on treated sawdust from coir pith [42].

3.4. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [43]. The adsorption isotherm study is carried out on two well-known isotherms, the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [44]. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [45]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Langmuir isotherm. The linear form of the Langmuir isotherm model is given by the following equation:

$$C_e/q_e = 1/Q_o b + (1/Q_o)\, C_e \qquad (3)$$

where C_e is the equilibrium concentration of the adsorbate (MB) (mg/l), q_e, the amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1}), and Q_o and b are the Langmuir constants related to the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When C_e/q_e was plotted against C_e, a straight line with slope of $1/Q_o$ was obtained (Fig. 7), indicating that the adsorption of the MB on treated sawdust produced from treated sawdust follows the Langmuir isotherm. The Langmuir constants 'b' and 'Q_o' were calculated from this isotherm and their values are given in Table 3.
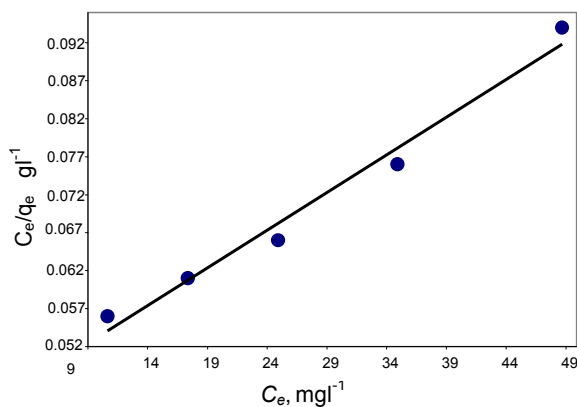

Fig. 7. The Langmuir adsorption isotherm of the MB using treated sawdust at 25 ^{0}C

Conformation of the experimental data into the Langmuir isotherm model indicates the homogeneous nature of the treated sawdust carbon surface, i.e. each dye molecule/treated sawdust carbon adsorption has equal adsorption activation

energy. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of activated carbon derived from sawdust. Similar observation was reported by the adsorption of acid orange 10 dye onto treated sawdusts prepared from agricultural waste bagasse [46] and by the adsorption of direct dyes on treated sawdust [41] and adsorption of the Congo red dye on treated sawdust from coir pith [42].

T a b l e 3

The Langmuir and the Freundlich isotherm constants for the MB at 25 ^{o}C

Langmuir isotherm	
Q_o (mg g^{-1})	263.16 ± **0.03**
B (L/mg)	0.007 ± **0.04**
R_2	0.9873 ± **0.02**
R_L	0.222 ± **0.01**
Freundlich isotherm	
$\dfrac{1}{n}$	0.5252 ± **0.02**
K_F [(mgg^{-1})(mg^{-1})$^{1/n}$]	58.56 ± **0.03**
R^2	0.9471 ± **0.01**

All values are means of triplicates ± SD

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [47, 48], which is defined by:

$$R_L = 1/(1 + bC_0) \qquad (10)$$

where b is the Langmuir constant and C_0 the highest dye concentration (mg l^{-1}). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.02 and confirmed that the treated sawdust is favorable for adsorption of the MB dye under conditions used in this study.

Freundlich isotherm. The well-known logarithmic form of the Freundlich model is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (11)$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MB) and K_F and n are the Freundlich constants, n giving an indication of how favorable the adsorption process and K_F (mg g^{-1} (l mg^{-1})^n) is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or a distribution coefficient and represents the quantity of dye adsorbed onto treated sawdust adsorbent for a unit equilibrium concentration.

The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [43]. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [44]. The plot of $\log q_e$ versus $\log C_e$ gives straight lines with slope of '$1/n$' (Fig. 8), which shows that the adsorption of the MB also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 3.
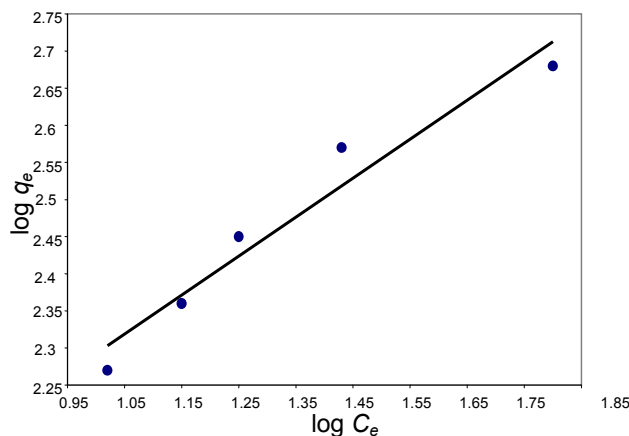

Fig. 8. The Freundlich adsorption isotherm of the MB using sawdust at 25 ^{o}C

Table 3 shows the values of the parameters of the two isotherms and the related correlation coefficients. As seen from Table 3, the Langmuir model yields a somewhat better fit ($R^2 = 0.9873$) than the Freundlich model ($R^2 = 0.9471$). As also illustrated in Table 3, the value of $1/n$ is 0.5252, which indicates favorable adsorption [48].

This work has shown that utilization of treated sawdust will be useful in the treatment of methylene blue dyes from industrial waste effluents; it will also eliminate various ecological problems that these waste effluents could cause.

4. CONCLUSIONS

The present investigation has shown that treated sawdust can be effectively used as a raw material for the removal of methylene blue dye from aqueous solution over a wide range of concentration. Methylene blue is found to adsorb strongly on the surface of treated sawdust. The effect of various reagents used for desorption studies shows that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. Also, the adsorbent exhibits a stable structure towards this reagent. The desorption of dyes by mineral acids indicates that the dyes are adsorbed onto treated sawdust by physisorption. The adsorption behaviour is described by a monolayer Langmuir type isotherm. Kinetic data follows the pseudo second-order kinetic model. The value of the maximum adsorption capacity, Q_o, (263.16 mg g^{-1}) is comparable with the values for commercial treated sawdust reported in earlier studies.

APPENDIX A.
Chemical structure of methylene blue dye
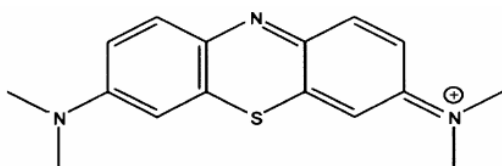
Methylene Blue [3, 9-bis dimethylaminophenazo thionium chloride]
Basic Blue 9, C.I. 52015, $\lambda_{max} = 668$ nm

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