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Modified Sawdust for Removal of Methyl Violet (Basic Dye) From Aqueous Solutions

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Sawdust an inexpensive material is currently being investigated as an adsorbent for removing undesired material from water. In this study, natural sawdust and modified ethylenediamine sawdust were used for sorption of methyl violet dye. The sorption characteristics of methyl violet by sorbent were studied under various experimental conditions. The effect of different parameters such as contact time, varying dye concentration, agitation time, pH of the medium and temperature was investigated. Simultaneous removal of methyl violet occurred at pH 10, contact time 1 h, 0.1 g of sorbent and room temperature (25 °C). Decreasing particle size increased the uptake of dyes. The kinetics of methyl violet dye sorption fitted a pseudo-second order rate expression. The equilibrium adsorption capacity of sawdust for methyl violet was obtained by using linear Freundlich and Langmuir isotherms.

Key Words: Adsorption, Dye removal, Sawdust, Modified sawdust, Methyl violet, Wastewater.

INTRODUCTION

The conventional methods of colour removal from industrial effluents include ion exchange, activated carbon adsorption, membrane technology and coagulation[1]. Amongst all the sorption process by an activated carbon has been shown to be one of the most efficient methods[2]. Adsorption techniques for colour removal are becoming popular and many adsorbents have recently been tested such as silica[3], hardwood sawdust[4], fly ash[5], chrome sludge[6] and waste red mud[7]. Although, activated carbon is a preferred adsorbent, its widespread use is restricted due to its high cost. In order to decrease the cost of treatment, some attempts have been made to find low cost alternative adsorbents[8]. A number of investigations have shown that agricultural by-products such as date pith, corncorb, barley husk, rice hull and biogases pith have the potential alternative sorbent for the removal of dyes in textile wastewater[9-11]. Chemical modifications of these materials enhanced their sorption capacities and thus usefulness in the treatment of wastewater. These materials, in general, posses' high sorption capacities for either positively or negatively charge dye molecules. It is very common for fine textile industries using a mixture of different types of dyes for different applications. Hence there is a need to have sorbents capable of removing different types of dyes either singly or simultaneously.

The aim of this work was to study the possibility of the utilization of sawdust and ethylenediamine modified sawdust for sorption of methyl violet from aqueous solutions.

EXPERIMENTAL

Synthetic basic dye solutions of methyl violet (MV) (basic violet 1) were used as the sorbates in this study (Fig. 1). The dye powder used in this study was purchased from Merck and used without further purification. Standard dye solutions of 1000 mg/L was prepared as stock solutions and subsequently diluted when necessary.

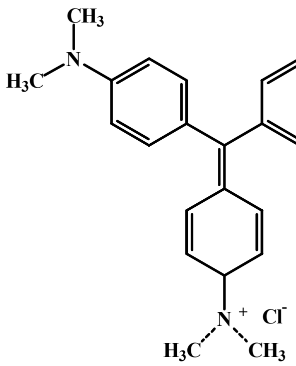

Fig. 1. Chemical structure of methyl violet

Sawdust is a by-product of wood industrials. Sawdust was collected and washed several times to ensure the removal of dust and ash. It was subsequently rinsed several times with distilled water and dried overnight in an oven at 50 °C. The dried sawdust was ground to pass through a 1mm sieve and labeled as natural sawdust. Modification of natural sawdust was optimized by varying the treatment temperature and the natural sawdust to ethylenediamine modified sawdust was prepared by treating natural sawdust with ethylenediamine in a ratio of 1.0 g sawdust to 0.01 mol of ethylenediamine in well-stirred water bath at 80 °C for 4 h.

Experimental procedure: Sorption experiments were preformed by agitating 0.1 g sorbent in 50 mL of 100 mg/L dye solution in a baker at 150 rmp on an orbital shaker for 2 h at room temperature (25 °C). The sorbent-sorbate mixture was then centrifuged at 3.0×10^3 rmp for phase separation. The supernatant was analyzed for its dye concentration using a Shimadzu 16A (Kyoto, Japan) double beam UV-Vis spectrophotometer.

All measurements were made at wavelength corresponding to maximum absorption. To study the effect of pH, a series of 100 mg/L dye solutions of methyl violet was prepared. The initial pH of dye solutions was adjusted to the range of 2-10 by adding dilute HCl or NaOH. At the end of experimentation pH of dye solutions were measured. Each dye solution was shaken with 0.1 g sorbent for 2 h. Contact time experiments were performed using methyl violet dye solutions with concentrations of 100 mg/L.

The effect of particle size on dye sorption was studied by sieving the modified sawdust into three different sizes ranging between 105-250 µm, 250-315 and 315-1000 µm. Sorption isotherms were obtained by varying the dye concentrations from 10 to 200 mg/L of dye solutions. The dependence of methyl violet sorption on sawdust concentration was studied at room temperature and fixed pH values by varying the sorbent amount from 0.02 to 2.0 g while keeping the volume (100 mL) of the dye solution constant. Linear regression analyses were carried out on the data in kinetic and isotherm studies and the correlation coefficient r^2 was calculated using Microsoft Excel Program.

RESULTS AND DISCUSSION

Comparative uptake of methyl violet dye by natural sawdust and modified sawdust: The comparative uptake of methyl violet by natural sawdust and modified sawdust of the dye solutions is shown in Fig. 2. At the end of the experiment, a decrease in pH was noted in dye solution, indicating that an ion-exchange process involving the carbonyl groups on the surface of the sorbent has occurred with the release of H^+ ions into the solution.

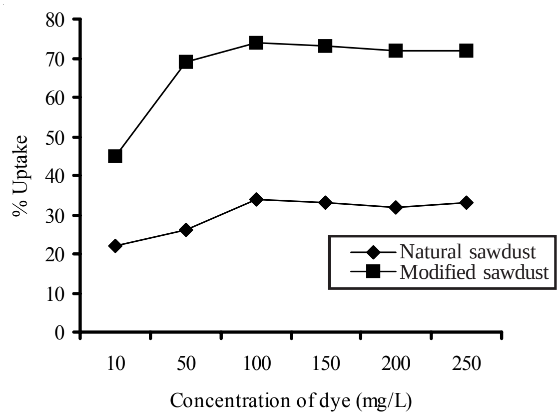

Fig. 2. Comparative study on the sorption of methyl violet dye by natural sawdust and modified sawdust

In aqueous solutions, the dye molecules of methyl violet dissociate into a positively charged component and Cl^-. The sawdust in its natural state sorbs positively charge species that is attributed to the presence of binding sites such as carboxyl and hydroxyl groups on the surface[12]. Modified sawdust appeared to be able to bind methyl violet dye solutions. It has been postulated that modified sawdust possesses both carboxyl and amine groups on its surface, the latter was introduced by modification process using ethyenediamine it thus appears that modified sawdust has different binding sites that are responsible for binding species. For that reason the modified sawdust can removed more than 70 % of the methyl violet dye, but natural sawdust can remove closely 30 % of dye.

Effect of particle size: The influence of particle size on dye sorption was investigated by using three different size ranges. Fig. 3. shows with decreasing particle size in dye solutions, sorption increases. This suggests that surface activity and thus surface area of sorbent plays an important role in the sorption of dye molecules. The small particles move faster in solution than large particles and thus there is more shears on their surface. It follows that the boundary layer thickness is thinner than that on the larger particles and this results in faster rate of sorption. Similar results were reported in the removal of dyes by modified rice hall[12], raw and activated date pits[9] and industrial waste products[13].

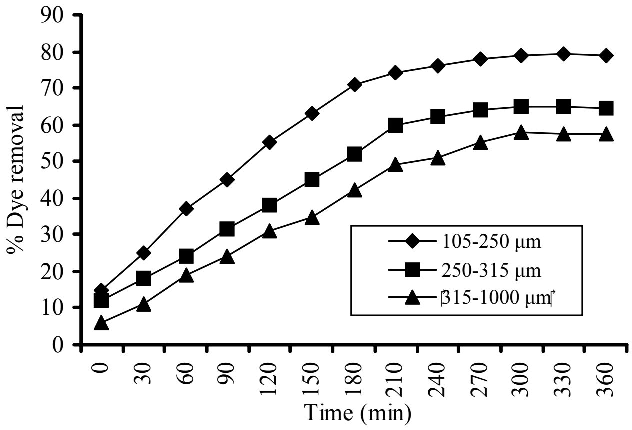

Fig. 3. Effect of particle size on the sorption of methyl violet onto modified sawdust

Effect of sorbent dosage: The effect of sorbent dosage on sorption of methyl violet dye solutions is shown in Table-1. It followed the usual pattern of increasing uptake as the sorbent concentration increased. This corresponds to an increase in active sites for sorption. With an initial dye concentration of 100 mg/L for methyl violet dye solution, saturation occurred at 0.1 g sorbent at which point further increase in sorbent dosage had little effect on sorption. Such a study should be useful for establishing the optimum amount of modified sawdust required in the removal of dye.

TABLE-1
EFFECT OF SORBENT DOSAGE ON THE % UPTAKE OF METHYL VIOLET DYE (DYE CONCENTRATION OF 100 mg/L AT ROOM TEMPERATURE)

Mass of sorbent (g)	0.01	0.025	0.05	0.075	0.1	0.25	0.5	0.75	1	1.5	2
%Uptake (NSD)	33	35	37	41	45	45	44	43	43	42	42
%Uptake (MSD)	46	52	59	68	75	74	73	72	72	71	70

NSD = Natural sawdust; MSD = Modified sawdust.

Effect of pH: The effect of pH on the uptake of methyl violet by modified sawdust is shown in Fig. 4. For methyl violet dye solution, the percentage uptake increased from 2.3 to 75.6 with increase in pH from 2 to 10. At low pH, the carboxyl groups

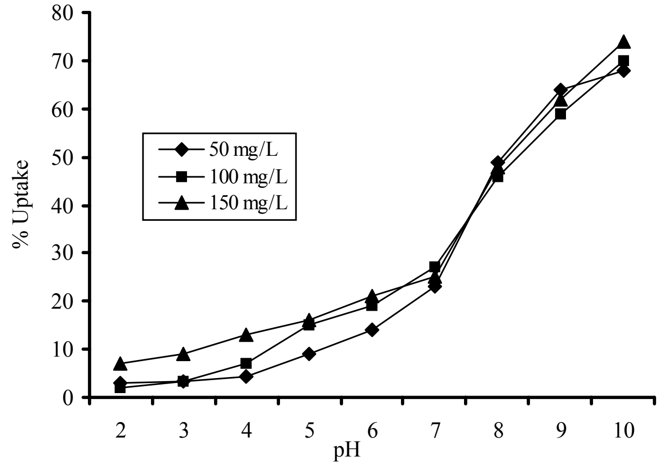

Fig. 4. Effect of pH on the sorption of methyl violet dye solution on the 0.1 modified sawdust at room temperature

on the surface of sawdust are responsible for binding with methyl violet is predominantly protonated (-COOH), hence incapable of binding dyes. As pH increased, sorption became favourable due to the deprotonation of the carboxyl groups ($-COO^-$), resulting in sorption sites that were available for binding with dye molecule. With increasing pH the number of positively charged sites decreased and the number of negatively charged sites increased. This phenomenon favours the sorption of positively charged dye due to electrostatic attraction[14].

Effect of contact time: The adsorption data of methyl violet *versus* contact time is presented in Fig. 5. The sorbate concentrations in solution were determined at different times from initial solutions of 100 mg/L and a sorbent dosage of 0.1 g. All the experiments conducted here were at pH 10. The plots representing adsorption of dye on sawdust and modified sawdust, visualize three distinct phases *i.e.*, the first phase indicates the instantaneous sorption of the dye within 10 min of contact time, the second one shows a gradual equilibrium and the third one indicates the final equilibrium. The uptake of dye on natural sawdust reaches equilibrium in 1.5 h with 35 % of dye removal, while on modified sawdust; it reaches equilibrium in 1 h with 86 % of dye removal.

Adsorption kinetics: In order to predict adsorption kinetic models of methyl violet dye solutions pseudo-first order and pseudo-second-order kinetic models were applied to the data. The pseudo-first order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time.

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \quad (1)$$

where q_e and q_t are the amounts of dye adsorbed per unit mass of the adsorbent (mg/g) at equilibrium and time 't', respectively and 'k_1' is the rate constant of adsorption (min^{-1}).

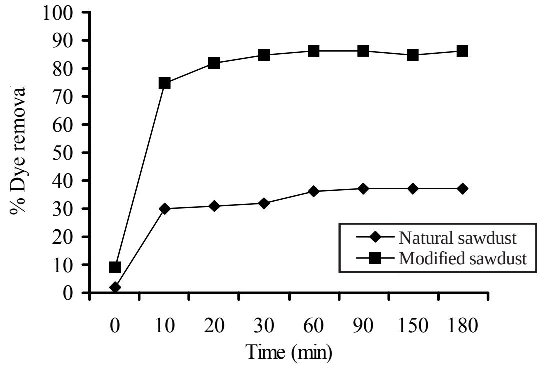

Fig. 5. Effect of contact time on % methyl violet removal by 0.1 g natural sawdust and modified sawdust at pH 10

The pseudo-second order model is based on adsorption equilibrium capacity:

$$1/C_t = 1/C_i + k_2 t \quad (2)$$

where C_i is the initial concentration (mg/L), C_t the concentration at time (mg/L) and k_2 is the rate constant of the pseudo-second order equation (l mg^{-1} min^{-1}).

The rates of sorption of methyl violet at different initial concentrations are shown in Fig. 6. It was found that application of pseudo-second order kinetics provides better correlation of experimental data than the pseudo-first order model for the methyl violet on modified sawdust. In addition, the equilibrium sorption capacities determined from the first order kinetic model were lower than those determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model, which was based on the assumption that the rate limiting step may be chemical sorption or chemisorption's involving valency forces through sharing or exchange of electron between sorbent and sorbate[15].

The values of rate constant were calculated from the slope of the plots, as 14.515 for natural sawdust and 26.745 for modified sawdust (l g^{-1} min^{-1}), respectively. The high rate constant of modified sawdust, indicates the high affinity for this dye, consistent with its high adsorption. Similar trends were observed in the adsorption of BB3 and RO16 12[12] and acid dye yellow 4 Gl[16]. The kinetic data (Fig. 7) do not fit the first order equation. The good correlation coefficients were obtained by fitting the experimental data to eqn. 2, indicating that the adsorption process on modified sawdust is pseudo-second order as shown in Fig. 6.

Adsorption isotherms: In the present investigation, the data have been correlated with a suitable isotherm. Equilibrium sorption data of methyl violet on modified sawdust is fitted into both Langmuir (eqn. 3) and Freundlich (eqn. 4) equations. The linear forms of the Langmuir and Freundlich isotherm are represented by the equations:

$$C_e/q_e = 1/Q\, b + C_e/Q \quad (3)$$

$$q_e = k_f + 1/n\, C_e \quad (4)$$

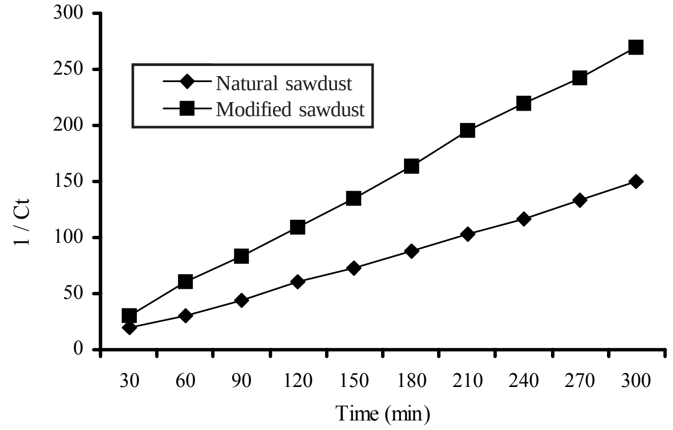

Fig. 6. Kinetics of pseudo-second order adsorption of methyl violet onto natural sawdust and modified sawdust at pH 10 and 25 °C

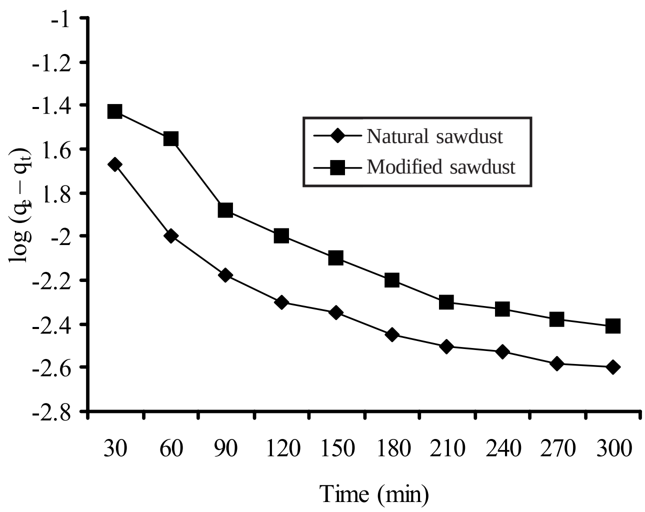

Fig. 7. Pseudo-first order kinetic of methyl violet onto modified sawdust for 50-200 mg/L of dye at pH 10 and 25 °C

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of the adsorbed adsorbate at equilibrium (mg/g) and Q (mg/g) and b (l/mg) are Langmuir constants related to the capacity and energy of the adsorption, respectively. The value of Q and b can be calculated from the slope and intercept of the plot of C_e/q_e *vs.* C_e. 'k_f' and 'n' are Freundlich isotherm constants. The values of 'n' and 'k_f' can be calculated from the slope and intercept of plot of log q_e *vs.* log C_e. The isotherm constants were calculated from the slope and intercept of Fig. 8 (Langmuir isotherm) and Fig. 9 (Freundlich isotherm) and presented in Table-2.

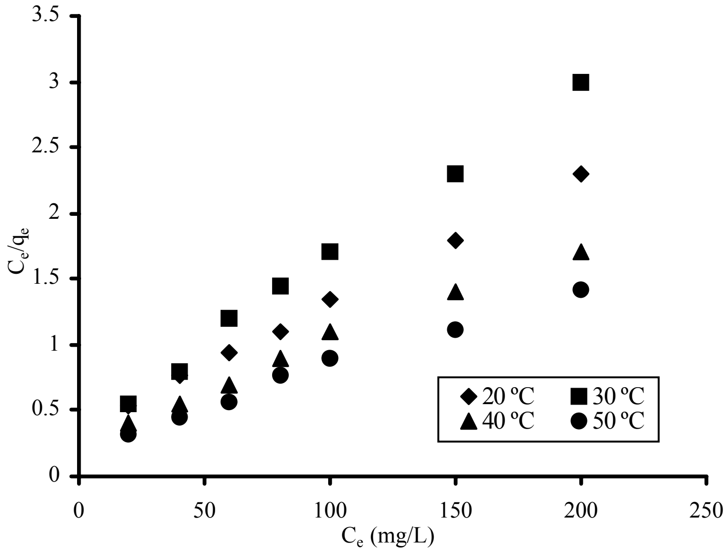

Fig. 8. Langmuir isotherm for the sorption of dye solutions at 30 ºC

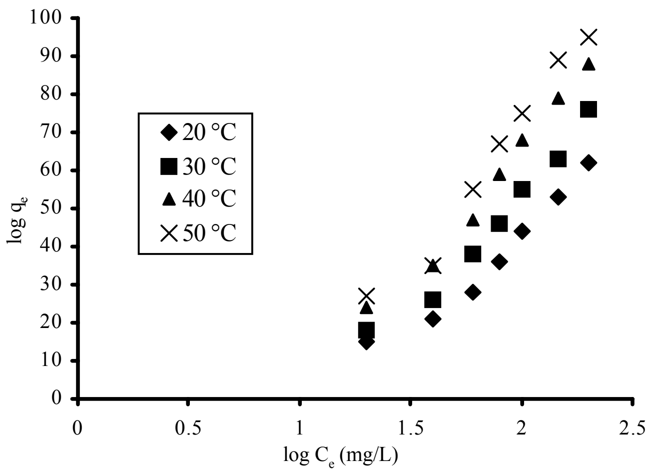

Fig. 9. Freundlich isotherm for the sorption of dye solutions at 30 ºC

TABLE-2
VALUES OF LANGMUIR AND FREUNDLICH ADSORPTION CONSTANTS FOR THE SORPTION OF METHYL VIOLET ONTO 0.1 g MODIFIED SAWDUST

Temperature (ºC)	Langmuir model			Freundlich model		
	Q (mg/g)	b (mg/L)	r^2	n	k_f	r^2
20	100.20	0.034	0.993	0.126	0.25	0.994
30	73.50	0.046	0.997	0.112	0.47	0.991
40	131.58	0.029	0.990	0.100	1.19	0.999
50	161.29	0.030	0.992	0.084	1.20	0.989

Applicability of both isotherms to sorption of dyes by agricultural wastes, activated carbons prepared from wastes and treated spent bleaching earth have been reported previously[2,14,17]. These two models are based on different assumptions *i.e.*, Langmuir model implies monolayer coverage and constant sorption energy while the Freundlich model deals with physico-chemical sorption on heterogeneous surfaces. However fitting the model to the sorption process does not necessarily imply any physical explanation attached to them since the biosorbent's surface is non-homogeneous and there could be more than one type of sorption sites on the biosorbent's surface. Langmuir model allows the calculation of limiting sorption capacities that could be useful for the comparison of the sorption efficiency of materials studied.

Conclusion

This study confirmed that modified sawdust was an excellent sorbent for removal of methyl violet from aqueous solution. Sorption was pH dependent and the optimal pH for removal of this dye was 10. The equilibrium data conform to both Langmuir and Freundlich isotherms. Analysis of data indicates that pseudo-second order kinetic model provided a better correlation of the experimental data than pseudo-first order equation of lagergren model.

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