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Research Article

Application of a Cost Effective Biosorbent for Basic Dye Removal from Textile Industries

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ABSTRACT

This article deals with application of sawdust (SD) as a very efficient and economical adsorbent for removal of methylene blue (MB) as a typical basic (cationic) and commonly used dye in textile industries from aqueous solutions. The operating variables studied were initial solution pH, adsorbent mass, initial dye concentration and contact time. The experiments were carried out using both batch and column systems at room temperature. In order to have a good comparison, a commercial grade of granulated activated carbon (GAC) was also used in this investigation. Adsorption of MB on the SD and GAC was examined by the pseudo-first-order and pseudo-second-order models and their respective rate constants of first-order adsorption (k_1) and second-order adsorption (k_2) were estimated. The experimental data fitted very well with the pseudo-second-order kinetic model. The experimental data were also analyzed by the Langmuir and Freundlich models of adsorption. Based on the correlation coefficient values obtained (R^2), it was found that equilibrium data for SD fitted well with both models. In order to find out the possibility of desorption for frequent application, the chemical regeneration of the used column was also investigated.

Keywords: Removal, wastewater, methylene blue, sawdust, activated carbon, biosorbent

1. Introduction

Due to the good solubility of synthetic dyes, they are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two percent of dyes that are produced are discharged directly in aqueous effluent. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [1]. The discharge of colored waste is not only damages the aesthetic nature of receiving streams, but also may be toxic to aquatic life. So, the removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Sorption process is proved to be one of the effective and attractive processes for the treatment of these dye-bearing wastewaters [2-10]. This method can be inexpensive, if the sorbent material used is of inexpensive material and does not require any expensive additional pretreatment step. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost, simple design and easy operation, less energy intensiveness, nontoxic, and superior removal of organic waste constituents as compared to the conventional biological treatment processes.

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent [11-18]. The adsorption process will provide an attractive technology if the lowcost sorbent is ready for use. However, physical and chemical processes such as drying, autoclaving, crosslinking reactions or contacting with organic or inorganic chemicals are proposed for improving the sorption capacity and the selectivity.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable [19-24]. There are several reported methods for the removal of pollutants from effluents. The technologies can be divided into three categories: biological, chemical and physical. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale. The chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use.

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation [25, 26]. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems. Furthermore, the combinations UV/TiO_2 and UV/H_2O_2 were found to be less efficient degradation of the dye waste.

Among all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [27-29]. In particular, the effectiveness of adsorption on activated carbons (AC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options. Because of their great capacity to adsorb dyes, AC is one of the most effective adsorbents. However, the adsorption capacities of an activated carbon depend on the different sources of raw materials, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure [21, 24].

The use of activated carbons based on relatively expensive starting materials is also unjustified for most pollution control applications. This has led many workers to search for more economic adsorbents. Research interest into the production of alternative sorbents to replace the costly adsorbents such as activated carbon has intensified in recent years. Certain by-products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents [19, 20].

Sawdust is easily available in the countryside at negligible price. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms. The sorption mechanisms can be explained by the presence of several interactions, such as complexation, ion-exchange due to a surface ionization, and hydrogen bonds [30, 31]. Chemical pretreatment of sawdust has been shown to improve the sorption capacity and to enhance the efficiency of sawdust adsorption [32-34].

In the current investigation, methylene blue (MB) was employed as a test probe for evaluation of sawdust for basic or cationic dye removal. As we have found in our preliminary investigation, sawdust or other waste biomaterials are not suitable adsorbent for anionic species such as anionic dyes. So, in this study, MB dye (a typical cationic textile dye) was used throughout the experiments. The data was then compared with those obtained from activated carbon (purchased from Merck Co.) which was used under the same operational adsorption conditions simultaneously.

2. EXPERIMENTAL

2.1 Materials and equipments

All chemicals used were analytical reagents grade and prepared in distilled water. MB [3, 7 bis (dimethyl amino) phenothiazin-5-ium ion] was purchased from Merck. Sawdust (SD), of balsam fir (Abies balsamea) origin was obtained from a local carpentry workshop (Iran).Sawdust was washed to remove dirt, dust and any possible waste adhered on the surface, rinsed copiously with doubly distilled water and finally dried at temperature about 70- 80°C for 2 h. After drying, the sawdust was then sieved through 35-50 μ m size fraction using ASTM standard sieve. A commercial grade activated carbon granulated form (termed as AC) obtained from Merck Co. A concentration of 100 mg L⁻¹ MB, C₁₆H₁₈Cl N₃S (MW =319.65 g mol⁻¹) was prepared in distilled water as stock solution. MB shows an

intense absorption peak in the visible region at 660 nm. This wavelength corresponds to the maximum absorption peak of the MB monomer (Figure 1).



A single beam Perkin-Elmer UV–Vis spectrophotometer with a 1 cm cell was used for measuring all of absorption data. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for showing pH values. pH adjustments were carried out using dilute NaOH and HCl solutions.

2.2 Determination of methylene blue (MB)

Concentrations of methylene blue solutions were analyzed by measuring their absorbance at 660 nm and using a calibration curve (Figure 2).





A calibration curve of optical densities against methylene blue concentrations was obtained by using standard methylene blue solutions at natural pH. Calibration curve shows that beer's law (A= ϵ bc) is obeyed in concentration range (0.0 – 2.5 mg L⁻¹). The experimental data reported in Figure 3 were fitted by a straight line with a high correlation coefficient (R² = 0.999).



Figure 3: Calibration curve prepared for analysis of MB

2.3 Adsorption experiments

In column experiments for preparing breakthrough curves, a glass column with dimensions of 1.0 cm diameter and 15 cm height was employed. 1.0 g sorbents SD and AC were packed in the column (bed volume \sim 5 cm³). Dye solution (MB) with known initial concentration was passed through the column with flow rate of 3 mL min⁻¹ at room temperature (23 ± 2 °C). The outlet solution was analyzed for unadsorbed MB. The following equations were used to calculate the percentage of sorption and the amount of adsorbed methylene blue, respectively:

%Sorption =
$$\frac{(C_o - C_e)}{C_o} \times 100$$
 (1)
 $\frac{x}{m} = \frac{(C_o - C_e)v}{m}$ (2)

Where C_o and C_e are the initial and equilibrium concentrations of the methylene blue, respectively (mg L⁻¹); x/m is the amount of methylene blue adsorbed onto unit amount of the adsorbent (mg g⁻¹) at equilibrium; and V is the volume of the solution used in the adsorption experiment (L). Alternatively, the following equations were used to calculate regeneration percentage of the used adsorbent:

%Desorption =
$$\frac{m^*}{m_o} \times 100$$
 (3)

$$\mathbf{m}^{\prime} = \mathbf{C}_{\mathbf{e}} \times \mathbf{V}$$
 and $\mathbf{m}_{o} = (\mathbf{C}_{o} - \mathbf{C}_{\mathbf{e}}) \times \mathbf{V}$ (4)
Where, \mathbf{m}_{o} is mg of the dye (MB) sorbed onto the adsorbent,

 m^* is mg of MB in the regenerated solution; V' is the volume of eluent solution (L). C_o and C_e are the initial (inlet) and equilibrium (outlet) concentrations (mg L⁻¹) of MB, respectively.

3. RESULTS AND DISCUSSION

3.1 Sorption of methylene blue by sawdust (SD), and activated carbon (AC)

3.1.1 Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity. For investigation the effect of pH, 0.8 g portions of dried sorbents (SD and AC) were treated separately with 50 mL of methylene blue solution (50 mg L^{-1}) at various pH values (2-12) using dilute HCl and NaOH solutions for pH adjustment. As our data show (Table 1), removal of MB by SD is increased with increasing pH of dye solution.

Under neutral or alkaline conditions (pH \leq 10) sorption capacity of SD is almost the same as AC. Removal of dyes by AC is mostly dependent on its high porosity and its great surface area (500- 1500 m²/g).

Table 1: Effect of pH on sorption of MB by SD and AC adsorbents

nН	2	4	6	8	10	12
P11			0	0	10	12
% Sorption	65.70	96.82	97.20	97.50	96.61	96.70
(SD)						
% Sorption	98.30	98.46	99.20	98.80	98.67	98.51
(AC)						

As the results indicate, the adsorbed methylene blue on sawdust after an adsorption period of 40 min was significantly lower for pH = 2. The lower adsorption of methylene blue at acidic pH can be attributed to the presence of excess H^+ ions that compete with the dye cation for adsorption sites.

As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favor the adsorption of MB dye due to electrostatic attraction. The increase in initial pH from 4.0 to 10.0 slightly increases the amount of dye adsorbed. In the case of granulated activated carbon adsorbent, the chemical nature of the surface is influenced by solution pH, which therefore plays an important role in the adsorption of solutes from aqueous solutions. Dye sorption by sawdust can be due to the presence of a number of acidic (phenolic, hydroxyl, and carboxylic acid) groups which is capable to sorb basic compounds such as cationic dyes. The low adsorption of dye in highly acidic solution also shows possibility of development of positive charge on the adsorbent, which inhibits the adsorption of dye over it. Based our BET analysis, the surface area of SD is very low (7-8 m^2/g). The sorption of MB dye by sawdust is therefore mainly due to the surface chemistry of the SD and molecular interactions between MB dye and various polar functional groups at the surface of SD. It is interesting to note that SD can compete with granulated activate carbon for MB dye removal in spite of its extremely low cost compared to GAC.

3.1.2 Effect of adsorbent dosage

In order to study the effect of adsorbent dosage on dye removal, various amounts of the SD and AC (0.1-1.0 g) were contacted with 50 mL MB solution with concentration of 50 mg L⁻¹ at pH 8.0 for SD and pH 6.0 for AC. It was observed that increasing the adsorbent dose, % removal increased. With increase in the adsorbent dose, additional sorbent sites are available for the adsorption and hence removal of dye molecules from the solution is increased. As our results indicate (Figure 4), 0.8 g of the used adsorbents (SD or AC) can decolorize 50 mL MB solution with an initial concentration of 50 mg L⁻¹.



Figure 4: Effect of adsorbent dosage on removal of MB

3.1.3 Effect of initial concentration

For performing this experiment 0.80 g sorbents SD and AC (mesh size 35-50) were treated with 50 mL of methylene blue solution with concentration of 20-100 mg L^{-1} at optimum pH values (pH 8 for SD and pH 6 for AC) for 40 minutes accompanied by mild

shaking at room temperature. The results obtained are summarized in Table 2. As our results show, with increasing the initial concentration of methylene blue (C_o), total amount of metal sorption (x/m) also increases linearly. As our data clearly show, both SD and AC can effectively and comparably remove MB from aqueous solutions under specified conditions.

It is interesting to note that decolorizing efficiency obtained for a very low cost agricultural waste such as sawdust obtained from Narra-wood is comparable or sometimes higher than AC which is a popular but very expensive adsorbent. An adsorption property of AC is mostly due to its great surface area.

Table 2: Effect of initial concentration of MB on sorption by SD and AC adsorbents

Adsorbent	$C_o (mg L^{-1})$					
	20	40	60	80	100	
%Sorption (SD)	98.05	97.80	97.14	96.44	95.70	
X/m (mg/g) (SD)	1.22	2.45	3.64	4.82	5.98	
%Sorption (AC)	99.50	98.72	97.64	97.30	97.0	
X/m (mg/g) (AC)	1.24	2.47	3.67	4.86	6.06	

3.1.4 Effect of contact time

For performing this experiment, 0.8 g of adsorbents (SD and AC) were treated with 50 mL of 50 mg L^{-1} MB at optimum pH values for different periods (10-60 minutes) accompanied by stirring at room temperature. The results of adsorption obtained from the analysis of unabsorbed MB solution are shown in Figure 5. It is seen that nearly 40 min are required for the equilibrium adsorption to be attained for MB. It is further seen from Figure 5 that adsorption is very fast initially, showing that more than 94% adsorption is completed in 20 min. After that it slowly attains equilibrium adsorption.



Figure 5: Effect of agitation time on removal of MB using SD and AC adsorbents

3.2 Adsorption dynamics

Kinetics of sorption is one of the important characteristics in defining the efficiency of sorption. Various kinetic models have been proposed by different workers where the adsorption has been treated as first-order and pseudo-first-order processes [35]. Different systems conform to different models. The Lagergren rate equation is the one most widely used for the sorption of a solute from a liquid solution. This first order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t$$
(5)

Where; \mathbf{q}_t and \mathbf{q}_e (mg g⁻¹) are the amounts of dye adsorbed per unit mass of the adsorbent at time t and at equilibrium, respectively, and \mathbf{k}_1 (min⁻¹) is equilibrium rate constants of pseudo-first-order adsorption. Hence a linear trace is obtained between the two values $\log(\mathbf{q}_e - \mathbf{q}_t)$ and t, provided the adsorption follows first order kinetics. In order to examine the efficiency of an adsorbent, this study is useful in removal of adsorbate species from aqueous solution by an adsorbent. Kinetic data were further treated with the pseudosecondorder kinetic model. The differential equation is the following [30]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$
(6)

Where k_2 is rate constant for pseudo second order adsorption (g mg⁻¹ min⁻¹). For the boundary conditions t=0 to t=1 & q_t = 0, q_t = q_t integrated form of equation is as follows:

$$\frac{1}{\left(\mathsf{q}_{\mathsf{e}} - \mathsf{q}_{\mathsf{t}}\right)} = \frac{1}{\mathsf{q}_{\mathsf{e}}} + \mathsf{k}_{2}t \tag{7}$$

The linear form of equation can be expressed as follows,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(8)

The plots of $\frac{t}{q_t}$ versus t should give straight lines where slopes and

intercepts are respectively $\frac{1}{q_{\mathsf{e}}}$ and $\frac{1}{\frac{1}{k_2 q_{\mathsf{e}}^2}}$.

The values of the rate constant k_2 and sorption capacity q_e are calculated from these parameters. The results obtained are summarized in Table 3. We could see that straight lines were obtained, with the coefficient (R^2) higher than 0.99, suggesting that adsorption of MB onto SD and AC followed the pseudo-second-order kinetics model.

Table 3: Adsorption kinetic parameters of MB onto SD and AC adsorbents

	Pseudo First order			Pseudo- Second order		
Adsorbent	k_1	q_{e}	R^2	k ₂	q_{e}	R ²
SD	0.032	0.185	0.4193	0.219	3.14	0.9996
AC	0.048	0.051	0.2510	0.171	3.21	0.9987

3.3 Treatment of data using adsorption isotherms

Both Langmuir isotherm and Freundlich models were employed for treatments of the equilibrium adsorption data [29, 30]. Langmuir model is represented by the following equation:

$$\frac{m}{x} = \frac{1}{x_{m}} + \frac{1}{x_{m}K_{L}}\frac{1}{C_{e}}$$
(9)

Where C_e is the equilibrium concentration of MB solution (mg L⁻¹), X is the amount sorbed by adsorbent (mg/g), X_m is the maximum amount sorbed, K_L a Langmuir's constant signifying energy of sorption. Values of K_L and X_m were calculated from the slope and intercept of the linear plot. The Langmuir model deals with monolayer adsorption and constant adsorption energy. The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is represented by the following equation:

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C_{e}$$
(10)

where, X/m is equilibrium adsorption capacity (mg g⁻¹), C_e is the equilibrium or residual concentration (mg L⁻¹) of MB dye in solution, and K and 1/n are empirical Freundlich constants indicating sorption capacity of adsorbent and intensity of adsorption (mg g⁻¹), respectively.

In Freundlich adsorption system, values of n and K are calculated from the slope and intercept of the linear plot of log X/m against log C_e . The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. For a good adsorbent it is usually between 1 and 10 [36-37]. The adsorption isotherms using both Langmuir and Freundlich equations (linear forms) obtained for removal of MB have been indicated in Figurers 6, 7 respectively. The calculated results of the Langmuir and Freundlich isotherm constants are also given in Table 3. In the case of AC, the correlation coefficient value R^2 obtained shows that the equilibrium data fitted better with the Freundlich model as compared to Langmuir equation under the concentration range studied.

The essential characteristics of the Langmuir isotherm and the favorable nature of adsorption can also be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by Eq. (11):

$$R_{L} = \frac{1}{1 + K_{L}C_{0}} \tag{11}$$

Where; K_L (L mg⁻¹) is the Langmuir constant and C_o is the highest dye concentration in solution (mg L⁻¹). The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The calculated value of R_L for highest concentration of 100 mg L⁻¹ obtained for both SD and AC indicates (Table 4) that both are suitable adsorbents for removal of MB from aqueous solutions and their isotherms are favorable.



Figure 6: Langmuir isotherm obtained for sorption of MB



Figure 7: Fruendlich isotherm obtained for sorption of MB

Table 4: Adsorption isotherm constants for the sorption of MB onto SD and AC adsorbents

Langmuir isotherm					Freundlich isotherm		
parameters				parameters			
Adsorbent	KL	X _m	R^2	n	Κ	R^2	R _L
SD	0.38	9.38	0.9993	1.53	2.44	0.9884	0.025
AC	3.36	4.86	0.9563	2.21	3.41	0.9906	0.003

3.4 Breakthrough curves for removal of MB using SD and AC adsorbents

Breakthrough curve is the plot of effluent solute concentration vs. time or volume of solution usually yields as S- shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion. This experiment was conducted at optimum conditions obtained from our preliminary batch studies. For performing this study, 1.0 g SD packed in a glass column, and then methylene blue solution with concentration of 50 mg L⁻¹ passed through the column with constant flow rate (3 mL min⁻¹) at optimum pH. Each time 10 mL was poured into the column. The outlet solution was analyzed for unabsorbed methylene blue solution in order to obtain the breakthrough curve. The breakthrough curves obtained for the SD is shown in Figure 8. The results for AC column has not been shown because of its break point happened quickly.



Figure 8: Breakthrough curve obtained for removal of MB using SD

According to the results obtained in this part of our study, each gram of SD is capable to remove more than 95% of MB from about 500 mL MB solution (50 mg L^{-1}) under a dynamic conditions (column system).

29

3.5 Effect of initial concentration of MB by SD on breakthrough curves

To perform this investigation, the column experiments were conducted as described previously using MB solutions of different concentrations (20-120 mg L^{-1}) with constant flow rate (3 mL min⁻¹) at pH 8.0. The results obtained are presented in Figure 9. As the results show, SD is more effectiveness when use for uptake of MB from aqueous solutions at low initial dye concentrations. On the other hand SD seems to be an effective low cost and environmentally friendly adsorbent for removal of basic or cationic textile dyes from wastewaters especially when the concentration of the dyes are not high.



Figure 9: Breakthrough curves for the sorption of MB by SD at different initial concentrations, $C_o: 20 (-), 50 (\bullet), 100 (\bullet)$ and 120 mg $L^{-1} (\bullet)$

Regenerant solution							
Adsorbent	Distilled water	Distilled water	HCl (1M)	C ₂ H ₅ OH	NaCl (1 M)		
	(T= 20 °C)	$(T = 60 \ ^{\circ}C)$		(96%)	(T = 60 °C)		
SD	0	5	0	12	80		
AC	0	3	0	10	0		

Table 5: Effect of different chemicals used for desorption of MB

3.6 Desorption studies

For any adsorption system, it is also very important to regenerate the adsorbent after use and also to recover the adsorbate. Desorption studies will help to elucidate the nature adsorption process. For performing this experiment, 1.0 g of adsorbents were first treated with 300 mL of MB solution with initial concentration 50 mg L^{-1} .

The analysis of the filtrate showed that more than 98% of MB has been removed. Desorption experiments were conducted by using HCl, NaCl and EtOH solution as the desorption agents. The results are summarized in Table 4.

It may be observed that the percentage of desorption is very low. This indicates a strong electrostatic attraction probably involves between both adsorbents and adsorbate. It was both interesting and amazing for us to find out that in the case of SD, desorption percentage can be improved considerably (at least 80%) when a hot solution of NaCl is used as desorption agent. In our further experiments, it was also very interestingly found that when regenerated sawdust was used for adsorption of MB, not any important loss in sorption capacity was observed. Maximum loss in sorption capacity was less than 5% for 3 cycles.

4. CONCLUSION

The present study shows that sawdust obtained from walnut is a very efficient adsorbent for removal of MB from aqueous solutions. The removal efficiency or adsorption capacity obtained for SD was interestingly comparable with the values obtained for activated carbon. Removal of MB using sawdust was more efficient under neutral or alkaline pH values. More than 80% of the MB dye can be recovered using a solution of 1 M NaCl at 60 °C. Application of sawdust obtained from carpentry workshops using walnut seems to be a very economical and promising adsorbent for treatment of textile industries wastewaters. In contrast to activated carbon, sawdust used in this study is very cheap material and easily regenerateable using hot NaCl solution efficiently. The effectiveness

of treatment depends not only on the properties of the adsorbent and adsorbate, but also on the following environmental conditions and variables used for the adsorption process: pH, ionic strength, temperature, existence of competing organic or inorganic ligands in solution, contact time and adsorbent concentration. Since industrial effluents contain several pollutants simultaneously, so development of the adsorption process requires further investigation in the direction of testing low-cost sorbents with real industrial effluents.

5. ACKNOWLEDGEMENT

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