

Methylene Blue Dye Removal from Aqueous Solution by Residue of Malaysian *Saccharum Officinarum*

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ABSTRACT

Saccharum officinarum (sugarcane) is abundant agricultural by-products in Malaysia. In this study, bagasse (the residue of Malaysian *saccharum officinarum*) was used as adsorbent for the removal of methylene blue (MB) from aqueous solutions. Batch studies were conducted to evaluate the adsorption capacity of unmodified bagasse (UMB) under different experimental conditions. Effect of various process parameters; contact time, initial metal ion concentration and adsorbent dosage have been studied for the removal of MB. Batch experiments were carried out at various dosage of adsorbent (0.2-2.0 g), initial MB concentration (10-50 mg^l⁻¹) and contact time (15-240) min. Then, the optimum conditions were applied to acid-modified bagasse (AMB) and base-modified bagasse (BMB) for the comparative study. The maximum MB removal capacity by UMB, BMB and AMB are 7.274, 5.599 and 5.514 mg g⁻¹ respectively. Adsorption process was expressed by using Langmuir and Freundlich isotherm. A Langmuir isotherm curve was found to be significant compared to Freundlich isotherm. The results indicate that such bagasse without modification could be employed as low cost adsorbent in wastewater treatment for the removal of colour and dyes.

Keywords: Adsorption, methylene blue, bagasse, isotherms

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Introduction

Colour is the most obvious indicator of water pollution. The discharge of coloured wastes into receiving streams not only affects the aesthetic nature but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity (Namasivayam, Radhika and Suba, 2001). Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing. Dyes can be classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) (Mishra and Tripathy, 1993).

In general, the methods for the treatment of wastewater containing dyes can be divided into two main groups (Gupta and Suhas, 2009; Sohrabnezhad and Pourahmad, 2010): (I) chemical or physical methods of dye removal, which refer to the process called decoloration and (II) dye removal by means of biodegradation. Physical methods of decoloration include different precipitation methods, adsorption, filtration, reverse osmosis, etc. Among the chemical methods of dye removal, there are processes such as reduction, oxidation, compleximetric methods, ion exchange and neutralization. Biological treatment can be conducted in the presence or absence of oxygen (Slokar and Majcen, 1998; Sohrabnezhad and Pourahmad, 2010). These processes have their disadvantages and limitations, such as high cost, generation of secondary pollutants, and poor removal efficiency. Thus adsorption has been found to be the most effective economic alternative with high potential for the removal and recovery of dyes from wastewater (Gupta et al. 2006; Han, Wang and Zou, 2007; Sohrabnezhad and Pourahmad, 2010)

Methylene blue (cationic dye) is the most commonly used substance for dyeing cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Ghosh and Bhattacharyya, 2002; Tan, Hameed and Ahmad, 2006).

Sugarcane is the family of *Saccharum officinarum* which is abundant agricultural by-products in Malaysia. Bagasse is the solid residue left after the extraction of juice from sugarcane. In this work, the potentials for the use of bagasse as a biosorbent for MB removal from aqueous

solution were investigated. The aim of the present work is to explore the possibility of utilizing bagasse for the adsorptive removal of MB from aqueous solution. The effect of such factors as adsorbent dosage, contact time, initial concentration and pretreatment was investigated. Experimental equilibrium data were fitted to the Freundlich and Langmuir isotherm equations to determine the best-fit isotherm.

Materials and Methods

Methylene Blue

Methylene blue (MB) supplied by Fisher Scientific was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all the solutions and reagents. MB was chosen in this study because of its known strong adsorption onto solids. MB has a molecular formula $C_{16}H_{18}ClN_3S$ and molecular mass of 373.9 g/mol, which corresponds to methylene blue hydrochloride with three groups of water. Chemical structure of MB is shown in Figure 1.

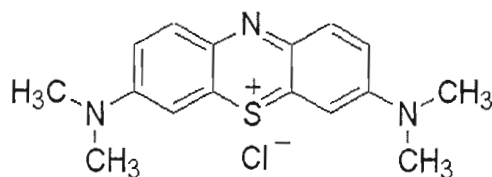


Figure 1: Chemical Structure of Methylene Blue Dye

Preparation of Raw Material

The adsorbent was prepared from bagasse, which is collected from Permatang Pauh, Pulau Pinang. The material was sieved to obtain the desired size fraction (150-212 μm), boiled and washed thoroughly with distilled water. Then, the adsorbent was dried in 90°C to 110°C in hot air oven for overnight.

Acid-treatment of Bagasse

For acid-pretreatment, 4.0 g of bagasse was immersed in 1000 mL 20% v/v H_2SO_4 in 2000 mL beaker on hot plate stirrer machine for 15 hours at

60°C temperature. The acid-modified bagasse (AMB) were extensively washed with deionized water and filtered thoroughly until a pH 7 was attained. Finally the resulting AMB was oven dried for 48 hours at 60°C to constant weight.

Base-treatment of Bagasse

For base-pretreatment, 4.0 g bagasse was immersed in 300 mL NaOH solution with very dilute concentration (0.15M or 0.6% w/v) in 500 mL conical flask on plate stirrer machine for 3 hours at room temperature. Fibres were then washed with deionised water until the pH value was 7. The base-modified bagasse (BMB) then was dried at 60°C in an oven for 48 hours before using as adsorbents.

Adsorption Studies

The adsorption experiments were carried out with batch method. A stock MB solution (1000 mg/l) was used in adsorption experiments. The concentration of MB was determined by Perkin Elmer UV-VIS RS Spectrometer 3000, wavelength 660 nm. A known amount of adsorbent and MB solution were taken in a 250 mL stoppered conical flask. The final volume was adjusted to 250 mL with distilled water and agitated at constant speed (150 rpm) on the orbital shaker GFL 3005 in room temperature over a period of time and then filtered. The initial pHs of all MB solutions were kept to pH 6-7. The concentration of MB in filtrate was determined and the amount of MB removal was calculated from the ratio of MB taken and that remaining in the solution. Adsorbed MB was calculated from mass balance. The experimental parameters studied are: contact time (15-240 min), initial MB concentration (10-50 mg/L), and the effect of dosage (0.2 – 2.0 g).

Equilibrium Adsorption Studies

The adsorption of MB from aqueous solutions by bagasse was carried out at room temperature, $27 \pm 1^\circ\text{C}$. In the experiments, 0.5 g bagasse was mixed with 250 ml solutions of various MB concentrations between 10 mg/L to 40 mg/L. After adsorption, the concentrations of MB remaining unabsorbed were determined.

Spectroscopic Studies

Fourier Transform Infrared (FTIR) was used to identify the characteristic functional groups in the fibers. Bagasse sample was powdered and then dispersed in dry potassium bromide (KBr) respectively. The mixture was thoroughly mixed in a mortar and pressed at pressure of 6 bars to form a KBr thin disc. Then the disc was placed in a sample cup of a diffuse reflectance accessory. The IR spectrum was obtained using Perkin Elmer 2000 infrared spectrometer. FT-IR spectra of each sample were obtained in the range of 4000–400 cm^{-1} . Spectral outputs were recorded in the transmittance mode as a function of wave number.

Results and Discussion

Effect of Contact Time on Adsorption Equilibrium

Effect of contact time for the removal of MB showed rapid adsorption in the first 30 min and the adsorption reached equilibrium in about 60 min as shown in Figure 2. From the Figure 2, we can see that some desorption happened but the values (% removal) are not much different with the percent removal at equilibrium time. After 30 min, almost more than 90% MB was removed. Available adsorption studies in literature

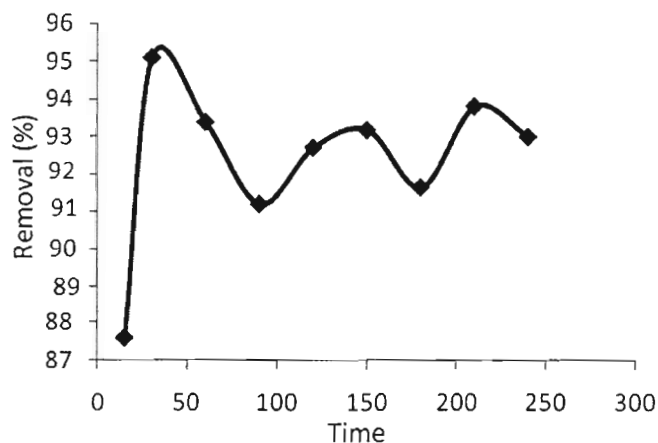


Figure 2: Effect of Contact Time on MB Removal Using UMB (pH = 6-7, temp = 27°C ± 1, particle size: 150-212 μm , MB concentration 50 mgL^{-1} and adsorbent dosage: 2 gL^{-1})

reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Mall, Srivastava and Agarwal, 2006).

Effect of Initial MB Concentration on Adsorption Equilibrium

The effect of initial MB concentration, C_0 on the removal of MB by UMB is shown in Figure 3. From the figure, it is evident that the MB removal decreased with the increase in C_0 . The maximum adsorption yields were determined as 91%, 92%, 62%, 46% and 11% for UMB at 10, 20, 30, 40 and 50 mg/L respectively. At lower concentrations, all MB present in the adsorption medium could interact with the binding sites so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites.

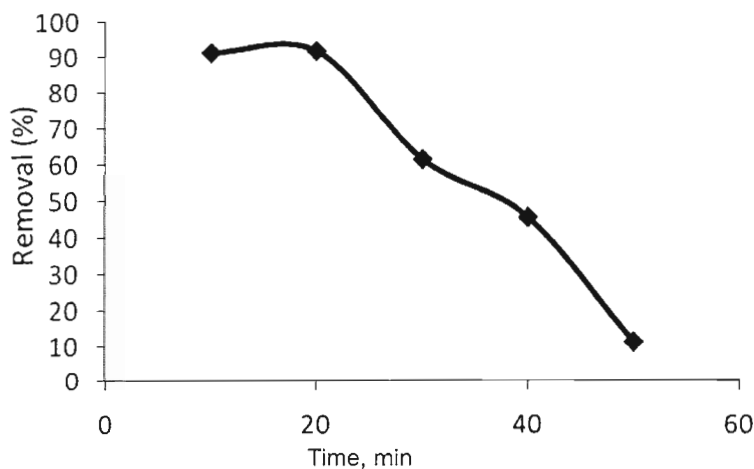


Figure 3: Effect of Initial MB Concentration Using UMB (pH = 6-7, temp = 27°C ± 1, particle size: 150-212 μm, contact time: 60 min and adsorbent dosage: 2 gL⁻¹)

Effect of Adsorbent Dosage, m on Adsorption Equilibrium

The effect of adsorbent dosage, m on the removal of MB by UMB at 50 mg L^{-1} is shown in Figure 4. It can be seen that the MB removal increases up to a certain limit and then it remains almost constant. An increase in the adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites (Mas and Sathasivam, 2009).

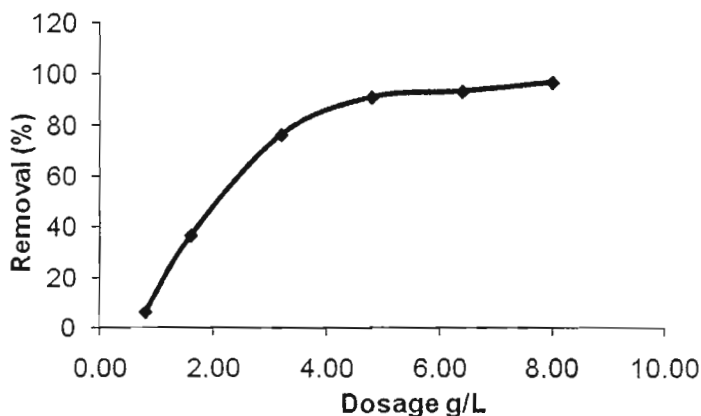
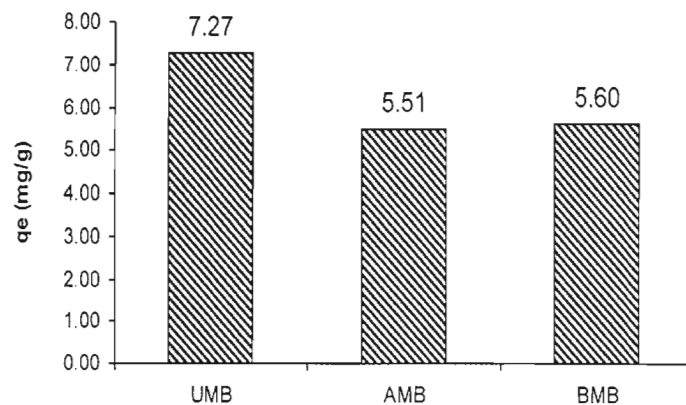


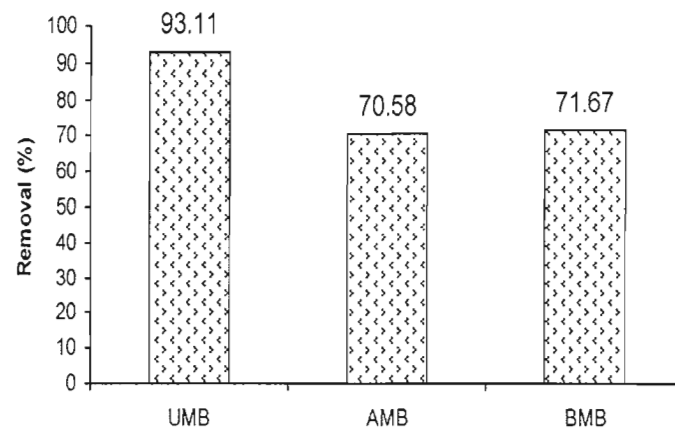
Figure 4: Effect of Adsorbent Dose on Adsorption of MB by UMB (pH = 6-7, temp = $27^{\circ}\text{C} \pm 1$, particle size: 150-212 μm , contact time: 60 min and MB concentration = 50 mgL^{-1})

Effect of Pre-treatment on Adsorption Equilibrium

To evaluate the effect of pretreatments on bagasse, 50 mgL^{-1} MB solution was shaken at 150 rpm with 6.4 g/L of UMB, AMB and BMB having size 150-212 μm at pH 6-7 for 60 min. Uptake capacity of adsorbent was significantly decreased after pretreatments (Figure 5a.). Acid pretreatment and base pretreatment of bagasse were resulted in decreased in percentage removal of MB by bagasse (Figure 5b). The results suggest that chemical modification (acid and base) should not be carried out for bagasse as the performance of AMB and BMB as adsorbents for the removal of MB decreased after modification. The chemical treatment seems to disturb the surface properties or functional group of bagasse which is responsible to its adsorption properties.



(a)



(b)

Figure 5: Effect of Pre-treatment (a) Adsorption Capacity, q_e (mg/g) of MB by UMB, AMB and BMB and (b) Percent Removal (%) of MB by UMB, AMB and BMB (pH = 6-7, temp = $27^{\circ}\text{C} \pm 1$, particle size: 150-212 μm , contact time: 60 min, MB concentration: 50 mgL^{-1} and adsorbent dosage: 2 gL^{-1})

Adsorption Isotherms

Langmuir Isotherm Model

Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. There is no transmigration of the adsorbate in the plane of the surface of the adsorbent (Langmuir, 1918; Mas and Sathasivam, 2009). On the other hand in the Langmuir model, it is assumed that intermolecular forces decrease rapidly with distance and this lead to the prediction that coverage of the UMB is of monolayer type. Once a particular site of the adsorbent is occupied by an adsorbate molecule, no further adsorption takes place at that site. The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

Where:

- C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
- q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
- Q_o and b = Langmuir constants related to adsorption capacity and rate of adsorption, respectively

When C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_o$ was obtained, as shown in Figure 6. The value of Q_o was determined from the Langmuir plot at the concentration range $10\text{-}50 \text{ mg L}^{-1}$ as 9.355 and then the b value was calculated to be 2.314 . The correlation coefficient of Langmuir isotherm, R^2 is 0.9983 . The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given as

$$R_L = \frac{1}{1 + bC_o} \quad (2)$$

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L =$

0). The value of RL was found to be 0.046 suggesting the isotherm to be favorable at the concentrations studied. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of UMB surface, i.e., each MB dye/UMB adsorption has equal adsorption activation energy; the results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of UMB.

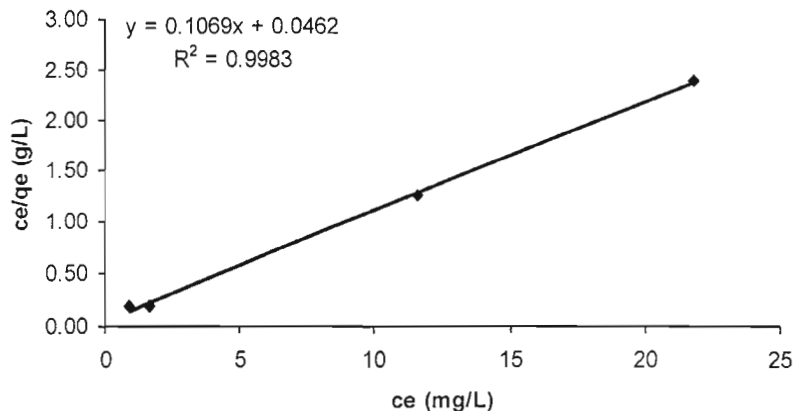


Figure 6: Langmuir Isotherms for the Removal of MB by UMB

Freudlich Isotherm Model

This model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption (Ahmad, Sumathi and Hameed, 2005). The Freundlich isotherm equation is written as

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (3)$$

Where:

- C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
- q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
- K_f (mg/g^{-1}) and n = Freundlich constants with n giving an indication of how favorable the adsorption process
- K_f = The adsorption capacity of the adsorbent

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the fibers for a unit equilibrium concentration. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Ajmal et al, 1998). When $\log q_e$ was plotted against $\log C_e$, a straight line with slope of $1/n$ was obtained, as shown in Figure 7. The Freundlich constants were derived from the slopes and intercepts of $\log C_e$ versus $\log q_e$ and are shown in Table 1. By analyzing the Freundlich isotherm, it describes the heterogeneous system and reversible adsorption.

Table 1: The Langmuir and Freundlich Parameters of Adsorption Isotherms

Isotherms	Constants			
	Q_o	b	R_L	R^2
<u>Langmuir</u>				
UMB	9.355	2.314	0.046	0.9983
<u>Freundlich</u>		k_f	n	R^2
UMB		0.783	6.258	0.4854

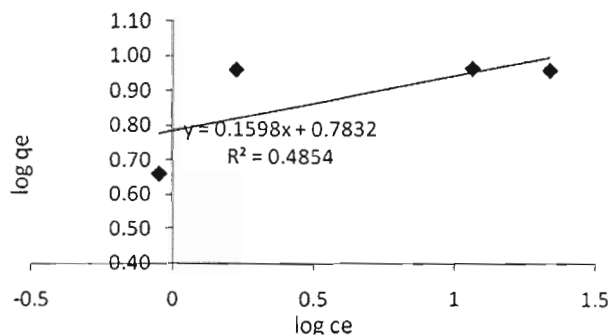


Figure 7: Freundlich Isotherms for the Removal of MB by UMB

As seen from the Table 1, a high regression correlation coefficient, R^2 (0.9983) was shown by the Langmuir model. This indicates that the Langmuir model was suitable for describing the sorption equilibrium of MB by the UMB.

Spectroscopic Study

Agricultural biomasses mainly consist of cellulose, hemi-cellulose, lignin and some proteins which make them effective adsorbent for dye. Bagasse mainly contains cellulose (45%), hemi-cellulose (28%) and lignin (18%) (Garg et al., 2008). Bagasse contains carboxylic and hydroxyl groups and hence shows efficiency towards removal of dye over wide range of pH.

Figure 8 shows the FTIR spectra for UMB in the form of KBr pallet. Identification of the most important peaks is based on previous studies of sugar cane bagasse (Garg et al., 2008; Gurgel et al., 2008), coconut husk (Shukla et al., 2005) and jute (Min et al., 2003).

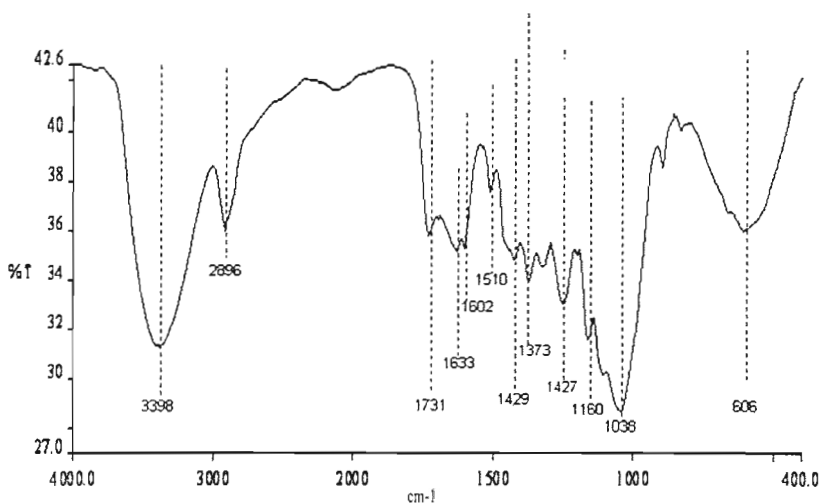


Figure 8: Infrared Spectra of UMB

For UMB, the broad adsorption at 3398 cm^{-1} is due to the stretching of hydroxyl groups and bonded O-H present in cellulose, hemicellulose and lignin. The peaks observed at 2901 cm^{-1} can be assigned to stretching vibration of the C-H. The peak around 1731 cm^{-1} corresponds to the C=O stretching of methyl ester and carboxylic acid in pectin or acetyl group in hemicellulose (Silverstein and Webster, 1998). The band at 1605 cm^{-1} related to the bending mode of the absorbed water. The peaks around 1633 cm^{-1} corresponds to the C=C stretching that may be attributed to the lignin aromatic groups. The small band at 1428, 1375

Table 2: Infrared Spectra Band of UMB

Wave number (cm^{-1})	Functional groups	Compounds	UMB Frequency, cm^{-1}
3600 - 3000	OH stretching	Acid, methanol	3398
2860 - 2970	C-H stretching	alkyl, aliphatic	2896
1700 - 1730	C=O stretching	aromatic	1731
1650 - 1600	Absorbed water	-	1602
1632	C=C	Benzene stretching ring	1633
1440 - 1400	OH bending	Acid	1373
1402	CH bending	alkyl, aliphatic	1427
1250	C-O stretching	Phenol	1250
	C-O		
1200-1100	antisymmetric stretching	-	1160
	C-O-C stretching	Pyranose ring	
1170, 1082	vibration	skeletal	1038
700-400	bending vibration	-	606

and 1321 cm^{-1} represent CH_2 bending, O-H bending, C-C and C-O stretching respectively. The absorbance at 1250 cm^{-1} is corresponds to C-O stretching in hemicellulose and lignin. The additional peak at 606 cm^{-1} and 833 cm^{-1} can be assigned to bending modes of aromatic compounds.

Conclusions

The present study shows that bagasse without modification is considerably efficient for removal of MB dye from wastewater. The adsorption is highly dependent on contact time, adsorbent dose and initial concentration. The equilibrium data for UMB fit well in the Langmuir model of adsorption, showing monolayer coverage of dye molecules at the outer surface of UMB. The result would be useful for fabrication and designing of spent textile dyeing wastewater for the removal of dyes. Since the raw material, bagasse, is freely available the treatment method seems to be economical.

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