

BIOSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS BY MODIFIED MESOPOROUS *SIMAROUBA GLAUCA* SEED SHELL POWDER

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ABSTRACT

The present study investigates the ability of formaldehyde treated *Simarouba glauca* seed shell powder for removal of methylene blue (MB) from aqueous solutions. Batch adsorption studies were carried out under various experimental conditions such as agitation time, dye concentration, adsorbent dose and pH. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), XRD, BET and CHNS analysis. The adsorption data were analysed using Langmuir, Freundlich, Temkin and Dubinin - Radushkevich isotherms. Equilibrium data fitted well to Langmuir isotherm with maximum adsorption capacity of 111.1 mg g⁻¹. Adsorption kinetic data were verified using pseudo first order, pseudo second order and Intraparticle diffusion model. The kinetic data were found to fit well with pseudo second order model.

Keywords: Biosorption, *Simarouba glauca* seed shell, Methylene blue, Adsorption isotherm, Kinetic studies

1. Introduction

The textile wastewater containing dyes are highly colored and considered as one of the major source for the environmental concern. The discharge of colored wastewater with high amount of suspended solids and high COD causes significant problems such as increasing the toxicity and chemical oxygen demand. The colored wastewater also affects the photosynthetic activity of aquatic life by reduced penetration. Moreover, dyes are toxic, mutagenic or carcinogenic and disturb the ecosystem (Al-Anber *et al.*, 2011; Garg *et al.*, 2004; Bhattacharyya and Sharma, 2005; Hameed and Ahmad, 2009). Synthetic dyes have low biodegradability due to complex molecular structure and are too hard to eliminate under aquatic environment. Therefore, the treatment of wastewater containing synthetic dyes is necessary and very important. As synthetic dyes have low degradability, conventional biological methods in treating dye wastewater are not efficient. The physico – chemical treatment methods such as ion exchange, ultrafiltration, electrocoagulation, photo-oxidation, reverse osmosis, microwave oxidation etc., have their own significant disadvantages like incomplete removal,

high energy requirement and production of toxic sludge as waste products require proper disposal (Al-Anber *et al.*, 2011; Hameed and Ahmad, 2009; Asgher and Bhatti, 2012).

Adsorption is one of the effective and economic techniques that have been successfully employed for treatment of textile wastewater. Although activated carbons have been recognized as effective commercial adsorbents for treating dye wastewaters, their high cost, limits their application. Biosorption technology has been found to be a cost effective and highly efficient method. The uses of biomass/ biomaterials in the treatment of wastewater are highly successful due to its low cost, high efficiency, regeneration of biosorbents and less chemical or biological sludge generation (Dogan *et al.*, 2009). A number of low cost biosorbents such as spent tea leaves (Hameed, 2009), modified wheat straw (Zhang *et al.*, 2011), peanut husk (Song *et al.*, 2011), Citrus sinensis bagasse (Bhatti *et al.*, 2012), Green pea peels (Dod *et al.*, 2012), oil palm empty fruit bunch fibers (Sajab *et al.*, 2013), pine saw dust (Witek-Krowiak, 2013), Cattail leaves (Guechi and Hamdaoui, 2013), egg shells (Podstawczyk *et al.*, 2014), breadnut peel (Chiang *et al.*, 2015) have been studied in the literature for their capacity to remove methylene blue from aqueous solutions.

Methylene Blue (MB) is a thiazine (cationic) dye which has been widely used including coloring paper, temporary hair colorant, dyeing cottons, wools and coating for paper stock. Though MB is not strongly hazardous, its acute exposure cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (Aksu *et al.*, 2010).

Simarouba glauca, commonly known as paradise tree is an edible oil seed bearing tree well suited for warm, humid and tropical regions. This eco friendly tree with well developed root system and with evergreen dense canopy efficiently checks soil erosion, supports soil microbial life and improves ground water position. The seed contains about 50 - 60% oil with 63% unsaturated fatty acid among which 59.1 % is oleic acid and is fit for human consumption. Many research studies are going on in efficient usage of biodiesel from *Simarouba glauca* seed oil (Devan and Mahalakshmi, 2009). The seed shell, a waste product from this eco friendly tree has been used for the present study for the removal of MB from aqueous solutions. The present study involves the potential utilization of formaldehyde treated *Simarouba glauca* seed shell in the removal of MB from aqueous solutions. The effect of pH, initial dye concentration, adsorption isotherm and kinetic parameters for the biosorption were evaluated.

2. Materials and methods

2.1. Materials

Simarouba glauca seed shells were collected from Gujarat, India and the dye MB were purchased from SFCL Limited, New Delhi.

2.2. Preparation of adsorbent - Steam Activated and Formaldehyde Treated Sorbent (SFTS)

The seed shells were powdered and were steam activated in a stainless steel autoclave at a temperature of 121 °C for 40 minutes and then washed well with distilled water. The washed material was then treated with 1% formaldehyde in the ratio 1:5 and was heated in hot air oven at 50 °C for 4 hours. The seed shell powder was filtered, washed again with distilled water to remove free formaldehyde and activated at 80 °C in hot air oven for 24 hrs. The treated material (SFTS) was sieved for the particle size 75 - 150 µm and stored in an air tight plastic container for further use.

2.3. Characterization of adsorbent

The adsorbent was characterized using FT-IR spectra and scanning electron microscopy (SEM, JSM-6390, JOEL). The infrared spectra of the sample were obtained using a Fourier transform infrared spectrometer (Shimadzu, model IRAffinity-1). The surface area, pore volume and average pore diameter were determined

by nitrogen sorption at 77K (Micromeritics, ASAP 2010). The X – ray diffractograms were obtained using PANalytical X'Pert PRO, PANalytical B.V., Almelo, The Netherlands. The surface morphological features of the sample were obtained using scanning electron microscopy. The elemental analysis of the sample was carried out using Elementar Vario EL III. The zero point of charge of the adsorbent was also determined.

2.4. Adsorption experiments

The adsorption experiments were carried out in a batch process of standard solutions of MB. A stock solution of the dye MB (1000 mg l^{-1}) was prepared by dissolving 1g of the dye in 1 litre of distilled water, which was diluted to desired concentration. Batch adsorption experiments were carried by adding 0.1g of SFTS into 250 ml Erlenmeyer flasks containing 50 ml of different initial concentrations ($150, 200, 250$ and 300 mg l^{-1}) of MB solution. The flasks were agitated in a rotary shaker at room temperature until equilibrium was reached. After equilibration time, the adsorbents were separated by filtration and the concentration of MB in the supernatant were determined at $\lambda_{\text{max}} 667 \text{ nm}$ by Visible spectrophotometer (Shimadzu Visible Spectrophotometer UVmini-1240V) and the amount of dye adsorbed was calculated.

The effect of pH on the removal of MB by SFTS were carried out using 50 ml of 200 mg l^{-1} of MB solution, agitated with 0.1 g of SFTS at initial pH values ranging from 2 to 11. The initial pH was adjusted by using 0.1 M HCl and 0.1M NaOH. The effect of adsorbent dose on the equilibrium uptake of 200 mg l^{-1} of MB was investigated using various adsorbent dosage between 0.05 g to 0.2 g respectively. All studies were carried out at equilibrium time of 60 min and at temperature $30 \pm 2 \text{ }^\circ\text{C}$.

2.5. Desorption studies

The dye loaded sorbents were prepared by agitating 0.2 g of adsorbent into 50 ml of dye solution for 60 min on a rotary shaker. The dye loaded sorbent was separated out by filtration using Whatman Filter paper No.42 and filtrate was discarded. The dye loaded sorbent was given a gentle wash with distilled water to remove unadsorbed MB if present. The dye loaded adsorbent was agitated with desorbing mediums such as distilled water, 0.1 M HCl and 0.1 M CH_3COOH for 60 min (Fernandez *et al.*, 2010). The desorbed MB in the solution was separated and analyzed as before. The percentage of desorption was calculated.

3. Results and discussion

3.1. Characterization of adsorbent

The FT IR spectra of adsorbent SFTS were taken before and after dye adsorption (Fig. 1).

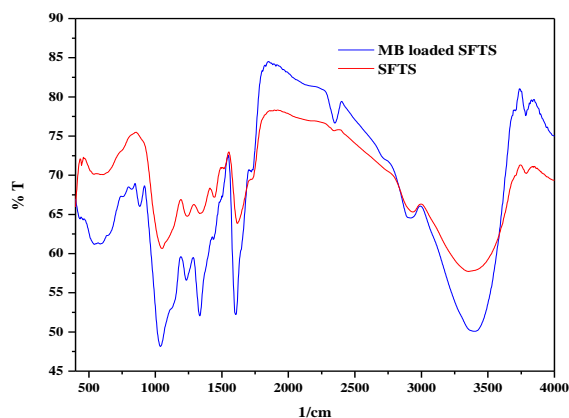
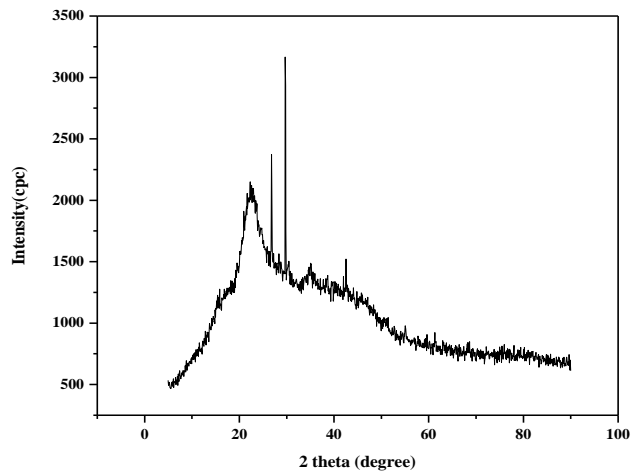
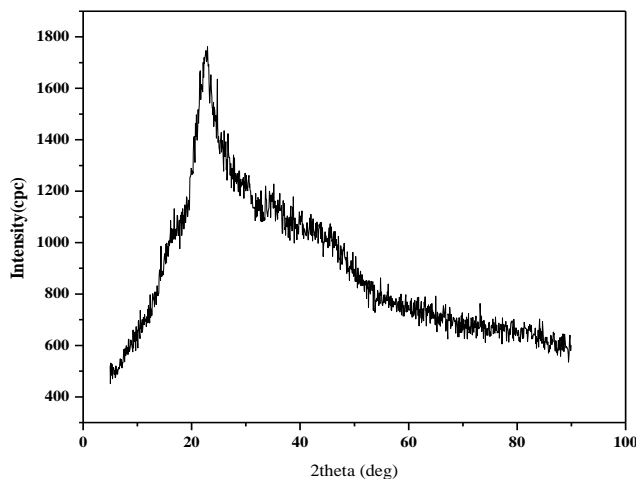


Figure 1. FT-IR spectrum of SFTS before and after adsorption

The broad and intense band at 3356 cm^{-1} corresponds to O – H stretching vibrations. The band at 2935 cm^{-1} represents symmetric or asymmetric C – H stretching vibration of aliphatic acids. The bands at 1616 cm^{-1} and 1516 cm^{-1} reveal the aromatic C – C stretching in phenyl ring of lignin. The absorption band at 1450 cm^{-1} is assigned to methoxy group of lignin (Anoop Krishnan and Haridas, 2008; Benyoucef and Amrani, 2011). A weak absorption band at 1722 cm^{-1} corresponds to C = O stretching of – COOH group. The FT IR spectrum well indicates the presence of hydroxyl and carbonyl groups in SFTS. The disappearance of peak at 1722 cm^{-1} and shifting of peaks confirms the involvement of functional groups in SFTS in adsorption process. The X-Ray diffractogram of SFTS (Fig. 2a) with sharp peaks confirms the crystalline nature of the adsorbent. The disappearance of these sharp peaks in X-Ray diffractogram of dye loaded adsorbent (Fig. 2b) confirms the effective adsorption of dye molecules onto adsorbent surface. The elemental analysis of SFTS was also done and the composition is shown in Table 1.



(a)



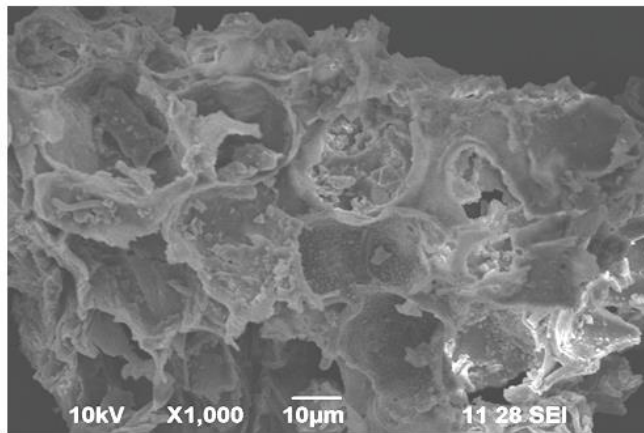
(b)

Figure 2. X- ray diffraction pattern of SFTS a) before adsorption and b) after adsorption

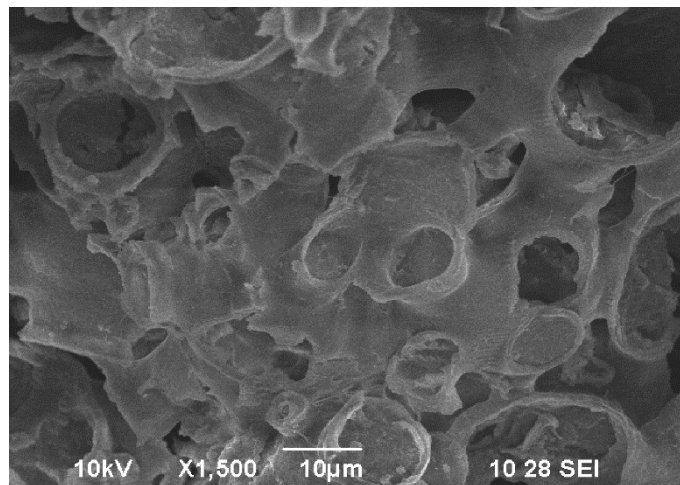
Table 1. Physicochemical characterization of SFTS

Parameters	Values
BET surface area	1.8704 m ² g ⁻¹
Total pore volume	0.003948 cm ³ g ⁻¹
Average pore diameter	8.4422 nm
Zero point of charge (pH _{zpc})	3.8
C %	52.21
H %	7.07
N %	1.32
S %	0.32

The SEM micrographs of SFTS before and after adsorption are shown in Fig.3.



(a)



(b)

Figure 3. SEM image of SFTS a) before adsorption and b) after adsorption

The availability of pores and rough surface of SFTS are clearly seen in Fig. 3a. The SEM micrograph of dye loaded SFTS clearly shows the coverage of pores and the surface by adsorption of dye molecules on to the adsorbent surface. The BET surface area, total pore volume and average pore diameter of SFTS were given in Table 1. The pore size distribution of SFTS is shown in Fig. 4. It is seen from the figure that most pores of SFTS are in the mesoporous range (diameter 2 – 50 nm) (Wang *et al.*, 2010). The average pore diameter of SFTS (Table 1) confirms the mesoporous nature of SFTS.

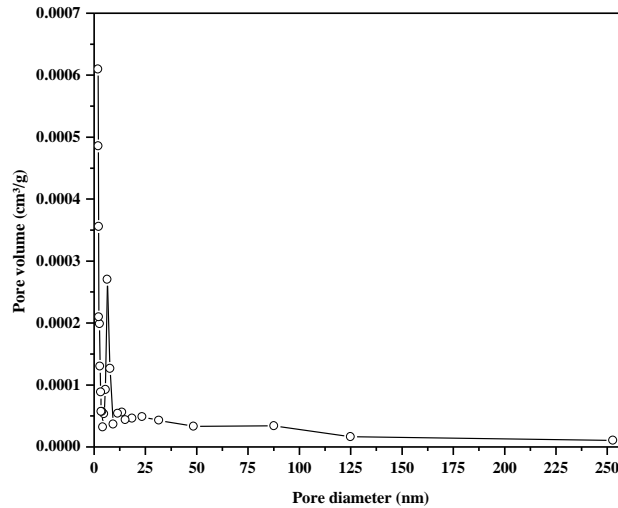


Figure 4. Pore size distribution of SFTS

3.2. Effect of initial dye concentration and contact time

The adsorption experiments were carried out for different contact time at initial dye concentration (150, 200, 250 and 300 mg l⁻¹) with adsorbent dose of 0.1 g at natural pH. Fig. 5 shows the effect of varying dye concentrations against the amount of MB adsorbed. The adsorption increases from 63 to 97 mg g⁻¹ with increase in initial MB concentration from 150 to 300 mg l⁻¹. This is due to the fact that with increase in concentration of MB, availability of MB at adsorbent interface also increases, thus increasing the amount of adsorption. The extent of adsorption reaches a saturated limit when the active sites in the surface of adsorbent are fully covered.

Fig.5 also represents the effect of contact time on the initial concentration of MB. The uptake of MB is rapid at the initial stages and thereafter it becomes near to the equilibrium. It can be explained based on the fact that a large number of vacant surface sites are available for adsorption during the initial stage and after a period of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between solute molecules on solid and bulk phases (Gusmao *et al.*, 2012). Fig.5 clearly shows the equilibrium time of 60 min for removal of MB by SFTS. The plots are single, smooth and continuous leading to saturation, suggesting the possibility of formation of monolayer coverage of the dye (Yamuna and Namasivayam, 1993).

3.3. Effect of pH

The pH of the aqueous solution is an important parameter in the adsorption of dyes on the biosorbents. The influence of the initial pH of solution on the adsorption of MB onto SFTS was studied in the pH range of 2 – 11(Fig.6). From the Fig. 6, it is clear that the adsorption capacity increases from 37 to 75 mg g⁻¹ with increase in pH 2 to 8, and then remains constant with increase in further pH of the solution.

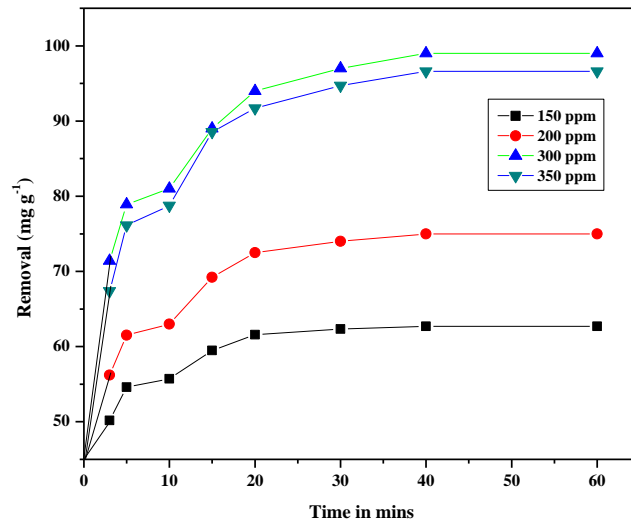


Figure 5. Effect of contact time on adsorption of MB onto SFTS (adsorbent dose = 0.1g/50 ml)

The influence of pH on the adsorption of MB can be explained on the basis of point zero charge (pH_{zpc}) of the adsorbent. The pH_{zpc} of SFTS was determined to be at pH 3.8. The surface of the adsorbent is positively charged at the pH lower than the pH_{zpc} , a high concentration of H^+ ions at acidic solution compete with dye cations on the surface of adsorbent, resulting in the suppression of dye adsorption at low pH. At pH higher than pH_{zpc} , the surface of the adsorbent becomes negatively charged and there exists a strong electrostatic attraction of dye cations with the adsorbent leading to the increased adsorption. Similar effect was observed in the adsorption of MB dye from aqueous solutions by succinylated sugarcane bagasse (Gusmao *et al.*, 2012), tea waste (Uddin *et al.*, 2009), EDTAD modified Bagasse (Xing *et al.*, 2010).

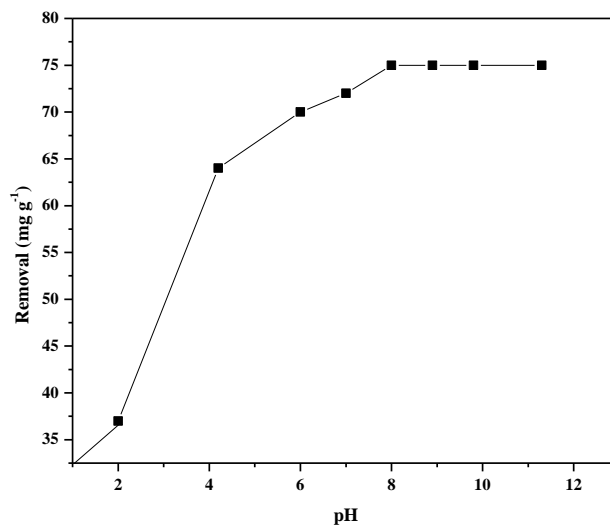


Figure 6. Effect of pH on adsorption of MB onto SFTS (adsorbent dose = 0.1g/50 ml, $C = 200 \text{ mg l}^{-1}$, $t = 60 \text{ min}$)

3.4. Effect of adsorbent dose

The adsorption of MB onto SFTS as a function of adsorbent dose is shown in Fig. 7. It is clear from the figure that the dye removal increases from 68 to 90% with increase in adsorbent dose from 0.05 to 0.2 per 50 ml of the dye solution. The reason for the increased adsorption may be attributed to greater surface area and large number of vacant sites thus favoring more adsorption.

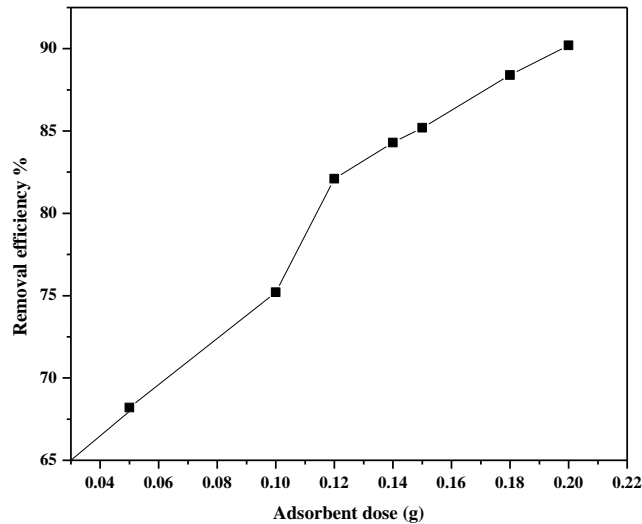


Figure 7. Effect of adsorbent dose on adsorption of MB onto SFTS ($V = 50$ ml, initial concentration = 200 mg l^{-1} , $t = 60$ min)

3.5. Isotherm analysis

The adsorption isotherms are used to indicate the distribution of molecules between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The amount of dye adsorbed at equilibrium reflects the maximum adsorption capacity of the adsorbent under operating conditions. The adsorption isotherms provide fundamental physiochemical data for evaluating the applicability of the adsorption process as a unit operation. The Langmuir, Freundlich, Temkin and D-R isotherm models were used to describe the data derived from the adsorption of MB by SFTS.

3.5.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interactions between sorbed molecules. The linear form of Langmuir adsorption isotherm is expressed as (Hameed *et al.*, 2008a)

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (1)$$

where q_e (mg g^{-1}) and C_e (mg l^{-1}) is amount of dye adsorbed per unit mass of adsorbent per unit mass of adsorbent and equilibrium concentration of dye. Q_0 and b are the Langmuir constants related to adsorption capacity and rate of adsorption respectively. The linear plots of C_e/q_e vs C_e (Fig. 8) shows that the adsorption obeys Langmuir isotherm and indicates the monolayer coverage of MB molecules at the outer surface of SFTS. The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in Table 2.

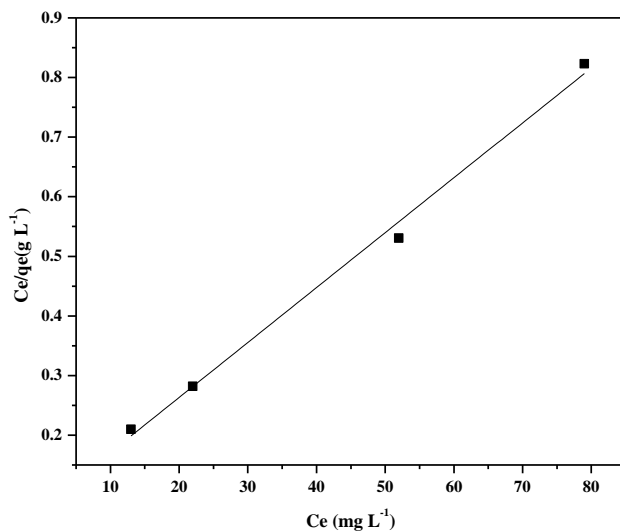


Figure 8. Langmuir adsorption isotherm for the adsorption of MB onto SFTS (adsorbent dose = 0.1g/50 ml, initial concentration = 200 mg l⁻¹, t = 60 min)

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (Hameed *et al.*, 2008a) by the following equation

$$R_L = 1 / (1 + b C_0) \quad (2)$$

where b (L mg⁻¹) is the Langmuir constant and C_0 (mg l⁻¹) is the highest initial concentration of dye. The R_L value indicates the shape of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values between 0 and 1 indicate favorable adsorption. The R_L value for the present study was found to be 0.026 indicating the favorable adsorption of MB onto SFTS. The comparison of adsorption capacities (Q_0) of various adsorbents for MB is presented in Table 3.

Table 2 Isotherm parameters for adsorption of MB onto SFTS

Isotherm	Parameters	Values
Langmuir	Q_0 (mg g ⁻¹)	111.1
	b (l ⁻¹ mg ⁻¹)	0.105
	R^2	0.993
Freundlich	K_F (l g ⁻¹)	33.35
	n	3.91
	R^2	0.937
Temkin	A (l g ⁻¹)	1.775
	B (KJ mol ⁻¹)	20.44
	R^2	0.929
D - R	Q_m (mol g ⁻¹)	94.63
	E (KJ mol ⁻¹)	0.222
	R^2	0.862

Table 3 Comparison of adsorption capacities of various low cost adsorbents for MB

Adsorbents	Q ₀ (mg g ⁻¹)	References
<i>Simarouba glauca</i> seed shell powder	111.1	This study
Defatted Jojoba	185	Al-Anber <i>et al.</i> , 2011
Silkworm exuviae	25.530	Chen <i>et al.</i> , 2011
Modified wheat straw	257.8	Zhang <i>et al.</i> , 2011
Citrus sinensis bagasse	112.36	Bhatti <i>et al.</i> , 2012
Green Pea Peels	163.94	Dod <i>et al.</i> , 2012
Peanut husk	72.13 ± 3.03	Song <i>et al.</i> , 2011
Banana stalk waste	243.902	Hameed <i>et al.</i> , 2008a
Garlic peel	82.64	Hameed and Ahmad, 2009
Sugarcane bagasse (SB)	27.29	Xing <i>et al.</i> , 2010
EDTAD-SB	115.3	Xing <i>et al.</i> , 2010
Palm kernel fiber	95.4	El-Sayed, 2011
Rice husk	8.07	Chen Shih, 2012
Coconut bunch waste	70.92	Hameed <i>et al.</i> , 2008b
Papaya seeds	555.557	Hameed, 2009
Rejected Tea	147	Nasuha <i>et al.</i> , 2010

3.5.2. Freundlich adsorption isotherm

The Freundlich isotherm is regarded as an empirical isotherm which indicates the surface heterogeneity of the adsorbent. The linear form of isotherm is expressed as (Senturk *et al.*, 2010)

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (3)$$

where K_f and n are Freundlich adsorption constants related to adsorption capacity and sorption intensity. The value of n varies with the heterogeneity of sorbent and gives an idea for the favorability of sorption process. The value of n less than 10 and higher than unity is favorable for adsorption (Senturk *et al.*, 2010). The values of Freundlich constants K_f and $1/n$ were obtained from the linear plot of $\ln q_e$ vs $\ln C_e$ and presented in Table 2. The Freundlich constant $1/n$ was smaller than unity indicates the favorable adsorption of MB onto SFTS.

3.5.3. Temkin adsorption isotherm

Temkin isotherm is based on the assumption that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbent interactions. The linear form of Temkin isotherm is commonly represented as (Anandkumar and Mandal, 2011)

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where $RT/b = B$, R is the gas constant ($8.314 \text{ J}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$) and $T(\text{K})$ is the absolute temperature. The constant B is related to the heat of adsorption and A is the equilibrium constant (min^{-1}) corresponding to the binding energy. The linear plot of q_e vs $\ln C_e$ enables the determination of constants A and B . The values of parameters are presented in Table 2.

3.5.4. Dubinin – Radushkevich (D-R) isotherm

D-R isotherm assumes that there is no homogeneous surface or constant biosorption potential. D-R isotherm was applied to characterize the process of adsorption and evaluate the type of interaction between dye and the adsorbent. The linear form of D-R isotherm is represented as (El Bakouri *et al.*, 2009)

$$\ln Q_e = \ln Q_m - \beta \epsilon^2 \quad (5)$$

where Q_m is the maximum adsorption capacity (mg g^{-1}), β is D-R isotherm constant and ϵ is the Polanyi potential. The constants β ($\text{mol}^2 \text{KJ}^{-2}$) and Q_m (mg g^{-1}) can be calculated from the slope and intercept of the plot $\ln q_e$ vs ϵ^2 and are presented in Table 2. ϵ , the Polanyi potential represents the work required to remove a molecule from its location, can be calculated as follows

$$\epsilon = RT \ln (1 + 1/C_e) \quad (6)$$

The mean free energy of adsorption (E) is the free energy when one mole of ion transferred from infinity in solution to the surface of the sorbent. E is calculated as follows

$$E = (-2 \beta)^{1/2} \quad (7)$$

The value of E would give information about the nature of adsorption as physisorption or chemisorption. The adsorption process would be physisorption when E lies between 1 and 8 KJ mol^{-1} , it would be chemisorption when E is higher than 8 KJ mol^{-1} . D-R isotherm parameters are presented in Table 2. The maximum adsorption capacity Q_m obtained using D-R isotherm for adsorption of MB onto SFTS is 94.63 mol g^{-1} . The value of E calculated is 0.22 KJ mol^{-1} indicates the physical adsorption of MB onto SFTS.

3.6. Kinetic studies

The adsorption kinetic studies were used to determine the adsorption behavior such as the adsorption type, rate and the capacity of the adsorption of the system (Malekbala *et al.*, 2012). In order to investigate the adsorption behavior, three kinetic models pseudo first order, second order and intraparticle diffusion models were used.

3.6.1. Pseudo first order kinetic model

The pseudo first order model was expressed as (Malekbala *et al.*, 2012)

$$\log (q_e - q_t) = \log q_e - (K_1 t) / 2.303 \quad (8)$$

The values of K_1 and q_e^{cal} can be obtained from the slope and intercept of the linear plot of $\log (q_e - q_t)$ vs t and represented in Table 4. The correlation coefficient is low and q_e^{cal} value did not show good agreement with the experimental one. This suggests that adsorption kinetics of MB on SFTS does not follow first order kinetics.

3.6.2. Pseudo second order kinetic model

The pseudo second order model is expressed as (Malekbala *et al.*, 2012)

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (9)$$

where K_2 is the rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), q_e and q_t are amount of dye adsorbed (mg g^{-1}) at equilibrium and time t (min). The values of K_2 and q_e^{cal} were calculated from the intercept ($1/K_2 q_e^2$) and slope ($1/q_e$) of the plot t/q_t vs t (Fig. 9) respectively and presented in Table 4. It can be seen from Table 4, there is an agreement between q_e^{exp} and q_e^{cal} for the pseudo second order model. The higher correlation coefficient also suggests the applicability of pseudo second order model for adsorption of MB on SFTS.

3.6.3. Intraparticle diffusion studies

Adsorption takes place in multisteps involving the transfer of solute from bulk of solution to surface of adsorbent. Intraparticle diffusion plays an important role in the extent of adsorption (Gupta *et al.*, 2012) and can be expressed as

$$q_t = K_{id} t^{0.5} + C \quad (10)$$

Where K_{id} is intraparticle diffusion constant ($\text{mg g}^{-1}\text{min}^{0.5}$) and C is the intercept (mg g^{-1}). The value of C gives an idea about the thickness of boundary layer, the layer the intercept greater the boundary layer effect. The value of K_{id} and C can be obtained from the linear plot of q_t vs $t^{0.5}$ (Fig. 10) and listed in Table 4.

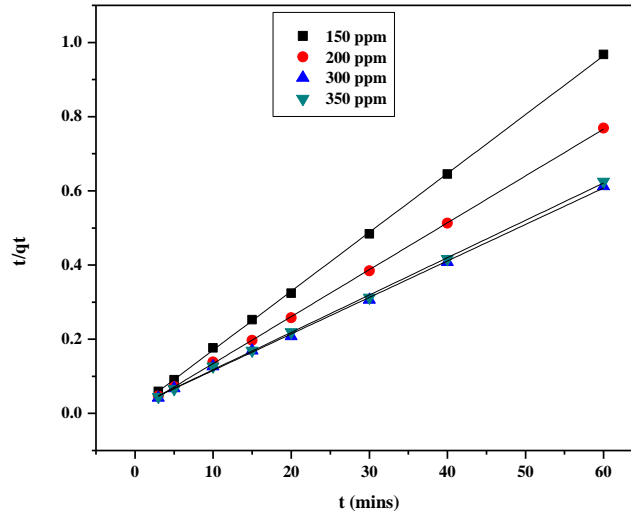


Figure 9. Pseudo second order plots for the adsorption of MG onto SFTS (adsorbent dose = 0.1g/50 mL, initial concentration = 300 mg l^{-1} , $t = 60$ min)

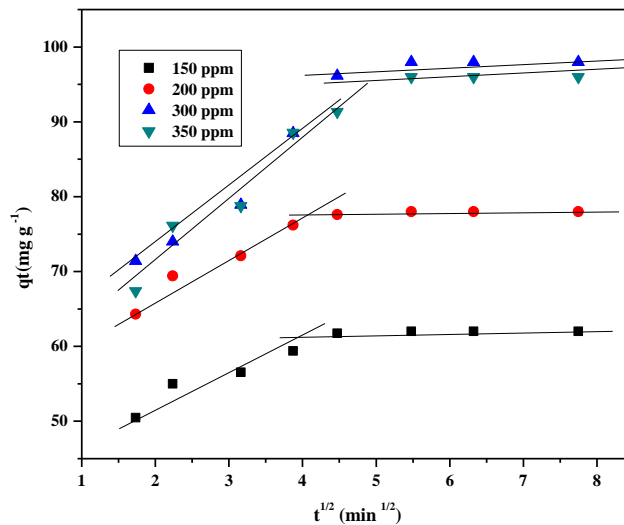


Figure 10. Intra particle diffusion plots for the adsorption of MB onto SFTS

The linear plot of q_t vs $t^{0.5}$ suggests that intraparticle diffusion might have a significant role in the adsorption of MB on SFTS. Since the linear plot did not pass through origin, it also suggests that although intraparticle diffusion was involved in adsorption process, it was not only the sole rate controlling step. It is clear from the Fig.10 that the adsorption processes involve more than one kinetic stage. The first linear portion was due to adsorption of dye molecules on to the adsorbent surface indicating boundary layer effect and the second linear portion is due to intra particle diffusion (Gupta *et al.*, 2012; Dogan *et al.*, 2009).

Table 4. Kinetic parameters for adsorption of MB onto SFTS

Concentration MG (mg l ⁻¹)	q _e ^{exp} (mg g ⁻¹)	Pseudo first order			Pseudo second order			Intraparticle diffusion	
		q _e ^{cal} (mg g ⁻¹)	K ₁ (min ⁻¹)	R ²	q _e ^{cal} (mg g ⁻¹)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²	K _{id} (mg g ⁻¹ min ^{-1/2})	R ²
150	62.7	11.38	0.069	0.634	66.66	0.014	0.999	2.025	0.798
200	75.4	27.86	0.106	0.979	83.33	0.075	0.999	3.279	0.848
300	98.7	38.82	0.099	0.979	111.1	0.0047	0.999	4.666	0.873
450	96.6	38.99	0.099	0.985	100.0	0.0055	0.999	4.866	0.840

3.7. Desorption studies

Desorption studies helps to clarify the mechanism of adsorption process. If the dye adsorbed can be desorbed by water, a weak interaction exists between dye molecules and the adsorbent. If the strong acid such as HCl can desorb the dye, interaction would be of ion exchange. The adsorption process might be chemisorption if the dye adsorbed can be desorbed by weak acid CH₃COOH (Chen *et al.*, 2011). In the present study, desorption of MB was found to be 0.32%, 32.1% and 22% for H₂O, HCl and CH₃COOH. The higher desorption in HCl compared to H₂O and CH₃COOH suggests the physical adsorption (ion exchange) of MB onto SFTS. Similar behavior has been observed in Silkworm exuviae (Chen *et al.*, 2011), wheat straw materials (Zhang *et al.*, 2011) and citric acid modified kenaf fibres (Sajab *et al.*, 2011).

4. Conclusion

The present study shows that the *Simarouba glauca* seed shell powder can be used as an effective adsorbent for removal of methylene blue from aqueous solutions. The equilibrium data showed best fit for Langmuir isotherm with maximum adsorption capacity of 111.1 mg g⁻¹. The optimum pH was found to be 8. The kinetic data were found to follow pseudo second order model and the adsorption of methylene blue was controlled by boundary layer effect and intraparticle diffusion. Desorption studies shows the predominance of physical adsorption of methylene blue onto the adsorbent surface.

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