Adsorption of basic Dye from Aqueous Solution using HCl Treated Saw Dust (*Lagerstroemia microcarpa*): Kinetic, Modeling of Equilibrium, Thermodynamic, INDIA

Kini Srinivas M.[1*], Saidutta M.B.[2], Murty V.R.C.[3] and Kadoli Sandip V.[1]
[1]Department of Chemical Engineering, Manipal Institute of Technology, Manipal-576 104, Karnataka, INDIA
[2]Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Karnataka, INDIA
[3]Department of Biotechnology, Manipal Institute of Technology, Manipal -576 104, Karnataka, INDIA

Abstract

In this work, experiments were conducted to explore the potential of saw dust activated with hydrochloric acid (ASD) as adsorbent for methylene blue (MB) removal. The influence of different variables like solution pH, MB concentration, contact period and ASD dosage were studied. Adsorption data were better fitted to the second order kinetics. Experimental equilibrium data were analyzed by various established isotherms and Langmuir isotherm was found to be better fitted one. Thermodynamic parameters like Gibbs free energy (ΔG), change in enthalpy (ΔH) and entropy (ΔS) were estimated and the adsorption of MB onto ASD was found to be exothermic and favorably influenced by decrease in the temperature. A mathematical model for MB transported by molecular diffusion from the solution to the surface of ASD was derived and the values of liquid phase diffusivity and external mass transfer coefficient were estimated.

Keywords: Methylene blue, Lagerstroemia microcarpa, kinetics, equilibrium, isotherms, mathematical model.

Introduction

Nowadays, environmental pollution is having an adverse effect on humans and ecosystems. Synthetic dyes are consumed in industries such as textile, leather, paper, plastics, etc., and hence are the major sources of water pollutants. Dye pollutants from the textile industries play a vital role in contaminating the environment. Due to their synthetic nature and structure mainly aromatic, the most of dyes are non-biodegradable and stable, having carcinogenic action[1]. In textile industries, the percentage of dye lost in the effluent during the dyeing processes is about 50% due to low levels of dye-fiber attachment[2]. The amount of dye lost is dependent upon type of dyes, the method of application and depth of shade required[3] and discharge of these dyes in the environment poses serious ecological concern[3,4]. Methylene blue (basic dye) is one such dye, used extensively in textile industry for coloring purposes. Wastewater containing methylene blue has adverse impact on humans and environment[5]. Therefore elimination of methylene blue from industrial wastewater in an optimum manner is a great challenge to the present day researchers.

Colored wastewater can be treated by convention treatment methods which encompasses several physical, chemical and biological methods but their use is restricted in textile industries due to their high cost and infeasibility. Amongst the above treatment methods, adsorption was found to be effective technique because of its low initial investment, greater flexibility in operation and simplicity of design of equipment, applicability on a large scale and insensitivity to toxic dye.

Liquid phase adsorption on granular or powdered activated carbon is a widely used method for the removal of color, but it is prohibitively expensive[6].

Numerous alternative materials from plant and agricultural wastes have been studied by various researcher's to adsorb dyes from aqueous solution. These waste material are assumed to be cost effective adsorbents since they are cheap, available in abundant quantities and contain various organic compounds such as lignin, cellulose and hemicellulose[7,8]. The saw dust untreated and treated, have been reported for removal of methylene blue dye from synthetic wastewater. These include, formaldehyde-treated sawdust[9], rattan[10], salt treated beech saw dust[11], chemically treated wood shavings[12], walnut and cherry tree, pine[13], Indian rosewood[14], biopolymer oak saw dust[15] and crude and monosodium glutamate functionalized saw dust[16] etc.

In the present research work, Benteak saw dust (Lagerstroemia microcarpa) was used. It is a deciduous tree, native to the moist forests of Western Ghats in India, growing to 10-15 m tall. The bark of this tree is generally used in furniture works. Batch experiments were conducted to find the effect of process variables such as pH, ASD dosage, initial MB dye concentrations and temperature. The influence of these parameters on adsorption capacity was investigated. The adsorption data were fitted using suitable isotherms. A new model was derived for adsorption for MB transported by molecular diffusion from the bulk of the solution to the surface of saw dust particle and the values of liquid phase diffusivity and external mass transfer coefficient were estimated.

Mathematical model: Since the particle is small, the flow in the vicinity of the particle is not turbulent. Thus we assume that the mass transfer to the particle can be modeled as a process of diffusion in a quiescent medium. Assuming pseudo-steady state, the differential equation is

$$(1/r^2) \, d(r^2 \, dc/dr)/dr = 0 \qquad (1)$$

Solving this equation with boundary condition,
B.C.: $c = c_\infty$; $r = \infty$., $c = c_e$; $r = R$.

where c_e is concentration on the adsorbent surface (kg/m^3) and R is the radius of particle. The concentration profile in the liquid is obtained as

$$c = c_\infty - (c_\infty - c_e) \, R/r \qquad (2)$$

The flux at the surface (r = R) is obtained as $D_L(c_\infty - c_e)/R$. This corresponds to a mass transfer coefficient k_c (m/s) ;

$$k_c = D_L/R \qquad (3)$$

Where D_L is the liquid phase diffusivity (m^2/s).

Material balance for the solute is;

$$\Phi \, (dq/dt) = - \, dc/dt \qquad (4)$$

Further, accumulation rate of solute on the solid is equal to the mass transfer rate from the liquid, i.e,

$$(dq/dt) \, \rho \, R^2 = D_L \, (c-c_e) \qquad (5)$$

Since equilibrium prevails on the surface, c_e and q are related by the Langmuir isotherm given by;

$$q = q_m * K_L * C_e / (1 + K_L * C_e) \qquad (6)$$

Where q_m is the maximum amount of dye adsorbed per unit mass of adsorbent corresponding to complete coverage of the adsorption sites in mg/g , K_L is the Langmuir constant related to energy of adsorption in L/mg. Therefore c_e in equation (5) can be substituted in terms of q. Thus we obtain equation (7). Using equation (4) in eqn.(7), we obtain equation (8)

$$dq/dt = (D_L/R^2\rho) \, (c - q/(K_L(q_m-q))) \qquad (7)$$
$$dc/dt = -\Phi \, (D_L/R^2\rho) \, (c - q/(K_L(q_m-q))) \qquad (8)$$

where Φ is solid loading (kg/m^3 of liquid).Solving eqn. (7) and (8) as an initial value problem using initial condition $c=c_\infty$; q=0; t=0 ,0 < r < R, with a help of numerical computer program in MATLAB, yields the bulk concentration as a function of time . The liquid phase diffusion coefficient D_L is obtained by matching the experimental concentration decay curve with that obtained from the model.

Material and Methods

Materials: Sawdust (Lagerstroemia microcarpa) which is a raw waste and usually thrown away was collected from carpentry work shop, Manipal, Karnataka, India and dried in a dryer at 110 ^{0}C for one day; Then sawdust was ground to fine powder and sieved to 150 μm size. Sawdust was chemically treated with hydrochloric acid (HCl) and was termed as acid activated sawdust (ASD). A suspension containing 20 gm sawdust, 400 ml of distilled water and 10 ml of 1.33M HCl was prepared in a beaker. The contents in the beaker was stirred for 1 hr at 80 ± 2^{0}C in a magnetic stirrer with hot plate. After cooling and filtering, the sawdust was washed several times with distilled water until the filtrate pH became neutral and then dried in air at room temperature. The material was stored in an airtight container for further experiments.

Preparation of MB solutions: The analytical grade methylene blue with 99.8% purity, was supplied by Hi-Media, Bangalore, India. A stock solution of 1000 mg/L of MB were prepared and then used for different experiments by diluting with distilled water.

Characteristics of ASD: The surface area of ASD were determined using BET apparatus (Smart Instruments, Mumbai) . The surface texture of ASD was found out by Scanning Electron microscopy (SEM) analysis. The structural information on the functional groups of ASD samples were detected by Fourier Transform Infrared (FTIR) spectroscope (Shimadzu, Japan). The FTIR analysis was done by using 150 mg KBr disks containing 2 % of ASD sample in the range 450-4000 cm^{-1} with 16 cm^{-1} resolution.

Adsorption experiments: Influence of pH: The amount of color removal were analyzed over a pH range of 2-10 by adjusting the pH using 0.1 N HCl and 0.1 N NaOH solutions. The experiments were conducted by agitating 100 mL of dye solution of 50 mg/L with 0.1 g ASD powder at temperature of 30 °C. The agitation was carried out for an equilibrium time of 6 hr and speed of 150 rpm. The samples collected were then filtered and analyzed using double beam U-V spectrophotometer (UV-1700, Shimadzu, Japan) by measuring the absorbance at 665 nm.

Influence of ASD concentration: The effect of ASD concentration on the amount of color adsorbed was studied by adding 0.1 to 0.6 g of ASD in 100 mL of MB solution of initial concentration of 200 mg/L . All the experiment were carried out at 30°C, pH of 7 and 150 rpm for 6 hr.

Adsorption equilibrium : The equilibrium experiments were conducted by agitating 100 mL MB solution with 0.1 g ASD at 150 rpm. The MB concentrations was varied from 50-300 mg/L. The amount of MB adsorbed per gram of ASD (q_e) at equilibrium was obtained by the following equation;

$$q_e = V * (C_o - C_e) / 1000 * M \qquad (9)$$

where V is the volume of MB solution (mL), C_o and C_e is initial and equilibrium concentration of MB in solution (mg/L) and M is the dry weight of the ASD powder (g). The percentage removal of the dye is given by;

$$\% \text{ Removal} = 100 * (C_o - C_e) / C_o \qquad (10)$$

Adsorption Kinetics: Kinetic experiments were performed by adding 1 g ASD powder to 1000 mL of the MB solution at 30°C at pH 7 and at constant agitation speed of 150 rpm. The MB concentrations were varied from 50 to 200 mg/L. The amount of MB adsorbed per unit gram ASD at any time (q_t) were obtained using the following expression;

$$q_t = V*(C_t - C_o)/ 1000* M \qquad (11)$$

where C_t is the MB concentration at any time t (mg/ L).

Effect of initial MB concentration: The experiments were conducted by adding 0.1 g ASD powder with 100 mL of MB solution of dye concentration ranging from 50- 200 mg/ , at four different temperatures (293K, 303 K, 313 K, 323 K) using shaking incubator for 6 hr.

Results and Discussion

Characterization of the adsorbent: The surface area of ASD was 1.12 m^{2}/g. Fourier-transform infrared (FTIR) spectra of the ASD before and after MB adsorption is presented in figure-1 and figure-2. FTIR spectrum of ASD before MB adsorption shows peaks at 3402 cm^{-1} due to O-H stretching , the peak at 2916 cm^{-1} was attributed to stretching of C-H bond of methyl and methylene groups, the peak observed at 1743 cm^{-1} was assigned to a carbonyl bond (C=O).The peak observed at 1550cm^{-1} is due to secondary amine group. The band at 1465 cm^{-1} was attributed to CH$_2$ group, and another band at 1427 cm^{-1} was due to aromatic ring of lignin. The band at 1242 cm^{-1} was due to bending modes of O-C-H, C-C-H and C-O-H[17]. The band at 1026 cm^{-1} was assigned to C-O stretching. As shown in figure-2, after adsorption, the peaks of the stretch vibration of C-H bond of methyl group and that of amine group were shifted from 2916 cm^{-1} and 1550 cm^{-1} to 2924 cm^{-1} and 1512 cm^{-1} respectively.
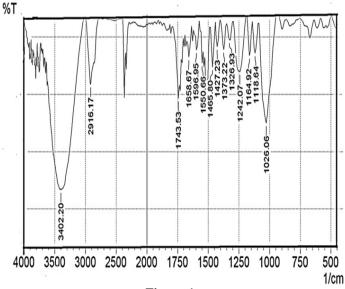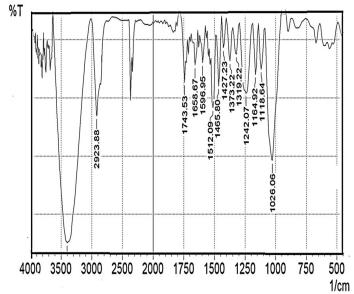

Figure-2
FTIR of ASD after adsorption of MB dye

In figure-3, scanning Electron Microscopy photographs before dye adsorption clearly revealed the surface morphology and the different level of porosity in ASD. The surface after MB adsorption shown in figure-4 however shows that ASD is loaded with MB dye.
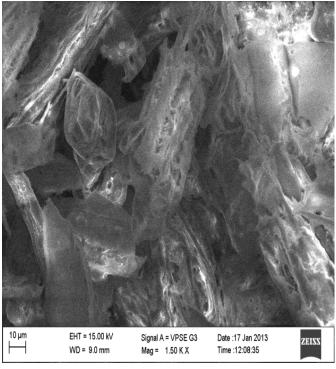

Figure-3
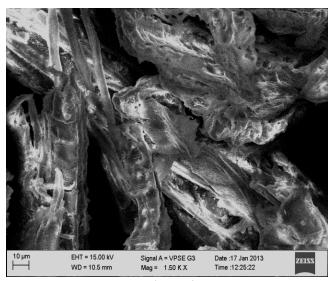**Scanning electron image of ASD before MB adsorption**

Figure-1
FTIR of initial ASD sample

Figure-4
Scanning electron image of ASD after MB adsorption

Batch mode adsorption studies: Influence of initial pH :
Effect of pH on MB removal is presented in figure-5. The MB adsorption by ASD enhanced with the increase in pH from 2 to 4 and thereafter remained nearly constant for pH greater than 4.0. The q_e value of 31.627 mg/g is minimum at pH 2 and is nearly constant in the range 48.69-49.19 mg/g for pH 4 – 10. At low pH, the surface charge may get positively charged, thus making H^+ ions and dye cation compete with each other for adsorption on active sites causing a decrease in amount of dye adsorbed[18]. At higher pH values, the ASD surface becomes negatively charged which increases the adsorption of positively charged dye cation through electrostatic force of attraction[19]. From figure- 6, it is observed that % removal of MB at an initial solution pH 7 was found to be maximum i.e. 98.3936 %. Therefore, further adsorption experiments were performed at pH 7.0.
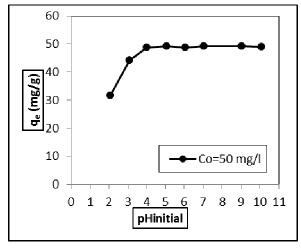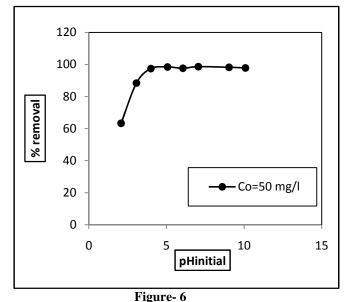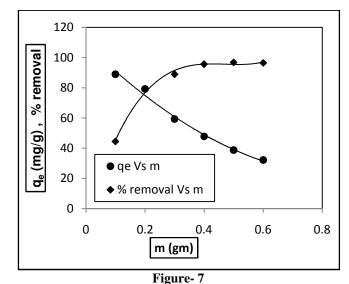
Influence of adsorbent dosage: The relationship of mass of ASD on the adsorption of Methylene blue onto ASD is presented in figure-7. From figure-7, for an increase in ASD dosage of 1-6 g/L, the q_e decreased from 88.95 mg/g to 32.162 mg/g, whereas the percentage removal increased from 44.47 % to 96.486 % respectively. The increase in % color removal was due to greater surface area and availability of more adsorption sites[20]. The decrease in adsorption capacity q_e with increasing ASD dosage may be due to overlapping of adsorption sites as a result of overcrowding of ASD particles[21].

Figure- 6
Plot of pH on the percentage adsorption of MB by ASD at temperature 303 K, time 6 h, initial concentration 50 mg/L and adsorption mass1 g/L

Figure -5
Plot of pH on the adsorption capacity of MB by ASD at temperature 303 K, time 6 h, initial concentration 50 mg/L and adsorption mass1 g/L

Figure- 7
Plot of ASD mass on the adsorption capacity of MB at concentration 200 mg/L and pH 7

Effect of Initial MB concentration and Contact time: The adsorption capacity versus time at different initial concentration were plotted in figure-8 and the result showed that as MB concentration increased, the q_t increased, primarily due to enhanced driving force to overcome mass transfer resistance and greater interaction between MB and ASD [15,22]. The MB adsorption rate onto ASD increased from 49.3976 to 189.0564 mg/g as MB concentration increased from 50 to 200 mg/L respectively.
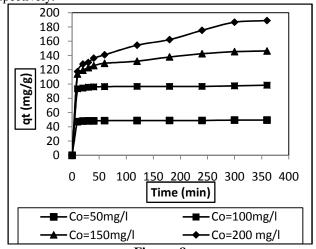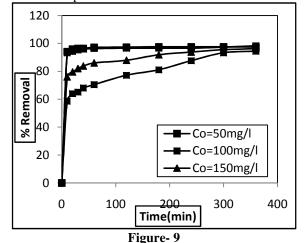

Figure- 8
Effect of mass of adsorption of MB dye with time at temperature 303 K and adsorbent mass 1 g/L

Figure-9 indicated very quick rate of adsorption of MB in the initial 15 min. and thereafter, the adsorption rate declined gradually and reached the equilibrium at about 6 hr. The higher adsorption rate at the initial stage may be due to availability of more number of vacant sites, as a result, there exists increased MB concentration gradient in solution and on the ASD surface. After a certain period of time, this gradient is reduced due to accumulation of MB dye in the vacant sites, leading to a decrease in adsorption rate[19,20].

Figure- 9
Plot of contact time on dye removal efficiency of ASD at temperature 303 K and adsorbent mass 1 g/ L

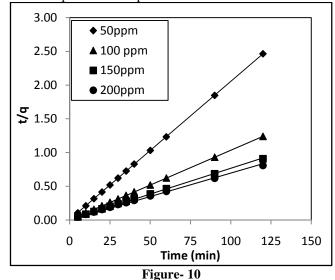**Adsorption dynamics:** The Lagergren 's [22] linear pseudo-first order expression is in the form:

$$\log (q_e - q_t) = \log q_e - k_{1*} (t / 2.303) \tag{12}$$

where k_1 is the rate constant of first-order adsorption (min^{-1}), q_e and q_t are the amounts of MB adsorbed on ASD at equilibrium and at time t (min), respectively. From the plot (figure not shown), values of k_1 were calculated. From table-1, the regression coefficient values R^2 were found to be in the range of 0.76-0.97 and the experimental q_e values deviated from the predicted q_e values. This shows that adsorption of MB onto ASD did not obey the pseudo –first order model. Therefore, the Lagergren's pseudo-second order equation was applied to describe the adsorption process, as given in equation. (13) and (14) [22];

$$t/ q = 1/ k_2 * q_e^2 + t/ q_e \tag{13}$$

and

$$h = k_2 * q_e^2 \tag{14}$$

Where k_2 is the pseudo-second-order rate constant (g /mg* min) and h is the initial adsorption rate at time approaching zero (mg /g*min). The intercept of the plot t/q versus t, figure-10 was used to calculate the rate constant k_2 and the initial adsorption rate h. Table-1 lists the value of rate constant k_2, initial adsorption rate and regression coefficients R^2. Due to higher $R^2 (> 0.99)$, the predicted $q_{e,cal}$ values were reasonably close to the experimental $q_{e,exp}$ values, suggesting very good agreement of the adsorption data for pseudo-second order model.

Figure- 10
Second order plot of MB adsorption onto ASD

Adsorption Isotherms[23]**:** In this study, adsorption data were fitted by five isotherms namely Freundlich, Langmuir, Dubinin-Radushkevich, Temkin and Redlich- Peterson. The Langmuir isotherm is given in equation (6) and the Freundlich isotherm is given by;

$$q_e= K_F * C_e^{1/n} \tag{15}$$

where K_F (mg/g*(L/mg)$^{1/n}$) and 1/n are constants related to adsorption capacity and intensity of adsorption, respectively. The Temkin isotherm is presented by;

$$q_e = B_1 * \ln (K_T * C_e) \tag{16}$$

where B_1 = (R *T/b), T (K) is the absolute temperature, R (8.314 KJ/Kmol K) is the universal gas constant, A (L/mg) is equilibrium binding constant and b (KJ/mol) is the variation of adsorption energy.

The Dubinin-Radushkevich isotherm is given by;

$$q_e = q_m * \exp (-D\mathcal{E}^2) \tag{17}$$

$$\mathcal{E} = R *T* \ln (1+C_e^{-1}) \tag{18}$$

Where the constant D gives the mean free energy of adsorption per molecule of the dye.

The three-parameter Redlich–Peterson isotherm is the following;
$$q_e = A* C_e/(1+B* C_e^g) \tag{19}$$

where A,B and g are Redlich-Peterson constants.
From the Langmuir's isotherm the dimensionless separation factor (R_L) is derived[23] as follows;

$$R_L = 1 / (1 + K_L*C_o) \tag{20}$$

The values of R_L lying between 0 and 1 indicates favorable adsorption. From the values of R_L given in table-2 and figure-11, the adsorption of MB onto ASD is favorable.

Isotherm Analysis : In recent years, the non-linear regression technique has been proposed as a better way to find the best fitting of adsorption equilibrium. In this method, the error distribution between experimental data and predicted isotherm is minimized by iterative procedure using the Microsoft Excel[20,24]. The various mathematically rigorous error function used in this analysis are given in table -3.

The figure-12 shows the experimental equilibrium data and the predicted Langmuir, Redlich-Peterson, Temkin, Freundlich and Dubinin–Radushkevich isotherm got by minimizing the R^2 function using non-linear method. In addition, from figure-12, the Langmuir and Redlich-Peterson isotherms were found to overlap with each other with the similar R^2 value. The isotherm parameters obtained at 303K are listed in table- 4. From table 4, it was observed that only R^2 value produces the g value equal to unity suggesting that the Redlich-Peterson isotherm is approaching the Langmuir isotherm whereas in the case of other error functions the value lies close to 1. The Langmuir and Redlich-Peterson isotherm describes the data in the best way based on R^2 value. The maximum q_m, value of 226.12 mg/g at

303K suggest that ASD is an effective adsorbent for dye removal.

Thermodynamic analysis: The thermodynamic values such as Gibbs free energy change ΔG (in KJ/ mol), change in enthalpy ΔH (in KJ/ mol) and change in entropy ΔS (in J/mol K) have been estimated using the following equations [21].
$$\Delta G = -R*T* \ln K \tag{21}$$

Where K is the equilibrium constant, related to the Langmuir constant, K_L by;
$$K = K_L *M_A \tag{22}$$

Where, M_A is the molecular weight of MB. The enthalpy and entropy values are given by Van't Hoff equation,
$$\ln K = (\Delta S/R) – (\Delta H/R*T) \tag{23}$$

The obtained results tabulated in table- 5 shows that since ΔG < 0, the adsorption was a spontaneous process. The slope and intercept of the plot of ln K versus 1/T in figure-13, gave the ΔH and ΔS respectively. The negative values of ΔH indicated that the ASD-MB interaction is exothermic in nature[19]. The ΔS > 0 indicates an increase in the degree of randomness of MB molecules at the ASD surface than in the solution.

Mathematical Model: The Langmuir isotherm described the equilibrium data very well with q_{m} = 229.8 mg/g and K_L= 0.461 at 30°C , and high correlation coefficient of 0.998. Equations (7) and (8) yielded the bulk concentration as a function of time and figure-14 (a),(b),(c),(d) shows the experimental decay- time profile of MB adsorption onto ASD at different initial solute concentration. The correlation coefficient for different initial solution concentration (50,100,150 and 200 mg /L) were computed and found to be in excess of 0.99, indicating satisfactory fit of model prediction and experimental data. The estimated value of D_L and K_c are $1.5x10^{-8}$ m^2/s and $1x10^{-4}$ m/s respectively.
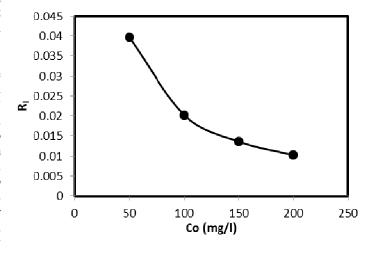

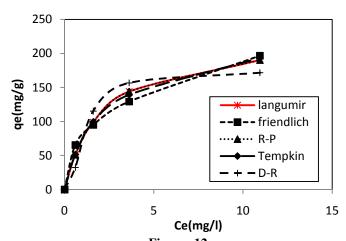**Figure- 11**
Plot of R_L Vs C_o

Figure- 12
Plot of predicted equilibrium isotherm for the adsorption of MB onto ASD
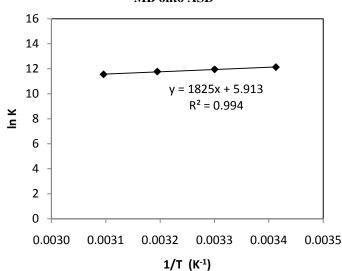

$y = 1825x + 5.913$
$R^2 = 0.994$

Figure- 13
Van't Hoff 's plot for the adsorption of MB onto ASD.

(a)

(b)

(c)

(d)

Figure-14
Effect of bulk concentration of MB with time for different initial concentration of
a) 50 mg/L. b) 100 mg/L c) 150 mg/L d) 200 mg/L.

Figure-15
Map of study area of our research work

Table-1
Kinetic constants for the adsorption of MB by ASD at temperature 30°C, agitation time 120 min. and adsorbent dose of 1 g/L

Conc.	$q_{e,exp}$	First order			Second order			
		$q_{e, cal}$	k_1	R^2	$q_{e, cal}$	k_2	R^2	h
50	49.40	1.86	0.0276	0.9063	48.78	0.0483	1.0000	114.88
100	98.39	4.21	0.0343	0.9729	97.09	0.0221	1.0000	208.42
150	146.39	28.15	0.0094	0.8457	136.98	0.0141	0.9989	264.94
200	189.10	64.63	0.0058	0.7752	175.43	0.0116	0.9959	358.23

Table-2
Seperation factor R_L

C_o	R_L
50	0.0397
100	0.02025
150	0.01359
200	0.01023

Table-3
Definition of error functions used[20]

Name of error function	Definition
The Sum square errors (ESQ)	$\sum_{i=1}^{p} (q_{e,cal} - q_{e,exp})_i^2$
The hybrid fraction error function (HEF)	$100/(n-p) \sum_{i=1}^{n} ((q_{e,exp} - q_{e,cal})^2 / q_{e,exp})_i$
Marquardt's standard deviation (MSD)	$100* (1/(n-p) \sum_{i=1}^{p} ((q_{e,exp} - q_{e,cal})^2 / q_{e,exp})_i)^{0.5}$
The average relative error (AE)	$(100/n) \sum_{i=1}^{p} |((q_{e,exp} - q_{e,cal}) / q_{e,exp})_i|$
The Sum of absolute errors (SAE)	$\sum_{i=1}^{p} |(q_{e,cal} - q_{e,exp})_i|$

p is number of parameter in the isotherm

Table-4
Isotherm values for adsorption of MB by ASD for initial concentration range of 50-200 mg/L, time of agitation 6 hr and adsorbent dosage 1g/L

	R^2	AE	HEF	MSD	SAE	SSE
			Freundlich			
K_F	79.4211	62.4588	62.6645	69.1641	83.6463	79.4213
n	2.6401	2.1604	2.1678	2.1678	2.9343	2.6401
MEF*	0.9429	10.9028	20.149	17.201	37.8421	623.6259
			Langmuir			
q_m	234.521	225.489	229.82	229.82	224.672	226.119
K_L	0.5777	0.4742	0.46	0.4607	0.4851	0.4842
MEF*	0.998	1.2638	0.0365	1.911	4.725	10.61
			Temkin			
B_1	48.877	49.9532	49.9536	50.2629	49.9543	48.8763
K_T	4.7612	4.4626	4.4625	4.4537	4.4625	4.7612
MEF*	0.993	1.9644	1.1845	4.0373	12.6693	76.3099
			Dubinin-Raduskevich			
q_m	173.93	157.343	158.236	155.825	155.8249	173.93
$D \times 10^4$	6.97	4.8	5.0	4.99	4.76	6.9
MEF*	0.9099	9.4950	0.5303	18.5741	55.2261	983.574
			Redlich-Peterson			
B	109.4786	108.1597	107.3691	107.105	108.8919	110.203
A	0.4842	0.4971	0.4971	0.4781	0.4846	0.4925
g	1.0	0.986	0.985	0.989	0.998	0.996
MEF*	0.999	1.5678	5.8654	3.1774	5.2312	11.8691

*Minimized / maximized error function

Table-5
Values of Gibbs free energy, enthalpy and entropy

T	ΔG	ΔH	ΔS
293	-29.5422	-	-
303	-30.1045	-15.1731	49.1607
313	-30.6089	-	-
323	-31.0057	-	-

Conclusion

The results demonstrates that ASD has the potential to serve as a promising low cost adsorbent for MB dye. The quantity of MB removed increased with increasing pH. The adsorption capacity increased with increasing dye solution concentration, contact period and decreased with increasing ASD dosage. The kinetics could be successfully fitted by a second order equation and the equilibrium data were well described by Langmuir isotherm with the monolayer adsorption capacity of 229.8 mg/g at 303K. Thermodynamically, the interactions are exothermic in nature, are entropically driven, and are supported by decrease in Gibbs free energy. The mathematical model derived gave a satisfactory fit of model prediction and experimental data thereby indicating that the adsorption is only taking place on the surface of the ASD.

References

1. Crini G., Non-conventional low cost adsorbent for dye removal: A review, *Bioresour. Technol.*, **97**, 1061-1085 (**2006**)

2. Mohan N., Balasubramanian N. and Basha C.A., Electrochemical oxidation of textile wastewater and its reuse, *J. Hazard. Mater.*, **147**, 644–651(**2007**)

3. Pearce C.I., Lloyd J.R. and Guthrie J.T., The removal of colour from textile wastewater using whole bacterial cell: a review, *Dyes and Pigments*, **58**, 179-196(**2003**)

4. Butani N., Chelliah P., Shah S., Randive B., Patel P., Microbial decolorization of disperse textile dye brown 21 by Enterbacter gergoviae isolated from textile effluents, *Int.Res.J.Env.Sci.*, **2(5)**, 31-36(**2013**)

5. Senthilkumaar S., Varadarajan P. R., Porkodi K. and Subbhuraam C. V., Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, *J. Colloid. Interface Sci.*, **284**, 78-82 (**2005**)

6. Song J., Zon W., Bian Y., Su F. and Han R., Adsorption characteristics of methylene blue by peanut husk in batch and column modes, *Desalination*, **265**,119-125 (**2011**)

7. Salleh M.A.M., Mahmoud D.K., Abdul Karim W.A.W., Idris A., Cationic and anionic adsorption by agricultural

solid wastes: A comprehensive review, *Desalination*, **280**,1-13 **(2011)**

8. Abeer A. and Ghadir A.E., Adsorption of citric acid rom aqueous solution onto activated P. Lentiscus leaves, *Int.Res.J.Env.Sci*., **1(4)**, 7-13(**2012**)

9. Garg V.K., Gupta R., Yadav A.B. and Kumar R., Dye removal from aqueous solution by adsorption on treated sawdust, *Bioresour. Technol.*, **89**, 121–124 (**2003**)

10. Hameed B.H., Ahmad A.L. and Latiff K.N.A., Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, *Dyes and Pigments*, **75** , 143-149 **(2007)**

11. Batzias F.A. and Sidiras D.K., Simulation of methylene blue adsorption by salts-treated beech sawdust in batch and fixed-bed systems, *J. Hazard. Mater.,* **149,** 8–17(**2007**)

12. Janos P. and Coskun S., Removal of basic (Methylene Blue) and acid (Egacid Orange) dyes from waters by sorption on chemically treated wood shavings, *Bioresource Technology,* **100**, 1450–1453(**2009**)

13. Ferrero F., Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust, *J. Hazard. Mater.*, **142** 144–152 (**2007**)

14. Garg V.K., Amita M., Kumar R. and Gupta R., Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes Pigments* ,**63**, 243–250(**2004**)

15. Abd El-Latif M.M., Ibrahim A.M. and El-Kady M.F., Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite, *J. American Sci.*, **6(6)** 263-287 **(2010)**

16. Gong R., Liu X. and Feng M., Comparative study of Methylene blue sorbed on crude and monosodium Gultamate Functionalized Saw dust, *J. Health Sci*., **54(6)** 623-628 (**2008**)

17. Bodiralau R. and Teaca C.A., Fourier transform infrared spectroscopy and thermal analysis of lignocellulose fillers treated with organic anhydrides, *Romanian J. Phys*., **54(1-2)**, 93-104(**2009**)

18. Namasivayam C., Prabha D. and Kumutha M., Removal of direct red and acid brilliant blue by adsorption on to banana pith, *Bioresour. Technol.*, **64,** 77-79(**1998**)

19. Mane V.S. and Vijay Babu P.V., Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust, *Desalination*, **273**, 321–329(**2011**)

20. Kumar K.V. and Porkodi K., Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, *J. Hazard Mater*, **146** , 214–226(**2007**)

21. Bulut Y. and Aydin H., A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, *Desalination*, **194**, 259–267(**2006**)

22. Qiu H., Lu L.V., Pan B., Zhang Q., Zhang W, Zhang Q. Critical review in adsorption kinetic models, *J. Zhejiang Univ. Sci. A*, **10(5)**,716-724(**2009**)

23. Foo K.Y. and Hameed B.H., Insights into the modeling of adsorption isotherm systems, *Chemical Eng. Journal,* **156**, 2–10 (**2010**)

24. Kumar K.V., Porkodi K., Rocha F., Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: comparison of various error functions, *J. Hazard. Mater*., **151**, 794–804(**2008**)