International Journal of Engineering Innovation & Research
Volume 2, Issue 1, ISSN: 2277 – 5668

Thermodynamic and Kinetic Analysis on the Removal of METHYLENEBLUE Dye Using Senna Alata Bark

M. Chidambaram and S. Arivoli

***Abstract* − The feasibility of using *Senna alata* bark for the cationic dye (Methylene Blue) adsorption has been investigated. Batch adsorption studies were conducted to study the effects of contact time, initial concentration, pH and adsorbent dose on the removal of methylene blue (MB) at temperature of 30^{0}C. The equilibrium data were analyzed by the Langmuir, the Freundlich. The data fitted well with the Langmuir model with a maximum adsorption. The pseudo-second-order kinetics was the best for the adsorption of MB by SAC with good correlation. The results demonstrated that the SAC is very effective to remove methylene blue from aqueous solutions.**

***Keywords* – MB-Methylene Blue, SAC-Senna Alata Bark Carbon.**

I. INTRODUCTION

The presence of dyes into streams and rivers constitutes a category of pollutants that cannot be neglected. For industrial liquid effluents, color is the first indication of water pollution. In the dyeing industry, ennobler discharge in the environment large volume of strongly colored effluents that are heavily loaded with pollutants and highly concentrated in salts. After reviewing the characteristics of these effluents, Hessel et al. [1] compare the current legislation on the dying industry emission. They examine more closely the discharge legislation, first in France and then in other countries around the world. Considering six of the most representative parameters (color, BOD5, COD, suspended solids, salinity, detergents and oil and grease) it was shown how different the applied constraints are in different countries. The industrial dumping of effluents containing dyes not only marks the natural aspect of the rivers but also perturbs the aquatic life interfering in the transmission of sunlight and thus reducing the action of photosynthesis because some azo dyes and their degradation products are highly toxic and even carcinogenic [2].

A convenient alternative for the classical treatment for the discoloration of wastewaters from the textile industry is the usage of some non-conventional adsorbents (natural materials, biosorbents and waste materials from industry and agriculture) with lower cost and high efficiency [3-6].

There exists an extensive research work in this field, systematized by Crini [3]. The review represents a critical analyses of these adsorbents with characteristics, advantages, limits and tendencies in their use, as well the possible mechanisms of sorption.

Our attention was focused on the **Senna alata** plant stem. This adsorbent obtained from the SA plants in and around Thiruvarur District, Tamilnadu, India.

II. EXPERIMENTAL METHOD

A. Preparation of Biosorbents:

Fig.1. Senna alata plant

Senna Alata used in this study was collected from the local Agriculture land of Thiruvarur, Tamilnadu, India. The raw biosorbent was cut into small sizes and then washed thoroughly with hot-distilled water followed by double-distilled water to remove any unwanted particles. It was then dried at 333 K in oven drier. The dried material was sieved to get uniform size particles <177µm (80mesh). The same **SAC** was used throughout the experiment.

B. Properties of Biosorbents:

Particle size analysis of the **SA** was carried out as per IS 2720 standard using standard sieves of different sizes. Scanning electron micrographs were obtained on a scanning electron microscope (Model Hitachi S-3000N) to understand the morphology of the original **SAC**. The particles were coated with gold using a sputter coater and the SEM images were then taken.

C. Preparation of Methylene Blue Solutions

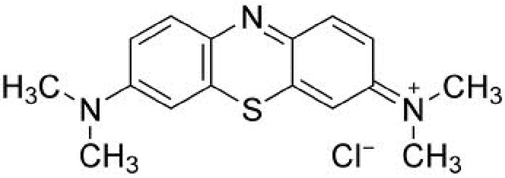


Fig.2. Structure of Methylene Blue

Methylene blue used in this study was of commercial purity (C.I 52015; FW, 319.86; MF, $C_{16}H_{18}N_3SCl$) and was used without further purification. Stock solution of methylene blue (500 mg L^{-1}) was prepared by dissolving the required quantity of the dye in double-distilled water.

Experimental dye solution was prepared by dilution the stock solution with suitable volume of double-distilled water to the desired concentration.

D. Determination of Methylene Blue Contents in the Solutions

The free dye content of the solution in the effluent before and after treatment was determined colorimetric ally using UV-Vis spectrophotometer (Model Hitachi 2800). Standard calibration curve was prepared by recording the adsorbance values of various concentration of methylene blue dye at maximum adsorbance of wavelength (663).

E. Influence of Agitation Speed

The biosorption capacity was determined at different agitator speeds ranging from 120 to 400 rpm using a fixed amount of **SAC** and methylene blue solution (20 mg L^{-1}) at 313 K in the incubator shaker, (Model Innova 42, New Brunswick Scientific, Canada). The initial and final concentrations of the solution were determined using UV-Vis spectrophotometer. Subsequently, adsorption capacities of the adsorbents were calculated based on the initial and final concentrations.

F. Influence of pH

Adsorption of dye on **SAC** was carried out through batch method. After loading the biosorbent, Acetic acid and sodium bicarbonate were added to adjust the initial pH of solution. The pH of the resulting mixture was determined by pH meter (model, EUTECH make digital microprocessor) for all the experiments. The pH meter was calibrated using different buffer solution (pH 4, 7, and 10 buffer tablets). 25 mg of **SAC** was added to 100 mL of 50 mg L^{-1} concentrated dye solution in each of the 250mL Erlenmeyer flasks, and pH was maintained using acetic acid and sodium bicarbonate. The pH of the resulting solution was measured for all the experiments at the before and after adsorption experiments. pH of the solution were varied from pH 3 to 10. These 250-mL flasks were stirred in a digital incubator shaker at 120 rpm at a constant temperature (313 K), and samples were collected from the flasks at particular time interval. The collected samples solution was analyzed using UV-Vis spectrophotometer to determine the dye concentration.

One hundred milliliters of different concentration of dye solution ranging from 50 to 250 mg L^{-1} were used, and dried **SAC (**25 mg) was added to Erlenmeyer flasks and agitated at 313 K and 120 rpm for 1 h. the initial and final concentrations of the solutions were measured using UV-Vis spectrophotometer, and adsorption capacities of the adsorbent were calculated. After the equilibrium was attained by each system, the dye uptake capacity for each sample was calculated.

III. RESULT AND DISCUSSION

A. SEM and FTIR of SAC

Fig.3. Shows the SEM micrographs of SAC sample before and after dye adsorption. It is clear that SAC has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye to be adsorbed. The surface of dye-loaded adsorbent, however, clearly shows that the surface of SAC is covered with dye molecules (Fig.4).

The FTIR spectrum of SAC (Fig.5b) shows that some peaks were shifted or disappeared and that new peaks were also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the SAC in adsorption process.

B. Effect of contact time and initial dye concentration

The effect of the initial MB concentration on the MB adsorption by SAC is shown in Fig.6 It could be seen that the amount of dye adsorbed (mg/g) increased with increased dye concentration provides and important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process. The equilibrium sorption capacity of the SAC increased with an increase initial dye concentration, while the % removal of dye showed the opposite trend. When the initial dye concentration increased from 50 to 250 mg/L, the loading capacity of SAC increased from 95.1 to 340.7 mg/g and the percentage removal decreased from 98.40 to 56.0%.

Fig.7 also indicated that the contact time needed for MB solution with initial concentrations of 50-250 mg/L to reach equilibrium was less than 1 hour.

G. Batch Adsorption Experiment

Table1. Equilibrium parameter for adsorption of METHYLENE BLUE on SAC

M_0	Ce(mg/L)				Qe(mg/g)				Removed(%)			
	30^0C	40^0C	50^0C	60^0C	30^0C	40^0C	50^0C	60^0C	30^0C	40^0C	50^0C	60^0C
50	2.419	1.73	1.14	0.78	95.1	96.5	97.7	98.4	95.1	96.5	97.7	98.4
100	17.75	14.8	10.92	8.11	164.4	170.7	178.1	183.7	82.2	85.1	89.0	91.8
150	40.69	34.2	27.98	22.49	218.6	231.5	244.0	255.0	72.8	77.1	81.3	85.0
200	78.35	70.1	61.50	52.93	243.2	259.7	276.9	294.1	60.8	64.9	69.2	73.5
250	109.9	99.5	89.09	79.61	280.0	300.8	321.8	340.7	56.0	60.1	64.3	68.1

C. Effect of solution pH on dye adsorption

The effect of solution pH on the equilibrium up-take capacity of **SAC** was studied at 50 mg/L initial dye concentration and temperature 30^0C between pH value of 2 and 10. As shown in Fig. , the dye up-take was found to increase with an increase in pH. It increased from 15.5 to 98.4 mg/g for an increase in pH from 2 to 10. A consistent increase in adsorption capacity of the SAC was noticed as the pH increased from 2 to 4, but further increase in pH from 4 to 9 seemed not affect the sorption in any wise. A similar trend was reported for the adsorption of MB onto wheat shells [29].

At lower pH as 2, the surface charge may be positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher pH the surface of SAC, may be negatively charged which enhance the positively charged dye cations through electrostatic force at attraction [30].

D. Adsorption isotherms

In order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system, two common isotherm models were tested: the Langmuir and Freundlich models. The applicability of the isotherm equations was compared by judging the correlation coefficients. R^2.

The Langmuir adsorption [32] model is based on the assumption that maximum adsorption corresponds to saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can describe by

$$Ce = \left(1/Q_0 b\right) + \left(1/Q_0\right) C_e \quad \text{----------} \ (1)$$

Table 2 : Langmuir and Fruendlich parameter

Tempe-rature ^{0}C	Langumuir Parameter		Fruendlich Parameter	
	Q_0	b	K_f	n
30	294.8477	0.0897	6.4991	3.5723
40	315.4495	0.1023	6.7999	3.5936
50	333.9590	0.1293	7.2070	3.6898
60	352.2694	0.1603	7.5732	3.7481

Where Ce (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent; Q_0 and b is Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig.9) shows that the adsorption obeys the Langmuir model.

The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in Table 2. The r^2 values (0.998) suggest that the Langmuir isotherm provides a good fit to the isotherm data. A similar observation was reported for adsorption of MB on fly ash [33], pomelo (citrus grandis) [26], silk worm [34], cedar sawdust and crushed brick [35].

The Freundlich isotherm [23] is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy system and is expressed by the following equation:

$$q_e = K_f Ce^{1/n} \quad \text{----------} \ (2)$$

Where K_F $(mg/g(L/mg)^{1/n})$ is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. In general, as the K_F value increases the adsorption capacity of adsorbent for a given adsorbate increases. The magnitude of the exponent, 1/n gives an indication of the favorability of adsorption. Value n>1 represents favorable adsorption condition [24-27]. The linear form or Eq.(3) is:

$$\log q_e = \log K_F + \left(1/n\right)\log C_e \ \text{----------} \ (3)$$

Values of K_F and n are calculated from the intercept and slope of the plot (Fig.) and are listed in Table 2. The value of Freundlich exponent n (2.97) is the range of n>1, indicating a favorable adsorption [28, 29, 30, 31].

The best equilibrium model was determined based on the linear square regression correlation coefficient R^2. From Table 2, it was observed that the equilibrium sorption data were very best represented by the Langmuir isotherm. The best fit isotherm expressions confirm the monolayer coverage process of MB onto SAC. A similar result was reported for adsorption of MB on adsorbents materials produce from sewage sludge [31- 34,].

Table 3: Comparison of adsorption capacities of various adsorbents for MB

Adsorbent	Q_0(mg/g)	T(^{0}C)	Reference
SAC	352.26	60^{0}C	This study
Orange peel	18.6	30	47
Rice husk	40.58	32	46
Pineapple stem	119.05	30	00
Sulfuric acid	88.29	26±1	29
treated	20.8	30	29
Parthenium(SWC)	16.56	30	31
Pathenium (PWC)	5.56	30	32
Wheat shells	0.0068	25	33
Raw Posidonia			
oceanica fibres	142.36	20	36
Yellow passion			
fruit peel	96.61	20	36
Cedar sawdust	102.04-	30-50	43
Crushed brick	136.98		
Waste apricor-		30	44
based activated	143.20	27	45
carbon	123.5		
Bamboo dust		25	48
carbon	0.80	25	48
Dehydrated	0.24		
peanut hull			
Eggshell			
membrane			

Table 3 lists a comparison of maximum monolayer adsorption capacity of MB on various adsorbents. SAC is found to have a relatively large adsorption capacity of 352.26 mg/g and this indicates that it could be considered a promising material for the removal basic dye from aqueous solution, mostly when compared with waste apricot based activated carbon (102.04-136.92 mg/g) [35] and dehydrated peanut hull (123.5 mg/g) [36,37,38].

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L [36] given by eq.(2)

$$R_L = 1/1 + bC_0 \ \text{----------} \ (4)$$

Where C_0 (mg/L) is the highest initial concentration of adsorbent, and b (L/mg) is Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm accordingly:

Table 4: Dimensionless Separation factor (RL) for METHYLENE BLUE on SAC

C_i	Temperature			
	30^0C	40^0C	50^0C	60^0C
50	0.1823	0.1634	0.1339	0.1109
100	0.1003	0.0889	0.0717	0.0587
150	0.0691	0.0611	0.0490	0.0399
200	0.0527	0.0465	0.0372	0.0302
250	0.0426	0.0376	0.0299	0.0243

$R_L > 1$ - Unfavorable adsorption
$0 < R_L < 1$ - Favorable adsorption
$R_L = 0$ - Irreversible adsorption
$R_L = 1$ - Linear adsorption

The value of R_L in the present investigation has been found to be 0.0426 at 30^0C showing that the adsorption on MB on **SAC** is favorable at the temperature studied.

E. Thermodynamic Treatment of the adsorption process

Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation

$$\Delta G^0 = -RT\ln K_0 \text{ --------------------- } (5)$$

Where ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the Universal gas constant (8.314 J $mol^{-1}K^{-1}$). The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of ln (qe/Ce) against Ce at different temperatures and extrapolating to zero Ce according to the method suggested by Khan and Singh [16] The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH^0) and entropy change (ΔS^0) as a function of temperature,

$$\ln K_0 = \left(\Delta H^0 / RT\right) + \left(\Delta S^0 / R\right) \text{ ------------ } (6)$$

Where ΔH^0 is the standard heat change of sorption (kJ/mol) and ΔS^0 is standard entropy change (kJ/mol), the value of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of plot of ln K_0 against 1/T. The values of thermodynamic parameter calculated from equations 5 and 6 are shown in Table. The thermodynamic treatment of the sorption data indicates that ΔG^0 values were negative at all temperatures.

From the results it can be made out that physisorption is much more favorable for the adsorption of Methylene Blue. The positive values of ΔH^0 show the endothermic nature of adsorption and they governs the possibility of physical adsorption for in the case of physical adsorption, while increasing the temperature of the system, the extent of MB adsorption increases, this rules out the possibility of chemisorptions. The low ΔH^0 value depicts that MB is physisorbed on to the adsorbent SAC [17, 18, 19, 20]

Table 5: Thermodynamic parameter for the adsorption of METHYLENE BLUE on SAC

C_0	ΔG				ΔS	ΔH
	30^0C	40^0C	50^0C	60^0C		
50	-7504.4	-8658.6	-10078.5	-11469.6	132.85	32.81
100	-3861.7	-4545.2	5634.2	-6717.0	96.04	25.35
150	-2488.8	-3172.4	-3953.7	-4809.6	77.04	20.89
200	-1107.9	-1602.9	-2179.8	-2829.0	57.20	16.26
250	-609.4	-1074.5	-1587.3	-2106.7	49.98	14.54

F. Adsorption Kinetics

Pseudo-first-order and second-order models were applied to test experimental data and thus elucidated the kinetic adsorption process. Lagergren proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren [36] in the form:

$$\log\left(q_e - q_t\right) = \log q_e - \left(k_1/2.303\right)t \text{ -------------- } (7)$$

Where k_1 (1/min), is the rate constant, q_e (mg/g) is the amount of solute adsorbed on the surface at equilibrium and q_t (mg/g) is the amount of solute adsorbed at any time. The value of k_1 for MB adsorption by SAC was determined from the plot of $\log(q_e\text{-}q_t)$ against t. Comparison of the pseudo-first-order adsorption rate constant and calculated and experimental q_e value obtained at different initial MB concentrations

Although the correlation coefficients (r^2) are generally greater than 0.858 for all initial concentrations under the limit of the experimental qe for the pseudo-second-order kinetic model. As such the adsorption of MB on SAC cannot be best described by the pseudo-second-order kinetic. In many cases the second-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [37]. Therefore, the pseudo-second-order kinetic model [38] as shown in eq.(6) was used to study the adsorption kinetic of the present system.

Table 6: The Kinetic Parameters for adsorption of METHYLENE BLUE on SAC

C_0	Temp ^{0}C	Pseudo second order				Elovich model		Intraparticle diffusion			
		q_e	K_2	r^2	h	α	B	r^2	K_{id}	r^2	intercept
50	30	95.16	0.044	0.9940	6.7645	16.0489	0.0392	0.9921	1.3645	0.9924	0.174
	40	96.54	0.050	0.9953	7.3409	18.9615	0.0410	0.9914	1.4118	0.9942	0.165

	50	97.71	0.057	0.9971	8.0160	22.7537	0.0429	0.9931	1.4554	0.9914	0.155
	60	98.44	0.066	0.9991	8.0381	22.4256	0.0422	0.9954	1.4539	0.9923	0.157
100	30	164.49	0.019	0.9984	10.1713	22.0267	0.0208	0.9912	1.2246	0.9918	0.176
	40	170.31	0.022	0.9975	11.0919	25.2672	0.0210	0.9961	1.2781	0.9924	0.170
	50	178.14	0.027	0.9983	13.0294	31.9661	0.0215	0.9943	1.3530	0.9917	0.161
	60	183.76	0.033	0.9997	13.8350	34.1256	0.0209	0.9917	1.3750	0.9934	0.163
150	30	218.61	0.013	0.9965	11.0838	22.6181	0.0139	0.9981	1.0582	0.9917	0.187
	40	231.57	0.015	0.9974	13.3830	28.1805	0.0142	0.9917	1.1593	0.9920	0.177
	50	244.03	0.018	0.9963	15.8040	34.7708	0.0142	0.9937	1.2425	0.9916	0.171
	60	255.02	0.021	0.9946	13.7137	36.1632	0.0152	0.9928	1.2835	0.9914	0.157
200	30	243.29	0.008	0.9958	8.7280	18.0554	0.0104	0.9914	0.7273	0.9911	0.209
	40	259.72	0.009	0.9919	10.7425	21.7238	0.0106	0.9925	0.8697	0.9921	0.199
	50	276.99	0.011	0.9946	12.9630	26.1700	0.0106	0.9916	0.9831	0.9934	0.192
	60	294.13	0.013	0.9986	16.3527	33.6239	0.0108	0.9935	1.1082	0.9921	0.181
250	30	280.09	0.007	0.9975	8.8469	19.0548	0.0085	0.9974	0.5897	0.9932	0.215
	40	300.89	0.008	0.9977	10.5726	21.9921	0.0084	0.9941	0.7110	0.9922	0.212
	50	321.80	0.009	0.9980	11.7216	24.2070	0.0080	0.9913	0.7758	0.9981	0.215
	60	340.78	0.011	0.9974	14.8567	29.7964	0.0082	0.9924	0.8204	0.9954	0.202

$$t/qt = 1/k_2q^2_e + (1/q_e)\ t \quad \text{----------}\ (8)$$

Where k_2 (g/mg min) is the second-order rate constant. The q_e and k_2 can be calculated from the slope and intercept of the plots t/qt verses t.

The constant k_2 is used to calculated the initial sorption rate h (mg/g min), as $t \to 0$ as follows:

$$h = k_2q^2e \quad \text{----------}\ (9)$$

The pseudo-second-order rate constant k_2, the calculated h values, and the corresponding linear regression correlation coefficients r^2 are given in Table 6. The r^2 values were found to be in the range 0.994-1.000. Moreover, the variations between the calculated q_e and experimental q_e were very minimal for this model.

The high correlations coefficient and high agreement that exist between the calculated and experimental q_e values of the pseudo-second-order kinetic model over the other model renders it best in adsorption of MB on SAC. This confirms that the sorption data are well represented by the pseudo-second-order kinetics for the entire sorption period. The increase in values of the initial adsorption rates, h (Table 4) with an increase in the initial dye concentration could be attributed to the increase in the driving force for mass transfer, allowing more dye molecules to reach the surface of the adsorbents in a shorter period of time [39].

The kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism [40].

$$q_t = k_{id}t^{1/2} + C \qquad \text{----------}\ (10)$$

Where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g $min^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [40]. For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [41]. The plots were not linear over the whole time range, implying that more than one process affected the adsorption.

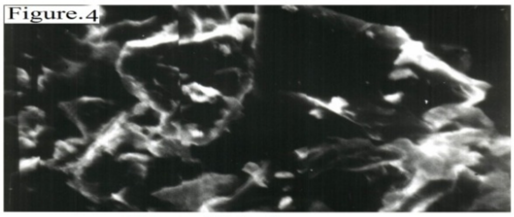
IV. CONCLUSION

The adsorption of MB from aqueous solution using SAC as low-cost adsorbent was investigated under different experimental conditions in batch process. The Langmuir adsorption isotherm was found to have the best fit to the experimental data with maximum adsorption capacity of 352.26 mg/g. the adsorption kinetics can predicted by pseudo-second-order kinetic. The results of the present investigation indicated that SAC, a low-cost adsorbent could be employed as an alternative to commercial-activated carbon for the removal of MB from aqueous solutions.

Figure.3

Senna Alata

Figure.4



Senna Alata +
Methylene Blue Dye

SEM images of before and after
adsorption of MB on SAC.

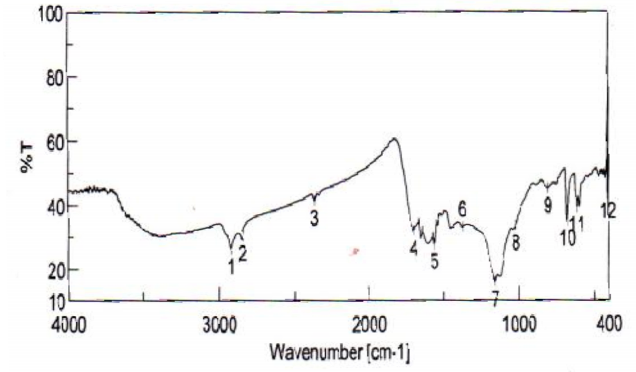


Fig.5a FT-IR spectra for raw Senna Alata Carbon

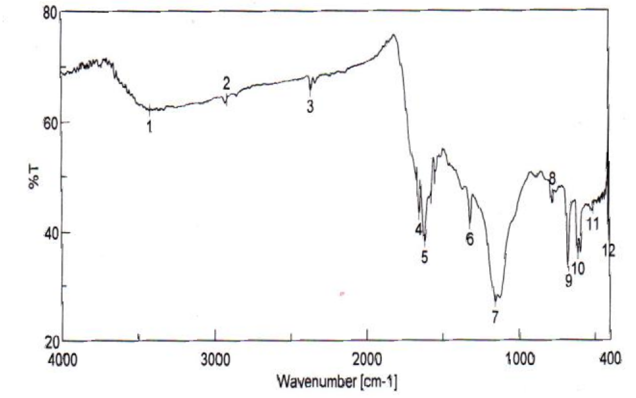


Fig.5b FT-IR spectra for the adsorption of Methyleneblue by SAC

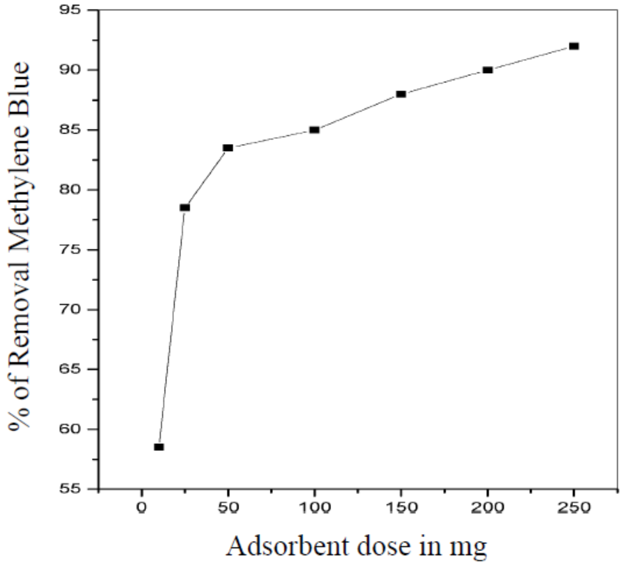


Fig.6. Effect of adsorbent dose on the removal of Methyleneblue 50mg/L: Contact time=60 min: pH=6.5: Temp=30^0C

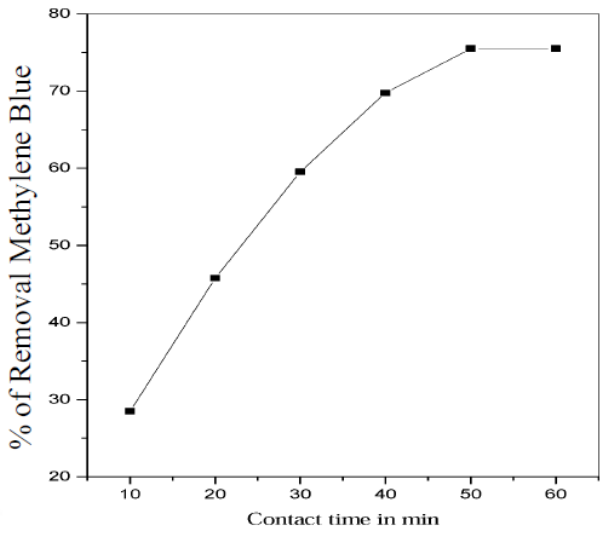


Fig.7. Effect of contact time on the removal of Methylene Blue 50 mg/L: adsorbent dose=50mg/50ml: pH=6.5: Temp=30^0C

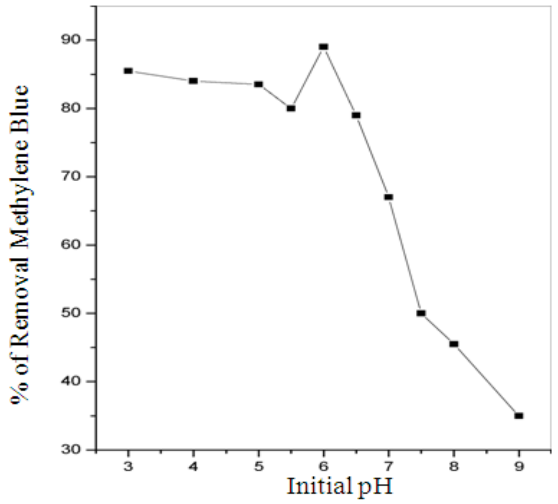


Fig.8. Effect initial pH on the removal of Methylene Blue 50 mg/L: Contact time=60 min: Adsorbent dose=50 mg/50 ml

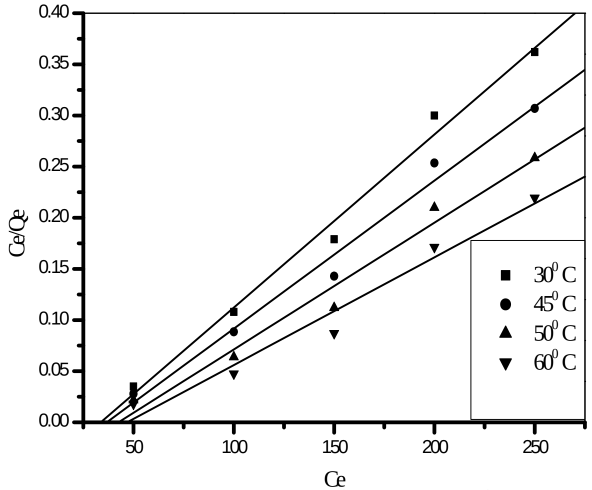


Fig.9. Linear Langmuir for the adsorption of Methyleneblue

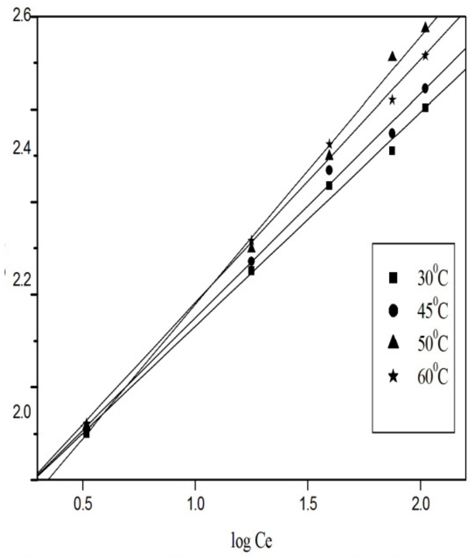


Fig.10. Linear Freundlich isotherm for the adsorption of Methylene Blue by SAC

REFERENCES

[1] C. Hessel, C. Allegre, M. Maisseu, F. Charbit, P. Moulin, “Guidelines and legislation for dye house effluents”, *J. Environ, Manage.* 83 (2007) 171-180.

[2] S.Nawar, H.Doma, “Removal of dyes from effluents using low-cost agricultural by-products”, *Sci. Total environ*. 79 (1989) 271-279.

[3] G.Crini, “Non-conventional low-cost adsorbents for dye removal” *a rewiew, Bioresourse Technol*. 97 (2006) 953-971.

[4] E. Forgacs, T. Cserhati, G. Oros, “Removal of synthetic dyes from wastewaters” *a review, Environ, Int*. 30(2004) 953-971.

[5] C.I. Pearce, J.R. Lloyd, J.T. Guthri, “The removal of colour from textile wastewater using whole bacterial cells” *a review, Dyes Pigments* 58 (2003) 179-196.

[6] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S. Shyam, “The role of sawdust in the removal of unwanted materials from water”, *J. Hazard. Mater*. 95 (2002) 137-152.

[7] F.A. Batzias, D.K. Sidiras, “Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems”, *J. Hazard. Mater.* 114(2004)167-174.

[8] F.A. Batzias, D.K. Sidiras, “Simulation of dye adsorption by beech sawdust as affected by Ph”, *J. Hazard. Mater.* 141(2007)668-679.

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

[10] F.A. Batzias, D.K. Sidiras, “Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems”, *Bioresource Technol*. 98(2007)1208-1217.

[11] V. Dulman, S. Cucu-man, V.I. Popa, R. Muresan, “Adsorption properties of beech wood sawdust related to some textile dyes”, *Anal. St. Univ. “Al. I. Cuza” lasi* VIII(2000)245-252.

[12] V.K. Kumar, S. Sivanesan, “Isotherms for Malachite Green onto rubber wood (Hevea brasiliensis) sawdust: comparison of linear and non-linear methods”, *Dyes Pigments* 72(2007)124-129.

[13] F. Ferro, “Dye removal by low cost adsorbents hazelnut shells in comparison with wood sawdust”, *J. Hazard. Mater.* 142(2007)144-152.

[14] M.Ozacar, I.A. Sengil, “Adsorption of metal complex dyes from aqueous solutions by pine sawdust”, *Bioresource Technol.* 96(2005)791-795.

[15] M.Ozacar, I.A. Sengil, “A kinetic study of metal complex dye sorption onto pine sawdust”, *Process Beochem.* 40(2005)565-572.

[16] Khan.A.A. and Singh.R.P., “Adsorption Thermodynamics of Carbafuran on Sn (IV) arsenosilicate in Li+, Na+ and Ca2+ forms,” *J. Colliod and Surface.*, 24 **(1987)** 33 – 42. 1987.

[17] Arivoli S and Hema M, “Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon”, *Intern J Phys Sci.*, 2007, 2, 10 – 17.

[18] Arivoli S, Venkatraman B R, Rajachandrasekar T and Hema M, “Adsorption of ferrous ion from aqueous solution by low cost activated carbon obtained from natural plant material”, *Res J Chem Environ* 2007, 17, 70-78.

[19] Arivoli S, Kalpana K, Sudha R and Rajachandrasekar T, “Comparitive study on the adsorption kinetics and thermodynamics of metal ions onto acid activated low cost carbon”, *E J Chem*, 2007, 4, 238 – 254.

[20] Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu, Chao yang, “Effect of chemical modification on dye adsorption capacity of peanut hull”, *Dyes and Pigments*, 2005,67,179.

[21] V. Dulman, S. Cucu-man, V.I. Popa, “sorption of some textile dyes by oak wood sawdust Cell”, *Chem. Technol*. 36(2002)515-525.

[22] V.G. Petrovici, V.I. Popa, “The chemistry and the chemical Processing of Wood”, *vol.II, Lux Libris, Brasov*, 1997(in Romanian).

[23] Dogan, M., Abak, H., & Alkan, M. (2008). “Biosorption of methylene blue from quesous solutions by hazelnut shells: equilibrium, parameters and isotherms”. *Water, Air, and soil pollution*, 192,141-1 53.

[24] Gong, R., Yi, D., Li, M., Yang, C., Liu, H., & Sun, Y. (2005a). “Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution”. *Dyes Pigments*, 64, 187-192.

[25] B.H.Hameed, M.I. El-Khaiary, “Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char”, *J.Hazard. Mater.* 153(2008)701-708.

[26] R.Han, D. Ding, Y. Xu, W. Zou, Y. Wang , Y. Li, L.Zou, “Use of rice husk for the adsorption of congo red from aqueous solution in column mode”, *Bioresour. Technol.*99(2008)2938-2946.

[27] H. Lata, V.K. Grag, R.K. Gupta, “Removal of a basic dye from aqueous solution by adsorption using Parthenium hysterophorus: an agriculture waste”, *Dyes pigments* 74(2007)653-658.

[28] B.H. Hameed, A.T.M. Din, A.L. Ahmad, “Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies”, *J. Hazard. Mater.* 141(2007)819-825.

[29] Y.Bulut, H. Aydin, “A kinetics and thermodynamics study of methylene blue adsorption on wheat shells”, Desalination 194(2006)259-267.

[30] M.C. Ncibi, B. Mahjoub, M. Seffen, “Kinetic and equilibrium studies of methylene blue biosorption by Posidonia oceanica (L.) fibres”, *J. Hazard. Mater*. 139(2007)280-285.

[31] F.A. Pavan, A.C. Mazzocato, Y. Gushiken, “Removal of Methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent”, *Bioresour, Technol*. 99(2008)3162-3165.

[32] I.Langmuir, “The adsorption of gases on plane surfaces of glass, mica and platinum”, *J. Am. Chem.* 57(1918)1361-1403.

[33] K. Vasanth Kumar, V. Ramamurthi, S. Sivanesan, “Modeling the mechanism involved during the sorption of methylene blue fly ash”, *J. Colloid Interface Sci*. 284(2005)167-174.

[34] B. Noroozi, G.A. Sorial, H. Bahrami, M. Arami, “Equilibrium kinetics adsorption study of a cationic dye by a natural adsorbent- Silkworm pupa”, *J. Hazard. Mater.* 139(2007)167-174.

[35] Q. Hamdoui, “Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick”, *J. Hazard. Mater.* 135(2006)264-273.

[36] H.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, “Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions”, *I&EC Fundam*,5(1966)212-223.

[37] H. Freundlich, “Dye adorption in solution”, *Z. Phys.Chem.* 57(1906)384-470.

[38] R.e. Treybal, *Mass Transfer Operations, second ed.*, McGraw Hill, New York, 1968.

[39] Y.S. Ho, G. McKay, “Sorption of dye from aqueous solution by peat”, *Chem. Ecg. J.*70(1998)115-124.

[40] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, “Kinetic and equilibrium modeling for the methylene blue removal from solution by adsorbent materials produced from sewage sludges”, *Biochem. Eng. J.* 15(2003).59-68.

[41] N. Kannanm, M.M. Sunduram, “Kinetics and Mechanism of removal of methylene blue by adsorption on various carbon-comparative study”, *Dyes Pigments* (2001)25.

AUTHOR’S PROFILE

Mr. M. Chidambaram

Received his B.Sc., degree in Chemistry from Islamiah College (Thiruvalluvar University), Vaniyambadi, Tamilnadu, India in 2006. He also completed his M.Sc., degree in General Chemistry from HH The Rajas College (Bharathidasan University) in 2009. He has been working as Lecturer in department of Chemistry from 2011 to till date in VAANI Polytechnic College, Vaniyambadi, Tamilnadu, India. His Area of Interest in Research is Adsorption of Dyes and Some Metal ions by Bio-adsorbent.

Dr. S.Arivoli

M.Sc., M.Phil., Ph.D.,

He has been working as Associate Professor and Head in PG and Research Department of Chemistry, Thiru vi ka Government Arts College, Thiruvarur. He has published more than 100 papers in well reputed journals. He has presented the 35 research articles in National and International Conferences and Seminars. At Present he has one UGC Major Research Project.