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Biosorption and Kinetic Study on Methylene Blue Dye Removal from Aqueous Solution using Activated Carbon Derived from Palm Flower (*Borassus Aethiopum)*

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Abstract

The methylene blue dye removal from aqueous solution by using activated carbon derived from a biodegradable agricultural waste material like palm flower (Borassus aethiopum) as bio- adsorbent was investigated in this work. The scanning electron microscopic analysis helps to identify the novel bio-adsorbent's surface. Batch experiments were carried out with different parameters like initial concentration, contact time, pH, adsorbent dosage and temperatures. The pseudo first order, pseudo second order, Elovich and intraparticle diffusion models were arrived with kinetic studies. The data obtained from equilibrium experiments were tested by Langmuir, Freundlich and Temkin adsorption isotherms. The maximum methylene blue dye removal is 92.50% at 0.1g/100ml adsorbent dose with 4mg/L dye concentration for 120min contact time at 7pH. The calculated adsorption capacity of the palm flower carbon was 10.42mg/g at 30^{0}C temperature. The equilibrium and kinetic data were well suited to the Langmuir, Freundlich isotherm, pseudo-second order and Elovich kinetic model. These studies confirmed that the activated carbon palm flower (Borassus aethiopum) is a potential low- cost adsorbent for methylene blue dye removal from industrial waste water.

Keywords: Methylene blue, palm flower, adsorption, isotherm, kinetic models

Introduction

Environmental studies provide a quantitative and qualitative approach of the environmental components and ecosystems. It works on pollution control, natural resource management and the effect of global climate change. The environment may be defined as follows "*The totality of circumstances surrounding an organism or group of organisms, especially the combination of external physical conditions that affect and influence the growth, development, and survival of organisms*". Pollution of environment occurs due to both natural phenomena and man-made activities. The natural phenomena like El Nino and La Nina, powerful volcanic eruptions, earthquakes, etc, causing pollution in environment are beyond our control. On the other hand, pollution due to man-made activities (e.g. agricultural activity, industrial activity, etc.) may be controlled to a large extent[1]. Now, pollution in different segments like atmosphere, lithosphere (soil) and hydrosphere is shocking the living bodies in biosphere. Metals and dyes are playing an important role for environmental pollution. Nowadays, water pollution is a very persistent problem. The industries like textiles, leathers, dyeing and paper were discharged wastewater containing dyes are the main cause for the pollution. Particularly, in textile industry about 10-15% of dyes is not binding during coloration and is released as wastewater. Dyes containing water reduces sunlight penetration and photosynthesis[2]. Under anaerobic conditions, dyes are decomposed into carcinogenic aromatic compounds which affect human beings and animals.

The cationic methylene blue dye is used in dyeing silk, wool, cotton, coloring paper. It is a laboratory reagent for microbiology, surgery, diagnostics and also used in photo oxidation of organic pollutants as sensitizer[3,4] . The harmful effects like jauandice, vomiting, heartbeat increase, shock, cyanosis, and tissue necrosis observed in human beings due to the usage of methylene blue dye[5]. Therefore, such harmful dyes removal from effluents prior to mixing with water sources is an important task. The removal of dyes by conventional method using alum, lime etc, is not economical and not feasible because of their complex structure and low bio degradability of dyes[6]. Adsorption is a newer technology developed for removal of pollutants from waste water because of its efficiency, simple design and very low initial cost. The abundant natural plant waste is inexpensive as they have very low economic value and widely used for water treatment process. The agricultural waste materials such as tea waste[7], wheat straw[8], grass waste[9], jackfruit peel, palm shell activated carbon[10], coir pith carbon, sugar cane stalks, neem leaf powder, saw dust activated carbon[11] and carrot stem powder were used in methylene blue dye removal from wastewater. The aim of the present investigation is to use the activated carbon produced from palm flower (*Borassus aethiopum)* as bio- adsorbent and to evaluate the effectiveness on methylene blue dye removal from aqueous solutions. So far, no work has been made by researchers on methylene blue dye removal from waste water using palm flower (*Borassus aethiopum)* an adsorbent.

Material and Methods

Preparation of adsorbent: The palm flower (*Borassus aethiopum)* was gathered from local area of Vellore District, Tamil Nadu. The matured palm flowers were cleaned and washed with water for free from impurities. The cleaned plant materials were sun dried for ten days and cut into small pieces. The dried materials were mixed with concentrated sulphuric acid in the ratio of 1:1 for 48 hours. The residual carbon was washed with distilled water until it reaches the neutralization point and then kept in hot air oven at 140^{o}C for 24 hours. The dry activated carbon from palm flower was powdered with machine and sieved with mesh size 100 micrometer and stored in desiccators. Here after the palm flower (*Borassus aethiopum*) is called as activated carbon palm flower (ACPF) powder. The produced ACPF adsorbent was characterized by SEM. The physical properties were analyzed by standard methods.

Adsorption studies: Analytical grade chemicals and reagents were used throughout the experiments. The dye solution was prepared by dissolving 1 g of methylene blue in 1000 ml standard flask using distilled water. The concentration of MB dye in the stock solution was 1000 mg/L. Different pH of the dye solutions were obtained with help of 0.1N H_2SO_4 and 0.1N NaOH solutions. From stock solution, working solutions of 2.0 to 12.0 mg/L concentration of the adsorbate were obtained by dilutions. The concentration of the dye was measured using UV-Visible spectrophotometer with 661 nm.

Batch equilibration method: All batch equilibrium experiments were performed at 30^{0}C. About 0.1g ACPF adsorbent was poured into the different 250 ml Erlenmeyer glass flasks. Then added 100 ml MB dye solution with concentration range of 2.0 to 12.0 mg/L to each flask. The mixture was agitated using rotary shaker at 120rpm for 120 min. The sample containing flasks were removed from the shaker and the adsorbent was separated through filter paper. The remaining concentration of MB dye in solution was measured by spectrophotometer. The Q_e (adsorption capacity in mg/g) and % removal were obtained by the following equations-1 and 2 respectively.

$$Q_e = [C_o - C_e] \times V/M \quad (1)$$

$$\% \text{ Removal} = [C_o - C_e] \times 100/C_o \quad (2)$$

Where, C_o and C_e are the MB dye concentration in solution (mg/L) at initial and equilibrium time, V is the volume of the test solution (L), and M is the dosage of the adsorbent used in these experiments (g). The various factors affecting the adsorption process was monitored by using adsorbent dosage, initial concentration, contact time, pH and temperatures. Duplicate experiments were performed and the mean values are presented in this paper.

Adsorption isotherm studies: The isotherm studies are highly significant in removal of dye by ACPF powder which was obtained using 2.0 to 12.0 mg/L of MB dye concentrations. The equilibrium data arrived from the experiments were fitted to Langmuir, Freundlich and Temkin isotherms:

Langmuir isotherm l:

$$C_e/Q_e = 1/Q_mK_L + C_e/Q_m \quad (3)$$

Langmuir isotherm ll:

$$1/Q_e = 1/bQ_mC_e + 1/Q_m \quad (4)$$

Freundlich isotherm:

$$\log Q_e = \log K_F + 1/n \log C_e \quad (5)$$

Temkin isotherm:

$$q_e = B\ln A + B \ln C_e \quad (6)$$

The shape of isotherm was identified with help of R_L value which is called as Dimensionless separation constant. It is one of the basic characteristic of Langmuir adsorption isotherm. It is expressed by the formula like $R_L = 1/ (1+bC_o)$, where b is the Langmuir adsorption constant and C_o is the initial concentration of the dye molecules. The relationship between R_L and shape of the isotherm is given as follows[12]

R_L value	Shape of isotherm
RL>1	Unfavorable
$R_L = 1$	Linear
$0<R_L<1$	Favorable
$R_L = 0$	Irreversible

Adsorption kinetics: The kinetic experiments describe the mechanism and rate of the adsorption at solid-solution interface. The kinetic models namely Pseudo first order, Pseudo second order, Elovich and Intra-particle diffusion were used to study the MB dye adsorption on ACPF.

Activation parameters: The free energy change ($\Delta G°$) was calculated from Langmuir constant b[13]. Other thermodynamic parameters like enthalpy and entropy were also analyzed.

Results and Discussion

Characterization of the adsorbent: Table- 1 shows the physicochemical properties of newly prepared adsorbent ACPF powder. The microstructure and adsorbent's surface morphology of the unloaded ACPF powder and MB dye loaded ACPF powder were identified by scanning electron microscope (SEM) and the images are depicted in figure- 1 and 2. The SEM image of unloaded ACPF powder reveals the nature of biomass which has micro pores and heterogeneous surface. The uptake of MB blue dye by ACPF was demonstrated by the change in morphology of the adsorbent's surface. Based on the surface morphology result of ACPF, it is suggested that the produced ACPF is a suitable adsorbent for MB dye removal from waste water.

Table-1
Physical characteristic of adsorbent

Properties	**ACPF**
Density	0.3243
Moisture content (%)	8.55
Volatile matter (%)	10.08
Acid insoluble matter (%)	2.58
Water soluble matter (%)	1.13
Ash content (%)	6.20
Fixed carbon (%)	75.17
pH	6.75

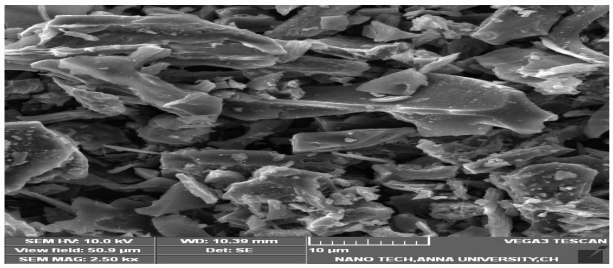

Figure-1
SEM images of Unloaded ACPF (above)

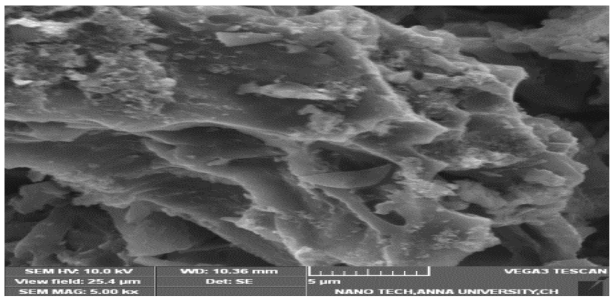

Figure-2
Dye loaded ACPF adsorbent (below)

Adsorption studies: Effect of pH: The pH of the solution is a vital role for controlling dye adsorption onto adsorbent. The changes on charge density of the surface of the adsorbent and ionization of pollutants are brought by pH variation of pollutants[14]. Different pH of the MB dye solutions (2 to 9) were prepared by using $0.1H_2SO_4$ and 0.1NaOH. The experiments with pH variation on removal of dye through adsorption was analyzed by mixing 0.1g of ACPF powder into flasks containing 100ml of 4mg/L MB solutions and agitated for 120minutes and the result was given in figure-3. The maximum adsorption of MB dye was 85.50% at 7pH and thereafter it decreases with further increases in pH. At initial pH, increases positive charge density due to protonation with negatively charged surface of the adsorbent and hence, decrease the removal efficiency due to electrostatic repulsion between positively charged surface of the adsorbent and positively charged dye with increasing pH[11] as well as the excess of H^+ ions competed effectively at low pH with MB dye to occupy sorption sites on bio-sorbent surface[14]. The MB dye removal decreases at higher pH (>7 pH) due an increase of –OH ions. The pH of the solution increases from 2 to 7, the negatively charged sites on adsorbent's surface increased and positively charged sites decreases. This indicates that more electrostatic attraction forec produced between MB dye and ACPF. Similar reports were given by other researchers[15].

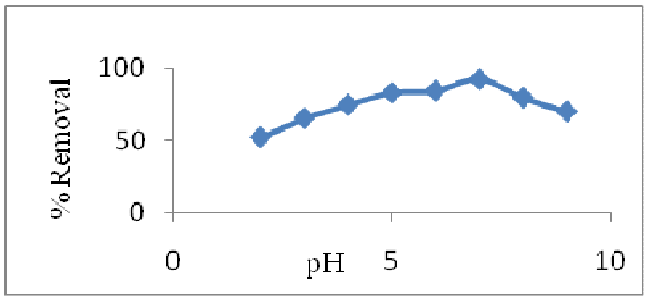

Figure- 3
Effect of pH (Dye=4mg/L; V=100ml; T=303K; t=2 h)

Effect of Dosage: The methylene blue dye adsorption on ACPF powder was conducted by varying the adsorbent dosages from 0.05 to 0.25g with 100ml of dye solution of 4mg/L concentration. The highest removal of MB dye was 92.50 % at 0.1g of activated carbon. A graph of % removal was plotted against the adsorbent dosage are given in figure- 4. It shows that the percentage adsorption increases with an increase in the ACPF dosage till 0.1g/100mL and then % adsorption decreased. This is because of overlapping or aggregation sites of the adsorbent which decrease the total surface area for adsorption[16].

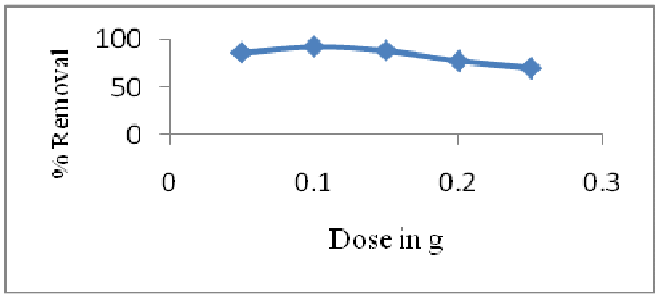

Figure-4
Effect of dose (Dye=4mg/L; V=100ml; pH 7; T=303K; t=2 h)

Effect of contact time with Initial concentration: Effect of contact time for removal of MB dye from aqueous solutions was reviewed with different initial concentrations and results are presented in figure-5. This reveals that the percent removal increases with increases from 30 to 120 min contact time or till equilibrium has been reached after that no significant adsorption taking place. The equilibrium time for methylene blue dye onto ACPF powder was found to be 120 minutes and highest removal of dye from aqueous solution was 85.00% at 4mg/L. Further it is also clear that the MB dye removal increased from 54.16 to 85.00% by decreasing the concentration of MB dye from 12 to 4 mg/L. Overcrowding of dye molecules at higher concentration are responsible for decreases the adsorption behavior. This is one of the important parameter for wastewater treatment system.

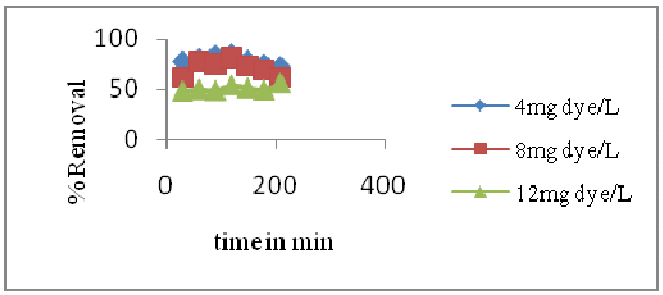

Figure- 5
Effect of contact time with initial concentration (Dose =0.1g/100ml; pH 7; T=303K)

Effect of Initial Ion concentration: The effect of initial concentration on percent removal of MB dye by ACPF was studied at 30° C with 2-12mg/L dye concentration at 7pH with 0.1g/100ml adsorbent dose and shown in figure- 6. It reveals that the removal process decreases gradually with increase of initial concentration. The removal is highly effective on 4 mg/L dye concentration at 0.1g dose after which decreases gradually. In low concentration, more adsorption sites are available for dye adsorption. But available sites are relatively very less for MB dye adsorption at higher concentration of dye solutions. Similar result obtained for MB dye removal by annona squmosa seed[22].

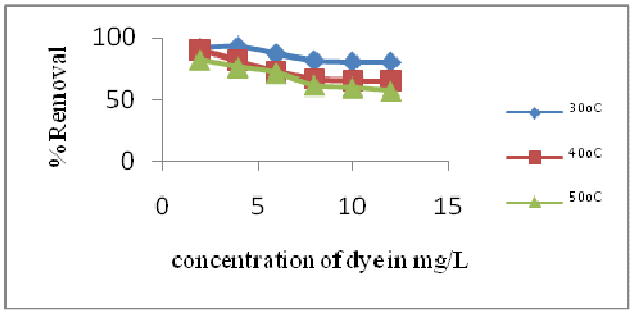

Figure-6
Effect of initial concentration with temperatures (Dose =0.1g/100ml; pH 7; 2 h)

Effect of temperature with initial concentration: The type of attraction force between the adsorbate and adsorbent was identified with help of physical and chemical sorption mechanism which are temperature dependent. If adsorption decreases with increasing temperature indicates that the physical adsorption and the opposite effect is chemisorption. The temperature parameters and influences on MB dye removal by ACPF powder were studied at 30°C, 40°C and 50°C for initial concentration 4, 8 and 12mg/L with 0.1g dose at 7pH. The temperature plot shows the decreasing trend for equilibrium adsorption capacity Q_e (mg/g) and the percentage removal of MB dye with increase in temperature (figure-6). Therefore, adsorption follows physisorption mechanism and favored at low temperature. Thus the adsorption comes under exothermic process. Similar results were reported by other researchers[17]. The above was explained with two reasons; 1. At higher temperature the electrostatic attraction forces are weakened between the dye and active sites of ACPF; 2. Forces between dye (adsorbate) and water (solvent) become stronger than that between dye and ACPF. Hence, the dye adsorption was more difficult on adsorbent[18].

Adsorption Isotherm Studies: Langmuir adsorption isotherm: Langmuir adsorption isotherm is developed by assuming that the homogeneous surface with fixed number of adsorption sites on solids. Only one molecule can be adsorbed on the surface site, and further adsorption not possible on those sites. Homogeneous adsorption occurs with same enthalpies and same activation energy. Saturation value is reached with monolayer adsorption. The following Langmuir isotherm equation-7 was used in this study

$$1/Q_e = 1/bQ_mC_e + 1/Q_m \quad (7)$$

Where, C_e is the concentration of the dye in solution (mg/L) and Q_e is the weight of dye adsorbed (mg/g) at equilibrium time. Q_m and b are the Langmuir constants corresponds to adsorption capacity and energy of adsorption or rate of adsorption. The constants b and Q_m are calculated from the slope and intercept of a linear plot of $1/Q_e$ against $1/C_e$, which are listed in table- 2.

The Langmuir adsorption isotherm plot of MB dye sorption onto ACPF was given in figure-7. The maximum adsorption capacity (Q_m) of MB dye on ACPF powder calculated from Langmuir graph was 10.42 mg/g at 30°C. Table- 3 proves the better adsorption capacity of ACPF powder with other adsorbents[19-26]. The recorded value of the present study of MB dye on ACPF powder have a reasonable removal capacity which suggests that this bio-sorbent (ACPF) could be used for dyes removal from waste water. From the constants, the adsorption follows the Langmuir model was confirmed. The correlation coefficient value [R^2=0.965] was close to unity prove the best fits for the Langmuir isotherm model. The parameter R_L values falls under the range between 0 and 1 indicate the favorable adsorption with all initial concentration (C_o) at various temperatures 30°C, 40°C and 50°C. The calculated R_L values are given in table-4.

Table- 2
Isotherm parameters of MB dye adsorption on ACPF at various temperatures

Isotherm model	Isotherm parameters		Temperature		
			30°C	40°C	50°C
Langmuir	Q_m	(mg/g)	10.42	8.62	10.00
	b	(L/mg)	1.37	0.963	0.448
	K_L	(L/mg)	1.391	0.674	0.597
	R^2		0.965	0.984	0.899
Freundlich	n		1.838	3.731	2.217
	K_F	(L/g)	5.689	4.045	3.459
	R^2		0.949	0.963	0.956
Temkin	A	(L/g)	1.603	1.443	1.537
	b	(J/mg)	186.5	264.5	293.2
	R^2		0.943	0.979	0.834

Table-3
Adsorption capacities of other adsorbents for MB dye

Adsorbent	Q_m (mg/g)	References
Sugar cane stalk	9.80	19
Raw beech Saw dust	9.78	20
Neem leaf powder	8.76	21
Annona squmosa seed	8.52	22
Coir pith carbon	5.87	23
Posidonia oceanice (L) fibers	5.56	24
Fly ash	2.63	25
Glass wool	2.25	26
ACPF powder	10.42	Present study

Table- 4
Dimensionless separation factor (R_L) for MB dye on ACPF

Con. of MB dye in mg/L	R_L values		
	30^{O}C	**40^{O}C**	**50^{O}C**
2	0.2674	0.3418	0.5274
4	0.1543	0.2061	0.3582
6	0.1085	0.1475	0.2711
8	0.0836	0.1298	0.2182
10	0.0680	0.0941	0.1825
12	0.0573	0.0796	0.1568

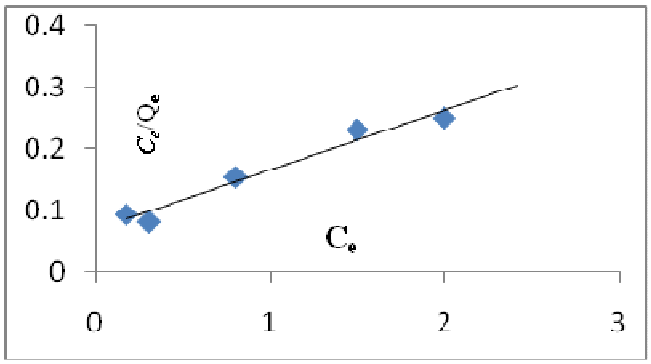

Figure-7
Langmuir adsorption isotherm

Freundlich adsorption isotherm: This isotherm relates with multilayer adsorption on heterogeneous surface, non-uniform distribution of adsorption heat and affinities over the surface of the adsorbent. The Freundlich equation expressed as

$$q_e = K_F C_e^{1/n} \quad (8)$$

The linear form of equation-8 is

$$\log Q_e = \log K_F + 1/n \log C_e \quad (9)$$

Freundlich isotherm constants K_F and 1/n are calculated from the linear plot of log Q_e against log C_e as shown in figure-8. The adsorption intensity or surface heterogeneity was measured and its value [1/n= 0.544] indicates that the surface is more heterogeneous. The 1/n value less than one, also indicate favorable adsorption. The correlation coefficient value for Freundlich plot (R^2=0.949) was comparable with Langmuir value (R^2=0.965) suggest that adsorption has taken place both monolayer adsorption and heterogeneous surface of multilayer adsorption. The Freundlich parameters were given in table- 2.

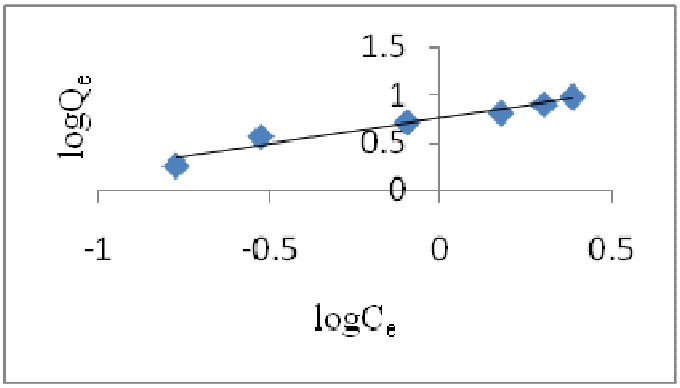

Figure-8
Freundlich adsorption isotherm

Temkin adsorption isotherm: This isotherm describes the interaction between dye (adsorbate) and ACPF (adsorbent) which provides the heat of adsorption decreases linearly with all the molecules. The linear form of Temkin adsorption isotherm can be written as

$$q_e = B \ln A + B \ln C_e \quad (10)$$

Where, A is the equilibrium binding constant (L/g), b is the heat of adsorption (J/mol) which is obtained from the equation; B = RT/b, R is the gas constant (8.314J/mol/L) and T is the absolute temperature (^{o}K), C_e is the concentration of adsorbate in solution at equilibrium (mg/L). Figure- 9 shows the Temkin plot of q_e versus log C_e which helps to calculate the constants A and b from the slope and the intercept. The data were listed in table- 2. The decreasing trend of values A with increase in temperatures, confirms the chemisorptions reaction between adsorbate and adsorbent[27]. The Temkin isotherm was fairly fitted well as compared to other isotherms like Langmuir, Freundlich isotherm due to low correlation coefficient (R^2 = 0.943) value from plot.

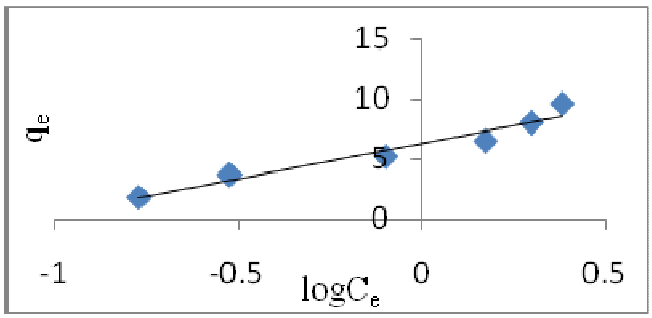

Figure-9
Temkin adsorption isotherm

Adsorption kinetic studies: The adsorption kinetic studies

help to identify the adsorption mechanism and evaluate the ability of adsorbent which depends on the physical and/or chemical properties as well as governed by surface adsorption on the pore wall of adsorbent. For determining the adsorption kinetics of methylene blue by ACPF powder was carried out with four kinetic models such as the pseudo first order and second order, the Elovich and intra particle diffusion.

Pseudo first order kinetic: The pseudo first order kinetic was analyzed by Lagergren whose linear form is represented as

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \quad (11)$$

Where, q_e (mg/g) and q_t (mg/g) are the amount of dye adsorbed at equilibrium and at a given time t (min) respectively and k_1 is the pseudo first order rate constant (min^{-1}). The linear plot of log (q_e- q_t) versus t (figure-10) shows the validity of Lagergren equation. The slope and intercept of the straight line of a plot gives q_e and k_1 values are given in Table- 5. The R^2 value (correlation coefficient = 0.998) is close to one but very high q_e value indicates that the adsorption process does not follow the pseudo-first order kinetic model.

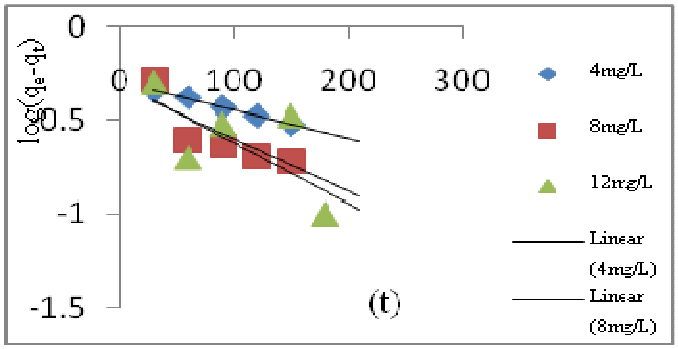

Figure- 10
Pseudo first order kinetic model

Pseudo second order kinetic: Analysis of adsorption mechanism was made by Ho and Mckay and proposed a pseudo second order kinetic model[28]. Integrated linear form of this model is given in eqution-12,

$$t/ q_t = 1/k_2 qe^2 + t/q_e \quad (12)$$

Where q_e (mg/g) and q_t (mg/g) are the weights of dye adsorbed at equilibrium and at a given time t (min) on the surface of the adsorbent and k_2 (g/mg/min) is the pseudo-second order rate constant. The linear plot of t/q_t versus t is shown in figure- 11 from which the parameters k_2 and q_e can be calculated. The h (initial adsorption rate) can be calculated using equation-13

$$h = k_2 q_e^2 \quad (13)$$

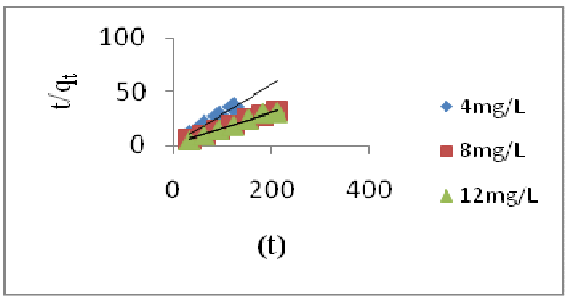

Figure-11
Pseudo second order kinetic model

h (mg/g/min) is the weight of dye adsorbed per unit mass of adsorbent at unit time. This value (h) can be utilized for comparison of initial sorption rate of MB dye with various adsorbents at similar conditions. The kinetic data are given in table- 5. The data put forth ideas about the rate controlling step is chemisorption involving valance forces through the exchange of electrons between adsorbent and adsorbate through chelation[29]. The good correlation coefficient (R^2= 0.999) value shows that the process follows the pseudo second order kinetic than the pseudo first order model.

Table- 5
Kinetic parameters of MB dye adsorption on ACPF at 303 K

Model	Parameters		Concen. Dye mg/L		
			4	8	12
Pseudo first-order	q_e	mg/g	1000	333.3	500
	K_1	min^{-1}	0.0023	0.0069	0.0046
	R2		0.998	0.748	0.438
Pseudo second-order	q_e	mg/g	3.53	6.667	6.623
	K_2	g/mg. min	0.057	0.017	0.020
	h		0.712	0.740	0.861
	R^2		0.999	0.993	0.985
Elovich	α	mg/g. min	44.78	4.27	25.98
	β	g/mg	1.927	0.399	0.808
	R^2		0.961	0.954	0.776
Intraparticle diffusion	K id	mg/g. $min^{0.5}$	0.057	0.144	0.120
	C		2.776	4.589	4.990
	R^2		0.976	0.715	0.840

Elovich model: The Elovich kinetic model also explains the chemisorptions kinetics. The simplified form of Elovich model is given in equation-14

$$q_t = 1/\beta (\alpha \beta) + 1/\beta \ln(t) \quad (14)$$

Where q_t is the amount of dye adsorbed at time t, the parameters α and β are Elovich constants are related to the initial adsorption rate (mg/g/min) and desorption constant (g/mg) which are calculated from the slope and intercept of a linear plot of q_t against log (t) (figure- 12). Equation- 14 is helps to study the

kinetics of MB dye sorption on ACPF. This equation explains the rate- controlling step in the diffusion process and obeying the chemisorptions mechanism between the adsorbents and solute from liquid solution[30]. Correlation coefficient (R^2 = 0. 961) of Elovich model for methylene blue dye adsorption by ACPF powder was found to be good fit with experimental data. The values of α, β and R^2 are listed in table-5.

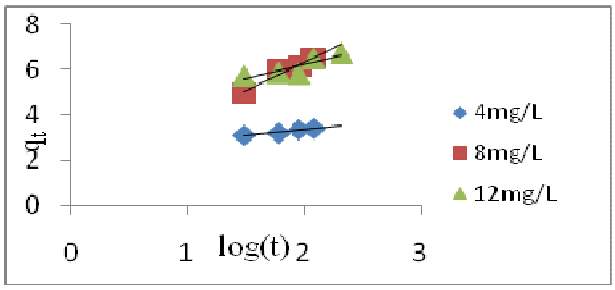

Figure-12
Elovich kinetic model

Intra particle diffusion kinetic model: Generally, the migration of adsobate from liquid phase to solid adsorbent' surface occurs in three consecutive steps: 1. film diffusion step, 2. movement of adsorbate within the pores of the adsorbent and 3. Intra particle diffusion step.The intra particle diffusion is the rate controlling step when negligible diffusion of the liquid film surrounding the adsorbent. The intra particle diffusion is investigated with its mathematical expression as follows:

$$q_t = K_{id}\, t^{0.5} + C \qquad (15)$$

Where q_t is the amount of dye adsorbed at time t, C is the intercept and K_{id} is the intra- particle diffusion rate constant (mg $min^{0.5}$ g^{-1}). The intra particle diffusion plot was arrived when plotting q_t against $t^{1/2}$ (figure- 13) which linear relationship. The slope K_{id} was used to identify the diffusion rate constant and the intercept C value gives thickness of the the boundary layer; the larger the intercept, the greater the effect of the boundary layer. The values of K_{id} and C are shown in table- 5. The plot shows the straight line not from the origin indicates that the intra particle diffusion is not the sole- rate determining step[31]. It can also be confirmed on the basis of C value. The intra particle diffusion is not the rate determining step when intercept C value is not equal to zero.

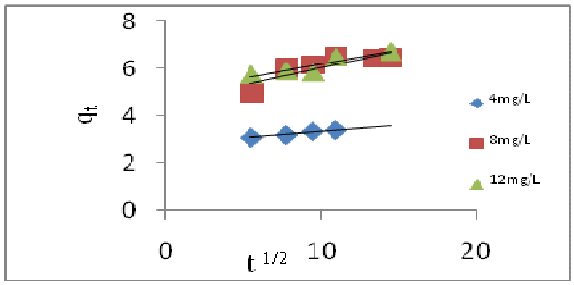

Figure-13
Intraparticle diffusion kinetic model

Thermodynamic parameters: The parameters were calculated using the equations-16, 17 and 18, their results are tabulated in table- 6.

$$k = 1/b \qquad (16)$$
$$\Delta G^0 = -RT\ Ink \qquad (17)$$
$$\Delta G^0 = \Delta H^o - T\Delta S^o \qquad (18)$$

Where, ΔG^0 gives the change of Gibbs free energy (KJ/mol), T is the temperature (^oK), R is the universal gas constant (8.314 J mol/K) and k is the equilibrium constant related to Langmuir constant, equal to 1/b[13]. Table-6 shows the ΔH^o and ΔS^o values obtained from the graph of log k against 1/T (figure-14) using slope and intercept. The negative value of ΔG° shows that adsorption process is highly favorable and spontaneous. The negative value of ΔH^o indicates the reaction is exothermic in nature and the low ΔH^o value depicts that MB dye undergoes physisorption. The negative value of ΔS^o also indicated randomness at methylene blue dye-ACPF interface[32].

Table-6
Thermodynamic parameters of MB dye adsorption on ACPF

Temp. (^oK)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
303	+0.793	-0.0453	-0.0028
313	-0.098		
323	-2.156		

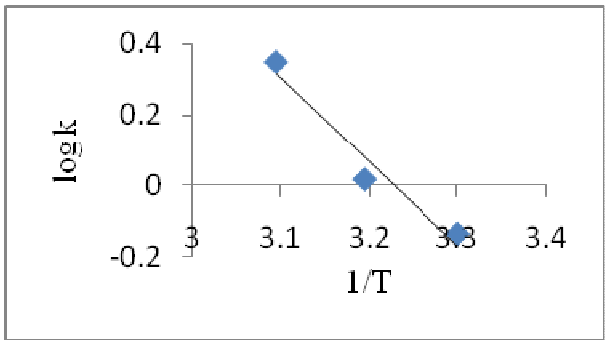

Figure-14
Thermodynamic analysis

Conclusion

The removal of methylene blue dye from aqueous solutions by activated carbon derived from palm flower (ACPF) was investigated. The sorption capacity on adsorption of MB dye by ACPF was 10.42mg/g. The effects of dye adsorption on ACPF by various factors were investigated. The equilibrium parameters have been evaluated and the data well fitted to Langmuir adsorption isotherm and Freundlich adsorption than other isotherms. Kinetic studies reveal the adsorption of dye by ACPF obeyed very much for pseudo second order kinetic and Elovich kinetic model than pseudo first order kinetic and intra-particle diffusion models. The parameters ΔG°, ΔH^o and ΔS^oS

reveals that the adsorption was spontaneous, exothermic process. Finally, it can be concluded that ACPF powder was one of the suitable bio-adsorbent for removing methylene blue dye from industrial waste water.

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