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Adsorption of methylene blue from aqueous solution using *Polyalthia longifolia* (Ashoka) seed powder

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ABSTRACT

The potential of Polyalthia longifolia (PL) seed powder to adsorb methylene blue (MB) from aqueous solution has been investigated through batch experiments. The MB adsorption was found to be dependent on adsorbent dose, contact time, initial MB concentration and temperature. The time required to obtain the maximum adsorption was found to be two hours at 298 K. The equilibrium data were described by Freundlich, Langmuir and Tempkin isotherm models. The Langmuir isotherm model was well fitted and maximum adsorption capacity was found to be 9.19 mg/g at 298 K.The kinetic processes of MB adsorption on PL seed powder were described by applying pseudo-first order and pseudo-second order equation. The adsorption process obeyed pseudo-second order kinetic equation. Thermodynamic parameters such as standard enthalpy (ΔH^0), standard entropy (ΔS^0) and standard free energy (ΔG^0) were evaluated.The adsorption interaction was found to be spontaneous and exothermic in nature. The adsorption capacity of Polyalthia longifolia seed powder as found from the result suggest a non-conventional and efficient biosorbent for the removal of MB from aqueous solution and can be used for the development of clean and cheap technology for effluent treatment.

Keywords: Adsorption; Equilibrium and kinetic; Methylene blue; *Polyalthia longifolia* seed powder.

INTRODUCTION

Dyes are widely used as colouring matter in textile, plastic, food, paper, printing, pharmaceutical and cosmetic industries [1]. The unspent colouring materials are discharged into the aquatic environment and considered as one of the important visible pollutants of industrial waste water. Dyes are highly coloured compounds which are non biodegradable [2], persist in water; retards photosynthetic activity, inhibit growth of aquatic biota and decrease recreation value of stream [3]. Methylene blue is an important basic dye used for printing calico, dyeing cotton and leather. It is not strongly hazardous but has various harmful effects such as eye burns, irritation to the gastrointestinal tract and to the skin [4]. Therefore it is necessary to remove methylene blue from waste water. The removal of dye can be achieved by chemical coagulation, ozonation, membrane filtration, ion-exchange, precipitation and adsorption [5]. Among these adsorption is the most effective and economical method [6]. Activated carbon is the most effective adsorbent for the removal of various pollutants from waste water [7] due to its highly porous nature, large surface area to volume ratio and presence of surface functional groups. The high cost of activated carbon however, restricts its application in developing countries including India [8, 9].This has promoted a growing research interest into the production of low – cost alternatives to activated carbon.

Literature survey revealed that adsorption processes using agricultural waste products are becoming the new alternative for wastewater treatment because they are cheap and cost effective. Some of the agricultural wastes which have been used as adsorbent material for the removal dyes from aqueous solution include, jackfruit peel waste [10], mansonia wood sawdust [11](Agustine E.Ofomaja 2009), treated sawdust [12], orange peel [13], chemical treated empty fruit bunch of oil palm [14], brewery waste [15], treated sugarcane bagasse [16], yellow passion fruit peel [17], jack fruit leaf powder [5], coconut husk [18], banana and orange fruit peels [19] , pine sawdust [20] etc. Various biological species such as algae, fungi and bacteria also find extensive use in the removal of contaminants [2].It could be considered as an eco-friendly device to the more expensive treatment technologies.

In the present work *P.longifolia* seed powder was selected as adsorbent as it is inexpensive, abundent and very common in India. The objectives of the present study were to investigate the potentialities of PL as biosorbent for MB removal by conducting batch experiments and to study various isotherms, kinetic parameters and to predict the maximum adsorption capacity.

EXPERIMENTAL SECTION

The plant material (*Polyalthia longifolia* seeds*)* was collected from Pune; Maharashtra, India in the month of July.It was authenticated at Botanical Survey of India, India. It's Voucher Specimen No.is BSI/WRC/Tech/2009/POLMK1. *P.longifolia* commonly called Ashoka (Annonaceae) is a tall, handsome plant commonly used as an ornamental street tree due to its effectiveness in controlling noise pollution and is planted throughout India. Each tree generates a large amount of seeds. The seeds were washed and dried in an oven at 100 ^{0}C. The dried seeds were then ground in a mechanical grinder and screened through a sieve to obtain fine powder of uniform particle size.The sieved material was then stored in an airtight plastic bottle for further experiments. The stock solution of MB (1000mg/L) was prepared in distilled water and diluted accordingly to obtain solutions of desired concentrations.

2.3. Characterization of biosorbent

2.3.1. Boehm titration

Boehm titration is one of the most widely used method to quantify and differentiate surface groups on activated carbon. In this study it was assumed that 0.05N sodium bicarbonate neutralizes strong acid groups, 0.05N sodium carbonate neutralizes both carboxylic and lactone groups, 0.05N sodium hydroxide neutralizes carboxylic, lactone and phenolic groups and 0.1N sodium ethoxide neutralizes carbonyl groups. Our method is similar to that used by Krisztina Laszlo and V.Strelko Jr [21, 22]. Adsorbent (0.500 gm) was mixed with 50 ml 0.05 N sodium hydroxide, sodium carbonate sodium bicarbonate, and sodium ethoxide solutions respectively. Corresponding solutions of 50 ml volume without solid samples were used as blanks. The flasks without solid samples were used as blanks. The flasks were covered with aluminium foil and were shaken for 24 h at 150 rpm.10 ml of supernatant from each flask was then titrated with 0.05 N Hydrochloric acid. The difference in blank and back was used to calculate milimoles of corresponding groups.

2.3.2. Fourier-transform infrared (FT-IR) analysis

FT-IR analysis was performed in order to characterize the functional groups of the biosorbent. A Perkin –Elmer spectrum RX/FT-IR system was used for FT-IR analysis.

2.3.3. Scanning Electron Microscope (SEM) analysis.

The scanning electron micrograph of adsorbent (0.063mm size) was obtained with the help of Scanning Electron Microscope (Model Leica-Stereoscan-440).

2.4. Batch biosorption studies:

The effect of adsorbent dosage were studied by agitating 100 Ml flasks containing different amounts of adsorbent with 50 ml MB (15.0mg/L) soultion for 10 minutes at 50 ml) To study the effect of time the 50 ml solution of MB (20, 30, 40 and 50 mg/L) was stirred with 0.200 gm seed powder at 200rpm for various intervals of time (from 2 to 120 minutes) at room temperature (25^{0}C). The effect of temperature on sorption studies of MB was performed at different temperatures (25, 35 and 45 ^{0}C) by shaking 0.050 gm of sorbent with 50 ml solution of MB (3.7 mg/L) at various intervals of time (2 to 120 minutes). The adsorption isotherm study was carried out at different concentrations of MB (10, 20, 30, 40 and 50 mg/L). A 0.200gm of seed powder with 50 ml solution of MB of various concentrations was shaken for 10 minute at room temperature (25^{0}C).All the experiments were carried out at original p H of solution. The flasks were agitated at 200 rpm. The reaction mixture was filetered through Whatman

filter paper (No.40).All the experiments were performed in duplicates. The concentrations of MB in the solutions before and after equilibrium were analyzed spectrophotometrically at 620 nm. (UV – Vis S1700 Pharma spectrophoto meter, Schimadzu).

2.5.1. Analytical method

The amount of dye adsorbed was calculated in percentage (%) and dye uptake (q_e) as in equation (1) and (2).

$$\% \text{ Adsorption} = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

$$q_e = (C_0 - C_e)\ V/\ 1000 \times w \quad (2)$$

Where C_0 is the initial concentration (mg/L)
C_e is the dye concentration at various time intervals (mg/L)
V is the volume of dye solution (m L)
W is the mass of adsorbent (g.)

2.5.2. Adsorption Isotherms

Freundlich Isotherm

The Freundlich equation is used in the linearised form [23], as,

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

Where q_e is the dye adsorbed (mg/g) at equilibrium
C_e is the equilibrium concentration (mg/L)
K_f (mg/g) is Freundlich constant indicating adsorption capacity
n is Freundlich constant indicating adsorption intensity

The values of K_f and n can be calculated from the intercept and slope of the plot log q_e versus log C_e.

Langmuir Isotherm

The Langmuir equation is used in the linearized form [24], as,

$$C_e/\ q_e = 1/\ (Q^0 b) + C_e/Q^0 \quad (4)$$

Where Ce is the equilibrium concentration (mg/L)
q_e is the amount of dye adsorbed (m/g) at equilibrium
Q^0 is the Langmuir constant related to maximum adsorption capacity (mg/g)
b is the Langmuir constant related to binding energy of the adsorption system (l/g.)

The values of Q^0 and b were obtained from the slope and intercept of the plot, $C_e/\ q_e$ versus C_e respectively.

R_L - The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter R_L, given by following equation [6];

$$R_L = 1 / (1 + b\ C_0) \quad (5)$$

Where C_0 is the initial concentration (mg/L)
b is the Langmuir constant (L /mg.)

If, RL , 1, indicates the shape of isotherm is unfavourable.
R_L is between 0 and 1, indicates a favourable shape of isotherm and adsorption process.
RL = 1 and 0, indicates the shape of isotherm is linear and irreversible.

Tempkin isotherm
Heat of adsorption and the adsorbate-adsorbent interaction on adsorption isotherm were studied by Tempkin and Pyzhev [25], who suggested that because of these interactions, the energy of adsorption of all the molecules decrease linearly with coverage.

The Tempkin isotherm has been used in the form as,

$q_e = RT / b \ln K_T + RT / b \ln C_e$ (6)

Where $RT / b = B$ (7)

The adsorption data can be analysed according to Eq. (6).The linear plots of q_e versus $\ln C_e$ able to determine the constant K_T and b.

2.5.3. Kinetic and thermodynamic study
Pseudo first order kinetic model:
The adsorption kinetics can be described by a pseudo- first order equation as suggested by Lagergren [26].

$\log (q_e - q) = \log q_e - K_{ad} t / 2.303$ (8)

Where, q (mg /g) is amount of sorption at time t
q_e (mg /g) is the amount of sorption at equilibrium time
K_{ad} ($min.^{-1}$) is the rate constant of pseudo first order sorption
The values of K_{ad} were calculated from the slope of linear plots of $\log (q_e - q)/q_e$ versus t.

Pseudo second order kinetic model:
The pseudo second order equation developed by Ho and McKay [27] has a linear form as;

$t / q = 1 / k_2 q_e^2 + 1 / q_e \times t$ (9)

Where, k_2 ($g\ mg^{-1} min^{-1}$) is the rate constant of pseudo second order reaction.

The plot of t / q verses t should give a straight line if pseudo second order kinetics is applicable and k_2 and q_e can be obtained from the intercept and slope of the plot.

Internal diffusion sorption model:
Assuming constant diffusion through adsorbent pores, the relation between amount adsorbed and the reaction time can be expressed as follows [28],

$q = K_w t^{1/2}$ (10)

Where, Kw ($mg\ g^{-1}\ min.^{-1/2}$) is the intra particle diffusion rate constant.

The plot of q ($mg\ g^{-1}$) verses the square root of time($t^{½}$) would give a straight line passing through the origin if the sorption process obeyed the intraparticle diffusion model. The slope of straight line gives K_w, the intraparticle diffusion rate constant.

Thermodynamic parameters:
For the calculations of thermodynamic parameters, the following equations were used:

$K_c = C_{ad} / C_e$ (11)

$\Delta G^o = - RT \ln K_c$ (12)

$\ln K_c = \Delta S^o / R - \Delta H^o / RT$ (13)

Where K_c is the equilibrium constant (unit less),
C_{ad} is the amount adsorbed on the adsorbent (mg/L) at equilibrium.
C_e is the equilibrium concentration in solution (mg/L)
ΔG^o, ΔH^o and ΔS^o are changes in Gibbs free energy (kJ/ mol), enthalpy change (k J / mol) and entropy change (J mol / K), respectively.
R is the gas constant (8.314 J / mol /K)
T is the temperature (K)

Energy of activation (Ea) plays an important role in determining whether the adsorption is diffusion controlled or involves chemical reaction. Here diffusion refers to the surface adsorption. Energy of activation, Ea, was calculated according to a relationship between Ea and ΔH^o for reactions in solution using the following equation [29], as,

$$Ea = \Delta H^o + RT \quad (14)$$

RESULTS AND DISCUSSION

3.1. Characterization of adsorbents

Characteristic properties of adsorbent (powdered material of *P. longifolia* seeds) are presented in **Table 1**. The biosorbent has low moisture adsorption capacity. Quantitative estimation of surface groups by Boehm titration showed that the carbonyl groups are present in high concentration followed by lactone, phenolic and carboxylic groups. IR spectrum displays the characteristic peaks of the compound. It also reveals the polymeric nature of compounds along with presence of hydroxyl, ketonic, acidic and ester functional groups. Such groups are capable of reacting with the functional groups of dye molecules. The FT-IR spectrum of powdered matrial (**Fig. 1**) shows a broad peak at 3550-3150 cm^{-1}, indicates presence of polyhydroxylated compound. The peak at 2937 cm^{-1} demonstrates the presence of saturated alkane C-H stretching. The peak at 1735 cm^{-1} indicates the presence of ester carbonyl functional group. The strong band at 1639 cm^{-1} depicts the presence of C=C bond. Association of peak at 1371 cm^{-1} displays presence of $–CH_3$ group. The peaks at 1246,1154 and a strong peak at 1018 cm^{-1} reveals the presence of – O –C = O acyl oxygen and etherial linkages of ester function confirms the presence of ester group.

Table 1.Characterization of Powdered Material

Physical Parameters	**Value**
p H	5.76
Bulk density (gm / ml)	0.5092
Moisture (%)	8.23
Ash content (%)	2.54
Matter soluble in water (%)	12.90
Matter soluble in acid (%)	23.93
Electrical Conductivity (at 25 ^{0}C)	3.90
Surface acid groups (meq/g)	
Millimoles of carbonyl group	0.4875
Millimoles of lactone group	0.1213
Millimoles of phenolic group	0.0049
Millimoles of carboxylic group	0.00065

The peaks in the FT-IR spectra ofadsorbent, strongly supports the presence of surface groups obtained by Boehm's titration. Scanning Electron Micrograph of adsorbent (**Fig.2**) shows that cavities are already present on the surface. This may be due to production of carbon of different porosity from ligno cellulosic material present in the seeds of *P. longifolia* [4]. Scanning Electron Micrograph of the adsorbent shows different structural features with non-uniform sizes and surfaces.

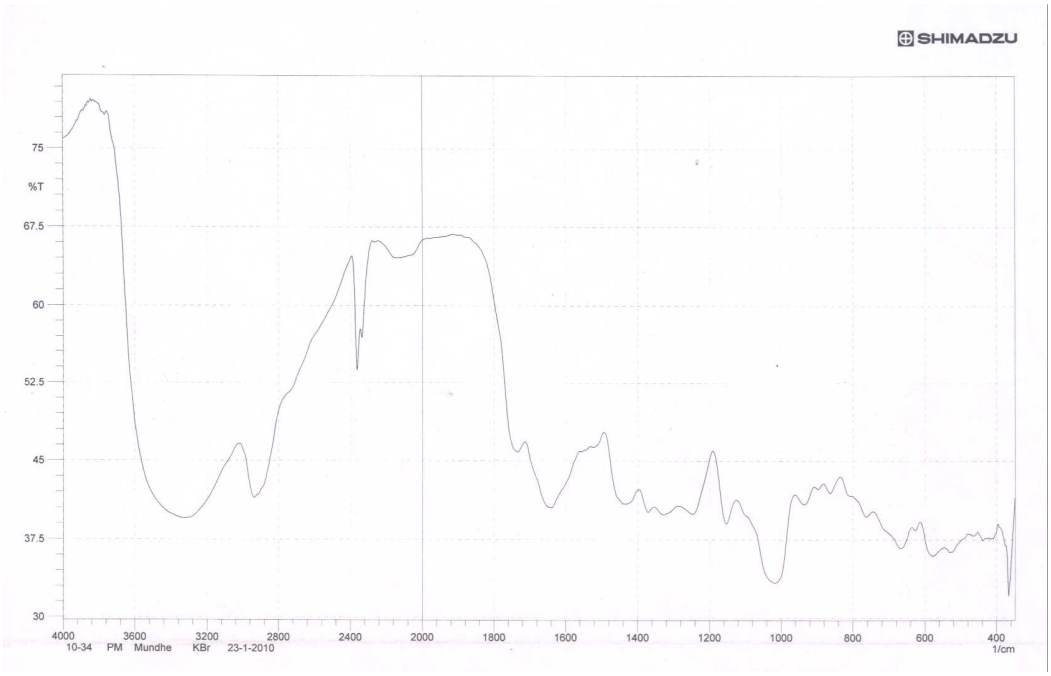

Figure: 1. FT-IR spectrum of *P.longifolia* seed biomass.

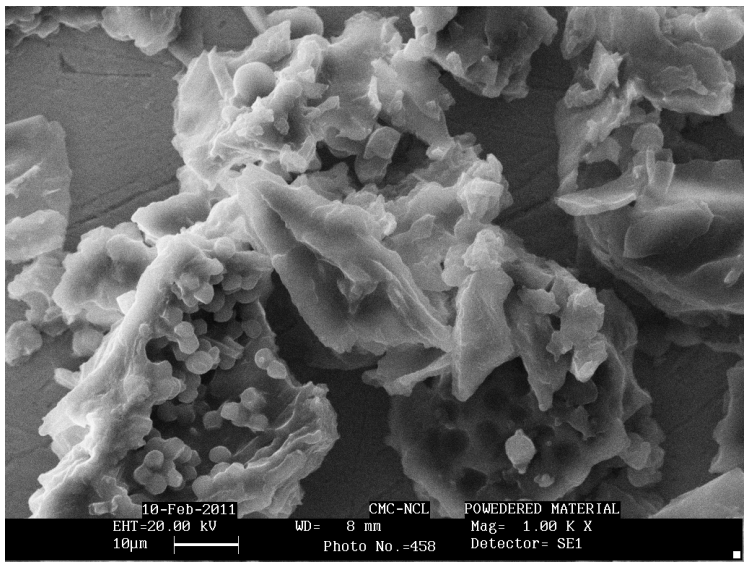

Figure: 2. SEM of *P.longifolia* seed biomass.

3.2. Batch Biosorption studies:

3.2.1. Effect of sorbent mass on dye sorption

Sorbent dosage is an important parameter due to its strong effect on the capacity of sorbent at given initial concentration of the sorbate; (**Fig.3)** shows the effect of sorbent dosage on the removal of MB. The amount of dye sorbed per unit mass of sorbent decreased with increase in sorbent dose, similar results were reported by M.M. Abd El-Latif [29]. Many factors can contribute to this adsorbent concentration effect. The most important factor is that adsorption sites remain unsaturated during adsorption. Also a fixed mass of adsorbent can sorbs only a certain amount of dye and equilibrium is attained between solute concentration in the solution and solute concentration on the surface of the sorbent. Figure 4, indicates that adsorbent mass has an influence on the time of contact necessary

to reach equilibrium. The smallest mass has (1g) attained the equilibrium after 60 minutes while the higher mass has (6g) achieved equilibrium within 30 minutes.

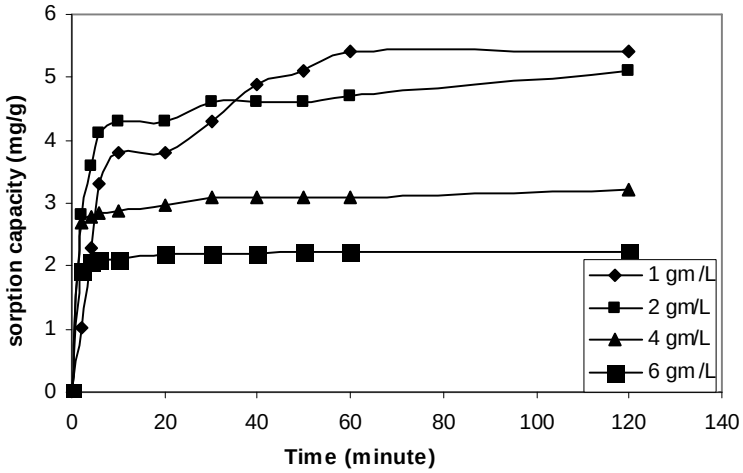

Figure: 3. Effect of sorbent dosage on the sorption capacity of methylene blue by *P.longifolia* seed biomass.

3.2.2. Effect of contact time and initial dye concentration

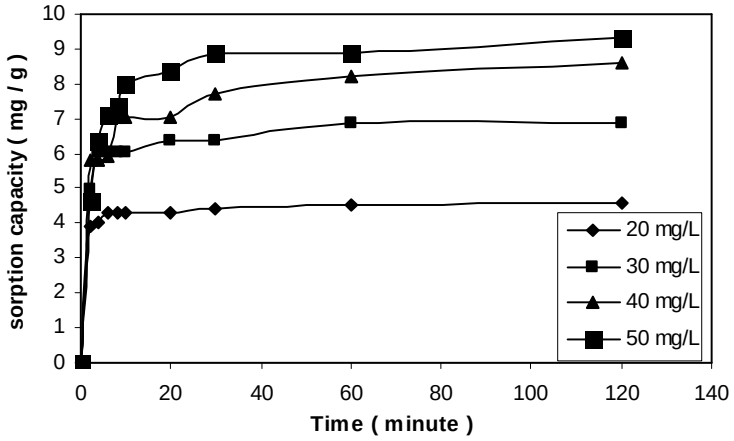

Figure : 4. Effect of initial concentration on the sorption capacity of methylene blue by *P. longifolia* seed biomass.

The experimental results of sorption of methylene blue by sorbent (*P.longifolia* seeds) at various initial concentrations with contact time are shown in **Fig.4.** It can be seen from Figure 5. that the amount of dye adsorbed (mg/g) increased with increase in initial dye concentration and remained constant after equilibrium time (30 minute) .The equilibrium sorption capacity is increased from 4.40 to 8.90 mg/g as the methylene blue concentration increased from 20mg/L to 50mg/L. The observed result indicates that the removal of adsorbate initially increases with time but attains equilibrium after 30 minutes. The adsorption process was found to be very rapid in the initial stages and a large fraction of the dye was removed in the first 10 minutes. The adsorption of methylene blue depends upon initial concentration of the dye. **Fig. 4**. shows same shape of curves indicating uniform process.

3.2.3. Effect of system temperature on dye sorption

One of the most important factor which affects largely on process of sorption is the temperature. The plots of time vs. sorbed amount at different temperatures (**Fig.5)** indicates that equilibrium is attained within 30 minutes.The

entire curve has similar shape. The equilibrium sorption capacity decreases from 3.32mg/g to 1.6mg/g. with increase in temperature. This is because room temperature is suitable for binding of dye on surface of adsorbent. This may be due to a tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution. Extent of adsorption varies inversely as temperature i.e. lower the temperature higher is the adsorption. From this it can be concluded that heat must be liberated during adsorption. This is in keeping with Le Chatelier's Principle which expects exothermic process to be favored at low temperature. This is true for physisorption.

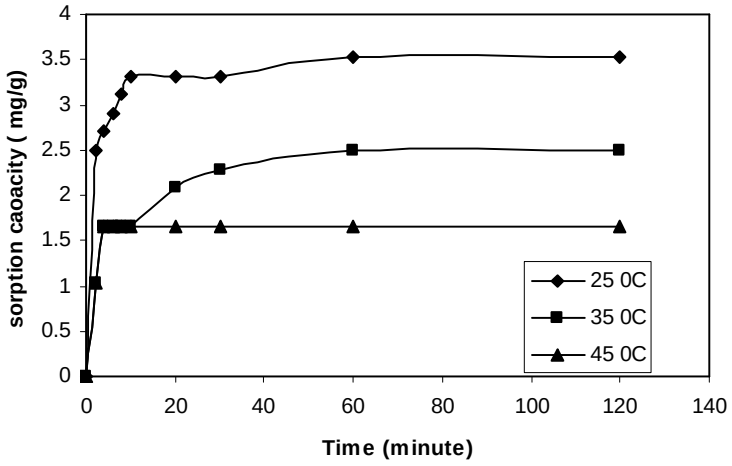

Figure : 5. Effect of temperature on sorption capacity of methylene blue by *P.longifolia* seed biomass.

3.2.4. Effect of solution pH on dye sorption

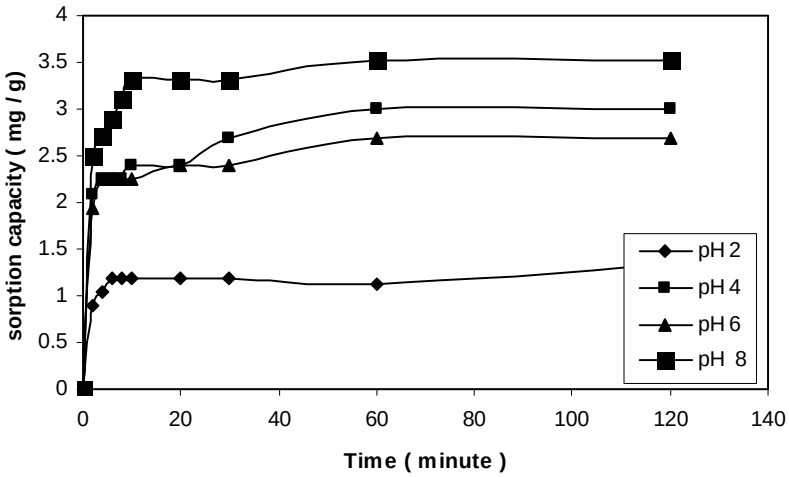

Figure : 6. Effect or pH on sorption capacity of methylene blue by *P. longifolia* seed biomass.

The solution pH is one of the most important factors which affect the sorption process. The percent removal was more in the pH range 6 to 8; (**Fig.6**) shows the effect of pH on the sorptiom capacity of dye. From the figure, it is observed that sorbed amount increases with increase in pH of solution. The equilibrium is attained at 30 minutes and the maximum amount is sorbed within 10 minutes. . The sorption capacity increases with increase of p H of solution. This can be explained as MB is a cationic dye, when p H of solution is lower, the surface of the sorbent is positively charged and therefore repulsion takes place. On the contrary, as the initial pH became higher, OH^- ions on the surface of adsorbent favor the adsorption of cationic dye due to ionic interaction between methylene blue

cation and negatively charged surface of sorbent. Adsorption of cationic dye was found to be favorable at higher pH. Several investigations have reported that methylene blue adsorption increases as pH increases.

3.3. Adsorption Isotherm data analysis

Table: 2. Values of Isotherm constants for methylene blue sorption by *P.longifolia* seed biomass at 25 ^{0}C.

Isotherm models	Parameter	Value
Freundlich	K(mg/g) 1/n R^2	3.0732 0.3611 0.9682
Langmuir	Q^0 (mg/g) b (l/g) R^2	9.19 0.3299 0.9964
Temkin	K_T (L mg $^{-1}$) B R^2	4.7989 1.8235 0.8967

Table: 3. For Langmuir isotherm the essemtial characteristics can be expressed in terms of dimentionless equilibrium parameter (RL), the values at various initial concentrations are as given in table.

Concentration (mg /L)	R_L
20	0.1316
30	0.0918
40	0.0704
50	0.0571

The equilibrium sorption isotherms are fundamentally important in designing bio sorption system and to investigate the maximum capacity of sorbent. Equilibrium relations between sorbent and sorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature.The isotherm shows the extent of the adsorbed layer that is the net result of adsorption and desorption processes [30]. In this study, analysis of equilibrium data for the biosorption of methylene blue onto the biosorbent has been under taken using the Freundlich, Langmuir and Tempkin isotherm models which are commonly usd for describing adsorption equilibrium.

The equilibrium data were analysed using linearized form of Freundlich isotherm (equation 3), by plotting log q_e vs. log Ce. The Freundlich equation assumes a logarithmic decrease in the enthalpy with increase in the fraction of occupied sites. The values of K_f and n obtained from the Freundlich plot are 3.07 mg/g and 2.7693, respectively. The value of correlation coefficient (R^2 = 0.96) obtained from Freundlich expression indicates that Freundlich isotherm provides good linearity. The value of n is greater than unity (n = 2.7693) indicating that the dye is favourably adsorbed on PMAS.

The equilibrium data were further analysed using linearized form of Langmuir isotherm (eq.4). The Langmuir constants maximum adsorption capacity (Q^0) and binding energy (b) were determined from linear plot of Ce/q_e vs and has the values as 9.19 mg/g and 0.3299(L /g). The high value of correlation coefficient (R^2 = 0.99) indicates Langmuir isotherm model was more suitable for experimental data than other isotherms.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter $R_{L,}$ (eq.5).The R_L values for the sorption of MB onto adsorbent(**Table 3**) are observed in the range of 0-1, indicating that the adsorption was a favourable process. This is in great agreement with the 'n' value obtained from Freundlich isotherm.

The adsorption data for MB on powdered material of *P. longifolia* seeds were also analyzed by a regression analysis to fit the Tempkin isotherm model (eq.5). The correlation coefficient was (R^2 = 0.8967) showing the poorest fit to

the experimental adsorption equilibrium data. The summary of data obtained from all isotherm plots is presented in **Table 2.**

3.4. Kinetic and themodynamic analysis

Table 4. Sorption kinetic constants for methylene blue sorption by of *P.longifolia* seed biomass obtained from pseudo second order kinetic model at different initial concentrations.
(particle size: 0.063 mesh; p H: 8.0; adsorbent dose: 0.200gm/50ml, temperature: 25 ^{0}C)

Concentration(mg/L)	k_2 (g mg^{-1} min^{-1})	qe (mg/g)	R^2
20	0.3889	4.6189	0.9998
30	0.1464	6.9108	0.9996
40	0.0563	8.66	0.9989
50	0.0688	9.4339	0.9995

Table 5. Intraparticle diffusion constants and Intercepts for methylene blue sorption by *P. lobgifolia* seed biomass

Concentration (mg/L)	Intraparticle diffusion rate constant (mg/g/minute)	Intercepts
20	6.0×10^{-2}	4.0
30	14.85×10^{-2}	5.49
40	30.71×10^{-2}	5.61
50	38.52×10^{-2}	5.91

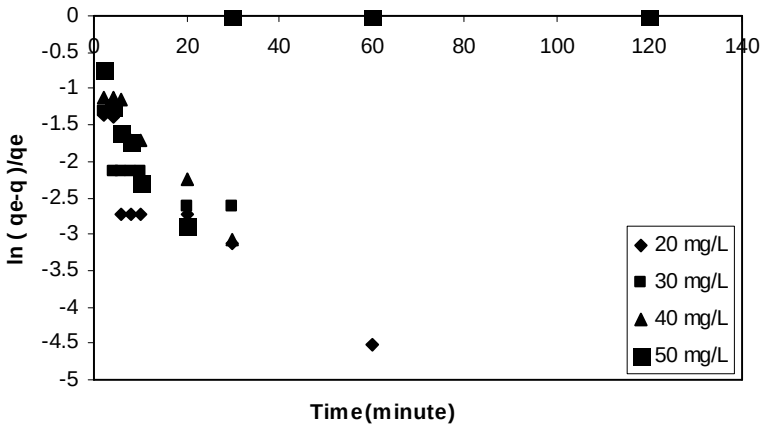

Figure:7. Application of pseudo-first order kinetic model for methylene blue sorption by *P. longifolia* seed biomass at different initial concentration

Adsorption is a surface phenomenon. Solid substances when broken into small pieces, new surfaces are created. In this process intermolecular bonds break and because of which valencies of molecules on the surface, remain unsatisfied. Thus on the surface unsatisfied valencies are present, this results in a tendency of the solid to attract other molecules or atoms on its surface, which help in decreasing its unbalanced forces and leads to adsorption.It is therefore a physicochemical process that involves the mass transfer of a sorbate from the liquid phase to the sorbent surface.

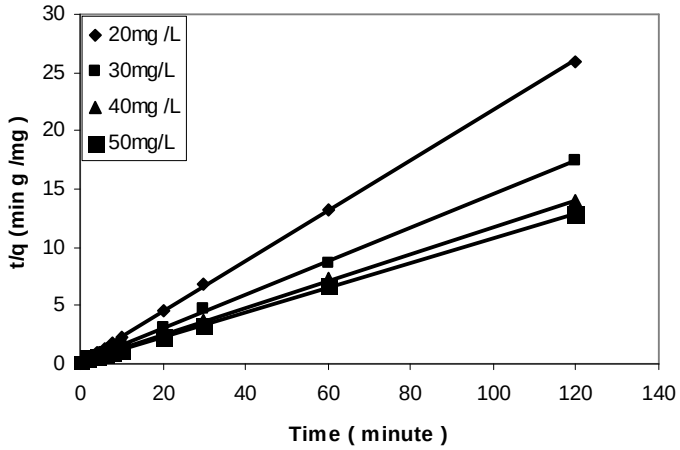

Figure: 8. Effect of concentration on pseudo-second order kinetics for methylene blue sorption by *P.longifolia* seed biomass.

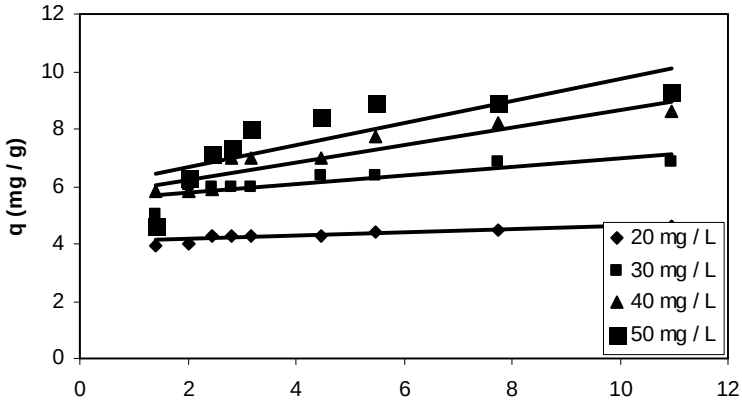

Figure: 9. Plots of sorption capacity versus square root of time for methylene blue sorption by *P. longifolia* seed biomass at various initial dye concentrations .

A study of kinetics of adsorption is important as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. The applicability of the pseudo-first order and pseudo-second order model was tested for the soprtion of MB on adsorbent. The best fit model was selected on the values of correlation coefficient, R^2.

The kinetics of MB sorption on adsorbent *(P.longifolia* seeds) was studied at different initial concentrations. Using equation (8), [ln $(q_e - q)/q_e$] versus t was plotted (**Fig.7**) at different initial methylene blue concentrations, which shows that the pseudo-first order model of Lagergren was not applicable to methylene blue sorption for various initial dye concentrations as the plots are not linear and the correlation coefficient, R^2 values are very small. Therefore the experimental kinetic data were further analyzed using pseudo second order model, (eq.9) The plot of t / q versus t for different initial MB concentrations (**Fig.8**), shows that a straight line was obtained in all cases with coefficient of determination better than 0.98, which clearly indicates that the sorption of methylene blue onto sobent can be better described by pseudo-second order model. The values of second order rate constant (k_2) and q_e were determined from the plots and the values along with correlation coefficent, R^2 (**Table 4**) showed that k_2 decreases with increasing initial MB concentration. The decrease in rate of MB sorption with increase in initial MB concentration may be due to association of molecules at the boundary surface, which get more pronounced at the high concentration. Similar results have been reported for sorption of MB on wheat bran [28] and on saw dust [29]. Kinetics of sorption can be explained on the basis of different diffusion mechanisms. Sorption kinetics is controlled by mechanisms, such as external and internal diffusion. Kinetic results analyzed using intraparticle diffusion model (eq.10) indicate that a plot of average particle loading, q (mg/g) versus square root of time, $t^{½}$ (**Fig.9**) would yield a straight line passing through origin if the sorption process obeyed the intraparticle diffusion model. Weber and Morris reported that if intraparticle diffusion is involved in the sorption process, then a plot of sorbate uptake versus square root of time would give linear relationship and the particle diffusion would be the rate controlling step, if this line passes through origin. From the Figure 13, it is clear that the plots are linear but do not pass through the origin. This indicates that intraparticle diffusion was involved in the sorption process but it is not the only rate controlling step. This confirms that sorption of methylene blue on the adsorbent involves other mechanisms involving adsorption on the external surface and diffusion into the internal sites. The intraparticle diffusion rate constants and the intercepts obtained from the plots are given in **Table 5**. The intercepts of the plots give an idea about boundary layer thickness. Larger the value of intercept greater is the contribution of the surface adsorption. From the Table 5, it seems that the values of intercepts increase with increase in initial dye concentration, indicating that the boundary layer effect increases with increase in concentration. Figure 13, shows that the curves has two shapes, initial curved portion and the next linear portion. The curved portion may be due to the mass transfer of the sorbate from the liquid phase to the sorbent surface and the linear portion may be due to slow diffusion of dye molecules in to internal sites of adsorbent.

From the above results it is concluded that the sorption of MB on powdered material process involves two stages, one is the sorption of dye molecules on the surface at a fast rate and the other was the slow diffusion of molecules through internal sites.

Thermodynamic study

Table: 6.Thermodynamic parameters for methylene blue sorption by *P. longifolia* seed biomass
(particle size: 0.063 mesh; p H: 8.0; adsorbent dose: 1 gm/L, concentration: 3.7mg/L, agitation time: 10 minute).

Temperature (K)	ΔG^0 (k J /mole)	Ea (k J /mol)	ΔH^0 (k J /mole)	ΔS^0 (J /mole/K
298	-5.1529	214.74	-91.5673	-292.89
308	0.5620	224.74		
318	0.58002	234.74		

Thermodynamic studies have been used to assess the spontaneity of the adsorptive process. The values of thermodynamic parameters for the sorption of MB onto PMAS at various temperatures were calculated and listed in Table 6. The Gibbs free energy change ΔG^0 was calculated using equation (12) while the values of ΔH^0 and ΔS^0 have been calculated from the slope and intercept of the plot lnKc vs. 1/T (**Fig.10**), which gives a straight line with acceptable coeffcient of determination ($R^2 = 0.7664$).The negative value of ΔG^0 at lower temperature indicates that sorption of dye on PMAS is a spontaneous process. The negative values of ΔH^0 and ΔS^0 indicate that the sorption process was exothermic and suggest probable occurrence of favourable adsorption. Energies of activation, Ea, below 42 kJ/mol, indicate diffusion controlled mechanism and higher than that represents chemisorption. In the present study activation values obtained are higher than 42 k J /mol as presented in **Table 6**, which indicate that the sorption of MB on powdered material is a chemically controlled process.

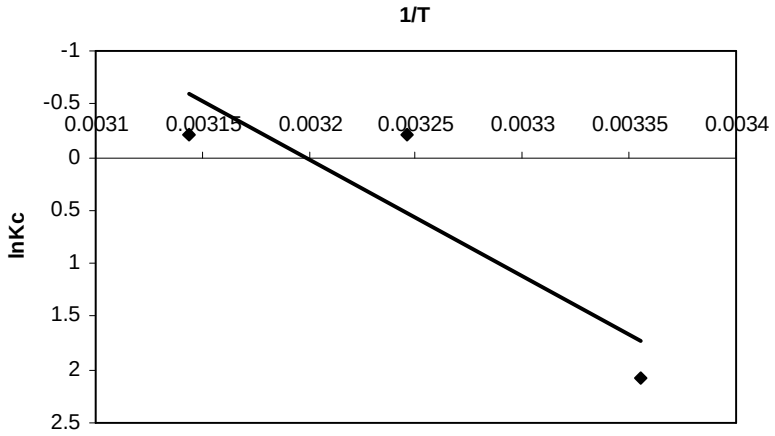

Figure: 10. Plot of lnKc versus 1/T for sorption of methylene blue by *P.longifolia* seed biomass

CONCLUSION

The preliminary studies performed in the present work, clearly indicate that the powdered material of *P.longiflolia* seeds can be efficiently used for the sorption of methylene blue from aqueous solution. The Boehm's titration and FT-IR analysis confirms the presence of active functional groups on surface of sorbent and SEM analysis shows the presence of large cavities on the surface. The parameters such as, initial sorbent dose, dye concentration, agitation time, temperature and pH affects the sorption process. The adsorption equlibrium data follows Langmuir isotherm model showing maximum sorption capacity of 9.19 mg/g. The R_L value between 0 and 1 indicates faourable adsorption.

The pseudo second order model provides the best fit for the experimental data obtained compared to first order Lagergren models shown by the correlation coeffecients. Intraparticle diffusion of MB occurs in two steps where the MB molecule diffused rapidly at a fast rate in the beginning and the the process slowed down due to intraparticle diffusion. The thermodynamic parameter (ΔG 0and ΔH 0) confirms the spontaneous and exothermic nature of adsorption process.

The negative value of ΔS^0 indicates favourable adsorption .The activation energy was found to be greater than 42 k J /mol indicating a chemically controlled process.
As *P.longiflolia* seeds are easily available, it has potential to be used for small scale industries which produce dyes as their effluent.Its adsorption capacity can be increased by chemical treatment.

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