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Removal of Methylene Blue Using Biosorbent Prepared From Seeds of *Polyalthia longifolia (Ashoka)*

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Abstact:

The present study describes the use of biosorbents prepared from waste material for the removal of Methylene Blue from aqueous solution. The seeds of *Polyalthia longifolia commonly* called as Ashoka were used for the preparation of biosorbent. Powdered Material (PM) is used for the adsorption of Methylene Blue from aqueous solution. The batch process is carried out in which various parameters like effect of adsorbent dose, effect of initial concentration and contact time, effect of temperature and pH were studied. It is observed that the optimum dose required for maximum percent removal of MB at equilibrium was found to be 4 g L^{-1} of PM. Initial rate of adsorption is high and as concentration is increased from 20 to 50 mg/L % removal at equilibrium decreases from 92 to 74.40 % for PM. The effect of temperature indicates that the process is exothermic involving physisorption. The optimum pH was found to be 8. Applicability of adsorption isotherms were studied. Q^0 value for PM (9.19) indicate better adsorption capacity for MB. R^2 value greater than 0.99 (Langmuir Isotherm) indicating applicability of process. The powdered material prepared from seeds of Ashoka is cost effective and ecofriendly biosorbent and can be used as an alternative to commercial adsorbents.

Index Terms:

Biosorption, Methylene Blue, Adsorption Isotherms, *Polyalthia longifolia* seeds.

Introduction:

Carbon materials are unique and have wide variety of applications in the field of industry. Industrial applications include: oil and natural gas, food, pharmaceuticals, water treatment, gold recovery, production of fine and bulk chemicals and catalysis[1]. Activated carbons due to high specific area and tunable porosity are effective in removing pollutants[2]. By using activated carbon as adsorbents in effluent treatment good quality effluent is obtained after treatment, design and operation of the process is simple[3]. High cost and large demand of activated carbon necessitates the need for the exploration of new sources of carbon materials with desired physicochemical properties. The carbon precursor and the method of preparation are the determining factors of the textural and surface properties of carbon materials[4]. In order to prepare low-cost carbon with desired properties various industrial and agro waste materials have been used as precursors. The adsorption of pollutants from an aqueous solution is frequently used to test the adsorption capability of various adsorbents[5].

Literature survey reveals that activated charcoal has been prepared from bagasse, coconut shell, coffee beans, cotton seed hulls, wood saw dust, walnut shell grapes seeds, eucalyptus, olive and peach stone have been found to be suitable precursors producing high carbon and low ash contents[6]. The materials like tree barks, cotton capsule shells, saw dust, rice straw, ground nut husk carbon and tea leaves have been investigated for the removal of pollutants from waste water in the last few decades[7]. In some cases the raw materials were used as an adsorbent with or without thermal/chemical treatment. Literature survey also

reports that the agro waste materials without any treatment can be effectively used for the removal of pollutants from waste water viz. maize bran for removal of chromium (II) ions[8]. Literature reports revealed that various researchers investigated the potential of biosorbents in removing pollutants from waste water. Adsorption on biosorbents is due to the various functional groups present on the surface[9]. Literature survey shows the excellent adsorption potential of various plants and plant derived materials. The effect of lignocellulosic structures on their carbons is also well recognized[10]. Use of such newer materials will result in carbons having diverse structures and thereby adsorption capacities.

Polyalthia longifolia is a garden tree generating large number of seeds. These are not useful as animal feed stock and thus become a potential source of garden waste. It was therefore thought worthwhile to investigate the potentials of these seeds – treated and untreated- for various applications.

Materials and Methods:

Preparation of biosorbent:

P. longifolia seeds have been used for the preparation of biosorbent. The seeds of *P. longifolia* were collected from the nearby garden in Pune Maharashtra, India during the months of July and August. The seeds were washed to remove all the dirt and earthy materials and air dried. The dried seeds were crushed, powdered and sieved to particle size 0.063mm and stored in air tight bottle for further use as an adsorbent, referred as Powdered Materia, 'PM'.

Preparation of solutions:

Methylene Blue (MB) (3,9-bisdimethylaminophenazo thionium chloride), having molecular formula $C_{16}H_{18}N_3SCl.3H_2O$ & molecular weight 373.90 g mol $^{-1}$, has been chosen as the sorbet (**Fig.1**). The stock solution of methylene blue was prepared (1000 mgL^{-1}) in distilled water. It was diluted accordingly to obtain solutions of desired concentrations. HCl and NaOH are used for variation of pH.

Experimental procedures:

Optimization of process parameters and the effect of, adsorbent dose, initial concentration & contact time, temperature and pH on adsorption are assessed by performing batch mode adsorption experiments. Appropriate amounts of sorbent is added and the solution is stirred using magnetic stirrer at 200 rpm. The solutions, after adsorption are filtered using Whatman filter paper No. 42. The absorbance is measured on colorimeter at 620 nm before and after adsorption to evaluate the initial concentration (C_0) and equilibrium concentration (Ce) of methylene blue. The pH of original MB solution is between 7.0 to 8.0 and it is not adjusted in other experiments except effect of pH.

Effect of adsorbent dose: The effect of adsorbent dose has been investigated by varying the amounts of adsorbent. 2 to 20 gL^{-1} PM and is taken in different 100 ml round bottom flasks. To each of the weighed adsorbent 50 ml of MB of known initial concentration (C_0) is added. The solutions are stirred for 30 min. and then filtered to measure the absorbance.

Effect of initial concentration and contact time: The effect of initial concentration and contact time on the adsorption of MB has been studied by stirring, 50 ml MB solution having initial concentrations 20, 30, 40 and 50 mgL^{-1} with weighed amount of adsorbents (4 gmL^{-1} PM) for different contact times (1 to 120 minutes) at room temperature. The solutions are then filtered and their absorbance is measured.

Effect of temperature and pH: The effect of temperature (25, 35 and 45 ^{0}C) and pH (2 to 8) of solution has been investigated for MB adsorption using PM. The 50 ml solution of MB (30 mgL^{-1}) is stirred with 4 gL^{-1} adsorbent dose of PM at different time intervals from 1 to 120 minutes with different temperature and pH. Absorbance of solution is recorded after filtration.

All the experiments were carried out in triplicate and mean values are reported.

Mathematical equations and Isotherm models used:

Analytical Method-

The amount of dye adsorbed is calculated in percentage (%) as,

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

Adsorption capacity (qe) is calculated from the mass balance equation as follows:

$$qe = (C_0 - Ce)\, V / 1000 \times w \quad (2)$$

Where, qe is the quantity of dye uptake by biosorbent (mg/g) at equilibrium

C_0 is the initial concentration (mgL^{-1}) of dye.

C_e is the concentration of dye after sorption at equilibrium (mgL^{-1})
V is the volume of dye solution (ml);
W is the mass of adsorbent (g.)
The results have been expressed in terms of amount of dye adsorbed on biosorbent at any time (q_t) or at equilibrium (q_e), mg/g and the concentration of dye that remain in solution at equilibrium (C_e, mgL^{-1}).

Adsorption Isotherms-

Data obtained from the effect of initial concentrations and contact time has been analyzed for adsorption isotherms. An adsorption isotherm is a graphical representation showing the relation at constant temperature between the amount of substance adsorbed by a unit weight of adsorbent and the concentration of sorbet remaining in the solution at equilibrium. To design a suitable reactor for waste water treatment, the knowledge about the equilibrium study is important. Consequently it is important to determine a suitable isotherm model which could describe the mechanism of adsorption involved in the solid-liquid system under various conditions. Adsorption isotherm parameters obtained from different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis. The important isotherms; Freundlich, Langmuir and Tempkin have been applied in this study.

Freundlich Isotherm Model

Freundlich equation describes heterogeneous surface energy terms and adsorption intensity of the adsorbate on the adsorbent surface & is expressed as,

$$q_e = K_F C_e^{1/n} \quad (3)$$

The linearized Freundlich isotherm is represented as,

$$\log q_e = \log K_F + (1/n) \log C_e \quad (4)$$

Where, K_F (mg/g) and 1/n are Freundlich constants including all factors affecting the adsorption capacity and favorability of adsorption onto biosorbents.
The plots of log q_e vs. log C_e are used to determine the values of K_F and 1/n from the intercept and slope. Freundlich parameter 1/n relates to the surface heterogeneity. When $0 < 1/n > 1$, adsorption is favorable; 1/n = 1 adsorption is homogeneous and there is no interaction between the adsorbed species and $1/n > 1$ adsorption is unfavorable.

Langmuir Isotherm Model

The Langmuir isotherm has been the most widely used adsorption isotherm. It determines the maximum capacity of adsorbent. The Langmuir isotherm theory is based on the assumption that,

- Adsorption takes place at specific homogeneous sites within adsorbent.
- There is negligible interaction among adsorbed ions.
- Adsorbent surface is saturated after adsorption.
- All sites are energetically equivalent.

The unmodified Langmuir equation is defined as:

$$q_e = Q^0 b C_e / 1 + b C_e \quad (5)$$

Where, Q^0 = Langmuir constant related to maximum adsorption capacity (mg/g)
b = Langmuir constant related to binding energy of the adsorption system (Lmg^{-1}) The Langmuir equation is used in the linearized form in order to evaluate adsorption capacity and Langmuir constant as,

$$C_e/ q_e = 1/ (Q^0 b) + C_e/Q^0 \quad (6)$$

The plot, of C_e/ q_e vs. C_e is used to determine the values of Q^0 and b from the slope and intercept respectively.
The Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (Halls Separation Factor) $\mathbf{R}_L$, which is defined as:

$$R_L = 1 / (1 + b C_0) \quad (7)$$

Where C_0 is the maximum initial sorbate concentration ($mg\ L^{-1}$). McKay et al.,

have shown that the value of parameter R_L indicates the type of isotherm as,

Value of R_L	Type of isotherm	Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable	$0<R_L < 1$	Favorable
$R_L = 1$	Linear	$R_L < 0$	Unfavorable
$R_L = 0$	Irreversible	-	-

Tempkin Isotherm Model

Heat of adsorption and the effect of adsorbate-adsorbent interaction on adsorption isotherm are studied by Tempkin & Pyzhev[7] 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:

$q_e = RT / b \ln K_T + RT / b \ln C_e$ (8) Where, $RT / b = B$, R = Gas constant (8.314 J / mol K),

T = Absolute température (K), K_T = Tempkin constant (Lg^{-1})

b = Tempkin constant related to heat of sorption ($Jmol^{-1}$)

The adsorption data is analyzed according to Eq. (8). The plot of q_e vs. ln Ce allows to determine the Tempkin constants K_T and b from intercept and slope.

Results and Discussion

Effect of adsorbent dose

Sorbent dosage is an important parameter which affects the removal efficiency of a sorbent at given initial concentration of the sorbate. The adsorption of MB using biosorbent PM at different dosages from 2 to 20 g L^{-1} has been studied at various initial MB concentrations (C_0 = 20, 30, 40 and 50 mg L^{-1}) at natural pH of solution, keeping other parameters viz. contact time (30 minutes), temperature (25 ± 2^0C) constant. The plots of % removal of MB at different doses of PM at various initial concentrations of MB (**Fig.2**) indicate that removal efficiency increases as the adsorbent dose increases. As the amount of PM is increased from 2 to 20 g L^{-1}, the percentage removal of MB increased from 80 % to 95% at C_0 = 20 mgL^{-1} of MB, however above 8.0 gL^{-1} dose no significant increase in the removal was noticed. Similar effect of adsorbent dose is observed for all initial concentrations (C_0) studied.

A fixed mass of adsorbent can sorbs only a certain amount of dye and equilibrium is attained between solute concentration in the solution and on the surface of the sorbent. Increase in adsorbent dose, increases surface area and availability of more adsorption sites[11] results in increase in the removal of dye.

Effect of initial concentration and contact time

The effect of initial concentration of MB and contact time on sorption efficiency of PM has been investigated by experiments carried out at various initial concentrations (C_0 = 20, 30, 40 & 50 mgL^{-1}) at original pH of solution, with 4 gL^{-1} dose of PM and at 25 ± 2^0C.The results presented in (**Figs. 3** and **4**), indicate that both the removal efficiency and uptake capacity (mg/g) increase with increase in contact time. The time required to attain equilibrium is found to be 60 min. over all the studied concentrations however, the initial rate of adsorption is very fast and major removal occurs within 10 min. Thus the adsorption process can be divided into three stages for all concentrations studied. First, where the rate of removal is rapid during the initial period within 10 min., second slow and stagnated within the range of 10–60 min. Finally, in the third stage adsorption efficiency does not vary significantly after 60 min., the adsorption was in a state of dynamic equilibrium between the dye desorption and adsorption. The reason for this could be that, during the adsorption, initially the dye molecules rapidly reach the boundary layer by mass transfer and then they slowly diffuse from the boundary layer film onto the adsorbent surface, as all the available external sites have been occupied and finally, they diffuse into porous structure of adsorbent[12].

A decrease in % removal of dye is recorded from 92 % to 74.40% with increase in initial concentration from 20 to 50 mgL^{-1} for 60 min. agitation time. This can be assigned to the fact that at low concentration, a large number of adsorption sites are available so that dye molecules get easily adsorbed on to surface of adsorbent, but at higher concentrations dye molecules are in large number as compared to available sites, therefore at higher concentration longer time is required to attain the equilibrium.

The equilibrium adsorption capacity (**Fig.4**) increases from 4.60 to 9.35 mg/g with the increasing initial MB concentration from 20 to 50 mgL^{-1}. This can be due to the mass transfer driving force become larger and the interaction between MB and adsorbent is increased, resulting in higher adsorption capacity[13].

Effect of temperature

One of the most important factors which affect largely the process of sorption is the temperature. The effect of temperature on percent removal of MB using PM, has been carried out at different temperatures 25, 35 and 45 ^0C, with varying contact time and at original pH of solution, keeping initial MB concentration (C_0 = 30.0 mg L^{-1}) and adsorbent dose (4 g L^{-1}) constant. The plots of % adsorption vs. contact time at different temperatures (**Fig. 5**) clearly reveal that with increase in temperature from 25 to 45 ^0C, percent removal of MB at equilibrium decreases from 88.90 to 44.47 %. This signifies that room temperature is most suitable for binding of dye molecules on the surface of the adsorbent and heat must be liberated during sorption process. This is because the tendency of dye molecules to escape from the solid phase to bulk phase increases with temperature indicating desorption. As temperature increases the weakening of electrostatic force of attraction between the dye molecules and active sites on adsorbent decreases, resulting in the substantial reduction in removal efficiency. This is in keeping with Le Chatelier's principle which expects exothermic process to be favored at low temperature, and is true for physisorption[14].

Effect of pH

The initial pH of solution affects and controls the sorption process, as the hydrogen and hydroxyl ions are adsorbed quite easily on the sorbent surface and compete with the sorbate ions in solution. Therefore to investigate the effect of pH on removal efficiency of PM for the dye becomes important. This has been studied over the pH range from 2 to 8 at optimized conditions of initial MB concentration (C_0 = 30mgL^{-1}) and 4 gL^{-1} adsorbent dose. The plots of percentage removal vs. contact time at varying pH (**Fig.6**) indicate that the increase in pH of solution is helpful for the adsorption of MB onto PM. As initial pH of MB solution is increased from 2 to 8 removal efficiency rapidly increased from 32 to 88.89 % within 10 minutes indicating large differences in adsorption efficiencies at acidic and basic pH. Equilibrium was attained within 60 minutes and thereafter % removal remains constant and the maximum removal of 94.44% is seen at 8 pH. This is because cationic dye interacts with OH^- ions in solution at this pH. Acidic condition produces more H^+ ions in the system and the surface of the adsorbent gathers positive charge by adsorbing H^+ ions, which prevent the adsorption of MB^+ ions onto adsorbent surface due to electrostatic repulsion between H^+ ions and MB^+ ions[15]. As the solution pH increases, the number of negatively charged surface sites on the adsorbent increase, which result in the increase in adsorption due to electrostatic attraction[16] between the OH^- and MB^+ ions.

Adsorption Isotherms

To optimize the adsorption system, it is important to set up the most appropriate correlation for the equilibrium curves. Various isotherms like Freundlich, Langmuir, Tempkin, Redlich-Peterson, Koble–Corrigan & Dubinin-Radushkevich have been used to describe the equilibrium characteristics of adsorption. They differ in basic assumptions. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and a logarithmic decrease in the enthalpy with increase in the fraction of occupied sites. The basic assumption of Langmuir theory is that, the sorption takes place at specific homogeneous sites within the adsorbent and it is helpful to determine the maximum adsorption capacity of adsorbent for the given adsorbate. Tempkin isotherm contains a factor that clearly takes into account the adsorbing species–adsorbent interactions. It assumes that (i) the adsorption is characterized by a uniform distribution of binding energies; (ii) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions. Adsorption is considered as satisfactory when the Freundlich constant 1/n takes a value within the range 0 - 1. For Langmuir type adsorption process, the efficiency of the adsorption process can be predicted by the dimensionless equilibrium parameter R_L (equation, 7).

The adsorption data obtained for MB using PM as adsorbent is analyzed in the light of Freundlich, Langmuir and Tempkin Isotherms. The applicability of the isotherm equation to describe the adsorption process is evaluated by the correlation coefficients, R^2 values. The isotherm constants and correlation coefficient, R^2 for all the studied isotherms are summarized in (**Table 1**).

Freundlich Isotherm

The equilibrium data is subjected to Freundlich model. The values of K_F and 1/n are obtained from the intercept and slope of the Freundlich plot, log qe vs. log Ce (**Fig.7**) which is the measures of sorption capacity and intensity of sorption respectively. The value of K_F is found to be 3.07 mg/g which indicates a

fairly good adsorption capacity lying in the same range as reported for adsorbents[17]. The value of 1/n is found to be 0.3611 i.e. in between 0 and 1 indicating that the dye is favorably adsorbed on adsorbent. The smaller value of 1/n indicates formation of relatively stronger bonds between adsorbent and adsorbate. The R^2 value (0.9682) indicates Freundlich isotherm provides fairly good linearity.

Langmuir Isotherm

The equilibrium data is further analyzed using linearized form of Langmuir isotherm (eqn.6). The linear plot of C_e/q_e vs. C_e, is obtained (**Fig. 8**), to determine Q^0 - maximum adsorption capacity (mg/g) and b - binding energy from the slope and intercept. The value of Q^0, 9.19 mg/g which is close to experimental value 8.90 mg/g indicates that sorption system is in ideal equilibrium. The Langmuir constant b, 0.3302(Lg^{-1}), which is between 0 and 1 and high value of correlation coefficient, R^2 = 0.9964, indicates Langmuir isotherm model is suitable for experimental data.

The dimensionless equilibrium parameter, Hall separation factor (RL), is evaluated by substituting the value of b and C_0, in eqn. 7. The value of R_L 0.0571 lying between 0 and 1 confirms the favorable conditions for dye sorption on sorbet. Smaller value of R_L or nearness to zero indicates more favorable conditions for sorption[18] which is in good agreement with '1/n' value.

Tempkin Isotherm

This isotherm helps to get an insight about interactions between adsorbing species and the adsorbent. The adsorption data for MB onto PM is also analyzed by a regression analysis to fit the Tempkin isotherm model (eq.8).From the plot of $\ln C_e$ vs. q_e (**Fig. 9**) the Tempkin constants B and KT are evaluated from the slope and intercept. The value of correlation coefficient R^2 = 0.8967 showing the poorest fit of Tempkin isotherm to the experimental adsorption equilibrium data. This also indicates non uniform energies at various binding sites[19].

The adsorbent is derived from natural material without any treatment and has a number of surface functional groups at which binding of the dye molecule will take place[20]. Due to the difference in nature of binding sites the energy of each binding site is expected to be different than that of other.

Following figures indicate adsorption of MB using PM

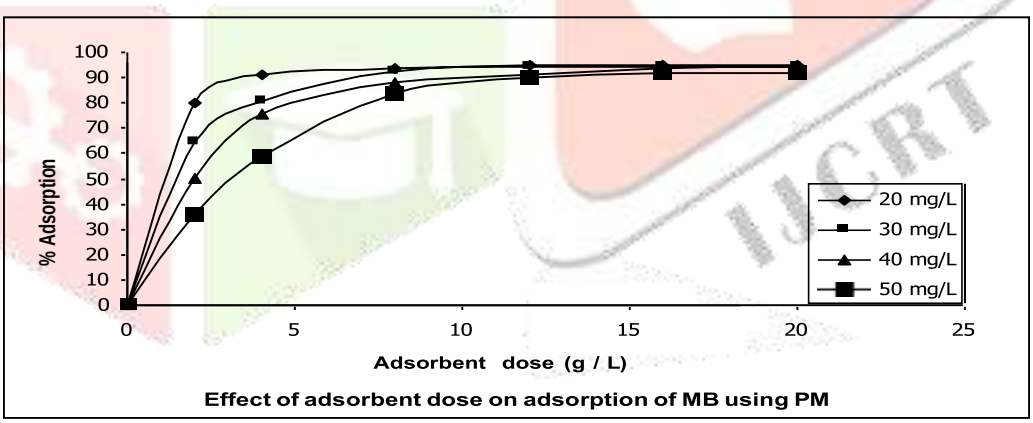

Figure 1: Effect of adsorbent dose on the percent removal of MB using PM (Contact time = 30 minutes, Temp. = 25 ± 2^{0}C)

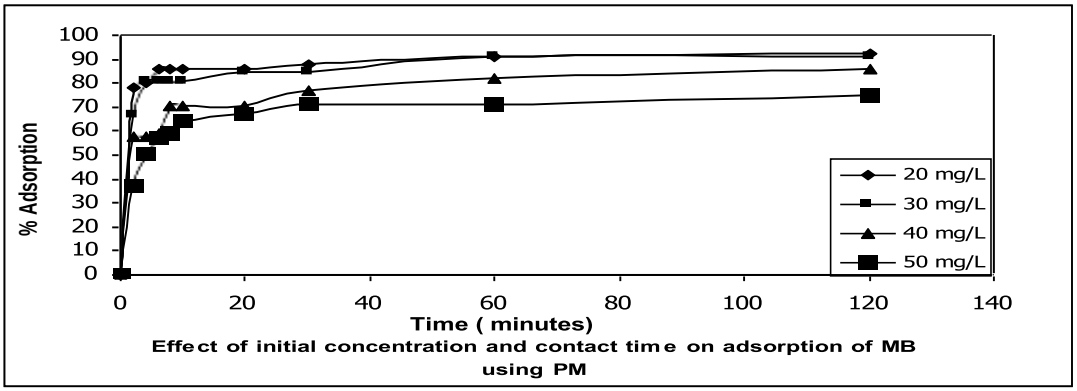

Figure 2: Effect of initial concentration and contact time on percent removal of MB using PM (Temp. = 25±2^{0}C, Adsorbent dose = 4 g L^{-1})

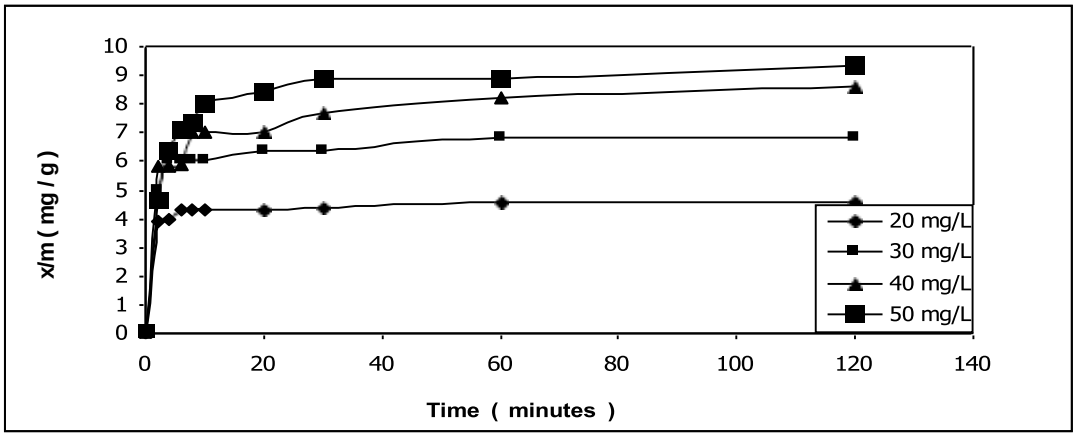

Figure 3: Effect of initial concentration and contact time on the adsorption capacity of PM for MB adsorption (Temp. = 25±2^{0}C, Adsorbent dose = 4 gL^{-1})

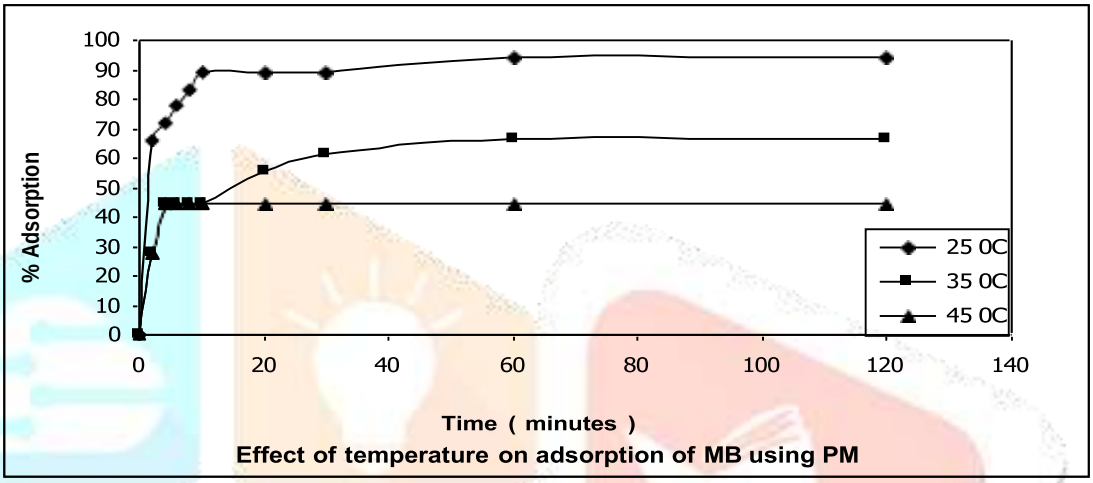

Figure 4: Effect of temperature on percent removal of MB using PM (C0 = 30 mgL^{-1}; Adsorbent dose = 4 gL^{-1})

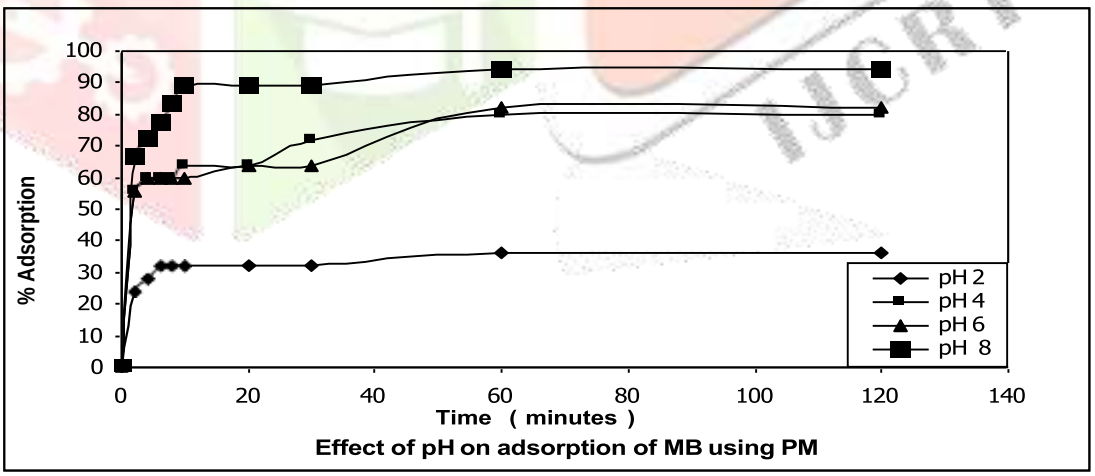

Figure 5: Effect of pH on percent removal of MB using PM (C0. = 30 mgL^{-1}; Adsorbent dose = 4 gL$^{-1,}$ Temp. = 25 ± 2^{0}C)

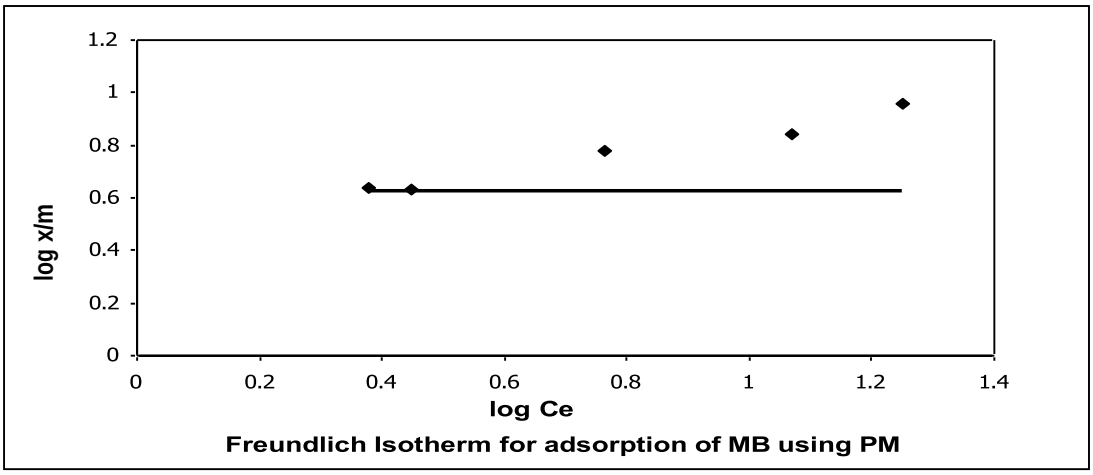

Figure 6: Freundlich Isotherm for adsorption of MB using PM (Temp. = 25 ± 2^{0}C)

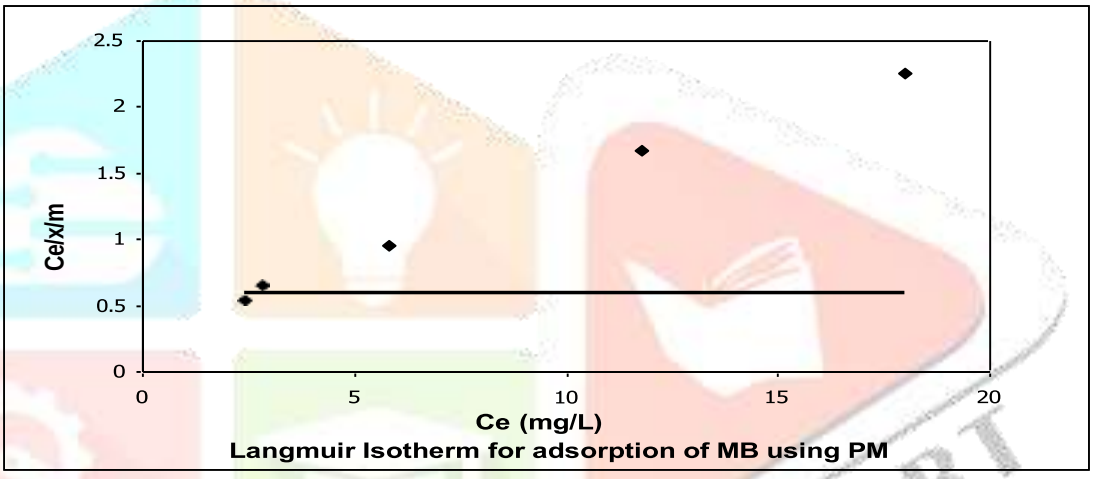

Figure 7: Langmuir Isotherm for adsorption of MB using PM (Temp. = 25 ± 2^{0}C)

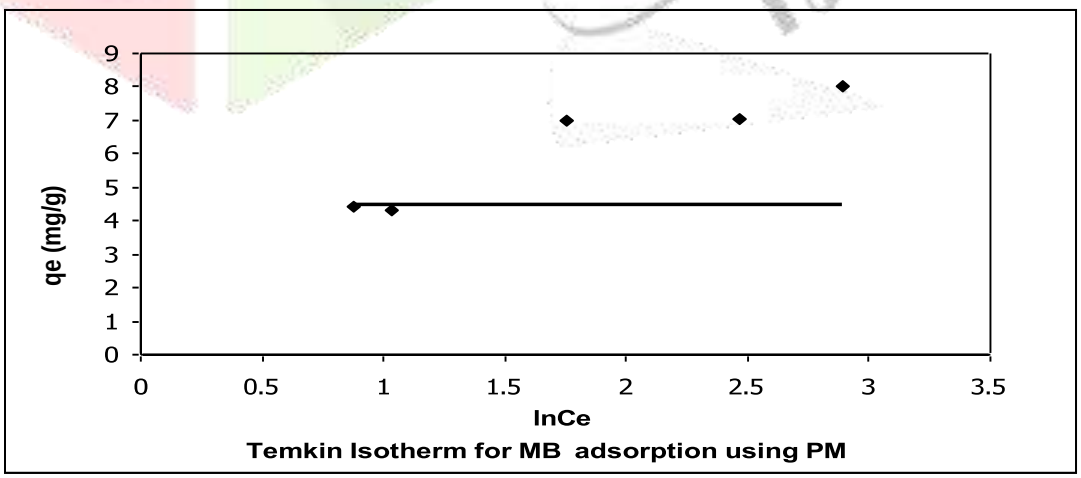

Figure 8: Temkin Isotherm for adsorption of MB using PM (Temp. = 25 ± 2^{0}C)

Table 1: Freundlich, Langmuir and Temkin isotherm constants for MB adsorption on PM at 25 ± 2^0C

Adsorption Isotherm	Parameter	Value
		PM
Freundlich	K_F (mg/g)	3.0732
	1/n	0.3611
	R^2	0.9682
Langmuir	Q^0 (mg/g)	9.19
	b (L/g)	0.3302
	R^2	0.9964
	R_L	0.0571
Temkin	K_T (L mg^{-1})	4.7989
	B	1.8235
	R^2	0.8967

Conclusions:

The adsorbent PM produced from waste biomass (*Polyalthia longifolia* seeds) is used for the removal of methylene blue from aqueous solution. The main conclusions of experimental results are as follows:

- The optimum dose required for maximum percent removal of MB at equilibrium was found to be 4 g L^{-1} of PM .
- For an increase in the dose from 2 to 20 gL^{-1} PM showed an increase in % adsorption from 80 to 95% at an initial concentration of MB, 20 mgL^{-1}.
- Initial rate of adsorption is high up to 10 minutes and then from 20 to 60 minutes the rate slow down and finally reaches equilibrium after 60 minutes.
- Increase in initial concentration of MB influences significantly the adsorption of the dye on PM. As concentration is increased from 20 to 50 mg/L % removal at equilibrium decreases from 92 to 74.40 % for PM.
- Rise in temperature from 25 to 45 ^{0}C leads to a decrease in % adsorption by PM indicates an exothermic process involving physisorption.
- The optimum pH for adsorption of MB on PM was found to be 8.
- 1/n value lie between 0 and 1 indicating favorable adsorption process using PM.
- R^2 value indicate Langmuir model was best for PM.
- RL values lies between 0 and 1 confirming the process to be a favorable one.
- Q^0 values for PM (9.19) indicate better adsorption capacity for MB.
- Heat of adsorption (B) 1.8325 indicates strong interactions due to physisorption.
- R^2 values are greater than 0.99 (Langmuir Isotherm) for PM indicating process follows pseudo second order kinetic model.

By considering all above results it can be stated that powdered material (PM) prepared from seeds of Ashoka is an alternative to commercial adsorbents used for the removal of dyes from waste water, also it is cost effective and ecofriendly.

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