WORLD JOURNAL OF PHARMACY AND PHARMACEUTICAL SCIENCES

SJIF Impact Factor 8.025

Volume 13, Issue 8, 864-876 Research Article ISSN 2278 – 4357

ADSORPTION OF METHYLENE BLUE ON CARBONIZED MATERIAL PREPARED FROM SEEDS OF *POLYALTHIA LONGIFOLIA*

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Article Received on 03 June 2024,

Revised on 23 June 2024,
Accepted on 13 July 2024

DOI: 10.20959/wjpps20248-27899

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ABSTRACT

In the present study an attempt has been made to investigate the potential of adsorbent, Carbonized Material prepared from *Polyalthia longifolia* seeds for the removal of Methylene blue from aqueous solution. In the present work batch mode studies are performed to develop all the supporting information on the sorption potential of prepared adsorbent. The effect of amount of adsorbent, initial concentration of dye solution and contact time, temperature and pH of solution is investigated. It is observed that as amount of adsorbent dose increases from 2 to 20 gL^{-1} percent adsorption increases from 74.55 to 92.73 % for a given initial MB concentration (Co = 20 mgL^{-1}). The equilibrium time for the initial concentration from 20 to 4 0 mgL^{-1} was found to be 60 min. while for 50 mgL^{-1} MB solution it takes 120 minutes. It is observed that as the temperature increases from 25 to 45^0C, % removal at equilibrium increases from 57.78 to 68.89 %. Removal of MB is favorable at basic pH. The correlation coefficient, R^2 = 0.9937 indicates applicability of Langmuir isotherm for the equilibrium sorption data of MB using prepared CM. Few reports are available on the use of *Polyalthia longifolia* seeds as biosorbents. Adsorption experiments indicates *Polyalthia longifolia* seeds were effective as biosorbents for the removal of basic dye methylene blue from aqueous solution. It is alternative to cost effective adsorbents.

KEYWORDS: Biosorbent, *Polyalthia longifolia* seeds, Adsorption Isotherms, Carbonized Material.

INTRODUCTION

In the last few decades, adsorption has proved to be one of the effective methods for removal of dyes from effluents. Adsorption involves accumulation of solute molecules at an interface which can be liquid-liquid, gas-solid, gas- liquid or liquid-liquid. The material being adsorbed is termed as adsorbate and the adsorbing phase, is adsorbent. Adsorbent surfaces are often physically and / or chemically heterogeneous and bonding energies may vary from one site to another. Dyes are one of the major pollutants coming from industries, particularly textile industries.[1] Among the various dyes, Methylene blue (MB) is one of the most frequently used cationic dye for dyeing cotton, wool and silk.[2] MB can have various effects on human being and animals. On inhalation, it can give rise to difficulties in breathing while acute exposure to MB can cause increased heart rate, shock, jaundice, cyanosis, eye burns, nausea, vomiting, diarrhea, tissue necrosis in human and methemoglobinemia.[3] It is therefore necessary to remove MB from industrial effluents from the environmental point of view. The treatment of wastewaters by adsorption using biosorbents is an excellent choice as compared to many other methods.[4] Biosorbents must come from nature or even has to be a waste material. In the last few years researchers are now focusing on removal of dyes from effluents using the low-cost adsorbents derived from various waste materials from industries[5], agriculture[6] and also by using marine organisms, yeast, bacteria, seaweeds[7] and mineral waste[8] having equivalent potential as that of commercial activated carbon.[9]

MATERIALS AND METHODS

Preparation of biosorbents

The carbonization of dried seeds was done in absence of air in an air tight bottle, till the constant weight is obtained.[10] The seeds were then ground and sieved to obtained uniform particle size of 0.063 mm. The carbonized material was stored in an air tight bottle and named as Carbonized Material, ‘CM’.

Preparation of Dye Solution

Methylene Blue (MB) (3,9-bisdimethylaminophenazo thionium chloride), having molecular formula $C16H18N3SCl.3H2O$ & molecular weight 373.90g mol^{-1}, has been chosen as the sorbet. 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.

Batch Study

The adsorption of Methylene Blue on Carbonized material were studied by considering the parameters like the effect of adsorbent dose, initial concentration & contact time, temperature and pH by performing batch mode experiments.

Effect of adsorbent dose: The effect of adsorbent dose has been investigated by varying the amounts of adsorbent (CM) from 2 to 20 gL^{-1} is taken in different 100 ml round bottomed 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 with initial concentrations 20, 30, 40 and 50 mgL^{-1} in weighed amount of adsorbents (4 gmL^{-1} CM) 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 Carbonized material. pH of solution is adjusted by using dilute solutions of HCl and NaOH. The 50 ml solution of MB (30 mgL^{-1}) is stirred with 4 gL^{-1} adsorbent dose of CM at different time intervals from 1 to 120 minutes. Absorbance of solution is recorded after filtration.

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

Analytical Method

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

$$\% \text{ Adsorption} = (C0 - Ce) / C0 \times 100 \qquad (1)$$

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

$$qe = (C0 - Ce)\, V / 1000 \times w \qquad (2)$$

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

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

Ce 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 (qt) or at equilibrium (qe), mg/g and the concentration of dye that remain in solution at equilibrium (Ce, mgL^{-1}).

Adsorption Isotherms

The important isotherms; Freundlich, Langmuir and Tempkin have been applied in this study.

Freundlich Isotherm

Freundlich equation is expressed as,

$$qe = KF\ Ce\ 1/n \qquad (3)$$

The linear form of Freundlich isotherm is represented as,

$$\log qe = \log KF + (1/n) \log Ce \qquad (4)$$

Where, KF (mg/g) and 1/n are Freundlich constants. The plot of log qe vs. log Ce are used to determine the values of KF 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.[11]

Langmuir Isotherm

The Langmuir equation is:

$$qe = Q0bCe / 1 + bCe \qquad (5)$$

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[5] in order to evaluate adsorption capacity and Langmuir constant as,

$$Ce/ qe = 1/ (Q0b) + Ce/Q0 \qquad (6)$$

The plot, of Ce/ qe vs. Ce 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[12] (Halls Separation Factor) **R**L, which is defined as:

$$RL = 1 / (1 + b\ C0) \qquad (7)$$

Tempkin Isotherm

The Tempkin isotherm has been used in the form as:

$$q_e = RT / b \ln K_T + RT / b \ln C_e \qquad (8)$$

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

Biosorption efficiency of Carbonized Material (CM) has been tested and the experimental results are-

Effect of adsorbent dose

Effect of adsorbent dose on adsorption of MB by CM, has been investigated by varying the adsorbent dose from 2 to 20 gL^{-1} for various initial MB concentrations (C_0 = 20, 30, 40 and 50 mgL^{-1}) at natural pH of solution, keeping other parameters viz. contact time (30 min.) & temperature (25 ± 2^0C**)** constants. The plots % removal of MB against adsorbent dose (gL^{-1}) of CM, (**Fig.1**) indicate that as dose increases from 2 to 20 gL^{-1} percent adsorption increases from 74.55 to 92.73 % for a given initial MB concentration (Co = 20 mgL^{-1}). The same trend of result has been observed for the various studied initial MB concentrations. It is noticed that as the adsorbent dose is increased from 2 to 20 gL^{-1}, the removal efficiency at equilibrium decreases from 92.73 to 76.99% with increase in initial MB concentration from 20 to 50 mgL^{-1}may be due to increase in collisions between the adsorbate molecules. Similar observations are reported.[13]

Effect of Initial concentration and contact time

The effect of initial concentration and contact time on removal efficiency of MB using CM has been investigated by performing the experiments at different initial concentrations of MB from 20, 30, 40 and 50 mgL^{-1} with varying contact time (1to180 minutes) at original pH of solution, keeping other parameters viz. adsorbent dose (4 gL^{-1}) and temperature (25 ± 2 ^{0}C) constant. The plots of % adsorption and adsorption capacity against varying contact time are depicted in (**Fig. 2** & **3**) respectively. It is observed that the percent removal of MB by CM increases with time and at equilibrium, it reaches a constant value beyond which no more MB is further removed from the solution. The contact time needed for MB solutions to reach equilibrium appears to depend upon initial concentrations of MB. The equilibrium time for the initial concentration from 20 to 4 0 mgL^{-1} was found to be 60 min. while for 50 mgL^{-1} MB solution it takes 120 minutes. This is because initially the dye molecules have to first accumulate at a fast rate at the boundary layer, then diffuse through film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent. Therefore, MB solutions of higher initial concentrations will take relatively longer contact time to attain equilibrium.

The % adsorption at equilibrium is found to have decrease from 83.93%, 73.33 %, 53.68% and 36.28 % with increase in initial concentrations from 20, 30, 40 and 50 mgL^{-1} respectively.[14] The decrease in % removal with increase in concentration was due to increase in collisions at higher concentrations which reduces removal efficiency. Adsorption capacity at equilibrium has been found to be 4.19, 5.50, 5.36 and 4.53 mg/g for the same initial concentrations.

Effect of Temperature

The effect of temperature (25, 35 to 45 ^{0}c) on removal efficiency of MB by CM at optimized conditions of solution pH, adsorbent dose (4 g L^{-1}) and initial MB concentration (C_0 = 30 mg L^{-1}) has been studied and the results are represented in (**Fig.4**). It is observed that as the temperature increases from 25 to 45 ^{0}C the % removal at equilibrium increases from 57.78 to 68.89 %. This may be due strengthening of sorbate-sorbent interactions which have contributed to chemical adsorption of the sorbate. Repeated experiments have however shown that with increase in temperature from 35 to 45 ^{o}C the rate of adsorption in the initial stages increases slightly. Within the first ten minutes % removal is 34.44% for 35^{o}C while at 45^{o}C % removal increased to 37.38%. These results depicts that with increase in temperature chemisorption emerges as the dominant mode of adsorption. Similar results are reported.[15]

Effect of pH

pH of solution plays an important role in the process of adsorption and it is one of the main variable affecting biosorption process. The effect of pH of solution from 2 to 8 on adsorption of MB by CM has been studied at optimized parameters and the experimental results are shown in (**Fig. 5**). As pH of solution increases from 2 to 8 the MB removal at equilibrium largely increases from 38.9 to 70%, indicating the removal of MB is favorable at basic pH. At low pH hydrogen ions compete with cationic dye molecules for sorption sites and restrict the dye removal. As pH of the solution increases, the number of OH^- ions on the adsorbent surface increases, resulting in the increase in adsorption of cationic species of the dye due to electrostatic attraction. Similar results are reported.[16]

Adsorption Isotherms

Analysis of the equilibrium data for the biosorption of MB using CM has been undertaken using adsorption isotherm models namely the Freundlich, Langmuir and Tempkin which are commonly used.

Freundlich Isotherm

The equilibrium is established between the adsorbed dye and that remained unabsorbed in solution is represented by the Freundlich adsorption isotherm. The Freundlich isotherm coefficient (K_F) and intensity of adsorption (1/n) have been evaluated from intercept and slope of the Freundlich plot (log C_e vs. log x/m), as depicted in (**Fig. 6**) using (eq.4). The value of K_F, 3.3635 indicates fairly good adsorption capacity and the 1/n value 0.183 which lies between 0 and 1 indicates favorable adsorption and correlation coefficient, R^2, 0.8785 indicated that the adsorption data of MB on the prepared CM fitted poorly in the Freundlich model.[17]

Langmuir Isotherm

The linear plot of C_e/q_e vs. C_e for MB sorption using CM follows Langmuir isotherm (**Fig.7**). The sorption capacity (Q^0) and b are evaluated from the slope and intercept of the Langmuir plot using (eq. 6). Q^0 has been found to be 6.38 mg/g which is in agreement with experimental value (5.895 mg/g). The value of b 0.3949 indicates good bonding between adsorbate and adsorbent. The correlation coefficient, R^2 = 0.9937 indicates applicability of Langmuir isotherm for the equilibrium sorption data of MB using prepared CM.[18] The values of, Hall separation factor[12], R_L is evaluated in the concentration range studied and is found to be 0.0388 indicating favorable conditions for sorption.[19]

Tempkin Isotherm

The adsorption equilibrium data for MB by CM has been also analyzed by a regression analysis to fit the Tempkin isotherm model (eq.8). ln C_e vs. q is presented in (**Fig. 8**) and the

Tempkin constants KT (L mg^{-1}) and B have been evaluated from the intercept and slope of the plot.[14] The Tempkin isotherm constants KT(L mg^{-1}) and B are found to be 16.4545 and 0.9051 respectively. The correlation coefficient R^2 = 0.8868, shows a poor fit to the experimental data.[20]

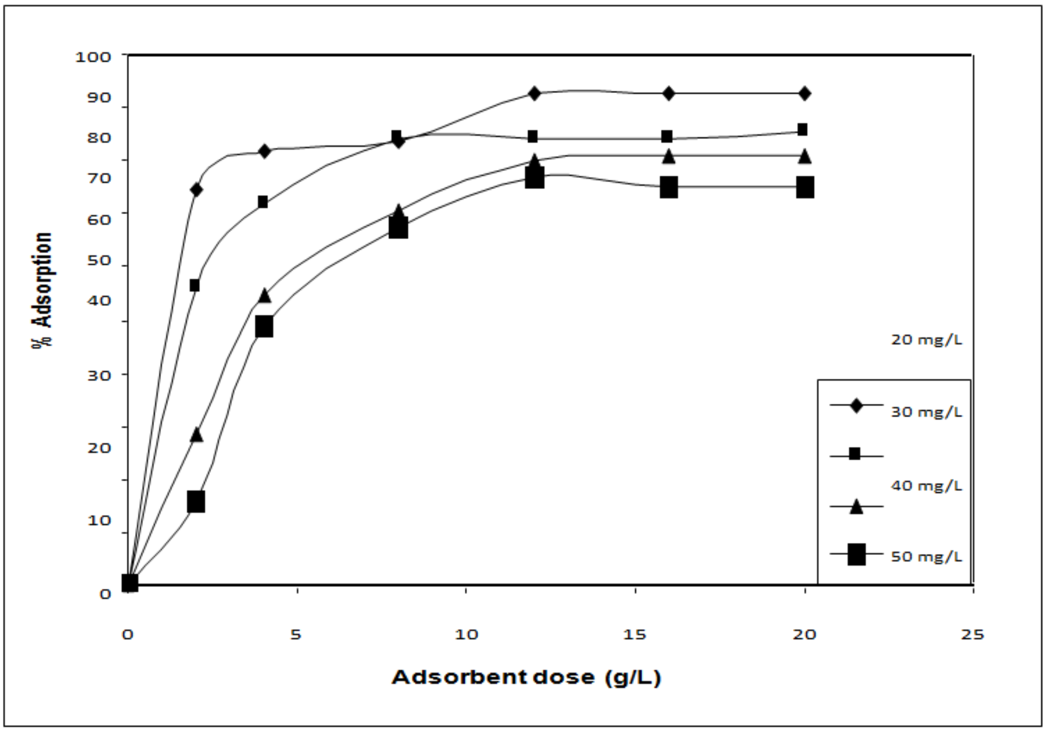

Figure 1: Effect of adsorbent dose on the percent removal of MB using CM (Contact time = 30 minutes, Temp. = 25 ± 2^0C)

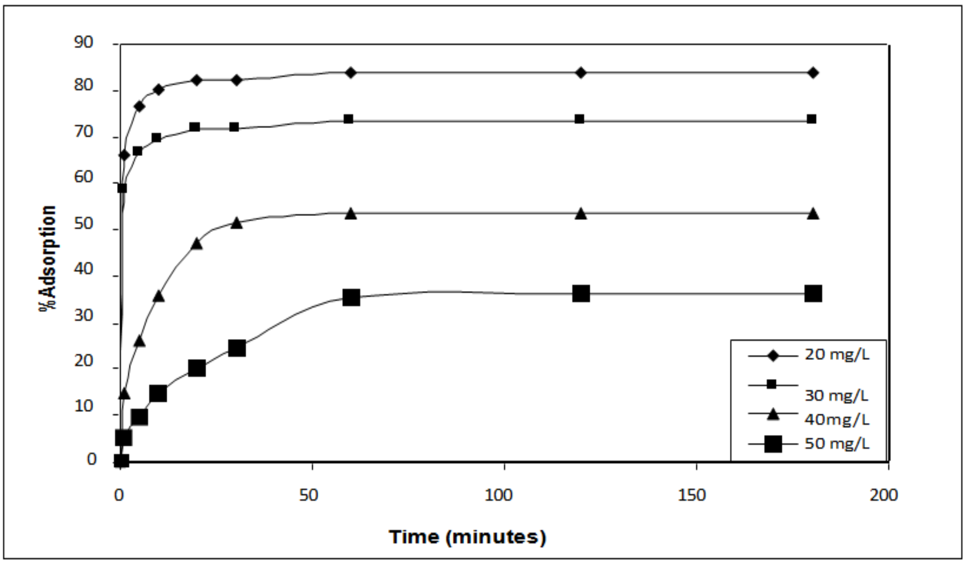

Figure 2: Effect of initial concentration and contact time on percent removal of MB using CM (Temp. = 25 ± 2^0C, Adsorbent dose = 4 g L^{-1})

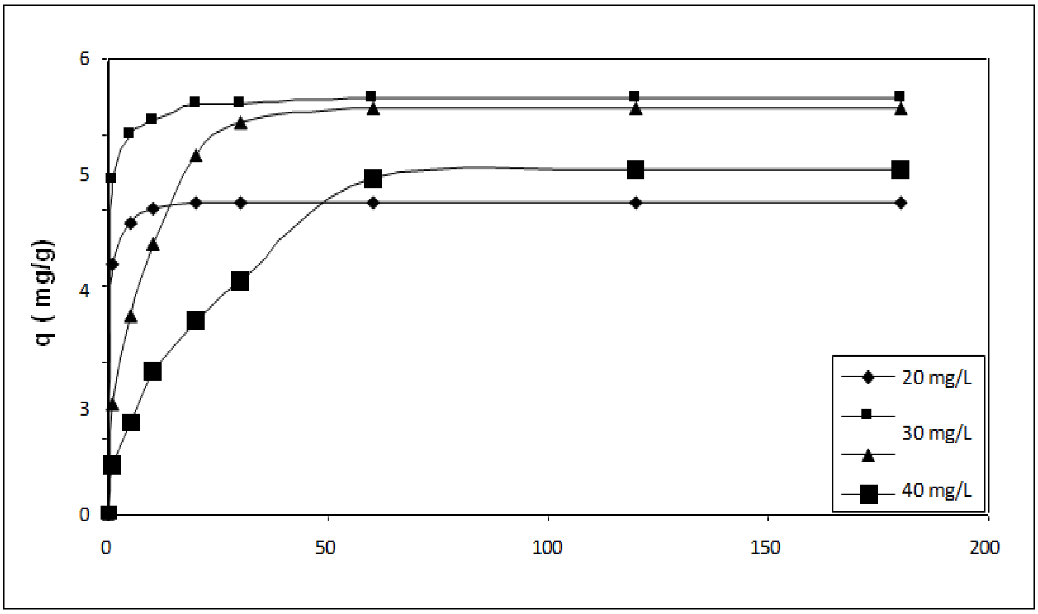

Figure 3: Effect of initial concentration and contact time on the adsorption capacity of CM for MB adsorption (Temp. = 25 ± 2^{0}C, Adsorbent dose= 4gL^{-1})

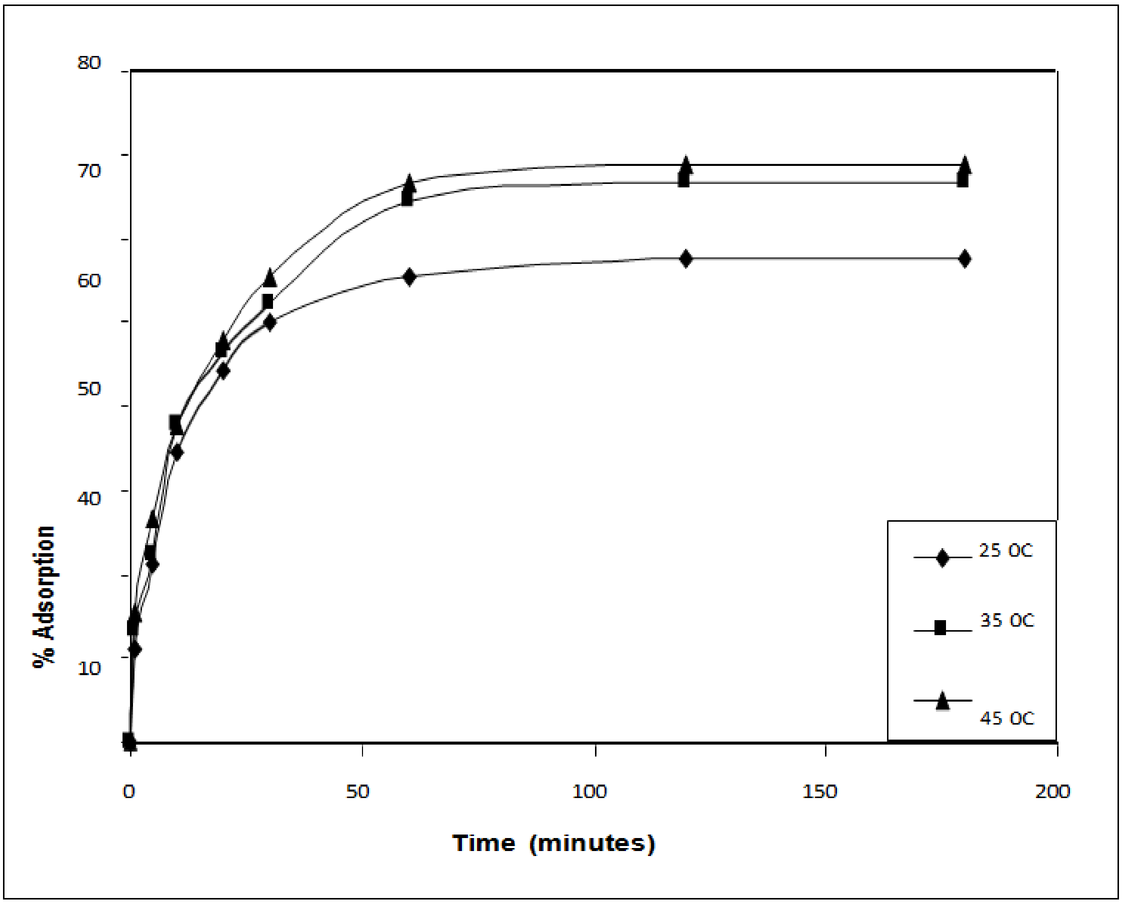

Figure 4: Effect of temperature on percent removal of MB using CM (C0 = 30 mgL^{-1}; Adsorbent dose = 4 gL^{-1})

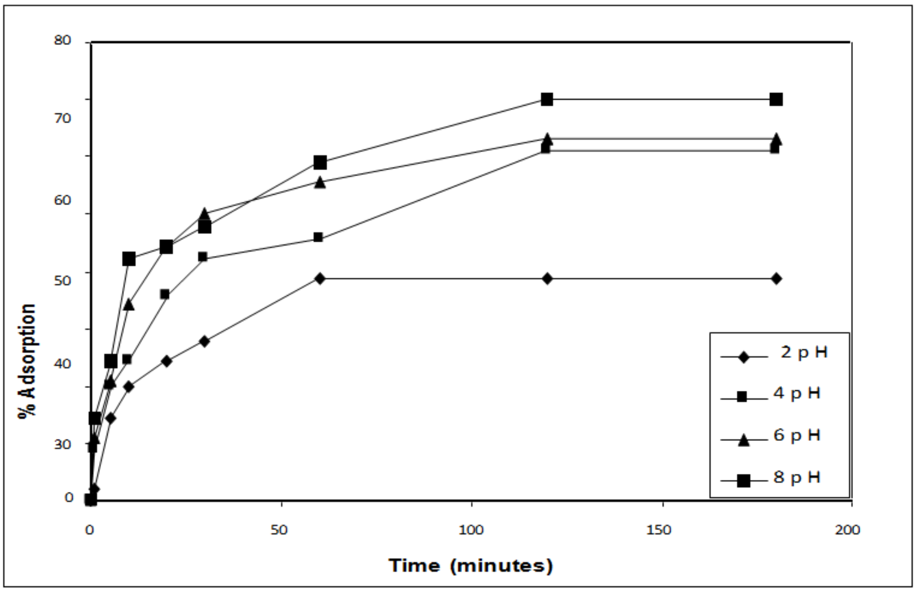

Figure 5: Effect of pH on percent removal of MB using CM (C_0. = 30 mgL^{-1}; Adsorbent dose = 4 gL^{-1}, Temp. = 25 ± 2^0C).

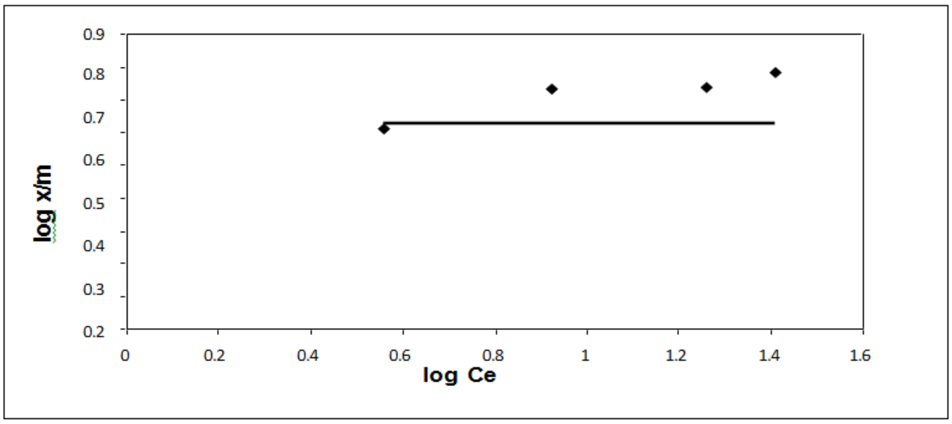

Figure 6: Freundlich Isotherm for adsorption of MB using CM (Temp. = 25 ± 2^0C).

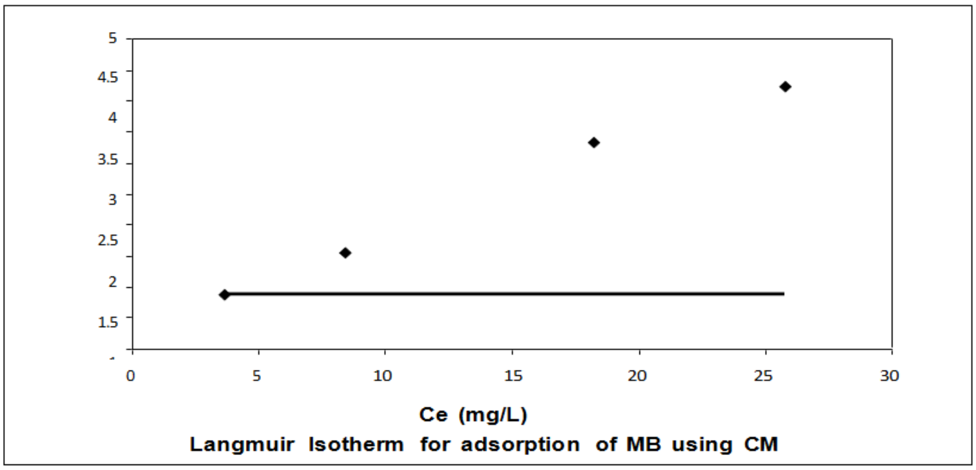

Figure 7: Langmuir isotherm for adsorption of MB using CM (Temp. = 25 ± 2^0C).

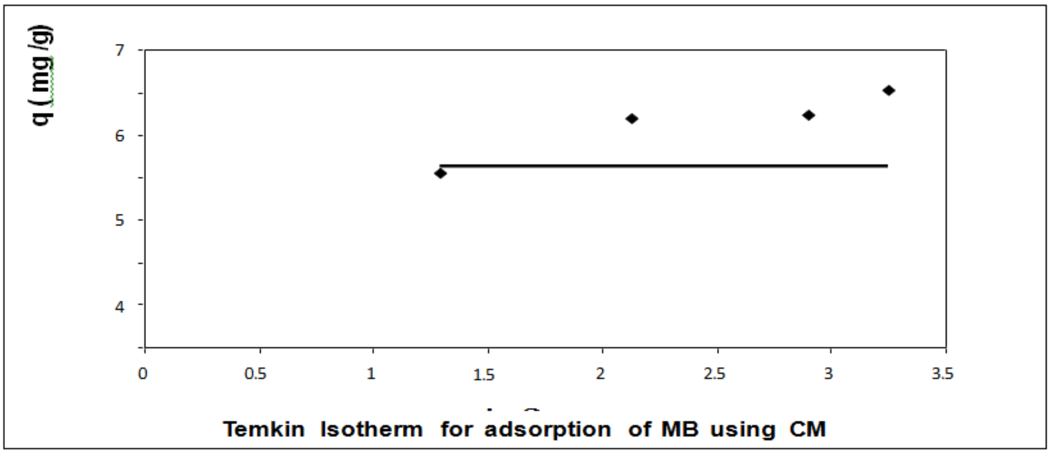

Figure 8: Tempkin Isotherm for adsorption of MB using CM (Temp. = 25 ± 2^{0}C).

CONCLUSIONS

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

- The optimum dose required for maximum percent removal of MB at equilibrium was found to be 4 g L^{-1} of CM.
- For an increase in the dose from 2 to 20 gL^{-1} CM shows an increase in % adsorption from 74.55 to 92.73%.
- 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 CM. As concentration is increased from 20 to 50 mg/L % removal at equilibrium decreases from 83.93 to 36.26% for CM.
- Rise in temperature from 25 to 45 ^{0}C increases % adsorption suggesting endothermic nature of adsorption process with chemisorption.
- The optimum pH for adsorption of MB on CM was found to be 8.
- 1/n value (0.183) lies between 0 and 1 indicating favorable adsorption process.
- R^2 value (0.9937) indicate Langmuir model was best for CM.
- R_L value lies between 0 and 1 confirming the process to be a favorable one.
- Q^0 value for CM (6.38) mg/g indicate better adsorption capacity for MB.
- Heat of adsorption (B) of MB for SATM was highest, 14.3890 indicating strong interactions between surfaces due to chemisorptions.
- R^2 value indicates process follows pseudo second order kinetic model.

ACKNOWLEDGEMENT

The authors are thankful to the Principal Anantrao Thopte College, Bhor, Dist. Pune and Principal S. P. College, Pune for their support and timely help. The authors are very much thankful to the Head, Dept. of Chemistry, S. P. College, Pune, Maharashtra, India for providing laboratory facilities for the research work

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