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Adsorptive removal of methylene blue from aqueous solution using activated carbon from *AnthacephalousCadamba* leaf powder: Equilibrium, Kinetic and Thermodynamic Studies

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ABSTRACT

The uncontrolled discharge of dyes into the natural water bodies is a global environmental concern due to their toxic effects. Increasing environmental awareness is forcing waste creators to consider new options such as adsorption for the disposal of colored wastewaters. Due to prohibitive costs of commercially available activated carbon, low-cost adsorbents with high adsorption capacities have gained increasing attention. The present investigation deals with adsorption of methylene blue on *AnthacephalousCadamba* leaf powder as activated carbon. The batch technique was adopted to know the influence of process parameter such as contact time, solution pH, initial dye concentration, dosage, temperature on biosorption capacity. Adsorption data were modeled using the Freundlich, Langmuir, Tempkin and pseudo first order and pseudo second order kinetic equations. The experimental data fitted well with pseudo second order kinetic model. Thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the systems were calculated. It was found that the adsorption process was feasible, exothermic and spontaneous.

KEYWORDS

Activated carbon;
Methylene blue;
Adsorption;
Isotherms;
Kinetics;
Thermodynamics;
AnthacephalousCadamba.

INTRODUCTION

India's dye industry manufactures various types of dyes, of which 50 % are reactive dyes. Approximately, 70 % of the synthetic dyes belong to the azo group and unfortunately, this class of dyes is the most unfriendly from the ecological point of view, as the effluents are slowly colored, contain high concentrations of salt and present high BOD/COD values[1]. Large amounts of dyes are annually produced and used in paper,textile, pharmaceutical, food, leather, cosmetics and other industries[2]. The textile industry accounts for two thirds of the total dye stuff market[3]. Even a very small amount of dye in water (10-50mg/L) affects the aesthetic value, water transparency and gas solubility in water bodies. Moreover, it may also affect photochemical activities in aquatic system by decreasing light penetration. It has been also described that several frequently used dyes are carcinogenic and mutagenic for aquatic organisms[4]. There are different conventional methods of removing dyes from aqueous solutions. Among these methods, adsorption isa good way the most flexible and widely used method because of its low cost and eases of operation. Therefore, there is the need to look for low

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cost option in easily obtainable bio-materials, which can adsorb dyes from wastewaters[5]. In this paper, we attempt to use activated carbon developed from *Anthacephalous Cadamba* leaves (ACL), as an adsorbent for the removal of dyes from water. The main objective of this study was to evaluate the possibility of using dried ACL to develop a new low-cost activated carbon and study its application to remove Methylene blue (MB) from simulated wastewater. The various parameters such as pH, adsorbent dose, initial dye concentration, time and temperature were investigated.

EXPERIMENTAL

Materials

ACL Activated Carbon (ACLAC) is used as adsorbent for dye removal. It is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

Preparation of activated carbon from leaf powder

Objective of an activation process is to increase the volume and diameter of the pores. The leaves were washed, dried and powdered. The powder was carefully weighed and put in beaker containing of chemicals such as $ZnCl_2$ and HCl.

The content of the beaker was thoroughly mixed until it forms a paste. The paste was then transferred to a crucible and the crucible was placed in a Muffle furnace and was heated to 600^0C for two hours activated sample was then cooled at room temperature, and washed with distilled water to a pH of 6 – 7, and dried in an oven at 90^0C for 24 hours. The final product was kept in an air tight polyethylene bag, ready for use. Before for the use of powder is crushed and sieved. The powder was screening through 150 mesh and retained pan. The powder is taken for the experimental analysis.

Dye solution

Stock solution of MB, concentration 1000 mg/L was prepared by dissolving 1g of MB in 1000 ml of distilled water. The range of concentration of prepared solutions varied between 10 and 50 mg/L.

RESULTS AND DISCUSSION

The experimental data on adsorption were obtained batch wise to study the effect of parameters on the removal of dye from the synthetic solutions prepared in the laboratory by ACLAC. All the experimental runs were conducted triplicate.

Adsorption studies

(a) Effect of contact time

The Figure 1 showed that a contact time of 30 min for MB was required to achieve an optimum adsorption and there was no significant change in concentration of the dye solution with for some time increase in contact time. A rapid uptake of adsorbate by an adsorbent is mainly predominant when applied to wastewater treatment by means of adsorption which signifies the efficacy of an adsorbent to be used in wastewater treatment[6]. Therefore, the uptake and unadsorbedMB concentration at the end of 30 min are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L). For further studies of adsorption with other variable parameters, the time of 30 min has been chosen for contact period. And lastly equilibrium time is one of the important considerations for economical water and wastewater applications.

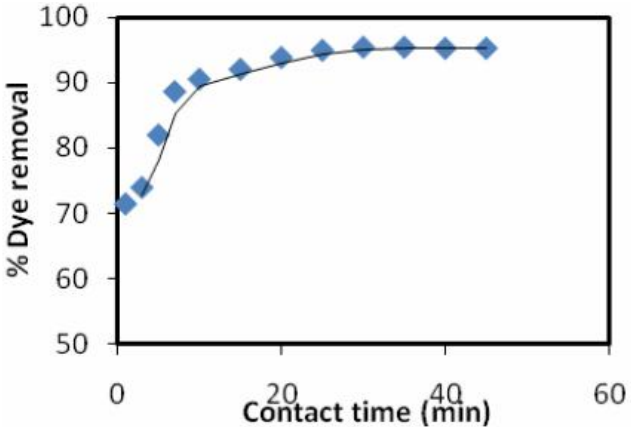

Figure 1 : Effect of contact time of MB dye removal and dye uptake by ACLAC for 10mg/L of dye at 0.1g/50ml of adsorbent concentration

(b) Effect of pH

The removal of MB as function of hydrogen ion concentration was examined at pH 4-12. The removal efficiency was found to be highly dependent on the hydrogen ion concentration of solution. The effect of pH on adsorption efficiency is shown in Figure.2. the high adsorption yield was obtained at pH 10. The maximum adsorption efficiency was 95.36% at pH 10

and this pH is selected as optimum pH for further studies. As the pH increased the ligands such as carboxylate groups would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of dye ions with positive charge and allowing the adsorption onto the cell surface[7].

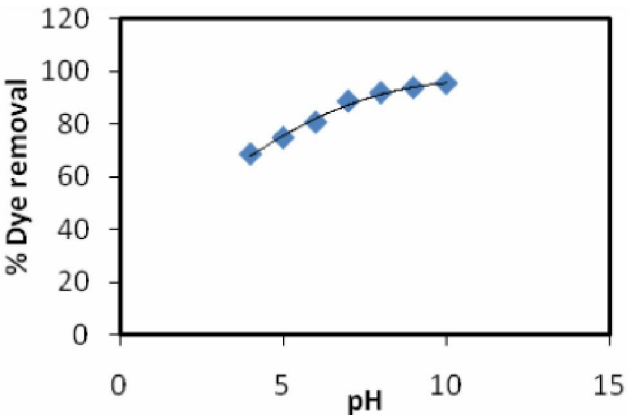

Figure 2: Effect of pH of MB dye removal and dye up take by ACLAC for 10mg/L of dye at 0.1g/50mL of adsorbent concentration

(c) Effect of initial dye concentration

In series to study the effect of initial concentration of MB in the solutions on the rate of adsorption on dye, the experiments were transfer out at a fixed adsorbent dosage (0.1g) and at different initial dye concentrations of MB (10,20,30,40,50mg/L) for optimum time contact (30min) at room temperature. Figure 3. shows the effect of initial dye concentration on the adsorption. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration.

(d) Effect of adsorbent dosage

For studying the effect of adsorbent dosage on removal of dye, the adsorbent dosage is varied from 0.02 to 0.1g, fixing the other parameters like initial concentration at 10mg/L, and pH 10. The contact time was 30min for MB stated earlier. The adsorption plot of Figure 4. Shows an increase in % adsorption with an increase in adsorbent dosage. This is because of availability of more binding sites for complexion of ions.

(e) Effect of temperature

The effect of temperature on % dye removal was shown in Figure.5. The percentage adsorption of MB on to ACLAC decreased from 95.36 to 90.6% as the temperature increased from 298 to 318K at 10mg/L. The percentage adsorption at higher temperature levels

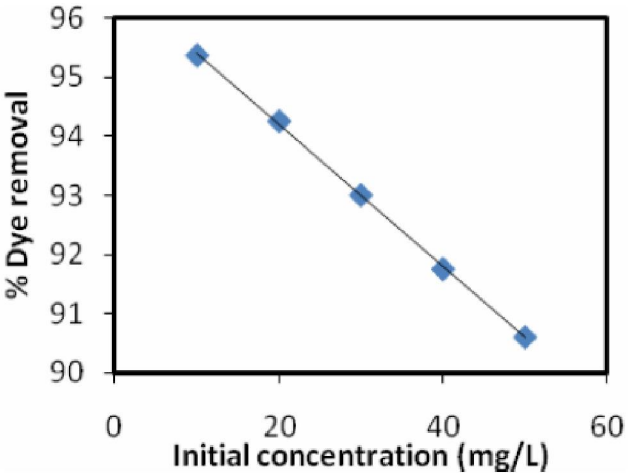

Figure 3 : Effect of initial concentration of MB dye removal and dye uptake by activated carbon for 10mg/L of dye at 0.1g/50mL of adsorbent concentration

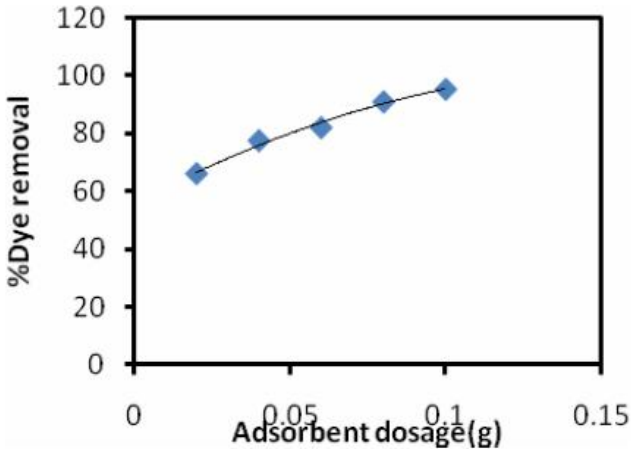

Figure 4 : Effect of adsorbent dosage of MB dye removal and uptake (mg/g) by ACLAC for 10mg/L of dye at 0.1g/50mL of adsorbent concentration

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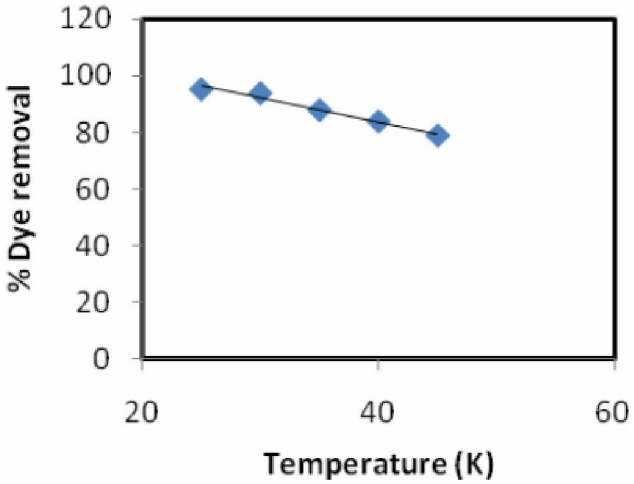

Figure 5

shows a decreasing trend because at lower temperatures, all dye ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher temperature. This happens because of more interaction of the ions with solution due to convection[8].

Adsorption isotherms

(a) Langmuir isotherm

Langmuir isotherm is a basic expectation that adsorption takes places at homogenous sites within the adsorbent. The Langmuir isotherm model is represented by the following equation[9].

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{k_L q_{max}} + \frac{1}{q_{max}} C_{eq} \qquad (1)$$

Where q_e (mg/g^{-1}) is the amount of dye adsorbed per unit mass of adsorbent, C_e(mg/L) is the equilibrium dye ion concentration in the solution, q_{max} (mg/g) is the Langmuir constant related to the greater monolayer adsorption capacity and k_L (L/mg) is the constant related to the free energy or net enthalpy of adsorption.

The Langmuir constants q_m and k_L are assess from the slope and intercept of the linear plot of C_e/q_e versus C_e.

(b) Freundlich isotherm

The linearized form of the Freundlich equation is as follows:

$$Log\ q_{eq} = log\ K_f + 1/n\ log\ C_{eq} \qquad (2)$$

WhereQe is the amount of dye adsorbed at equilibrium, Ce is the concentration of the dye solution at equilibrium and 1=n is empirical constant and indicate adsorption capacity and intensity, respectively. Their values were obtained from the intercepts (ln versus lnCe.K) and slope (1=n) of linear plots of lnq_e.

(c) Tempkin isotherm

The derivation of the Tempkin isotherm concluded that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation[10]. The Tempkin isotherm has normally been applied in the Freundlich equation. The Tempkin isotherm has generally been applied in the following form[11].

$$q_{eq} = \frac{RT}{b_T} \ln\left(A_T C_{eq}\right) \qquad (3)$$

This can be written as,

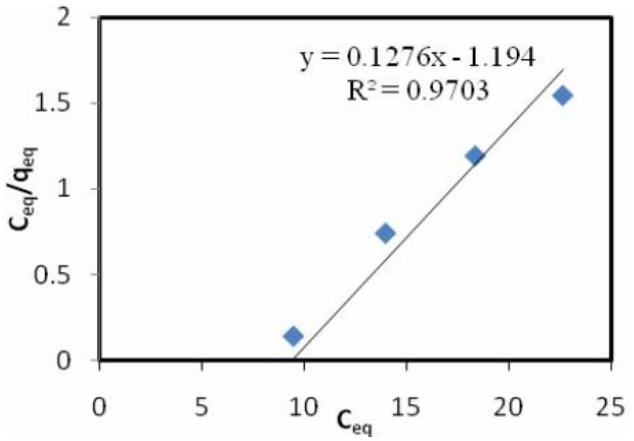

Figure 6 : Langmuir isotherm for MB dye by ACLAC for various concentrations of dye at 0.1g/50ml of adsorbent concentration

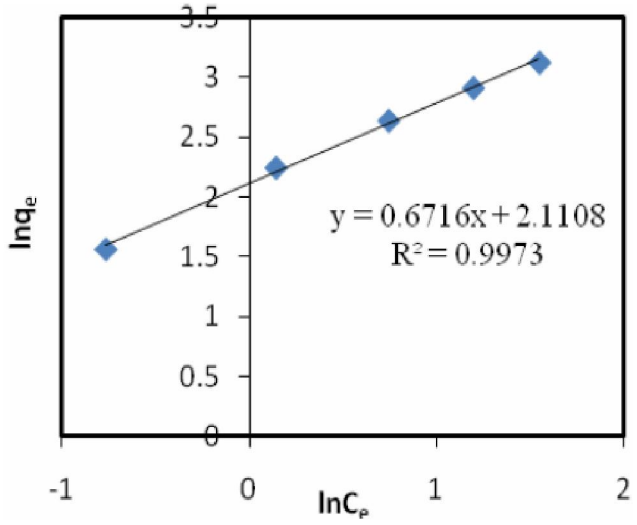

Figure 7 : Freundlich isotherm for MB dye by ACLAC for various concentrations of dye at 0.1g/50ml of adsorbent concentration

$$q_{eq} = \frac{RT}{b_T} \ln C_{eq} + \frac{RT}{b_T} \ln A_T. \quad (4)$$

Where A_T (L/mg) and b_T are Tempkin isotherm constants.

For Tempkin isotherm the constants A_T, B_T were observed as 0.3387 and 151.60. The correlation coefficients obtained from the Tempkin Isotherm model are 0.8688 for MB.

The correlation coefficients obtained from the Langmuir, Freundlich and Tempkin Isotherm models were found to be 0.9703, 0.9973 and 0.8688. Freundlich model was observed to be more suitable, followed by Langmuir model for the experimental data.

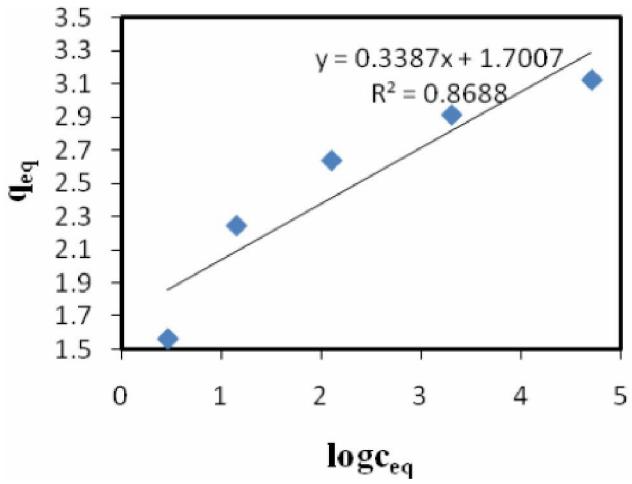

Figure 8 : Tempkin isotherm for MB dye using ACLAC powder for various concentrations of dye at 0.1g/50ml of adsorbent concentration

Adsorption kinetics

Kinetics of adsorption data was examined using two kinetic models, pseudo-first order and pseudo-second order. These models correlate solute uptake, which are predominant in forecasting the reactor volume. These models are explained as follows:

(a) Pseudo-first order model

The possibility of adsorption data following [12]pseudo-first order kinetics is given by

$$\frac{dq}{dt} = K_1(q_{eq} - q) \quad (5)$$

Integrating Eq. (5) with respect to integration conditions q=0 to q=q at t=0 to t=t, the kinetic rate expression becomes

$$\log(q_{eq} - q) = \log q_{eq} - \frac{K_1}{2.303} t \quad (6)$$

In order to obtain the rate constant, the straight-line plot (Figure-4.1.14) of log (q_{eq}-q) versus time (t)was made of ACLAC powder for initial MB concentrations, 10mg/l. The intercept of the above plot should be equal to log q_{eq}. However, if q_{eq} from intercept does not equal to the equilibrium MB dye uptake then the reaction is not likely to be first order, even this plot has high correlation coefficient with the experimental data. The correlation coefficient was found to be 0.9675, but the calculated q_{eq} is not equal to experimental q_{eq}, suggesting the insufficiency of Pseudo-first-order model to fit the kinetic data for the initial MB concentration examined.

(b) Pseudo-second order model

A pseudo-second order model suggested by[13] was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorption. The pseudo-second order model can be expressed as

$$\frac{dq}{dt} = K_{II}(q_{eq} - q)^2 \quad (7)$$

Separating the variables in Eq. (7) gives:

$$\frac{dq}{(q_{eq} - q)^2} = K_{II} dt \quad (8)$$

Where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) are the amount of dye adsorbed at equilibrium and at any time, t. The correlation coefficients were found to be 0.9997 for initial concentrations 10 mg/L. therefore pseudo second order kinetic model fitted well with the adsorption process. TABLE 1 gives the comparison of kinetic constants and dye uptake.

Thermodynamic studies

Thermodynamic parameters such as Enthalpy change (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o) can be calculated using equilibrium constants become different with temperature. The free energy change of the sorption reaction is given by the following equation:

$$\Delta G^o = -RT \ln K_c \quad (9)$$

Where ΔG^o is standard free energy change in J, R the universal gas constant, 8.314 $Jmol^{-1}$ K^{-1}, and T the absolute temperature, K. The free energy change indicates the degree of spontaneity of the adsorption process and the negative value reflects more firmly favorable adsorption.

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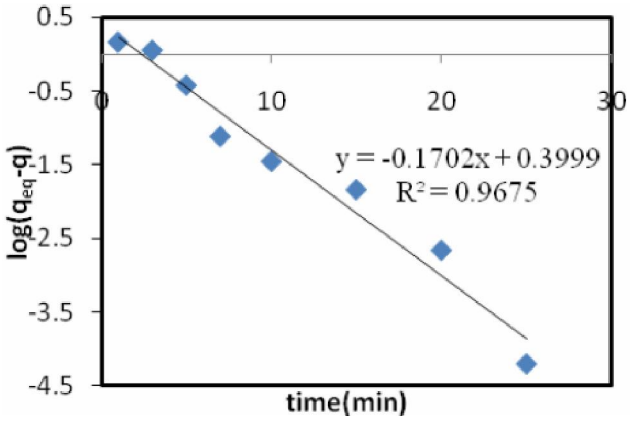

Figure 9 : Pseudo first order kinetics for MB dye by ACLAC for 10mg/l of dye at 0.1g/50ml of adsorbent concentration

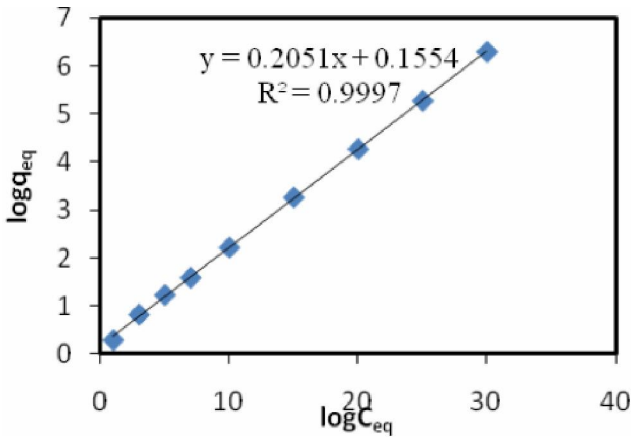

Figure 10 : Pseudo second order kinetics for MB dye by activated carbon for 10mg/l of dye at 0.1g/50ml of adsorbent concentration

TABLE 1 : Comparision of kinetic studies

Psuedo first order	Psuedo second order
K_1 = 1.1702	K_2 = 0.27
q_e = 1.490mg/g	q_e = 4.87mg/g
R^2 = 0.9675	R^2 = 0.997

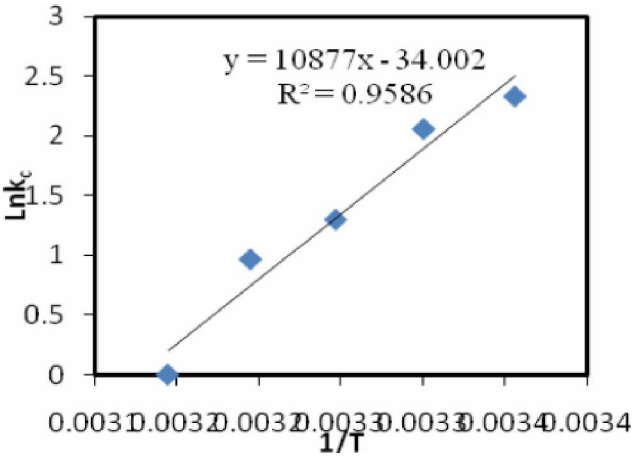

Figure 11 : Plot of Lnk$_c$ vs 1/T

$$\ln K_a = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (10)$$

From the Figure.11 (i.e lnK$_c$ versus 1/T) standard Gibs energy change was found to be -22.91KJ/mol, the standard enthalpy change ΔH^o was obtained as -66.266KJ /mol, while the standard entropy change ΔS^o was insisted as -145.47 kJ /mol K at pH 10. The value of ΔH^o is negative, indicating that the sorption reaction is exothermic.

CONCLUSION

This study established that the adsorbent prepared fromACLAC, a low cost agricultural waste, could effectively remove MB from an aqueous solution. Effects of process variables such as contact time, pH, dosage, initial dye concentration and temperature influence the adsorption process. Removal of MB using ACLAC can be best fitted by the Freundlich model. The kinetics of adsorption of MB onto ACLAC described well with the pseudo second order model. The adsorption of MB onto adsorbent is a feasible, spontaneous and exothermic process.

REFERENCES

[1] S.Saraf, V.K.Vaidya; Int J.Ind.Chem, **6**, 93–104 **(2015)**.
[2] P.K.Malik; Dyes and Pigments, **56**, 239-249 **(2003)**.
[3] P.Chulhwan, M.Lee, B.Lee, S.Kim, A.Howard, J.Lee, S.Kim; Biotech Engineering Journal, **36**, 59-65 **(2007)**.
[4] R.Aravindhan, J.Raghava Rao, U.N.Balachandran; Journal of Hazardous Materials, **142**, 68-76 **(2007)**.
[5] T.Santhi, S.Manonmani; Chemical engineering research bulletin, **13**, 1-5 **(2009)**.
[6] L.B.L.Lim, N.Priyantha, D.T.B.Tennakoona, H.I.Chienga, M.K.Dahria, M.Suklueng; Arabian Journal of chemistry, **39(9)**, 6757-6765 **(2014)**.
[7] K.Vasanthkumar, S.Sivanesan, V.Ramamurthi; Process Biochemistry, **40**, 2865-2872 **(2005)**.
[8] A.Ozer, G.Akkaya, M.Turabik; Dyes and pigments, **71**, 83-89 **(2006)**.
[9] C.Aharoni, M.Ungarish; J.Chem.Soc.Far.Trans, **73**, 456-464 **(1977)**.

[10] C.Aharoni, D.L.Sparks; Madison WI, 1-18 **(1991)**.
[11] I.Langmuir; J.Am.Chem.Soc, **40**, 1316-1368 **(1916)**.
[12] S.Lagergren, S.S.Kungliga; Handling Band, **2(4)**, 1 **(1898)**.
[13] Y.S.Ho, G.Mckay; Can J.chem. Eng, **76**, 822-827 **(1998)**.