Equilibrium, Kinetic and Thermodynamic studies of biosorption of Methylene Blue dye using plant biomass as biosorbent: Optimization using Response Surface Methodology (RSM).

Kalpana Polipalli, King Pulipati

Abstract—The use of low cost and eco-friendly biosorbent was investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. In this study, the sorption of Methylene Blue (MB) on Bauhinia purpurea L. (BPL) biomass was investigated in a batch system. The rate of biosorption was investigated under various parameters such as temperature, biosorbent dosage, pH, contact time and initial dye concentration on the sorption of MB. Response surface methodology (RSM) was used to optimizing the process parameters. BPL was characterized by using scanning electron microscope (SEM) and Fourier Transfer for infrared spectrophotometer (FTIR). Equilibrium isotherm was analyzed using the Langmuir, Freundlich and Temkin isotherm models. The characteristic parameters for each model have been determined. The sorption kinetics of MB onto BPL was described by pseudo-second order kinetic equation. Thermodynamic activation parameters such as ΔG^0, ΔS^0 and ΔH^0 were also calculated.

Index Terms— Response surface methodology, Bauhinia purpurea, methylene blue , biosorption, kinetics, isotherms, thermodynamic studies.

1 INTRODUCTION

Concern about environmental protection has increased over the years from a global view point. Today, rapidly changing technologies, industrial products and practices generate waste that if improperly managed, could threaten public health and the environment. Therefore, elimination of heavy metals and synthetic compounds are attempted by many researchers.

Effluents from industries such as dyestuff, textiles, leather, paper, printing, plastic and food contain various dyestuffs. Dye, a highly coloured and synthetic substance contains at least one chromophores (colur bearing group) and auxochromes (colour helpers) which impart intense colors to them and are undesirable and disgusting in wastewater. There are various conventional methods of removing dyes from waters. Among these methods, adsorption is by far the most versatile and widely used method because of its low cost and eases of operation. A number of agricultural waste and by-products of cellulose origin have been studied for their capacity to remove dyes and heavy metals from aqueous solutions, such as peanut hulls [1], maize bran [2], sawdust [3], sugar beet pulp [4], crab shell [5], cornstarch [6], rice husk [7], chitin [8], orange waste [9], Araucaria cookii bark [10] and aqua cultural shell powders [11].

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The aim of the present study is to investigate the influence of pH, contact time, dosage, initial dye concentration and temperature on the biosorption of MB by the BPL. Different isotherms were used to derive the adsorption parameters. The process optimization was also studied. The materials were characterized by FTIR and SEM techniques.

2. MATERIALS AND METHODS:

2.1. PREPARATION OF ADSORBATE

A cationic dye, MB, having molecular formula $C_{16}H_{18}N_3SCl.3H_2O$ was chosen as adsorbate. MB (Basic Blue 9) was purchased from Fischer inorganics and Aromatics Ltd. Chennai, India. The MB was chosen in this study because of its known strong adsorption onto solids. The dye stock solution was prepared by dissolving accurately weighted MB in distilled water to the concentration of 1000 mg/L. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations.

2.2. PREPARATION AND CHARACTERIZATION OF BPL

The BPL was collected from GMR Institute of Technology campus of Rajam, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt and sun dried. Then the dried leaves were powdered using domestic grinder to the powder size of 81-212 µm and used as biosorbent without any pretreatment for MB adsorption. Infrared (IR) spectra of the BPL samples were recorded in the region 4000 to 500

cm^{-1} on a spectrum – 100 FTIR spectrometer. SEM analysis was carried out on the BPL to study its surface texture before and after MB adsorption.

2.3. Experimental Procedure

Batch biosorption experiments were carried out at room temperature. The stock solution of MB (1000 mg/L) was prepared and suitably diluted to the required initial concentrations (20 –100 mg/L). The experiments were carried out in 250 ml flasks containing 30 ml of synthetic dye solution. The flasks were agitated on a shaker at constant speed of agitation for 60 min. The final equilibrium concentrations were measured spectrophotometrically at 665 nm using UV spectrophotometer. Various experimental conditions such as initial dye concentrations, dosage, pH and contact time were studied. The percentage removal of dye and amount adsorbed (mg/g) were calculated using the following relationships:

$$\% \text{ color removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad \text{---------- (1)}$$

$$\text{Dye uptake, } q = \frac{(C_i - C_f)\frac{v}{m}}{} \quad \text{---------- (2)}$$

Where C_i is the initial sorbent concentration (mg/L), C_f is the final sorbent concentration (mg/L), v is the volume of the solution (L) and m is the mass of the biosorbent (g).

2.4. Experimental design and data analysis

The aim of RSM is to find out the optimum operating conditions for a given system, or the way in which a particular response is affected by a set of variables. The quadratic response surface model over some specific region of interest was fitted to the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \quad \text{----------(3)}$$

Where Y is the predicted response ; X_1, X_2, X_3, and X_4 are independent variables; b0 is an offset term; b_1, b_2, b_3 and b4 are linear effects; b_{11}, b_{22}, b_{33} and b_{44} are squared effects; and b_{12}, b_{13},b14, b_{23}, b_{24} and b_{34} are interaction terms.

The ''Design Expert'' software (statistical package STATISTICA 6.0 (Stat Soft Inc.) was used for regression and graphical analysis of the data obtained. The operational conditions were independence variables which were X_1 (temperature), X_2 (pH), X_3 (dosage) and X_4 (initial dye concentration). The intervals of reaction parameters were selected as 30 – 50^0C for temperature, 8 -12 for pH, 0.02 to 0.1 for dosage and 20 -100 mg/L for initial dye concentration. The experimental range and levels of the independent variables are indicated Table 1.

Table.1: Levels of different process variables used in CCD for removal of MB dye.

Factor	Symbol	Level				
		-2	-1	0	+1	+2
Temperature, ^{0}C	x_1	30	35	40	45	50
pH	x_2	8	9	10	11	12
Dosage, g	x_3	0.02	0.04	0.06	0.08	0.10
Initial dye concentration mg/L	x_4	20.00	40.00	60.00	80.00	100.00

3. Results and Discussion:

3.1. Surface Characterization

The FTIR spectra(Fig.1a) of BPL showed peaks at 3298, 2900, 2350, 1610, 1317, 1242, 1149, 1052, 779, 648, 594 cm^{-1} which may be assigned to the OH group, CH stretching, CH_2 group, C= O stretching, NO_2 aromatic nitro compound, C – O stretching, C- N stretching, CH bendng vibrations(aromatics) respectively [12] . The intensity of the peaks were either minimized or shifted slightly in case of adsorbed BPL (Fig. 1b). These results are similar to the ones reported earlier [13,14].

Fig. 2 shows the SEM micrographs of BPL sample before and after dye adsorption. It is clear that BPL has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye to be adsorbed. The surface of dye-loaded adsorbent, however, clearly shows that the surface of BPL is covered with dye molecules (Fig. 2b).

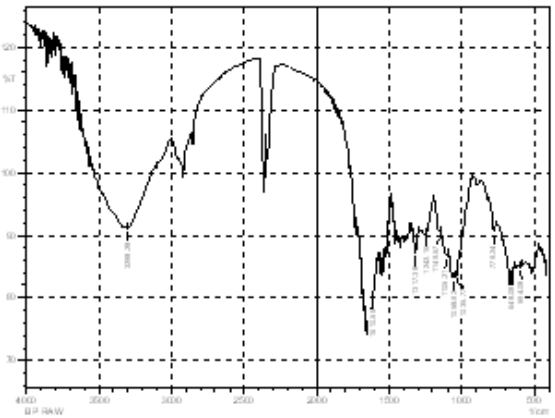


Figure.1a.FTIR Spectra BPL before adsorption

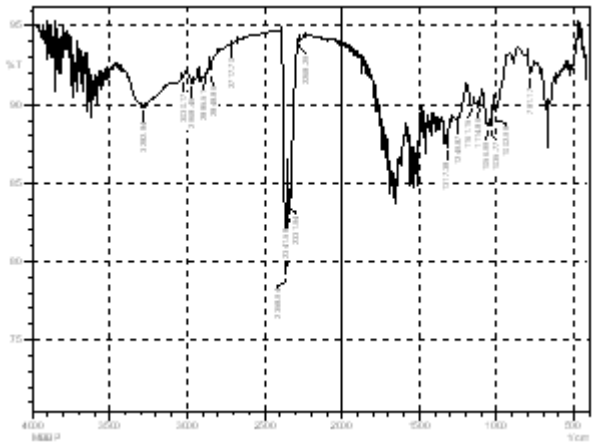


Figure. 1b FTIR Spectra BPL after MB adsorption

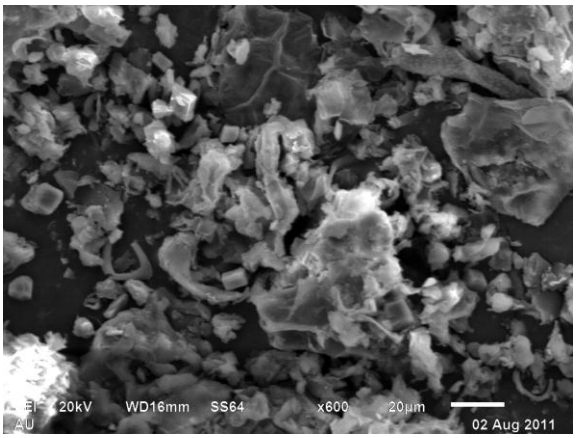


Figure.2a. SEM OF BPL before adsorption

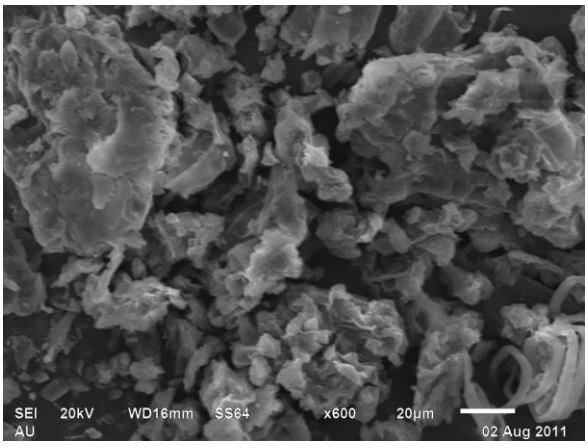


Figure.2b. SEM of BPL after MB adsorption

3.2 EFFECT OF CONTACT TIME AND CONCENTRATION

The data obtained from the biosorption of MB on the BPL showed that a contact time of 20 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and un -adsorbed MB concentrations at the end of 20 min are given as the equilibrium values (q_e, mg/g; C_e , mg/L), respectively (Fig.3) and the other adsorption experiments were conducted at this contact time. A large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [15, 16, 17]. This results in the slowing down of the adsorption during the later period of adsorption [18].

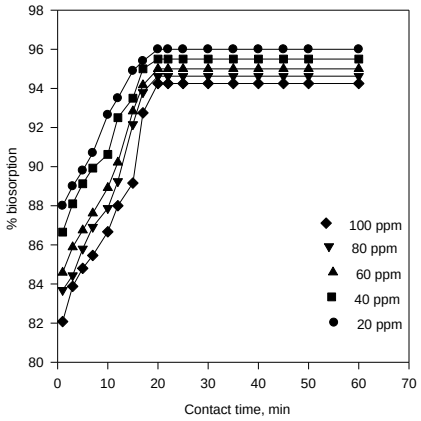


Figure.3. Effect of contact time

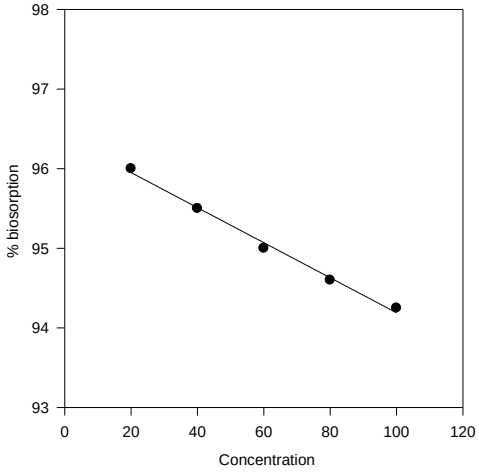


Figure.4. Effect of initial dye concentration

Fig. 4 shows the effect of initial dye concentration on the adsorption of MB by BPL. The percentage removal of dye is highly dependent on the initial amount of dye concentration. The data shows that the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. At a 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 lack [19]. On the other hand the increase in 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 transfer at a high initial dye concentration [20].

3.3 Effect of pH and dosage

MB is a cationic dye, which exists in the aqueous solution in the form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH [21]. Fig. 5 shows the effect of pH on the BPL adsorption capacity of MB. It was found that, the removal of MB increased with the increase of pH. Lower adsorption of MB at low pH is probably due to the presence of H+ ions competing with the cations groups on the dye for adsorption sites [22]. As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged MB and the surface of the BPL is lowered, this may result in an increase in the rate of adsorption. The maximum percentage of biosorption was observed at pH 10. Above this point, adsorption of MB on BPL decreases. Similar trends were reported in the literature for the adsorption of basic dyes, methylene blue onto jute fiber carbon. [23].

The adsorption of the dyes on BPL biomass was studied by varying the sorbent dosage (0.02 to 0.1 g in 30 mL). The percentage of adsorption was increased as the adsorbent concentration increased shown in Fig.6. This increase is due to the availability of larger surface area with more active functional groups at higher adsorbent dosages.

3.4 Effect of temperature

Fig.7 shows the effect of temperature on the biosorption kinetics of BPL at a pH of 10. It was observed that with increasing temperature from 30 to 500C the adsorption capacity of BPL decreased. This indicates that adsorption of dyes onto BPL is controlled by exothermic process and the maximum adsorption is nearly 96% at 20 min at 300C. Results shows that temperature plays an important role on the dye adsorption capacity of BPL. At high temperatures, the thickness of the boundary layer decreases, due to the increased tendency of the dye to escape from the biomass surface to the solution phase, which results in a decrease in temperature as temperature increases. The decrease in adsorption with increasing temperature suggests weak adsorption interaction between biomass surface and the dye.

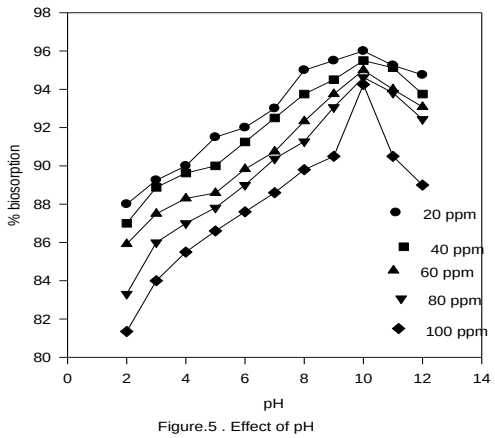


Figure.5 . Effect of pH

Figure.6. Effect of biosorbent dosage

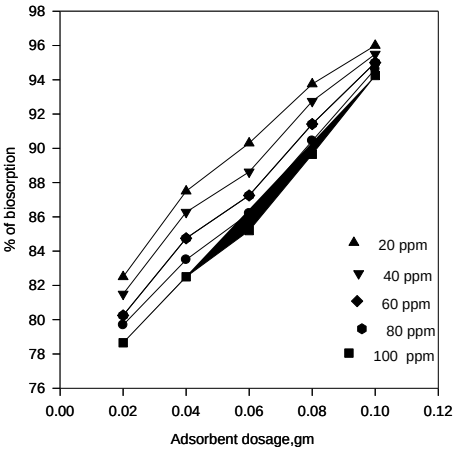
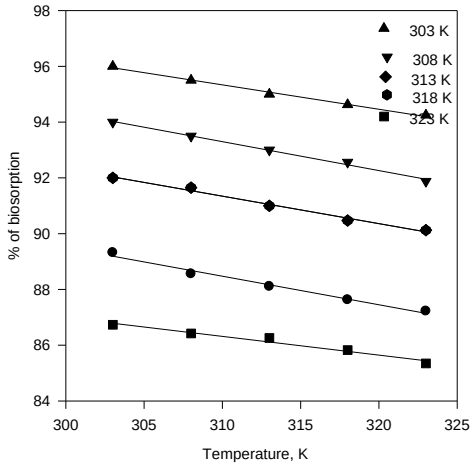


Figure.7. Effect of Temperature



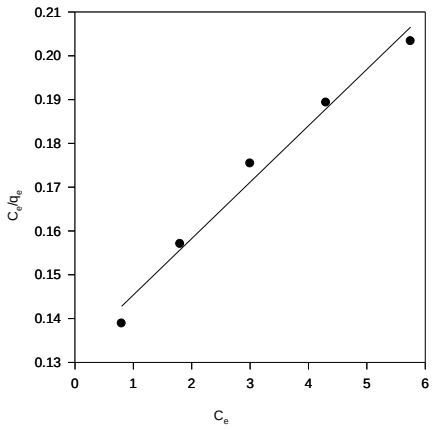
3.5 Modeling Adsorption Isotherms

In order to indicate the adsorption behavior and to estimate the adsorption capacity, adsorption isotherms were studied. The analysis of the isotherm data through fitting with different isotherm models is an important step in finding the suitable model that can be used for design purpose. The isotherm data were fitted to the Langmuir, Freundlich and Temkin isotherms. Langmuir isotherm [24] is represented by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad \text{---------- (4)}$$

where q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively (Fig. 8). The Langmuir constants b and q_m were calculated from this isotherm and their values are listed in Table 2.

Figure.8. Langmuir isotherm for adsorption of MB on BPL



The Freundlich model can take the following form [25]:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{---------- (5)}$$

where kf is the Freundlich constant (mg/g (mg/L)n) and 1/n is the heterogeneity factor. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [26]. The plot of $\ln q_e$ versus $\ln C_e$, (Fig. 9), gives straight lines with slope 1/n. Accordingly, Freundlich constants were calculated and recorded in Table 2.

Temkin isotherm [27] is represented by the following equation:

$$q_e = A \ln K_T + A \ln C_e \quad \text{---------- (6)}$$

The adsorption data were analyzed according to Eq. (6). A plot of qe versus lnCe , Fig. 10, enables the determination of the isotherm constants K_T and A. K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy and constant A is related to the heat of adsorption. The values of the parameters are given in Table 2, indicating that the Freundlich isotherm model yielded the best fit with the highest r^2 value (0.9994) compared to the Langmuir and Temkin models.

Figure.9 Freundlich isotherm for adsorption of MB on BPL

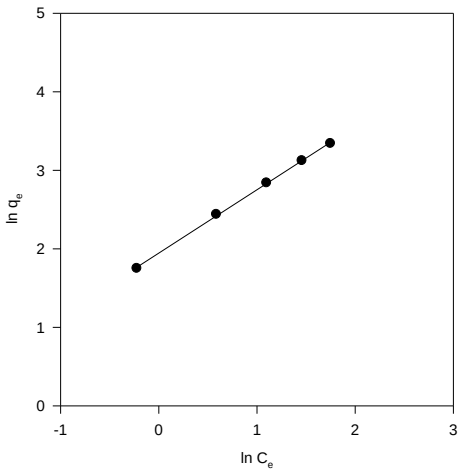


Figure.10. Temkin isotherm for adsorption of MB on BPL

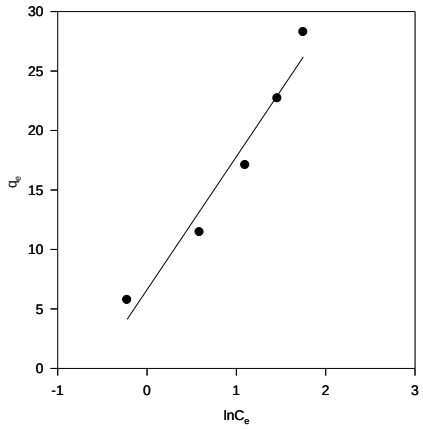


Table.2: Adsorption isotherms and corresponding parameters for MB binding by BPL.

Langmuir model	Freundlich model	Temkin model
$q_m = 77.63$	$1/n = 0.8066$	$A = 11.1833$
$k_L = 0.097$	$K_f = 6.9947$	$K_T = 1.8064$
$r^2 = 0.9815$	$r^2 = 0.9994$	$r^2 = 0.9577$

3.6. ADSORPTION KINETICS:

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models were used to test experimental data [28]. The experimental data were also analyzed using the pseudo-first and pseudo-second-order adsorption kinetic models. These models correlate solute uptake, which is important in predicting the reactor volume. These models are explained below

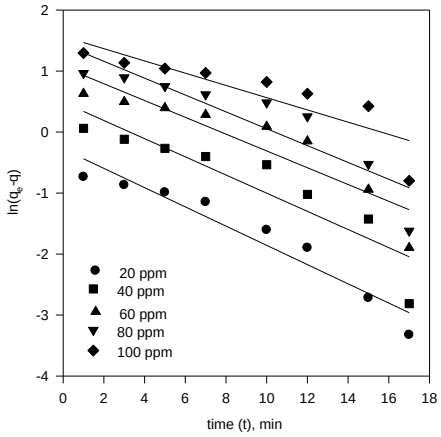
The pseudo-first-order equation

The linear form of pseudo-first-order equation of Lagergren is generally expressed as follows:

$\ln(q_e - q) = \ln(q_e) - k_1 t$ ---------(7)

The pseudo-first-order rate constant k_1 can be obtained from the slope of the graph between log(qe −q) versus time, t (Fig.11). The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 3. Based on the q calculated and experimental values this model cannot be applied to predict the adsorption kinetic model.

Figure.11. Pseudo first order kinetic model



The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [29]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad \text{---------- (8)}$$

where t is the contact time (min), q_e(mg/g) and qt (mg/g) are the amount of the solute adsorbed at equilibrium. Eq. (10) does not have the problem of assigning an effective q_e. If pseudo-second-order kinetics is applicable, the graph t/qt against t of Eq. (8) should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot (Fig. 12) and there is no need to know any parameter beforehand.

The pseudo-second-order rate constant k, the calculated qe value and the corresponding linear regression correlation coefficient value R_2^2 are given in Table 3. At an initial MB concentration of 20 mg/L, the linear regression correlation coefficient R_2^2 value was higher. The higher R_2^2 value confirms that the adsorption data were well represented by pseudo-second order kinetic model.

A comparison of the maximum capacity qm of BPL with those of some other adsorbents reported in literature is given in Table 4. Differences of dye uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

Figure.12. Pseudo second order kinetic model

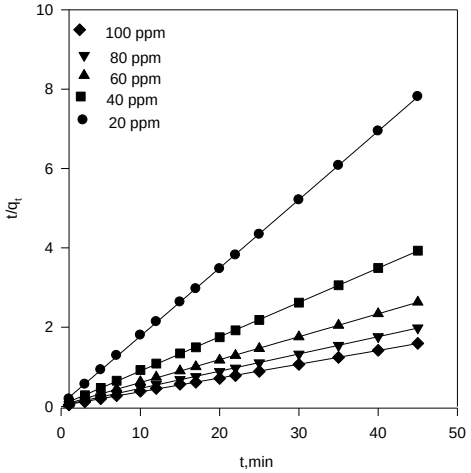
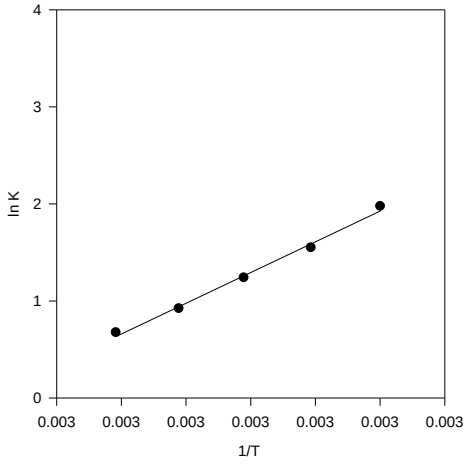


Figure.13. Van't Hoff plot for the adsorption of MB onto BPL



Initial conc^n (mg/L)	20		40		60		80		100	
Rate constant	k_1	k	k_1	k	k_1	k	k_1	k	k_1	k
	0.157	0.508	0.149	0.227	0.137	0.114	0.138	0.079	0.100	0.058
q (calc)	0.755	5.839	1.628	11.61	2.91	17.41	4.207	23.11	4.796	28.6
q (expt)	5.76	5.76	11.46	11.46	17.1	17.1	22.71	22.71	28.27	28.27
R^2	0.928	0.999	0.820	0.999	0.830	0.999	0.802	0.999	0.752	0.999

Table.3: Parameters of pseudo first order and pseudo second order kinetic model.

3.7. THERMODYNAMIC STUDIES

In order to gain an insight into the mechanism involved in the adsorption process, thermodynamic parameters for the present system were calculated. The adsorption free energy (ΔG^0), adsorption enthalpy (ΔH^0) and adsorption entropy (ΔS^0) were determined from the slope and intercept of the van't Hoff plot of ln K versus 1/T(Fig.13) [39, 40].

It was observed that all ΔG^0 values are negative indicates that the biosorption process is feasible and the adsorption process is spontaneous in nature. ΔH^0 and ΔS^0 were calculated as -52.628 KJ/mol and -157.66 J/mol, respectively. The negative value of adsorption enthalpy shows that the adsorption process is exothermic.

3.8. RSM:

The application of the RSM based on the estimates of parameters indicated an empirical relationship between the response and the input variables expressed by the following fitted second order polynomial equation

$$Y = -560.33 + 5.02\ X_1 + 95.16\ X_2 + 1225.81\ X_3 + 1.22\ X_4 - 0.07X_1^2 - 4.34\ X_2^2 - 5963.62\ X_3^2 - 0.01\ X_4^2 - 0.01\ X_1X_2 - 0.03\ X_1X_3 - 0.01\ X_1X_4 - 19.42\ X_2\ X_3 - 0.06\ X_2X_4 + 0.31X_3X_4 \quad \text{------ (9)}$$

The student t- distribution and the corresponding p-values, along with the parameter estimates, are listed in Table-5. The significance of each parameter was determined via p-values and the student t- test. A larger t-value and smaller p-value identifies the effect that appears to be very important [41, 42]. For our data, it was observed that the first order main effects of variables, namely pH (X_2), Dosage (X_3) and Concentration (X_4) and their second order main effects X_{22}, X_{32} are highly significant since their respective p-values are very small. The quantities X_1, X_2, X_3 and X4 have positive influence while X_{12}, X_{22}, X_{13}, X_{14} , X_{33} etc. shows a negative influence on adsorption. In order to determine whether or not the second order polynomial equation was significant to fit with experimental result, it is necessary to conduct an analysis of variance (ANOVA). The ANOVA indicates that the equation represents adequately the actual relationship between the response and the significant variables. The coefficient of determination (R^2) is found to be 0.97 which is very high and has advocated high correlation between the observed and the predicted value [43].

Biosorbent	Biosorption capacity (mg/g)	References
Saw Dust	67.5	30
Natural Tripoli	16.6	31
Gypsum	38	32
Ulva Lactuca and Sagassum	26	33
Modified lignin from sugar cane Bagasse	34.2	34
Treated activated carbon	45.9	35
Carbon prepared from Guava Seeds	46.3	36
Bamboo based Activated Carbon	55.9	37
Sheep fiber	57.1	38
Araucaria cookii bark powder	91.35	10
Bhaunia Purporial L	78.37	Present study

Table4: Comparison of the biosorption capacity of present work with those reported in the literature

Term	Constant	SE	T value	P value
b_0	-560.33	132.836	-4.21820	0.001441
b_1	5.02	2.895	1.73458	0.110710
b_2	95.16	16.321	5.83061	0.000114
b_3	1225.81	553.436	2.21491	0.048798
b_4	1.22	0.553	2.21181	0.049063
$b_1 * b_1$	-0.07	0.029	-2.49591	0.029722
$b_2 * b_2$	-4.34	0.737	-5.88110	0.000106
$b_3 * b_3$	-5963.62	1842.926	-3.23595	0.007931
$b_4 * b_4$	-0.01	0.002	-3.01629	0.011733
$b_1 * b_2$	-0.01	0.154	-0.06395	0.950158
$b_1 * b_3$	-0.31	7.699	-0.03976	0.968998
$b_1 * b_4$	-0.01	0.008	-0.76266	0.461706
$b_2 * b_3$	-19.42	38.497	-0.50451	0.623853
$b_2 * b_4$	-0.06	0.038	-1.66251	0.124611
$b_3 * b_4$	0.31	1.925	0.16258	0.873801

Table.5 : Response surface regression of percentage color removal of MB dye.

4. Conclusions

The present study confirmed that the BP has an effective biosorbent for removal of MB from aqueous solution. Removal of MB dye is pH dependent and maximum removal was attained at pH 10. The equilibrium adsorption is achieved through a contact time of 20min. The percentage removal of dye is also a function of dosage, dye concentration and temperature. The adsorption kinetics could be quite successfully fitted by a pseudo-second order kinetic model. The equilibrium data were well described by the Freundlich model with adsorption capacity of 78.37 mg g-1. The determination of thermodynamic parameters indicates the spontaneous and exothermic nature of the adsorption process. RSM results showed that the optimum values of the process variables were an initial MB concentration of 35.34 mg/L, a pH value of 10.48, a dosage of 0.085g and a temperature of 31.8 ^{o}C.

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