

## “Removal of aqueous solution of Methylene blue dye using “*Clitoria ternatea*”: A Novel Adsorbent”

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### ABSTRACT

Textile, paper, plastic and paint industries discharge large amount of waste water containing dyes. Dyes are stable to light, non-biodegradable and difficult to degenerate hence they should be removed before discharging the effluents into the environment to diminish health damage and demolition of the environment. The existing work establishes the use of acid treated *Clitoria ternatea* leaves powder (ATCTLP) for the removal of methylene blue (M.B.) dye from its aqueous solution. For this purpose, batch adsorption process was used. The study revealed that maximum removal of the M.B. dye ( $5 \text{ mg L}^{-1}$ ), was found to be 90.86 % at pH 7, contact time 60 min, adsorbent dose 0.02 g and particle size  $105 \mu\text{m}$ . The adsorbent was characterized using FESEM, EDX, FTIR, X-RD techniques before and after adsorption which clearly indicates effective adsorption of dye on it. The studied adsorbent is cost effective and can be applied for effluent treatment from dye industry.

**Key word:** Methylene blue, *Clitoria ternatea*, Adsorption, Dye removal

### 1. Introduction

A Huge quantity of waste water containing dyes is produced by textile industries. About 60,000 tons of dyes are discharged in to the environment, 80% of which are azo dyes<sup>1</sup>. Trace quantity of dyes also affects plant and animal life<sup>2</sup>. The dyes are carcinogenic and genotoxic<sup>3</sup>. Chemical precipitation, solvent extraction, flocculation, coagulation, membrane filtration, chemical oxidation, ion-exchange, reverse osmosis and adsorption are some methods used for waste water treatment. However, most of these methods are neither environmentally friendly nor economically feasible. Amongst all these methods, more effective and superior technique is Adsorption<sup>4</sup>; in terms of efficiency and cost effectiveness. It is a sludge free clean operation with maximum removal of dye even from very dilute solutions. Several investigators have reported variety of agricultural waste as adsorbents; in view point of their good adsorption capacity such as almond gum<sup>5</sup>, rice biomass<sup>6</sup>, neem sawdust<sup>7</sup>, rice husk<sup>8</sup>, and

wheat shell<sup>9</sup>. Removal of different dyes using various adsorbents was reported from our laboratory<sup>10-12</sup>. Natural low-cost adsorbents are one of the best applicants for the removal of dye from wastewater. Natural adsorbents were basically composed lignocellulose material such as lignin cellulose and hemicellulose<sup>13, 14</sup>, which improve adsorption capacity. In the present work, *Clitoria ternatea* Leaves (local name: Gokarn) were used as an adsorbent after chemical treatment.

## **2. Experimental**

### **2.1. Materials**

Fresh leaves of *Clitoria ternatea* were collected from home garden. The Methylene Blue ( $\lambda_{\text{max}}= 661\text{nm}$ ) dye used in this study was obtained from Fisher Scientific (Qualigens fine chemicals).

### **2.2. Preparation of adsorbent**

The garden-fresh leaves of *Clitoria ternatea* were thoroughly washed with water, dried under sunlight and soaked with 1:1 ortho-phosphoric acid for 24 hours and were then filtered through Whatman filter paper no. 42. The soaked leaves were boiled and washed with distilled water until free from organic components. It was then dried in an oven and sieved through mesh (size 105- 710 $\mu\text{m}$ ) to get uniform particle size. It was stored in air tight glass container until further use.

### **2.3. Preparation of dye solution:**

A stock solution was prepared and diluted further as per the requirements. For absorbance measurement a UV-Visible double beam spectrophotometer (Shimadzu) was used. The concentration of dye was determined, before ( $C_o$ ) and after ( $C_e$ ) batch adsorption process, at 661nm.

### **2.4. Batch Adsorption process**

Batch Adsorption process was used to study the maximum removal of dyes under optimized conditions. Various parameters viz. pH, contact time, adsorbent dose, particle size, concentration and temperature were optimized to obtain maximum removal of dye. Each adsorption experiment was carried out with 25 mL dye solution in 100 mL round bottom flask.

### **2.5. Characterization of adsorbent**

The various physico-chemical techniques were used to characterize (before and after adsorption) chemically treated *Clitoria ternatea* adsorbent. FTIR spectrophotometer (Shimadzu 8400) was used to study IR spectrum (wave length 4000-400 $\text{cm}^{-1}$ ) of adsorbent,

using KBr disk for reference. Field Emission Scanning Electron Microscopy (FET Nova nanoSEM-450) was used to study surface morphology of adsorbent. Presence of different elements was determined with the help of energy dispersive X-ray spectrum (Brouker SLASH-6130) detector

### 3. Experimental procedure

#### 3.1. Adsorption of Dye:

25 ml of desired concentration of MB was stirred for different time intervals by adding the desired quantity of adsorbent. pH of the solution was adjusted by means of 0.1N HCl and 0.1N NaOH. The solution was stirred using magnetic stirrer at constant speed (1100 rpm) for various time interval. After centrifugation (3000 rpm) for 10 minutes, supernatant solution was filtered through Whatman filter paper No. 42 and filtrate was analyzed with UV-Visible spectrophotometer. The following equation was used to calculate extent of dye removal

$$\% \text{ dye removal} = \frac{C_o - C_e}{C_o} \times 100 \quad \text{----- (1)}$$

Where,  $C_o$  = Initial concentration of dye solution ( $\text{mg L}^{-1}$ ),

$C_e$  = Concentration of dye solution ( $\text{mg L}^{-1}$ ) after adsorption.

At a time only one parameter was varied keeping others constant.

**3.2. Recovery of Dye:** Dye was recovered at optimum condition of adsorption by using 25 ml of water, 0.1N NaCl, 0.1 N NaOH and 0.1 N HCl solutions and contact time 40 min.

Recovery of dye was determined by measuring the absorbance with UV- Visible spectrophotometer and following equation

% recovery of dye was calculated using the equation given below,

$$\% \text{ Recovery} = \left( \frac{C_d}{C_a} \right) \times 100 \quad \text{----- (2)}$$

Where:  $C_d$  is amount of dye desorbed ( $\text{mg L}^{-1}$ ) and  $C_a$  is amount of dye adsorbed ( $\text{mg L}^{-1}$ ).

### 4. RESULTS AND DISCUSSION:

The effect of various parameters on removal of dye is discussed below

**4.1. Effect of pH:-** Fig.1 shows % removal of dye as a function of pH

As can be seen from above Fig. the extent of adsorption of dye increases with increase in pH and remains almost constant after pH 7 indicating maximum removal at this pH. Similar results are also reported by Rajurkar et.al.<sup>12</sup>, At lower pH adsorption of MB was lower due to  $\text{H}^+$  ions competing with the MB cationic group at absorption site which decreases the dye adsorption. H. Dargo et. al.<sup>15</sup> and Reddy et. al.<sup>16</sup>.

**4.2. Effect of contact time:-** The % removal of dye as a function of contact time is presented in Fig.2

Fig.2, indicates a rapid increase in % removal up to 60 min. and then a gradual decrease in it. Similar results were reported by Rajurkar et. al,<sup>12</sup>. Around 82.4 % of MB was removed within 60 min, due to strong attractive forces between the adsorbate and adsorbent<sup>17</sup>. Initially, adsorption increases with increase in contact time. At optimum contact time, surface area of adsorbent, gets completely adsorbed by dye. At this point, adsorbed and desorbed dyes are in equilibrium with an adsorbent. After optimum contact time, further no adsorption takes place.

**4.3. Effect of adsorbent dosage: -** Fig.3 presents effect of adsorbent dose on dye removal.

An examination of Fig.3 shows that after certain amount of dose, % removal decreases and the optimum dose is 0.02 g.

**Adsorbent dose plays important role in the removal of dye.** Initially adsorption sites are not saturated and are available for adsorption. After equilibrium, with increasing adsorbent dose, the amount of adsorbent adsorbed per unit mass of adsorbate decreases due to saturation of adsorption sites due to aggregation of adsorbate and decreases the total surface area of adsorbent. Thus, in turn, increases diffusion path length which decreases percentage removal<sup>18, 19</sup>. The equilibrium state was found to be at 0.02 g adsorbent dose.

**4.4. Effect of particle size on adsorbent: -**

Fig.4 depicts effect of adsorbent particle size on the removal of dye.

It is seen from Fig.4, that % removal of dye decreases with increasing particle size, the maximum dye removal being at 105 $\mu$ m particle size of adsorbent. It is attributed to decrease in surface area and less availability of adsorption sites for adsorption with particle size increase<sup>13</sup>.

**4.5. Effect of concentration on adsorbent: -** Effect of initial concentration on % removal is shown in Fig.5

The experiments were carried out using various initial concentrations of adsorbate (MB dye). The study of Fig.5 indicates that, removal of adsorbate decreased from 90.86% to 79.5% (30 mg L<sup>-1</sup>). Adsorption is more predominant at 5 mg L<sup>-1</sup>, due to strong driving forces of concentration gradient. Similar results are reported by earlier researchers<sup>20, 21</sup>.

**4.6. Effect of Temperature on adsorbent: -**Effect of temperature (298 °K to 318 °K), on % removal is shown in Fig.6

To study the effect of temperature on the adsorption of MB on adsorbent, adsorption experiments are carried out over temperature range 25°C to 45°C. An examination of Fig.6, reveals that the amount of dye adsorbed decreases with increase in temperature as the

solubility of MB increases at high temperature. Optimum adsorption temperature was observed at 25°C. (93.83% removal)

**5. Application of the developed method to actual industrial sample:**

The developed method was applied for removal of MB dye from textile industrial effluent. For this purpose, sample was collected from Akkalkot M. I. D. C. area, Solapur district, before and after Effluent Treatment Process (ETP).

Sample collected from textile industry before effluent treatment procedure for MB was found to have MB concentration 5.2 mg L<sup>-1</sup> while after ETP it was 1 mg L<sup>-1</sup> indicating 80.55% removal.

Removal of MB from collected sample before ETP was carried out by using developed method under optimized conditions which showed 93.15% removal.

Thus, our developed method is found to be more effective than that used in the industry.

**6) Adsorption Isotherms studies:** -To study the adsorption isotherms, optimized conditions were used in adsorption experiments.

**6.1. Freundlich isotherm:** The linearized form of equation is given by following equation,

$$\log q_e = \log K_f + 1/n \log C_e \text{ -----(3)}$$

Where:- $q_e$  = Amount of MB adsorbed at equilibrium,

$C_e$  = equilibrium concentration of MB in solution,

$K_f$  &  $n$  = Constant indicates the adsorption capacity and intensity of adsorption respectively.

The graph  $\log q_e$  verses  $\log C_e$  is shown in Fig.7. The adsorption of dye obeys Freundlich adsorption isotherm ( $K_f = 12.11$ ). The  $K_f$  value which is a measure of the amount of dye absorbed per unit weight of adsorbent, indicates favorable adsorption process<sup>22</sup>. The ‘ $n$ ’ is the adsorption intensity ( $1/n = 0.81$ ) found in the range of  $1 < 1/n < 10$ . The values of  $R^2 = 0.991$ ,  $K_f = 12.11$ ,  $1/n = 0.81$  are shown in Table 1

**6.2. Langmuir Isotherm:** Langmuir equation is given below,

$$1/q_e = 1/ab \times 1/C_e + 1/b \text{ ----- (4)}$$

Where:- $q_e$  = Amount of dye adsorbed at equilibrium,

$C_e$  = Equilibrium dye concentration,

$a$  = Langmuir constant ( $K_L$ ),

$b$  = The maximum adsorption capacity,  $q_m$  (mg/g)

As can be seen from Graph of  $1/q_e$  verses  $1/C_e$ ,  $R^2=1$  and hence adsorption of MB on studied adsorbent does follow Langmuir isotherm.

**6.3. Temkin isotherm:** Temkin isotherm is expressed by the following equation

$$q_e = B \ln A + B \ln C_e \quad \text{-----(5)}$$

Where:  $B = RT/b$ ,

A and B are the Temkin isotherm constants, b is the constant related to heat of adsorption,

R is the gas constant (8.314 J/mol k),

T is the absolute temperature (K),

$q_e$  is the amount of dye adsorbed at equilibrium (g/g),

$C_e$  is the equilibrium concentration of the dye ( $\text{g L}^{-1}$ ).

Linear graph ( $R^2 = 0.913$ ) indicates the adsorption process obeys Temkin isotherm. The values of  $A = 3.23$  and  $B = 12.42$  are shown in Table 1

**6.4. Dubinin-Radushkevich (D-R) isotherm:** D-R model decides whether adsorption process is either physical or chemical adsorption process<sup>23</sup>. D-R isotherm equation is as follows:

$$\ln q_e = \ln Q_{DR} - K\varepsilon^2 \quad \text{-----(6)}$$

Where  $q_e$  = the amount of dye adsorbed (g/g),  $Q_{DR}$  is the maximum adsorption capacity of dye (g/g), K is the Dubinin-Radushkevich constant ( $\text{kJ}^2/\text{mole}$ ) and  $\varepsilon$  is Polanyi potential given by the equation

$$\varepsilon = RT \ln (1 + 1/C_e) \quad \text{----- (7)}$$

Where R is the gas constant in J/mol K. T is the temperature in kelvin and  $C_e$  is equilibrium concentration of dye solution ( $\text{g L}^{-1}$ ).

A graph of  $\ln q_e$  versus  $\varepsilon$  (Fig.10) gives a straight line ( $R^2 = 0.895$ ) with a slope of K (0.21) and an intercept (3.3) of  $Q_{DR}$ . Biosorption mean free energy E(kJ/mol) is calculated from D-R constant K and is calculated by following equation

$$E = 1/\sqrt{-2k} \quad \text{----- (8)}$$

Where: E is the biosorption mean free energy (kJ/mol) and K is the D-R constant.

The transfer of one mole of solute from solution to the surface of adsorbent is due to the biosorption mean free energy (E) which describes the adsorption performance of the system.

Value of  $E < 8$  indicates physical adsorption and  $E > 8$  indicates chemical adsorption process<sup>20</sup>. The value of the mean free energy of MB dye was calculated (1.55 kJ/mol) and indicates physical adsorption process.

Study of Table 1 reveals that adsorption of MB on the *ATCTLP* obeys Freundlich ( $n < 1$ ), Temkin and Dubinin-Radushkevich (D-R) isotherm ( $E < 8$ ).

**7. Adsorption Kinetic studies:** Adsorption mechanism and adsorption characteristics of adsorption were studied by using various kinetic models.

Adsorption kinetic of MB onto the adsorbent is express by following equation,

$$\log(q_e - q_t) = \log q_e - K_1 / (2.303)t \quad \text{-----(9)}$$

Where:-  $q_e$  and  $q_t$  are amount of dye adsorbed ( $\text{mg g}^{-1}$ ) on adsorbent at equilibrium at time  $t$  respectively,  $K_1$  is rate constant of pseudo –first order adsorption ( $\text{min}^{-1}$ ).

A plot of  $\log(q_e - q_t)$  verses time ( $R^2 = 0.23$ ) was used to determine pseudo-first order rate constant ( $k_1 = 4.9 \times 10^{-6} \text{ min}^{-1}$ ,  $q_e = -6\text{g/g}$ ) which indicates that it does not follow pseudo-first order kinetics ( $R \neq 1$ ).

Adsorption capacity on the solid phase is determined by Lagergren pseudo-second order equation. It is given by following expression as<sup>24</sup>,

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \quad \text{-----(10)}$$

Where,  $K_2$  is rate constant of second order adsorption ( $\text{g mg}^{-1} \text{ min}^{-1}$ ).

Second order rate constant is determined from Fig.11. The value of rate constant  $K_2 = 0.23$ ,  $q_e = 5.88$  and  $R^2 = 1$  shows good linearity of plot and better fit to Lagergren pseudo –second order kinetic model.

### 7.1. Intraparticle diffusion model:

Diffusion of the adsorbate from the outer surface into the pores of the adsorbent was studied on examination of plot  $q_t$  verses  $t^{1/2}$  (fig.12), The slope ( $k_{id} = 0.03$ ) and the intercept value (5.53) indicate that the line does not pass through origin which indicates, there are some other factors affecting the adsorption. The sorption process has a tendency to be followed by two phases. The two phases in this plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The intraparticle diffusion equation is given by

$$q_t = k_{id} t^{0.5} + C \quad \text{-----(11)}$$

Where:  $k_{id}$  = Particle diffusion rate constant in  $\text{mg/g/min}^{0.5}$ ; and  $C$  is intercept.

A plot of  $q_t$  verses  $t^{0.5}$  gives values of  $k_{id}$  (slope) and  $C$  (intercept) from the equation.

The value of  $k_{id}$  and  $C$  is found to be 0.03 and 5.53 respectively.

### 7.2. Thermodynamic studies:

Thermodynamic parameters such as change in free energy ( $\Delta G^\circ$ ) kJ/mol, enthalpy ( $\Delta H^\circ$ ) kJ/mol, and entropy ( $\Delta S^\circ$ ) kJ/mol K, were calculated by using following equations.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \text{----- (12)}$$

$$\Delta G^\circ = -R T \ln K \quad \text{----- (13)}$$

$$K = \frac{q_e}{C_e} \quad \text{----- (14)}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{----- (15)}$$

Where:  $K$  is equilibrium constant,  $R$  is gas constant,  $T$  is temperature in K.

$\Delta G^\circ$  is calculated from equation (12) while  $\Delta H^\circ$  and  $\Delta S^\circ$  values were obtained from the slope and intercept of plot  $\ln K$  versus  $1/T$ , the negative value of  $\Delta G^\circ$  indicates the adsorption is spontaneous and thermodynamically favorable for adsorption of MB. The negative value of  $\Delta H^\circ$  indicates physisorption and endothermic nature of adsorption. The negative value of  $\Delta S^\circ$  indicates change in surface morphology and increase in randomness at liquid solid interface<sup>20</sup>.

A plot of  $\ln K$  versus  $1/T$  is shown in Fig. 13

The thermodynamic parameters obtained from above plots are recorded in following Table.2 Above data reveals that, the  $\Delta G^\circ$  values are negative representing the spontaneous nature and thermodynamically favorable adsorption for MB<sup>20</sup>. The negative value of  $\Delta H^\circ$  shows exothermic process<sup>24</sup>. The negative value of  $\Delta S^\circ$  designates decreased disorder at liquid solid interface<sup>25</sup>.

The distribution coefficient  $K$  values for adsorption process of MB on *ATCTLP* at different temperatures were calculated and it is reflected in following table

Table 3 reveals that, maximum adsorption was observed at temperature 298 °K due to maximum distribution coefficient value (20.52).

## 8. Recovery of Dye:

Recovery of dye was carried out by using various eluents (25 ml); water, 0.1N NaCl, 0.1 N NaOH and 0.1 N HCl solutions. The results are shown in Figure 14.

An examination of Fig. 14 shows that, HCl was found to be most efficient solvent for recovery of adsorbed dye. It was further used to recover a dye (5 mg L<sup>-1</sup>) from loaded adsorbent at optimized conditions using various volumes of HCl (0.1N). A study of Fig.15 shows that, 50.22 % MB dye was recovered using 25 ml of 0.1N HCl. The result shows that the adsorbed dye can be effectively recovered. Thus, bio adsorbent can be regenerated and reused for further removal.

## 9. Characterization studies

### 9.1. FTIR Studies:

FTIR spectrum of virgin adsorbent (a) shows a peak at 3410 cm<sup>-1</sup> which indicates the presence of H-bonded –OH stretching vibration in phenolic compound present in cellulose of adsorbents. In spectrum (b), Strong broad band at 3437 cm<sup>-1</sup> due to -OH stretching vibration. There are two inflections observed in Fig. (a) and (b). in figure (a) band at about 2851-2916



due to medium –CH stretching and In figure (b), the absorption bands at 2853 and 2918  $\text{cm}^{-1}$  can be assigned to symmetric and asymmetric vibrations of the C–H<sub>3</sub> bonds in the dimethylene groups of MB molecules<sup>26</sup>. An examination of Fig.16 shows considerable change in the peak intensity indicating adsorption of MB on the adsorbent

**9.2. FESEM Studies:** The morphological characteristics of adsorbent were studied with FESEM and corresponding micrograph is shown in Fig.17.

An observation of Fig. 17a shows, SEM micrograph of virgin adsorbent possess irregular plate like long narrow shallow depression and highly porous rough surface structure indicates better opportunity for adsorption. The appearance of a dark molecular cloud over the superficial layer of the dye loaded adsorbent (Fig.17b) confirms the adsorption of dye on to the surface of adsorbent. There are no empty porous spaces left on the surface of adsorbent because 90.86 % dye adsorb on to the surface of adsorbent.

**9.3. EDX studies:** The EDX spectrum of *ATCTLP* and MB loaded *ATCTLP* is shown in the Fig. 18a & 18b respectively

Energy dispersive spectrum of adsorbent (18a) shows the elements Ca, C and O. While Energy dispersive spectrum of adsorbent loaded with MB (18 b), confirms presence of ‘N’ in the dye.

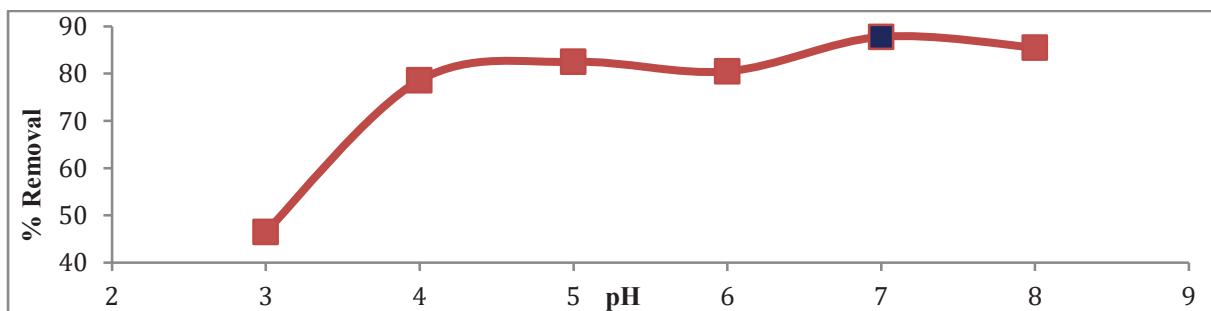
## CONCLUSIONS:

The present study shows the effectiveness of *ATCTLP* in the removal of methylene blue dye from aqueous solutions. The maximum dye removal (90.86 %) of MB (5  $\text{mg L}^{-1}$ ) was observed at pH 7, contact time 60 min, adsorbent dose of 0.020 g, particle size of 105  $\mu\text{m}$ . The adsorption isotherm study indicates that, adsorption of MB on *ATCTLP* is physical adsorption process. It follows Freundlich, Dubinin-Radushkevich and Temkin isotherms. The adsorption kinetic study shows adsorption of MB follows pseudo–second order kinetics and Intraparticle diffusion model. Thermodynamic studies revealed that adsorption is spontaneous and endothermic process. *ATCTLP* is efficient adsorbent for removal of MB dye. The adsorbed dye can be effectively recovered using 0.1 N HCl solutions as an eluent.

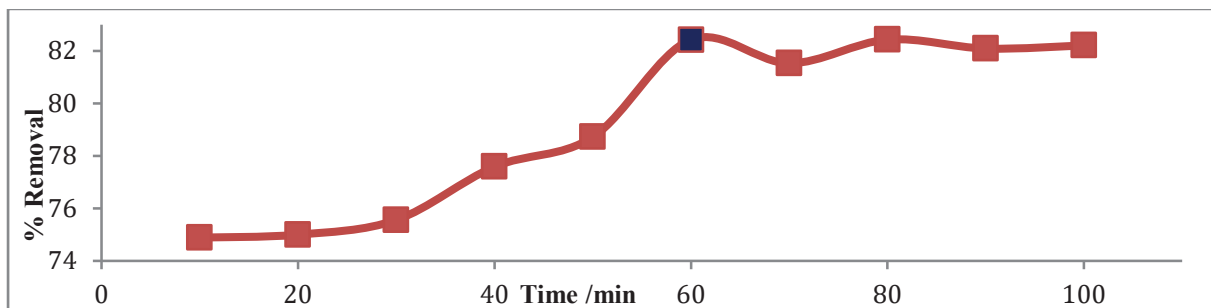
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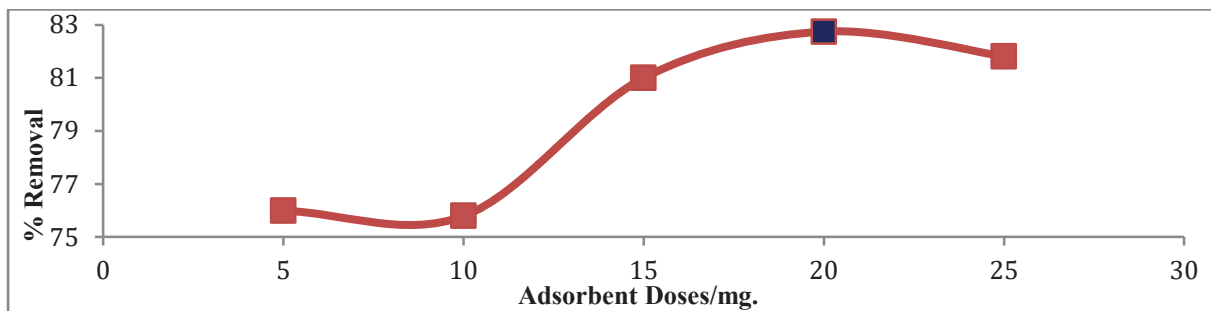
Figures:



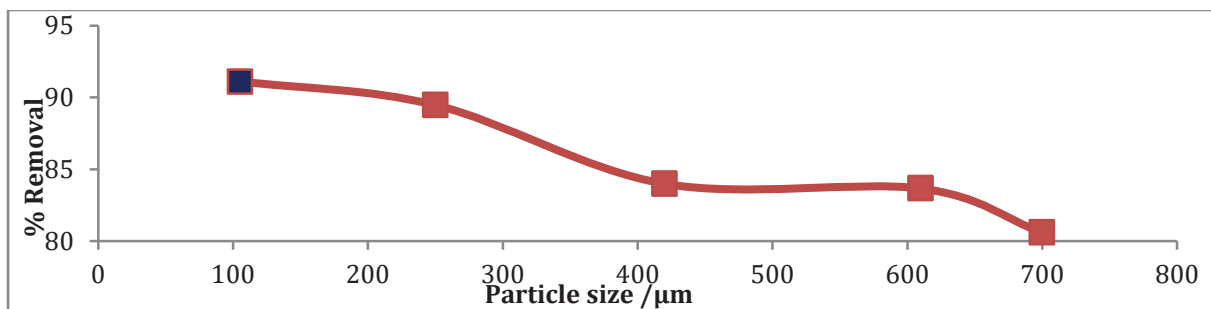
**Fig.1.**Effect of pH on removal of MB  
 [Contact time: 30 min, Adsorb. dose:10mg, Particle size: 420 $\mu$ m, Concentration: 5mg L<sup>-1</sup>]



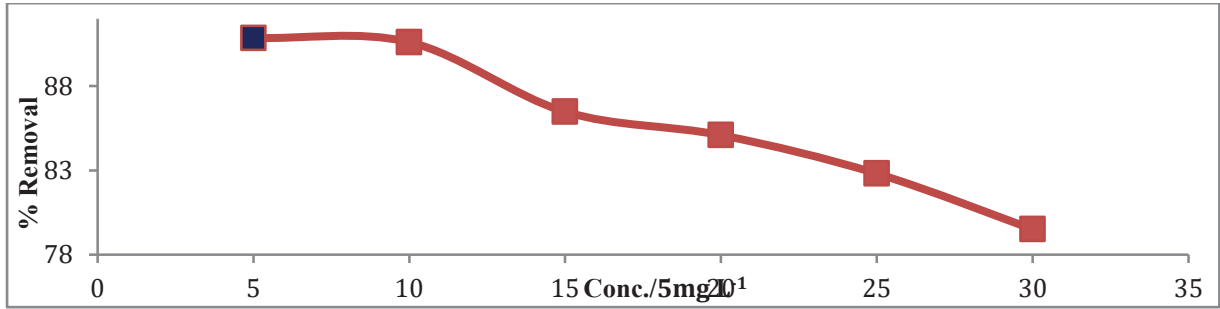
**Fig.2.** Effect of contact time on removal of MB  
 [pH: 7, Adsorbent dose: 10 mg, Particle size: 420  $\mu$ m, Concentration :5 mg L<sup>-1</sup>]



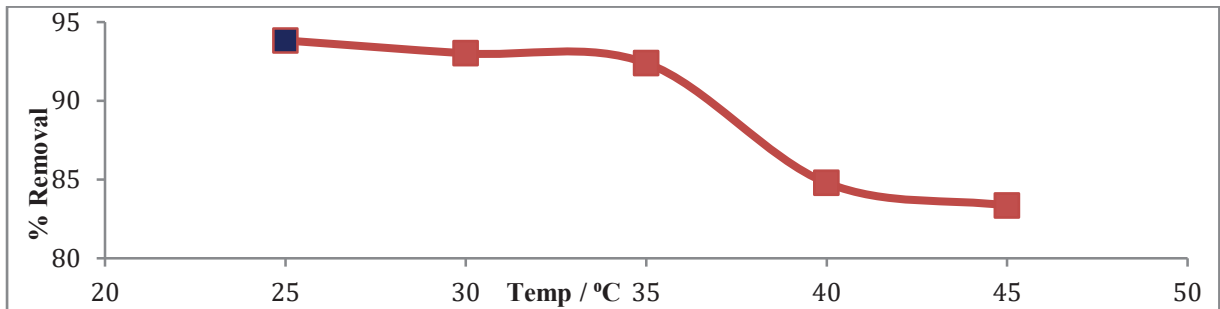
**Fig.3.** Effect of adsorbent doses on removal of MB  
 [pH: 7, Contact time: 60 min, Particle size: 420 $\mu$ m, Concentration:5 mg L<sup>-1</sup>.]



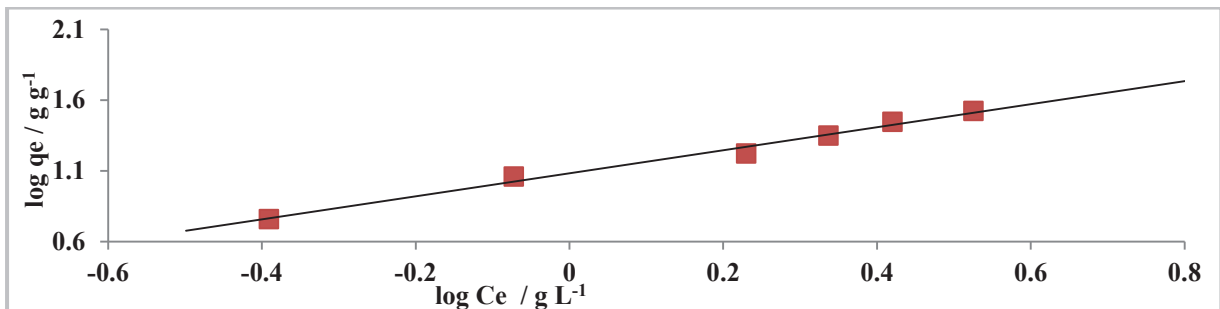
**Fig.4.** Effect of particle size of adsorbent on removal of MB  
 [pH: 7, Contact time: 60 min, Concentration: 5mg L<sup>-1</sup>. Adsorbent dose: 20mg]



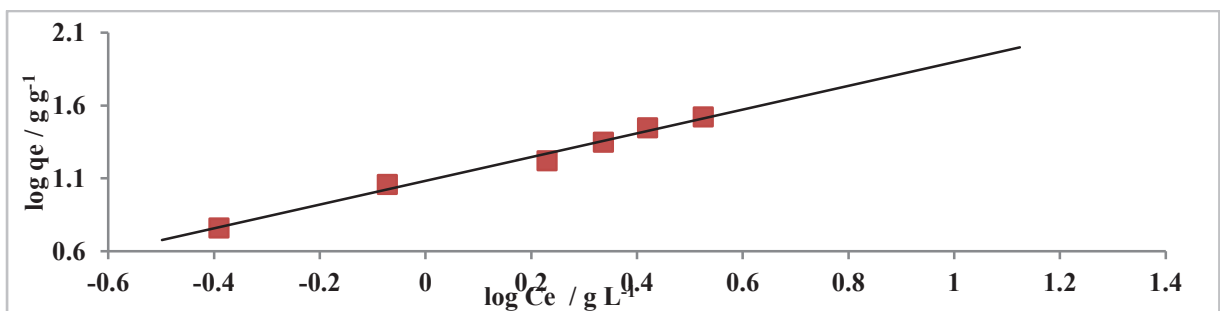
**Fig.5.** Effect of concentration, on removal of MB  
[pH: 7, Contact time: 60 min, Adsorb. dose:20mg, Particle size: 105 $\mu$ m.]



**Fig.6.** Effect of temperature on % removal of MB  
[pH:7, Cont. time: 60 min, Adsorb. dose: 20 mg, Particle size: 105  $\mu$ m, Conc: 5 mg L<sup>-1</sup>.]



**Fig.7.** Freundlich isotherm plot for adsorption of MB on *ATCTLP* under optimized condition.



**Fig.8.** Langmuir isotherm plot for adsorption of MB on *ATCTLP* under optimized condition.

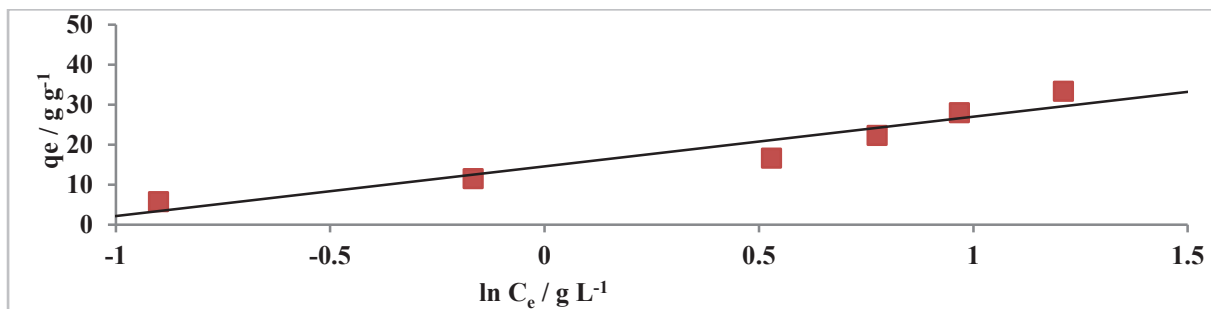


Fig.9. Temkin isotherm plot for adsorption of MB dye on *ATCTLP* under optimized condition.

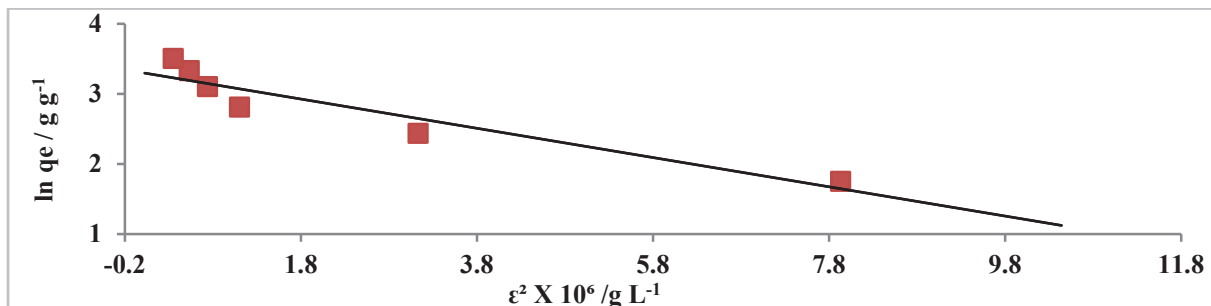


Fig.10. D-R Isotherm plot for adsorption of MB dye on *ATCTLP* under optimized condition.

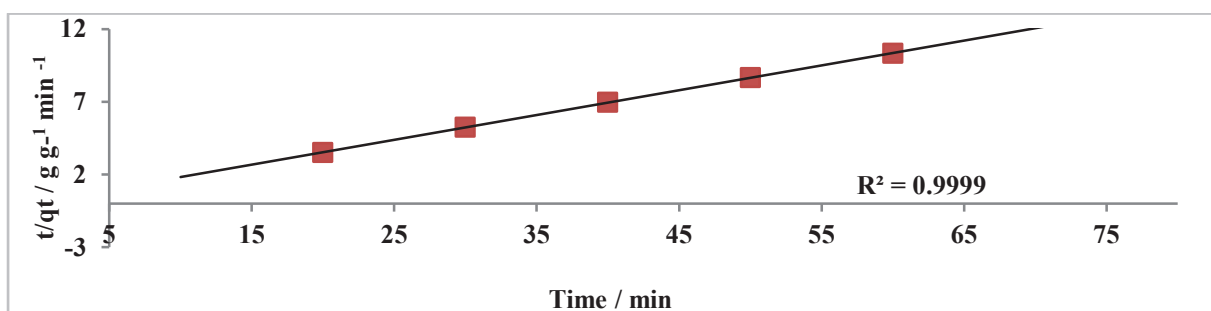


Fig.11. Pseudo –second order plot for adsorption of MB dye on *ATCTLP* under optimized condition.

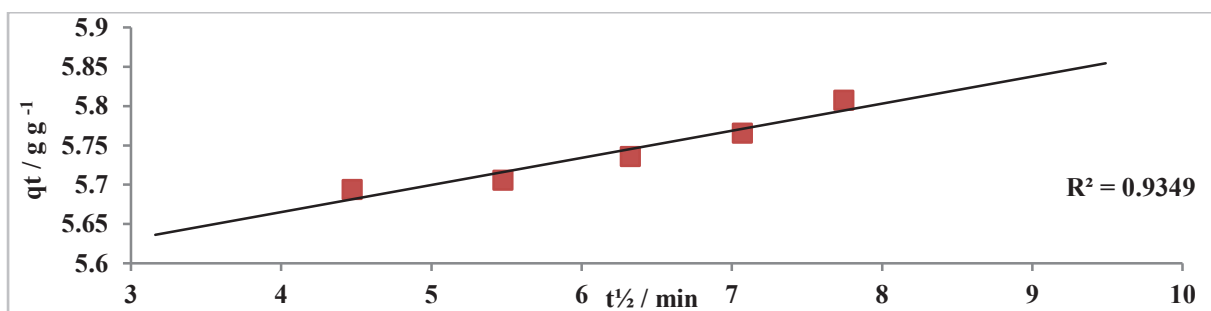


Fig.12. Intraparticle diffusion plot for adsorption of MB dye on *ATCTLP* under optimized condition.

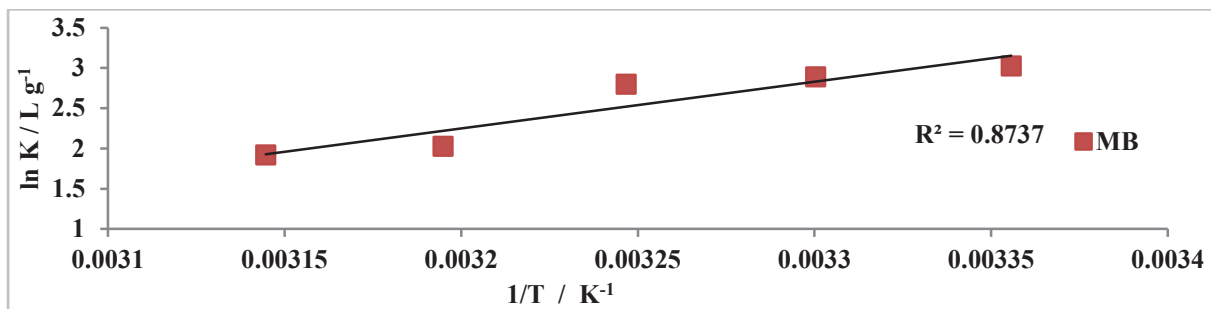


Fig.13. Plot of ln K verses 1 /T for adsorption of MB dye on ATCTLP under optimized condition.

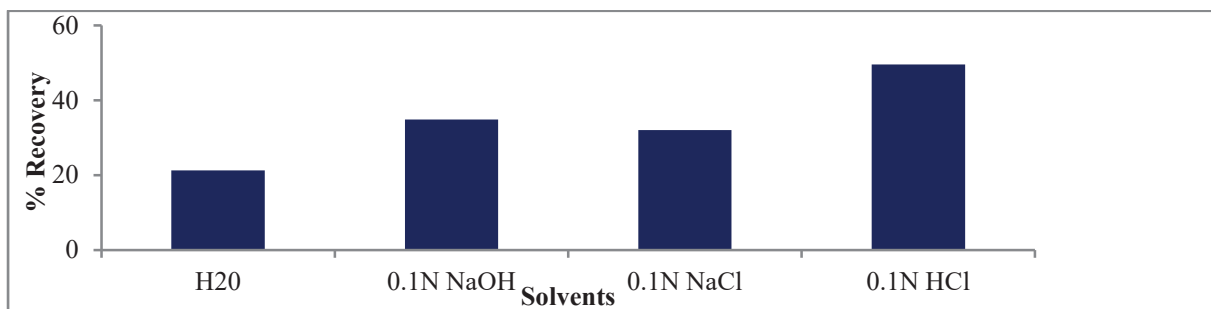


Fig.14. % Recovery of dye from dye loaded adsorbent using different eluents.

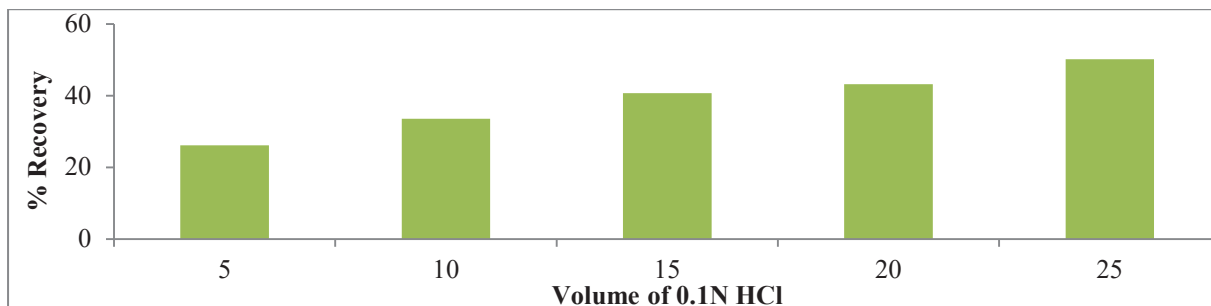


Fig.15. % Recovery of MB dye from dye loaded on adsorbent using 0.1 N HCl.

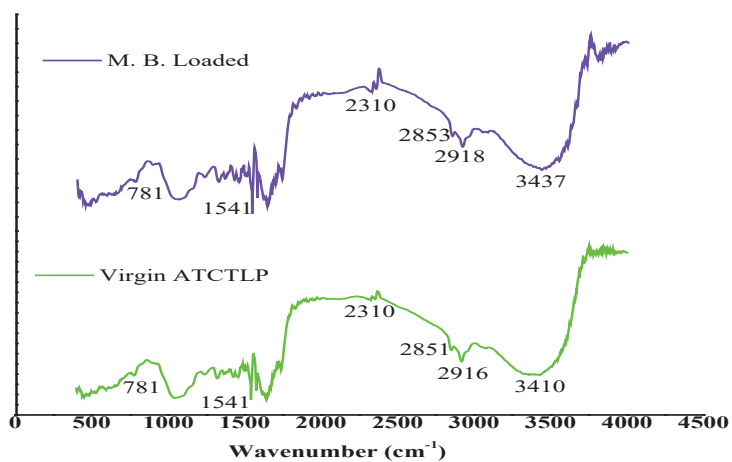


Fig. 16. FTIR Spectrum of ATCTLP (a) and MB loaded ATCTLP (b).

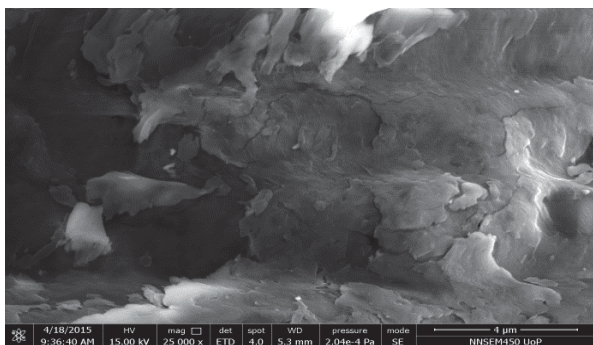


Fig.17a, SEM micrograph of Virgin ATCTLP

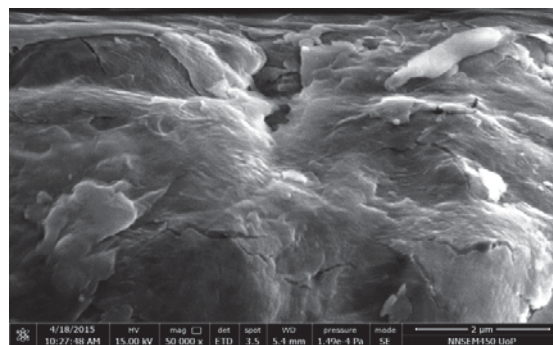


Fig.17b, ATCTLP loaded with MB.

### Virgin adsorbent

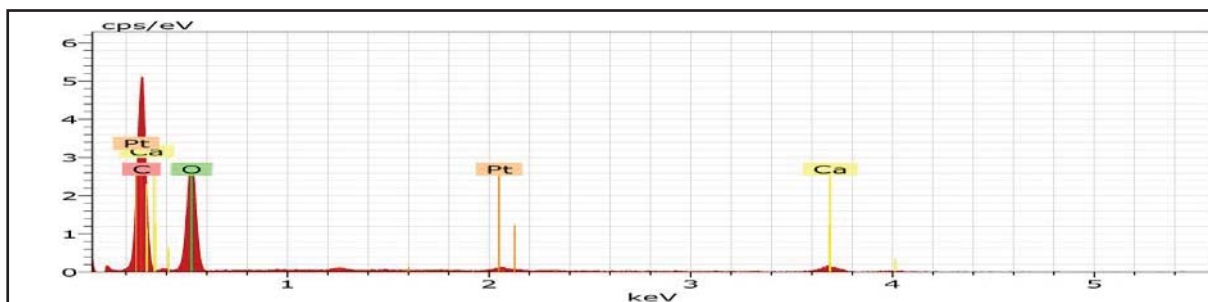


Fig. 18a, EDS of ATCTLP

### M.B. loaded adsorbent

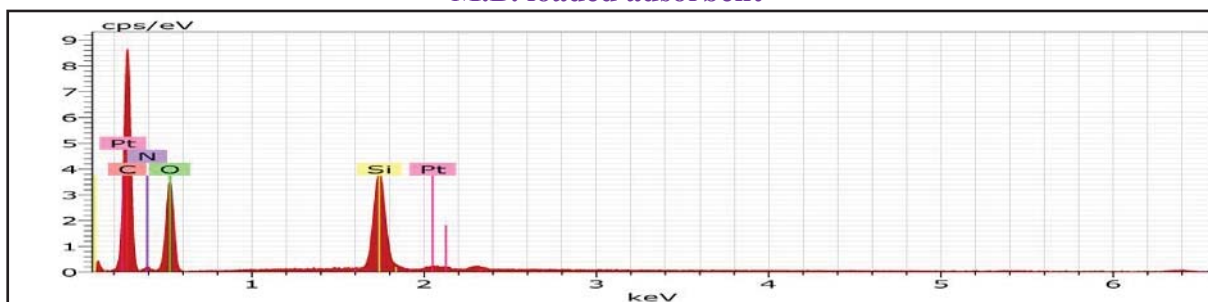


Fig. 18b, EDS of ATCTLP loaded with MB

**Tables:**

**Table: 1.** Isotherm constants for absorption of MB dye on *ATCTLP* adsorbents.

Adsorption Isotherm	Constants	Values
Freundlich Isotherm	$R^2$	0.989
	$K_f$	12.11
	$1/n$	0.81
Langmuir Isotherm	$R^2$	1
	A	0.19
	B	78.92
Temkin Isotherm	$R^2$	0.912
	A	3.23
	B	12.42
D-R Isotherm	$R^2$	0.895
	$Q_{DR}$ (g/g)	27.19
	$K$ (kJ/mol)	0.21
	E (kJ/mol)	1.55

**Table:2.** Thermodynamic parameter for MB sorption by *ATCTLP* adsorbents.

Sr. No.	Temp. (°K)	$\Delta G^\circ$ (kJ/mol )	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol k )
1.	298	-7.81	-48.17	-0.12
2.	303	-7.13		
3.	308	-6.46		
4.	313	-5.78		
5.	318	-5.10		

**Table:3.** Variation of K with temperature for adsorption on MB dye on *ATCTLP* adsorbents.

Temp. (°K)	298	303	308	313	318
$K / L \text{ mg}^{-1}$	20.52	17.96	16.40	7.58	6.81

**REFERENCES:**

1. Quiang Liu, IOP vof. Ser.: Earth Environ. Sci. 514, 052001, 2020
2. R. Jain, S. Sikarwar, Int. J. Environ. Pollut., 27, 158, 2006.
3. Amr A. Essawy, A. El-Hag Ali, M. S. A. Abdel-Mottaleb, J. Hazard. Mater., 157 (2-3), 209.2008.
4. Robinson, T., McMullan, G., Marchant, R. and Nigam, P., Bioresource Technology, 77, 247, 2001.
5. F. Bouaziz, M. Koubaa, F. Kallel, F. Chaari, D. Driss, R. E. Ghorbel, S. E. Chaabouni,

- Industrial crops and products, 74, 903, 2015.
6. MSU Rehman, I. kim, J. Han, Carbohydr, Poylm.; 90(3), 1314, 2012.
  7. S. D. Khattri, M. K. Singh, J. Hazard. Mater., 167, 1089, 2009.
  8. O. Abdelwahab et al., J. Aquat res; 31, 1, 2005.
  9. Y. Bulut and H. Aydin, Desalination, 194, 259, (2006).
  10. Borkar D. J., Rajurkar N. S. and Adhyapak P. V., J. of Applicable Chemistry 5 (5), 1064, 2016. (10)
  11. M. R. Pawar J. ISAS 1 (1), 97, 2022
  12. N. S. Rajurkar, M. R. Pawar, Env. Obsever. 13, 215, 2013.
  13. N. S. Rajurkar and N. S. Walvekar, J. Applicable. Chem, 3(6), 2602 2014.
  14. N. S. Rajurkar and Asha Desai, Journal of Applicable Chemistry, 4 (5), 1446, 2015.
  15. L. Oliveira, N. Cordeiro, A. J. D. Silvestre, I. C. Torres and D. Evtuguin, Industrial Crop Prod, 26, 163, 2007.
  16. Hayelom Dargo, Nigus Gabbiye, and Adhena Ayalew, International Journal of Innovation and Scientific Research, 9 , 317, 2014.
  17. B. Srinivasa Reddy, V. Krishna Veni and K. Ravindhranath, Journal of Chemical and Pharmaceutical Research, 4(11), 4682, 2012.
  18. M. M. Abd El-Latif, A. M. Ibrahim, M.F.E1-Kady, J. American Sci. 6, (6), 267, 2010.
  19. S. Saiful Azhar, A. Ghaniey Liew, D. Suhardy, K. Farizul Hafiz and MD. Irfan Hatim, American J. Appl. Sci., 2(11), 1499, 2005.
  20. H. Runping et al., J. of Hazardous Materials. 141, 156, 2007.
  21. N. S. Rajurkar and D. R. Mahajan, J. Applicable.Chem, 4(4),1206, 2015.
  22. G. Kavitha, V. Venkateswaran, Journal of Applied Chemistry, 10 (9), 68, 2017.
  23. P. Velmurugan, V. Rathinakumar, G. Dhinakaran, Int. J. of Environ. Sci, 1(7), 1492, 2011.
  24. Narayan saibaba K. V. and King P., International Journal of Research in Engineering and Technology, 1(3), 17, 2013.
  25. Nitin Sharma, Tanveer Alam, Arshi Rastogi, Hina Tarannum and Gita Sain., J. Applicable. Chem, 4, (3), 871, 2015.