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Investigation of Sorption of Methylene Blue onto Crushed Biomass of Ailianthus Exelsa

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ABSTRACT

The adsorption capacity of untreated Crushed biomass of Ailanthus excelsa was studied for the removal of methylene blue from aqueous solution. In the present work effects of parameters such as Biomass dose, Contact time, and concentration of MB solution, pH, and temperature were investigated. Methylene blue removal increased with the increased in contact time and the maximum removal observed at 20 minutes. Removal of dye is dependent upon the concentration of the MB dye. The sorption increases with decreasing temperature. The maximum adsorption is observed at pH is 2. The adsorption isotherm data was better fitted to the Langmuir and Freundlich isotherm with the R^2 values 0.8944 and 0.8977 respectively. It has been observed that an average 79.6% removal of methylene blue under the different conditions in the batch experiment. The data fit well in the Freundlich isotherm. The Langmuir and Freundlich equations were found to have the correlation coefficient value in good agreement. Adsorption of MB onto Powdered Biomass of Ailanthus excels followed pseudo second order kinetics with R^2 value 0.9973. The equilibrium data were also fitted to the Freundlich equation and it was observed that the sorption process is spontaneous and exothermic in nature. It has been observed that the untreated crushed biomass of Ailanthus excelsa is simple, cheap, easily available, ecofrieindly very good biosorbent for methylne blue removal.

Key Words: Adsorption, Methylene Blue (MB), Ailanthus excelsa, crushed biomass.

INTRODUCTION

Of various pollutants contained in industrial wastewaters, colour is considered to be Very important from the aesthetic point of view and is stated as 'visible pollutant'. Almost every industry uses colouring matter to colour their products. Unspent colouring. Materials are usually discharged, with/without treatment into the aquatic environment. Dyes are highly coloured polymers and low biodegradable. Colour/dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream. As a cationic dye, methylene blue ($C_{16}H_{18}ClN_3S$, MB) is widely used in chemical indicators, dyes and biological dyes. A large amount of organic dye wastewater is produced in the processes of the printing and dyeing industries. The dye wastewater has characteristics such as large discharge, high chromaticity, high organic matter concentration, and poor biodegradability, and greatly affects the water body health and the photosynthesis of microorganisms in the water environment [1, 2].At present; many researchers have used different methods to treat the dye wastewater [3]. Typical treatment methods include physical, chemical, and biological methods, such as flocculation [4], membrane filtration [5, 6], advanced oxidation [7], Ozonation, photo catalytic degradation [8], and biodegradation.

These traditional methods have inherent limitations [9] such as the complex and uneconomical of nature of the technology, and thus it is necessary to seek efficient and simple dye wastewater treatment methods [10].Compared with other treatment methods, the adsorption method is considered as prevailing over other dye wastewater treatment technology due to its advantages such as high efficiency, low cost, simple operation, and insensitive of toxic substances [11]. Activated carbon is the most commonly used adsorbent, and is widely used to remove the organic and inorganic pollutants in water phase. Adsorption capacity is an important index to evaluate the adsorption efficient of adsorbent. Various low-cost alternative adsorbents from agricultural solid waste, industrial solid waste, agriculturally-products and biomass are used in wastewater treatment. For example, clay [12], sludge [13], montmorillonite [14], flax fibre [15], zeolite [16, 17], and biochar (rice husk) [18, 19], pinewood [20], wheat [21], sugarcane bagasse [22], switch grass [23], Ficus carica baste [24]), Ailanthus excelsa crushed biomass is used as adsorbents for adsorption methylene blue dye from aqueous solutions [25], Ailanthus excelsa was found ample tree at state of Chhattisgarh and Himachal Pradesh in India.

MATERIALS AND METHODS

Ailanthus excelsa was collected from the locally available planting. The stalk part of Ailanthus excelsa was dried and washed several times with distilled water to remove adhered impurities from its surface. This was then milled and sieved through mesh 850-micron particle size. This biomass was dried at 100^0C for 12 hand used for sorption study.

Adsorbate:

Methylene blue (C16H18N3SCl.3H2O) was obtained from E.Merck, India and was used for sorption study. The required concentrations were prepared by dissolving MB dye in distilled water. The MB stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/L. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations like 15 mg/L, 20mg/L, 25mg/L and 30mg/L.

Experimental:

The batch adsorption experiments were conducted in a set of 250 ml of Erlenmeyer flask containing adsorbent and 100 ml of MB solution with various initial concentrations. The flasks were agitated in an isothermal water-bath shaker at 100 rpm and 270C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 665 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 1N HCl and 1N NaOH solutions. The amount of dye adsorbed and percentage removal of MB were calculated using Equations. (1) and (2), respectively:

$$qe = (Co\text{-}Ce)\frac{v}{m} \qquad (1)$$

$$\% \text{ Removal} = \frac{Ci - Ce}{Ci} \qquad (2)$$

RESULTS AND DISCUSSION:

Effect of Time:

The amount of dye adsorbed at various intervals of time indicates that, the removal of dye (adsorbate) initially increases with time but attains equilibrium within 20 minutes. The adsorption process was found to be very rapid initially, and a large fraction of the total concentration of dye was removed in the first 15 minutes. Though it was observed that adsorption of, MB increased with an increase in dye concentration in the solution, which shows that removal of dye is dependent upon the concentration of the dye solution. However, as a whole the percent removal decreases with the increase in dye concentration as observed in the fig-1. The adsorption of methylene blue onto crush biomass reached equilibrium in 20 minutes.

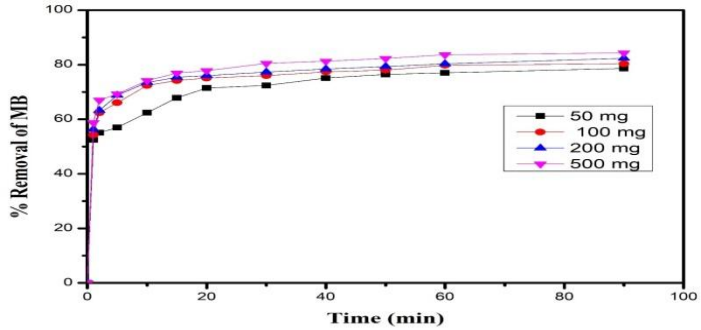

Figure 1:- Effect of Contact time on MB removal

Effect of concentration:

For a particular experiment, the rate of adsorption decreased with time, it gradually approached a maximum adsorption, and owing to continuous decrease in the concentration driving force and it also indicate that the adsorbent is saturated at this level. In addition, it is observed initial rate of adsorption was greater for higher dye concentration because as the resistance to the dye uptake decreased, the mass transfer driving force increased. The time variation, adsorption capacity increases continuously and seems to be smooth which is indicative of the formation of monolayer coverage on the surface of adsorbent. The Crushed biomass could remove a maximum of 79.6 %MB at initial dye concentration of 15 ppm, while for dye concentrations of 30 ppm; the adsorption of the dye was above 79.6 % in 60-90 minutes. Both concentrations were studied at temperature 25°C and adsorbent dose of 100 gm/L. Further increase in dye concentration

showed no significant changes in removal efficiency (Fig. 2). This is because with increased dye concentration, the driving force for mass transfer also increases. At low concentrations, there will be unoccupied active sites on the adsorbent surface. Above optimal MB concentration, the active sites required for the adsorption of dye will lack (Barka al., 2011; Iqbal et al., 2011)

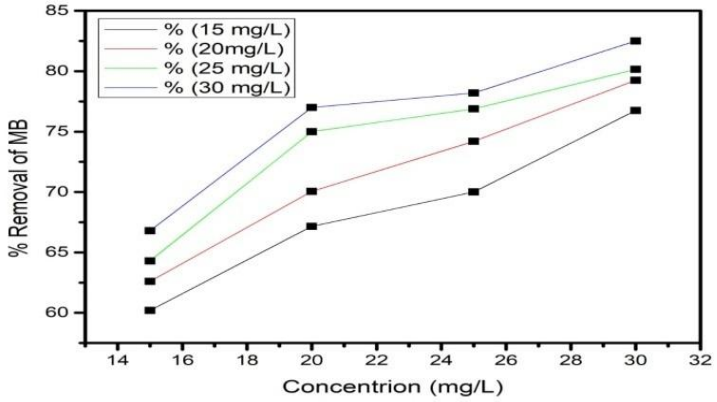

Figure-2 Effect of Concentration on MB removal:

Effect of adsorbent dose:

The initially rate in the percent dye removal increases rapidly which is then slow down as there is increase in the material dose. This phenomenon can be explained, because at lower adsorbent dose, the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. The initial rise in adsorption with adsorbent dose is probably due to bigger driving force and lesser surface area. Larger surface area of the adsorbent and smaller size of adsorb ate favour adsorption. The rate of adsorption is higher in the beginning Fig.3 as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rate become equal at a stage called adsorption equilibrium. The subsequent slow rise is observed in percent removal, which states that adsorption and intra-particle diffusion-taking place simultaneously with dominance of adsorption. Thus, the results obtained from this section of experiment indicate that crushed biomass has a good potential as an adsorbent for dye removal.

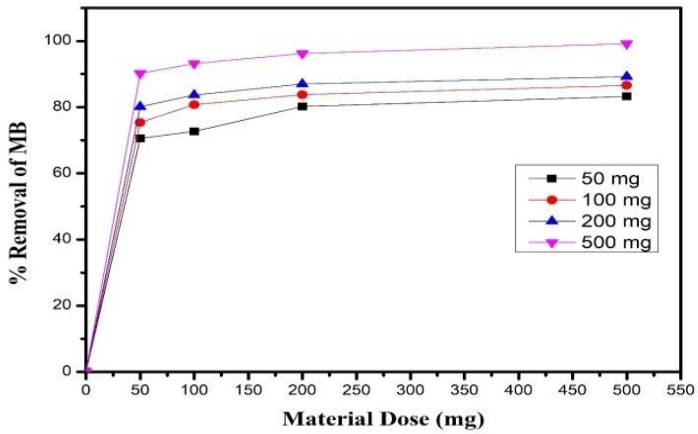

Figure 3 Effect of material dose on MB removal

Effect of Temperature:

Temperature dependence of adsorption process is a complex phenomenon. Thermodynamic parameters, like heat of adsorption and energy of activation play an important role in predicting the adsorption behaviour and both are strongly dependent on temperature. Temperature rise affects the solubility and chemical potential of the adsorbate, the latter being a controlling factor for adsorption. It have been reported that if solubility of the adsorbate increases with increase in temperature, then chemical potential decreases and both of these effects work in the same direction, causing a decrease in adsorption [17]. On the other hand if temperature has the reverse effects on the solubility than both the said effects will act in the opposite direction and adsorption may increase or decrease depending upon the predominant factor. In the present experiments the adsorption rate at four different temperatures (15°,25°,35^0,45°C) have been analysed as presented in data Table. 2. For the crushed biomass, the rate of dye uptake decreases with an increase in temperature from 82.32% to 72.4% at 15°C to 45°C with100 gm dose in 45 60 minutes for 25-ppm dye solution, indicating that the process is exothermic in nature [18]. This may be due to a tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution.

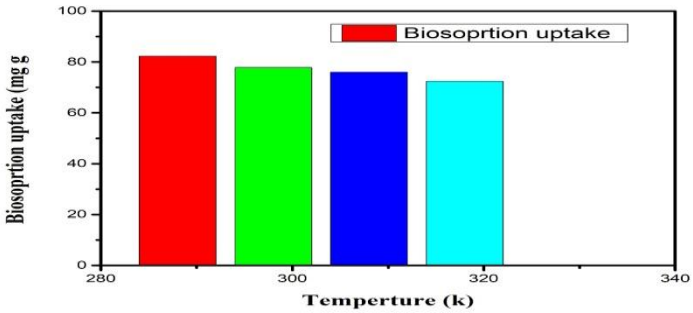

Figure 4: Effect of temperature on MB removal.

Effect of solution pH:

The effect of pH on the amount of MB adsorbed onto crush biomass was investigated over the pH range from 2 to 10. The pH was adjusted using 0.1 mol l^{-1}, NaOH or 0.1 mol l^{-1} HCl solutions. In this study, 25ml of MB solution of 25 mg l^{-1} was agitated with 100m g $l^{-1}$of crushed biomass. Agitation was made for 15 min and the adsorption mixture was filtered and absorbance was measured. It was found that the higher adsorption of MB observed at pH 2. As shown in fig.5

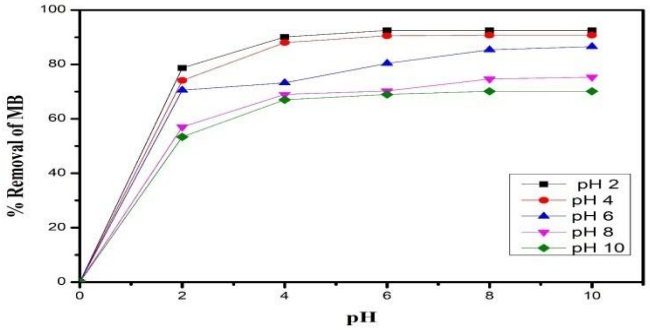

Figure-5 Effect of pH on methylene blue removal.

Adsorption isotherms:

Langmuir isotherm:

The Langmuir (1916) sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites .constitution and fundamental properties of solids and liquids. The Langmuir equation is written as

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{KLqmCe} \qquad (3)$$

The shape of this isotherm can also be expressed in terms of separation factor (RL), which is given as follows

$$RL = \frac{1}{1 + KLCO} \qquad (4)$$

Where KL is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. qe is dye concentration at equilibrium onto bio sorbent (mg/g). Ce is dye concentration at equilibrium in solution (mg/l).qm is dye concentration when monolayer forms on biosorbent (mg/g).

Freundlich isotherm:

The Freundlich equation for heterogeneous surface energy systems shown by is given by Eq. (5).

$$Ln = \ln KF + \frac{1}{n} \ln Ce \qquad (5)$$

The KF and n are Freundlich constants, determined from the Plot of ln qe versus ln Ce. The parameters KF and 1/n are related to sorption capacity and the sorption intensity of the system. The magnitude of the term (1/n) gives an indication of the favourability of the sorbent/adsorbate systems

Temkin isotherm:

X.S. Wang, Y. Qin. (2005) Equilibrium sorption isotherms for crush biomass. The linearized Temkin equation is given by the following equation

qe =β ln α+ β ln (6)
Where
β = RT/b
T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), and b is the Temkin constant related to heat of sorption (J/mg). The Temkin constants a and b are calculated from the slope and intercept of qe versus ln Ce.

Adsorption kinetics:

The pseudo first order rate expression is given as:
Log (qe-qt) = log qe – k1t/2.303 (7)

Where, qe and qt are the amount of dye adsorbed on sorbent at equilibrium and time t (mg/g) and k1 is the first order rate constant (min^{-1}). A plot of log (qe/qt) versus t gives a linear relationship, from which the value of k1 and qe can be determined from the slope and intercept. The linearized form of pseudo second order rate expression is given as

$dq1= k2 (qe-qe)^2$ (8)

$t/qt =1/k2q^2e + t/qe$ (9)

where qe is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), qt is the amount of adsorbate adsorbed at contact time t (mg/g) and k2 is the pseudo second order rate constant (g/mg min). A plot of t/qt versus t gives a linear relationship, from which qe and k2 can be determined from the slope and intercept. The data for the adsorption of MB on of crush biomass were applied to pseudo first and pseudo second order kinetic models and the results are presented in Table-1.kinetic model is greater than for first order kinetic model (Table-1, Figure- 6). This confirmed that the rate-limiting step is chemisorptions, involving valence forces through sharing or exchange of electrons.

Table- 1 Kinetic and thermodynamic parameters for the sorption of MB onto crush biomass of Ailanthus excelsa. Pseudo first order and Pseudo second order model:

Pseudo first order model k1 (min_1) 0.024	qe(mg/g) 3.0471	R^2 0.8229
Pseudo second order model k2 (g/(mg/min) 0.06644	2.4176	0.99997
Interparticle diffusion model kd (mg/g min) -0.08055	C(mg/g) 5.33	0.3460
Thermodynamic parameters ΔH^0 (kJ/mol) -7.789.91	ΔS^0 (J/mol K) -2.91788	DG^0 (kJ/mol) -806.2052

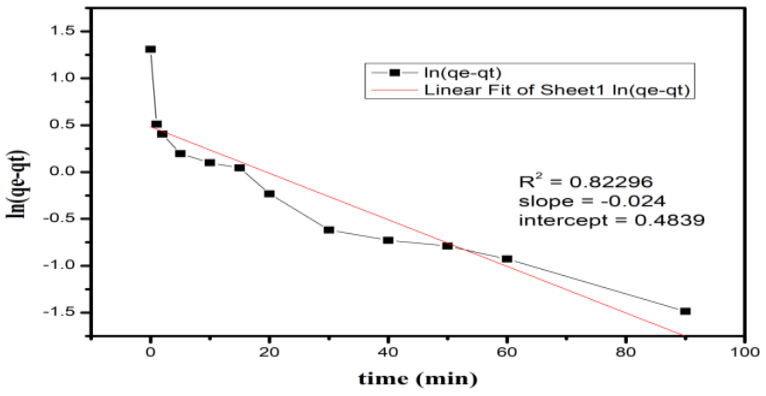

Figure 6: Pseudo-first order

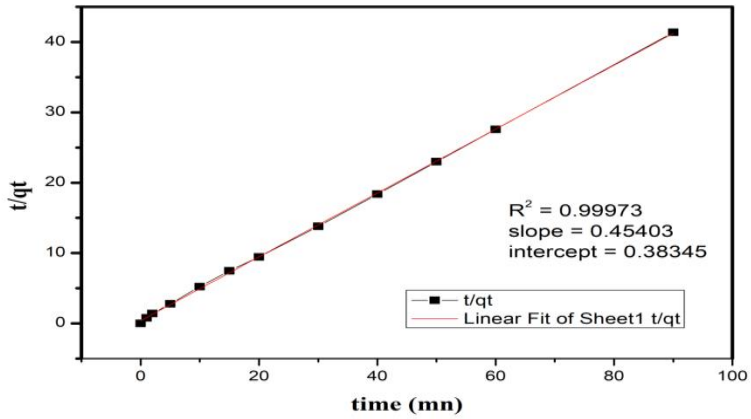

Figure 7: Pseudo-second order

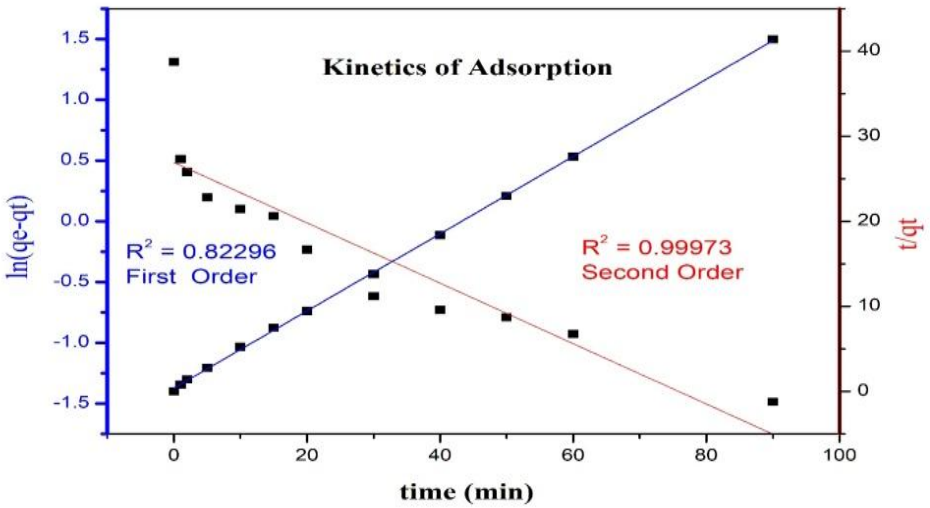

Figure 8: Kinetics of Adsorption:

ADSORPTION ISOTHERM:

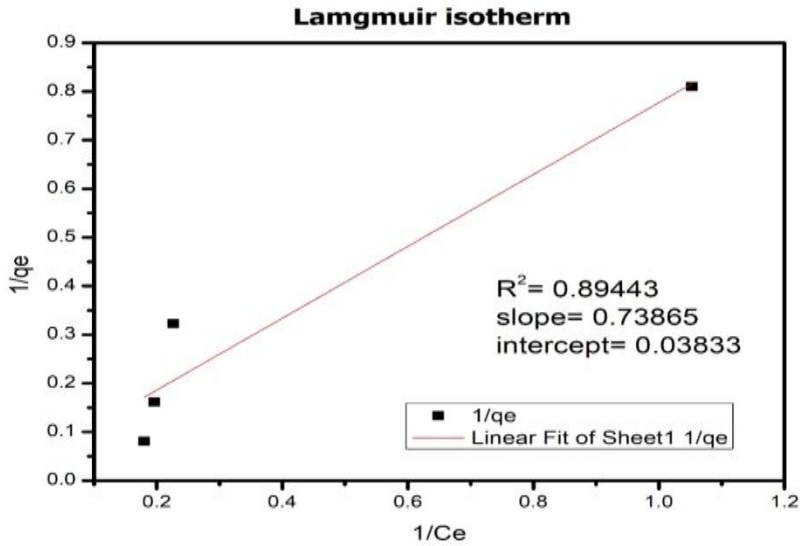

Fig-9: Freundlich Isotherm.

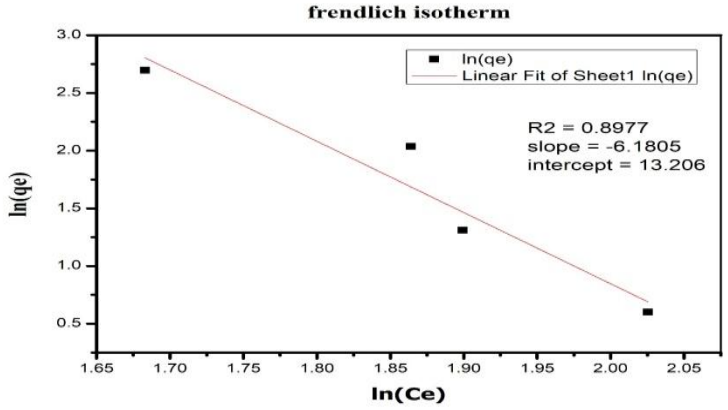

Fig-10: Temkin Isotherm

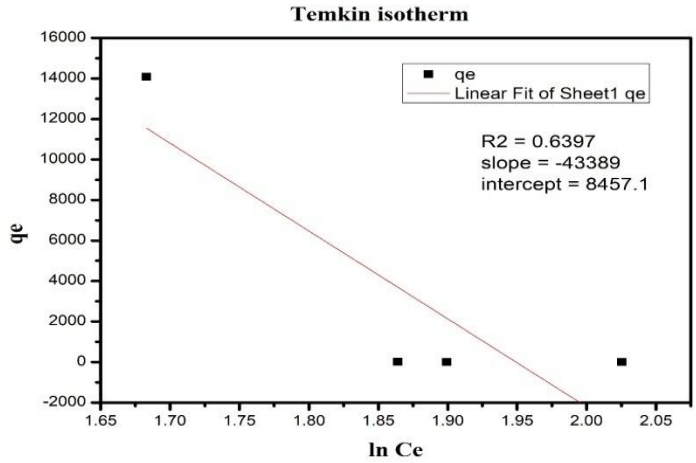

Fig-11: Freundlich Isotherm.

Adsorption capacity:

The sorption capacity and other parameters were evaluated using Langmuir, Freundlich and Temkin isotherm models is explain following table -2 . Biosorption of Hg2+ions by Sulphonated biomass of Stalks of Prunus cerasus [26] studied with the Langmuir, Freundlich and Temkin isotherm models**.**

Table -2 Results of various isotherm plots for the adsorption of MB onto crush biomass of Ailanthus excelsa.

Models		**Isotherm constants**		
Langmuir	q_m(mg/g) 1.3539	KL(L/mg) 19.2715	RL 0.002071	R^2 0.8944
Freundlich	q_m(mg/g) -6.1805	KL(L/mg) -0.1617	RL -0.3286	R^2 0.8977
Temkin	Intercept 8457.1	Slope -43389	----	R^2 0.6397

The high value of correlation coefficient 0.9907 (Fig-6) indicates the applicability of Langmuir isotherm which assumes a monolayer coverage and uniform activity distribution on the sorbent surface. In the present study, favour the adsorption of MB onto of crush biomass Eq. (5) was used to evaluate Temkin isotherm. The value of correlation coefficient R2 obtained from Temkin isotherm was found to be 0.9762 constant b is related to heat of sorption indicating physic–chemical nature of the sorption process. The equilibrium data were also fitted to the Freundlich equation. The parameters KF and n indicated the sorption capacity and the sorption intensity of the system. The magnitude of the term (1/n) gives an indication of the favourability of the sorbent/adsorbate systems. The correlation coefficient value (0.946) is lower than Langmuir and Temkin values. Therefore, adsorption onto crush biomass does not follow Freundlich isotherm closely.

CONCLUSION

In this work it has been observed that the crushed biomass of Ailanthus excelsa shows, promising adsorption capacity for methylene blue removal. The maximum sorption for MB solution concentration (0.025m g/100 ml), sorbent dosage (0.10 g/100 ml), the optimum contact time (20 minutes) and optimum temperature (288 K) were observed. The maximum removal of methylene blue dye was attained at pH 2.0. The equilibrium data were fitted well in the Langmuir, Freundlich and Temkin isotherm models, which confirmed that the sorption is heterogeneous, and occurred through physico–chemical interactions. The adsorption isotherm data was better fitted to the Langmuir and Freundlich isotherm with the R^2 values 0.8944 and 0.8977 respectively. It has been observed that an average 79.6% removal of methylene blue under the different conditions in the batch experiment. The data fit well in the Freundlich isotherm. The Langmuir and Freundlich equations were found to have the correlation coefficient value in good agreement. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value R^2 is 0.9997. The negative DG° values indicated that the sorption of dye onto biosorbent was feasible and spontaneous. The negative ΔH^0 value depicted exothermic nature of the sorption. The entropy change negative, making the reaction spontaneous only at low temperatures**.** The parameters KF and n indicated the sorption capacity and the sorption intensity of the system.

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