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Adsorptive Removal of MethyleneBlue through Biosorption from Aqueous Solution using Lysiloma Latisiliquum Seed Powder.

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ABSTRACT
In this present study, Lysiloma Latisiliquum (LL) seed powder is chosen as the adsorbent for removal of Methylene Blue (MB). Studies were conducted in Batch Mode process for various experimental conditions such as contact time, initial dye concentration, pH, adsorbent dosage and temperature to determine the potentiality and efficiency of the adsorbent for removal of MB from aqueous solutions. Consequently, the experimental data obtained was analyzed using the adsorption isotherms and kinetic models. The adsorption process is found to be optimum at pH of 6 for an equilibrium time of 50 mins with an adsorbent dosage of 20g/lit. Based on regression coefficient, adsorption of MB onto LL seed powder followed Pseudo-Second-Order kinetics. The experimental data obtained fitted well with Langmuir isotherm model and Freundlich isotherm model. The maximum adsorption capacity was found to be 20.703 mg/g.

Keywords - Adsorption, Kinetic Models, Adsorption Isotherms, Lysiloma Latisiliquum.

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I. INTRODUCTION

Globally, more than 10,000 synthetic dyes with distinct chemical structures and forms are being produced and available commercially [1-7]. Dyes find their place in industries like textile, paint, cosmetics, paper, ceramic in order to color their products [8-10]. The effluents emerging out from these industries are highly colored, possess carcinogenic properties and toxic for the environment. Hence, the removal of these dyes is of great environmental significance [11,12].

Biological treatment methods are gaining significant importance as conventional methods such as coagulation and flocculation, reverse osmosis, membrane filtration, electro flotation irradiation, ozonation, microbiological degradation and active carbon adsorption are restricted to extensive applications due to their high capital investment and operational costs [13-17]. On the other hand, biosorption has being a promising alternative for its low-cost, flexibility, operational simplicity and high adsorption capacity [18-20]. Many biosorbents have been reported in the literature for the biosorption process. Few of them are Tea waste [21], Mango seeds [22], Peanut husks [23], Marine seaweed [24].

In this study, Lysiloma Latisiliquum seed powder is chosen as the biosorbent. The main purpose of this study is to find the potentiality of this biosorbent and its influence on adsorption process. Various parameters like contact time, initial dye concentration, pH, dosage of adsorbent, temperature was taken into account for evaluation of adsorption capacity.

II. MATERIALS AND METHODS.

2.1. Preparation of Biosorbent:

The adsorbent used here is Lysiloma Latisiliquum (LL) seed powder. The Lysiloma Latisiliquum plant was collected in its raw form near West Bengal. In the beginning, the plant was washed with normal ground water to remove fine dust and thereafter cleansed with distilled water for several times. Then, it is dried in an oven at 65^0C for 72h. It is then grounded using a household grinder. The adsorbent was stored in a moisture- free surrounding any used in experiments without any further pre-treatment.

2.2. Preparation of Dye Solutions:

Methylene Blue (MB) was used as the dye in this experiment. MB is purchased from a dealer and is used in the experiment without any further purification. Stock solution of 1000ppm of MB was prepared by dissolving 1.0g of MB in 1L of distilled water. This solution is stored in a volumetric flask. Further desired concentrations in this experiment were prepared by serial dilution of stock solution

with distilled water. The final dye concentration in the solution is measured by using a UV spectrometer at a specified wavelength of 600 nm.

2.3. Biosorption experiments:

The experiments were conducted in batch process using a 250mL conical flask filled with 100mL of MB solution with 25ppm initial concentration. Experiments were carried out for varying concentrations: 25ppm, 50ppm, 100ppm, 150ppm with 1.0g of Nicotiana tabacum powder. The pH of the solution is kept at its original value (6). The solutions were agitated using an orbital shaker spinning at constant 180 rpm for equilibrium time. Also, keeping the procedure same, experiments were done for different pH values: 6, 7, 8.5 and temperatures: 30^0C, 40^0C, 50^0C. The adsorption kinetics were performed at equilibrium conditions. Samples were collected at pre-determined time intervals and subjected to centrifugation to estimate the final dye concentration in the supernatant solution using UV spectrometer.

The adsorption capacity (q_e) is estimated by using:

$$q_e = \frac{C_i - C_e}{m} V$$

The percent removal (%) of dye was calculated using the following equation:

$$\% = \frac{C_i - C_e}{C_i} \times 100$$

III. RESULTS & DISCUSSIONS

3.1. Effect of Contact Time:

Determination of contact time was investigated by adding certain amount of Wild Tamarind Seeds powder (1.0g/100mL) to conical flasks containing 50 mg/L concentration of Methylene Blue dye with a base pH of 6 at a temperature of 303K. The dye solution is agitated in an Orbital Shaker and the samples are centrifuged. The clear is subjected to analysis for residual dye concentration. The same is repeated for different time intervals: 1,3,5,10,20,30,40,50,60,90,120,150 and 180 mins and the samples were analyzed. From these intervals, equilibrium time is determined. From Fig 1., the percentage biosorption revealed that it increases with increase in agitation time from 1-50 mins and percentage of biosorption observed was 75.40%.

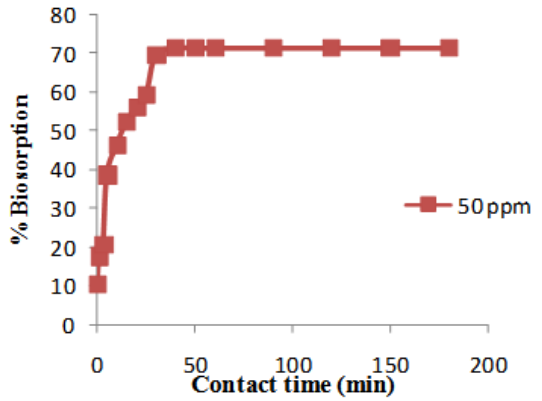

Fig 1. Effect of contact time on the adsorption of MB onto LL seed powder (Experimental Data: initial concentration = 50 mg/L).

3.2. Effect of initial concentration:

The effect of initial dye concentration was measured by varying concentrations of MB dye solution. Initially, 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L concentration solutions were taken for the experiment. Then, to these solutions (100ml) containing different concentrations, a known weight of Latisiliquum seed powder (1.0g) is added. The solutions were agitated for equilibrium time at a temperature of 303K and centrifuged for measuring final dye concentration.

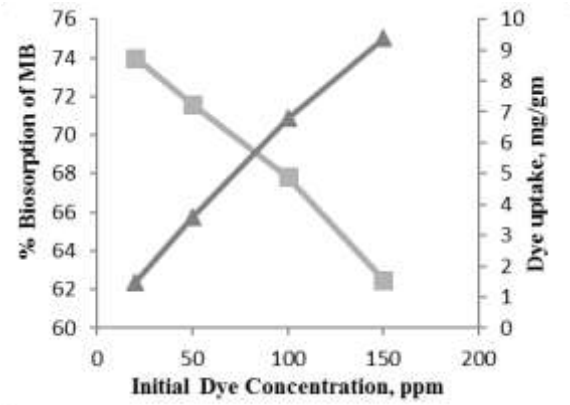

Fig 2. Effect of initial concentration on the adsorption of MB onto LL seed powder. (Experimental Data: Adsorbent Dosage = 1g/100mL, Contact time = 50 mins).

3.3. Effect of pH:

The charge on the surface of adsorbent and the degree of ionization of different components in the solution are affected by the Ph of the solution. The varying pH effects the adsorption process through the dissociation of functional groups onto the biosorbent's surface active sites. The adsorption of MB is studied in the pH ranges of 2-9. The orbital shaker is used for agitation of solutions at a speed of 180 rpm for equilibrium time. UV spectrometer is

used to measure the residual dye concentrations. As pH increased from 2 to 5, the biosorption capacity of MB increased and later declined from 5 to 9. Therefore, acidic medium is favorable for biosorption of MB. The results are illustrated in Fig 3.

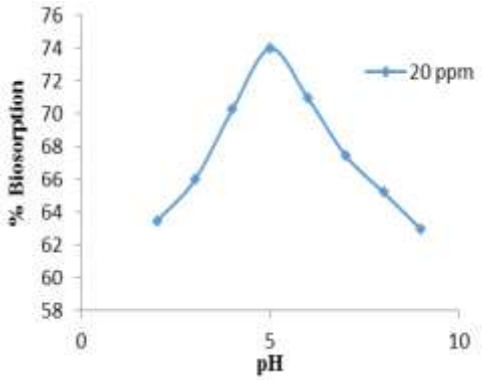

Fig 3. Effect of pH on the adsorption of methylene blue onto LL seed powder. (Experimental Data: Adsorbent Dosage = 1g/100mL, initial concentration = 20mg/L, Contact time = 50 mins).

3.4. Effect of adsorbent dosage:

The dosage of biosorbent is a key parameter as it helps in determining the adsorption capacity of the biosorbent. Experimental results are represented in Fig 4. The biosorption yield increased from 65.55% to 86.75%, when biosorbent dosage was increased from 0.5g to 2.5g. This sudden rise may be due to an increase in number of possible binding sites and surface area of adsorbent. Increase in biosorbent mass from 2g to 2.5g showed no appreciable improvement in biosorption yield. This may be attributed to a restricted aggregation of biomaterial, which ultimately results in a decreased effective surface area for biosorption.

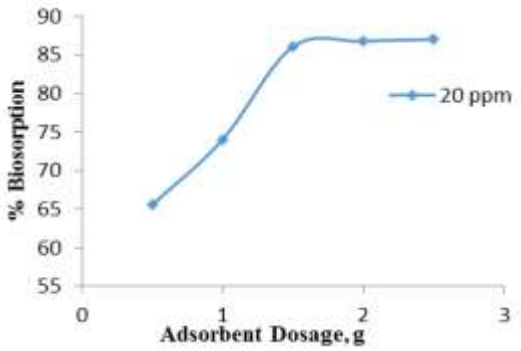

Fig 4. Effect of Adsorbent Dosage on the adsorption of methylene blue onto LL seed powder. (Experimental Data: Initial concentration = 20mg/L, Contact time = 50 mins, pH =5).

3.5. Effect of Temperature:

In the process of biosorption, temperature is one of the major governing factors effecting the potentiality of adsorbent. The change in temperature affects the equilibrium capacity of the adsorbent. The adsorption rate constant of removal of MB with initial concentration of 20mg/L at pH 5 and temperatures 298K to 318K on Latisiliquum seed powder has been studied for this purpose. The removal of MB increases from 80.55% to 92.80% by LL Seed Powder with an increase in temperature from 298K to 318K. The results are illustrated in Fig 5.

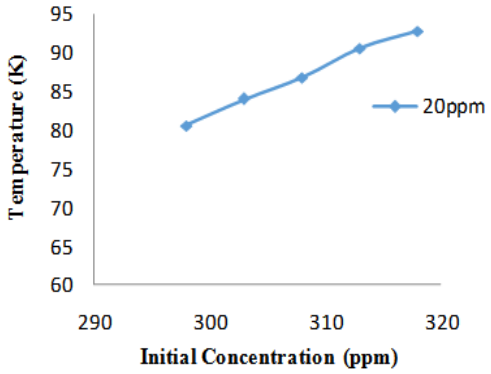

Fig 5. Effect of Temperature on the adsorption of methylene blue onto LL seed powder. (Experimental Data: Adsorbent Dosage = 2g/100mL, initial concentration = 20mg/L, Contact time = 50 mins, pH =6).

3.6. Biosorption Kinetics:

The study of kinetics plays a pivotal role in analyzing the reaction pathways and also the mechanism involved. For obtaining optimum conditions for full-scale process, data on kinetics is required. Kinetic studies were performed in conical flasks containing 100 mL MB solutions of 20 mg/L concentration. The flasks were agitated in an orbital shaker at 180rpm. Samples were taken at regular intervals, centrifuged and analyzed for the residual MB concentrations. The Lagergren first order rate equation and pseudo-second-order equations were used for modelling MB biosorption kinetics and kinetic data obtained were analyzed using regression coefficient (r^2).

The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows (Lagergren, 1898):

$$\frac{dq}{dt} = K_1(q_e - q)$$

After integrating and applying the boundary conditions, for q=0 at t=0 and q=q at t=t, the integrated form of the above equation becomes:

$$q = q_e(1 - e^{-Kt})$$

where q_e and q (both in mg/g) are respectively the amounts of dye adsorbed at equilibrium and at any time 't', and k_1 (1/min) is the rate constant of biosorption.

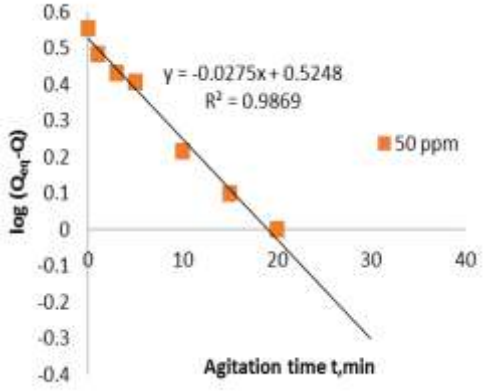

Fig 6.1. First Order plots for the adsorption of MB onto LL seed powder.

The Pseudo-second-order is based on the assumption that the adsorption process follows second order chemisorption. This model can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

Integrating the above equation with similar boundary conditions, the following is obtained:

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_2 t}$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption.
The experimental data and correlation coefficients are provided in Fig6.1. The table shows that the correlation coefficients for the second order kinetics are more appropriate than the first order kinetics. Hence, from these we can say that the pseudo-second-order model holds good than the Lagergren first order for the systems studies in this work.

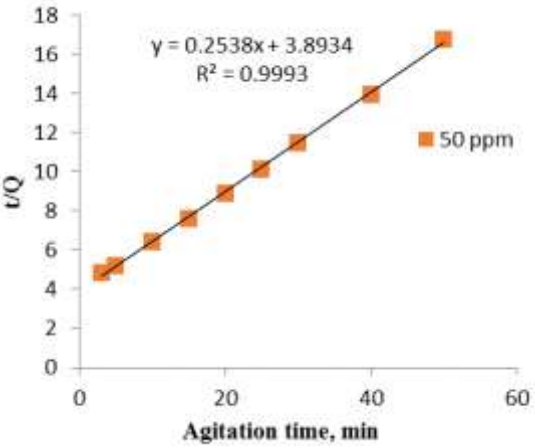

Fig 6.2. Pseudo Second Order plots for the adsorption of MB onto LL seed powder.

Table 6.3. Kinetic Parameters for adsorption of MB onto LL seed powder.

Conc MG (mg/L)	q_e^{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_e^{cal} (mg/g)	K_1 (min^{-1})	R^2	q_e^{cal} (mg/g)	K_2 (min^{-1})	R^2
50	3.579	3.34	0.06333	0.98	3.9401	0.0165	0.9993

3.7. Biosorption isotherms:

Adsorption is typically modelled by isotherms as they relate the relative concentrations of solute adsorbed onto the solid (q_e) and in solution (C_{eq}) Throughout the literature, many models have been established in order to get suitable correlations for the equilibrium curves. In this study, isotherms data were analyzed using three models: Langmuir, Freundlich and Temkin.

Biosorption isotherm studies were performed by contacting 2.0g of Latisiliquum seed powder with 100mL MG solutions of 20 mg/L concentration at pH 5 and temperature of 303K. For obtaining equilibrium time, the solution is agitated using orbital shaker at constant rpm of 180. Entire procedure is repeated in the temperature range of 298K to 318K.

i) The Langmuir Model:

It is based on the assumption that the sorption process is homogenous and monolayer with a fixed number of biosorption sites. The governing equation is as follows:

$$q_e = \frac{q_{max} K_a C_{eq}}{1 + K_a C_{eq}}$$

where q_{max} is the monolayer biosorption capacity (mg/g) and the Langmuir constant K_a is related to energy of biosorption. Linearized equation of Langmuir Model is:

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{K_a q_{max} C_{eq}}$$

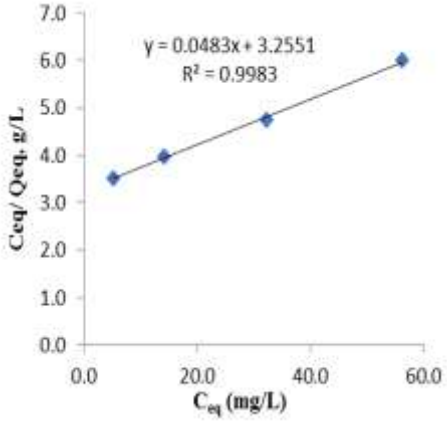

Fig 7. Langmuir adsorption isotherm for the adsorption of MB onto LL Seed Powder.

ii) The Freundlich Model:

It was proposed by Boedecker in 1895 and later modified by Freundlich. It is an empirical equation based on sorption onto a heterogeneous surface. Its equation is:

$$q = KC_{eq}^{\frac{1}{n}}$$

The linearized form is:

$$lnq = lnK + \frac{1}{n} lnC_{eq}$$

where 'q' is the equilibrium biosorption capacity (mg/g), C_{eq} is the equilibrium concentration of the adsorbate in the solution. 'K' and 'n' are constants related to biosorption process such as biosorption capacity and intensity capacity.

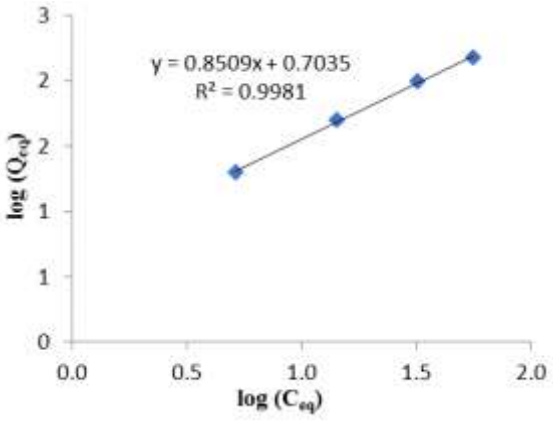

Fig 8. Freundlich adsorption isotherm for the adsorption of MB onto LL seed powder.

iii) Temkin Model:

It was proposed by Temkin and Pyzhev. They suggested that due to the interactions between adsorbate/biosorbent indirectly, the heat of biosorption of all the molecules in the layer would decrease linearly. It's of the form:

$$q = \frac{RT}{b} \ln(A_T C_{eq})$$

where A_T (L/mg) and b are Temkin isotherm constants. 'T' is the absolute temperature in Kelvin and 'R' is the universal gas constant (J/mol.K). C_{eq} is the equilibrium concentration of the adsorbate.

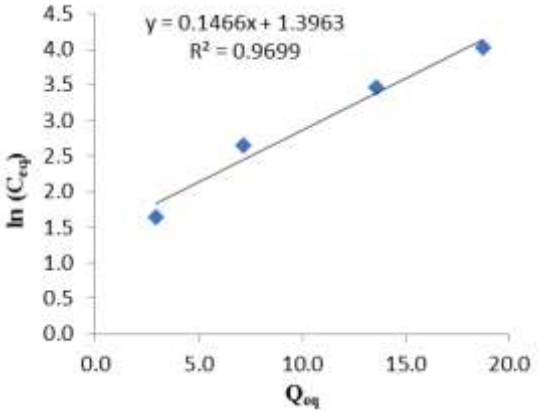

Fig 9. Tempkin adsorption isotherm for the adsorption of MB onto LL seed powder.

Table 10. Isotherm Parameters

Isotherm	Parameter	Values
Langmuir	q_{max} (mg/g)	20.703
	K_a	0.015
	R^2	0.9983
Freundlich	K	5.0524
	n	1.1752
	R^2	0.9981
Tempkin	A_T (L/g)	1.1107
	b (KJ/mg)	17.183
	R^2	0.9699

IV. CONCLUSIONS

From the above results, it is evident that Lysiloma Latisiliquum seed powder is potent for removal of MB. An optimum pH of 6 is observed for the removal of MB. Based on regression coefficient, Pseudo Second-Order-Kinetics fits the adsorption process. Langmuir, Freundlich and Tempkin models were studied for analyzing equilibrium data. Both Langmuir and Freundlich models indicated best fits with maximum removal of 20.703 mg/g.

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