



Adsorption of Malachite Green onto *Lysiloma latisiliquum* seed powder from aqueous solution

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Abstract

In this present study *Lysiloma latisiliquum* seed powder, a low-cost agricultural byproduct, was used as the adsorbent for the removal of cationic dye malachite green (MG) from aqueous solutions. The adsorbent was characterized by Fourier Transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), XRD analysis. Batch mode adsorption studies were performed under various experimental conditions such as contact time, initial dye concentration, pH, adsorbent dose, and temperature to assess the potentiality of the adsorbent for the removal of MG from aqueous solutions. Optimum absorption of MG was found to be at pH of 6.0, for an equilibrium time of 90min with an adsorbent dosage of 20 g/L. Kinetic data were studied using pseudo first order and pseudo second order models. The experimental results showed that it followed pseudo second order kinetics. The data fitted well with Freundlich model with a maximum adsorption capacity of 35.5871 mg/g.

Keywords: bio sorption, kinetic studies, adsorption isotherms, *Lysiloma latisiliquum* (LL) seeds, malachite green (MG)

1. Introduction

Dyes are the substances which add a specific color to a material. The usage of dyes can be traced back since the debut of civilization^[1]. All the dyes used today, apart from one or two exceptions, were discovered in the late nineteenth century. The introduction of reactive dyes in 1954 and their launch in 1956 indicated a major breakthrough in the cotton dyeing industry^[2]. Dyes play a prominent role in textile, leather, paper and paint industries. Consequently, immense volumes of effluents are being released and discharged straight into water bodies^[3]. The discharged colored wastewater possesses a huge threat to both human and aquatic life due to its toxicity, carcinogenicity and mutagenic nature^[4, 5]. It is therefore of significant relevance to treat these effluents before routing them directly to waterbodies. But most of the synthetic dyes comprises of complex aromatic structures and possess xenobiotic properties^[6]. Malachite Green (MG), a triphenylmethane, is a cationic dye, also called as basic green 4, is enormously consumed as biocide in aquaculture industries for its effectiveness against parasitic treatment, fungal and bacterial infections in fish and fish eggs. MG is an environmentally sustained dye and is venomous to various aquatic and terrestrial animals as it was found to be toxic to mammalian animals and may trigger liver tumor formations^[7, 8]. Though MG has been banned in several countries and not approved by US Food and Drugs Administration, it is still being used for its low cost, immediate availability and efficacy and unavailability of conventional alternative^[9, 10]. This cause has driven researchers to conduct studies on removal of MG from aqueous solutions using physical, chemical and biological methods^[11-15]. Several conventional methods have been employed to

remove dyes from aqueous solutions: Ion-exchange, electrocoagulation, Ultrafiltration, Photo oxidation, Reverse Osmosis, Microwave Oxidation etc. These methods have considerable disadvantages such as producing by-products, high power requirement and expensive equipment costs^[16, 17]. Adsorption, on the other hand, is one of the efficient methods for removal of dyes. Activated carbon has been used extensively as the adsorbent due to its high surface area and porosity. For the sake of its economical constraint, its use is limited^[18].

Lysiloma latisiliquum commonly known as wild tamarind is an edible oil seed-bearing plant well suited for humid, warm and tropical regions. Its seeds contain 9.4% - 11.3% of moisture, 13.3% - 26.9% of protein, 4.5% - 16.2% of Fat/oil, 7.4% - 8.8% of crude fiber, 50% - 57% of carbohydrates and 2.4% - 4.2% of ash^[19]. The seeds of this ecofriendly tree which are considered to be a waste material has been used for the present study for the removal of malachite green from aqueous solution. The main objective of the study is to investigate the feasibility of formaldehyde – treated *Lysiloma latisiliquum* seed powder in the removal of malachite green from aqueous solutions. The effects of contact time, initial dye concentration, pH, Dosage, temperature, kinetic parameters and adsorption isotherms were evaluated in this study.

2. Materials and methods

2.1 Preparation of Biosorbent

The seeds of *Lysiloma latisiliquum* are collected near Kolkata in West Bengal. First, the seeds are washed numerous times with distilled water to remove any dust particles. Subsequently, it is dried at 75°C for 48h. The dried seeds are then powdered into fine particles using a

household blender. Further, the obtained powder is stored in a glass bottle for experiment purpose without any pre-treatment.

2.2 Preparation of Dye Solutions

Malachite Green was purchased from a local dealer and is of analytical grade. Stock solution is prepared by dissolving appropriate quantity of the dye without any further purification in distilled water and the concentrations were obtained by serial dilution of stock solution. The pH of the solutions was adjusted by addition of 0.1N NaOH and 0.1N HNO3.

2.3 Biosorption experiments

The biosorption experiments were performed in 250mL conical flasks at a constant agitation speed. The experiments were carried out by varying contact time from 0 to 180 mins and biosorbent dosage from 0.5 to 2.5 g/100 mL, the pH ranges from 2-9, the initial concentration from 20 to 150 mg/L and the temperature from 25°C to 45°C. The temperature is controlled by using incubator. After each batch process completed, the samples were centrifuged at a speed of 2500 rpm for 10 min to separate solid phase from the liquid phase.

2.4 Analyses

The residual amount of dye in each flask was investigated using UV spectrometer (ANTECH) of 619.5 nm wavelength. The amount of dye adsorbed per unit tobacco powder was calculated according to mass balance on dye

concentration using the equation:

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

Where Ci is the initial dye concentration (mg/L), Ce is the equilibrium dye concentration in solution (mg/L), V is the volume of solution of solution (L) and m is mass of adsorbent in g.

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

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

3. Results & Discussion

3.1 Characterization of *Lysiloma latisiliquum* seed powder

The particle size of *Lysiloma latisiliquum* seed powder was observed to be 100 - 120 μm (Average: 110 μm), which is used as adsorbent in many experiments. Figs (1) & (2) depicted FT-IR spectra of *Lysiloma latisiliquum* seed powder, in which the bend near bend near 3600 cm-1 was revealed, is due to hydroxyl group, a broad bend near 3000 - 3200 cm-1 of amino and carboxylic acid group, a 1653 and 1541 cm-1 are due to primary amine and nitro compound and also, 1064 cm-1 of primary alcohol (C-O) stretching. The adsorbent containing these bends are usually utilized for color removal. The SEM images of *Lysiloma latisiliquum* seed powder (Fig. 3) at higher magnifications 500X shows that the surface of materials is porous.

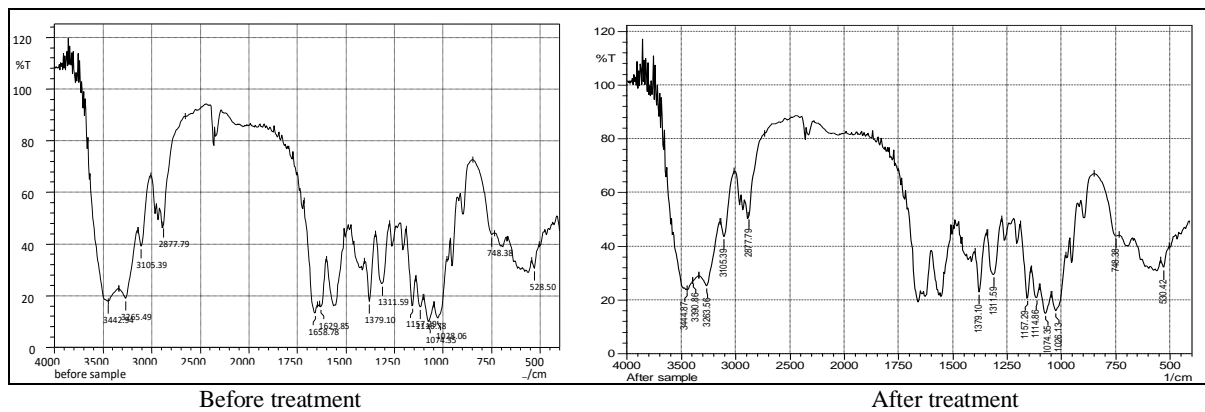


Fig 1: FTIR Images of biosorbent

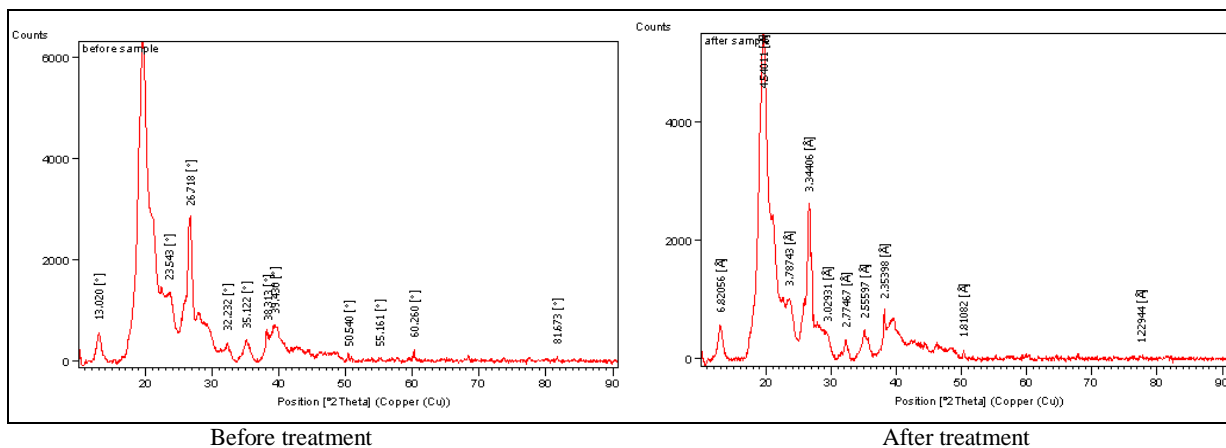


Fig 2: XRD images of biosorbent

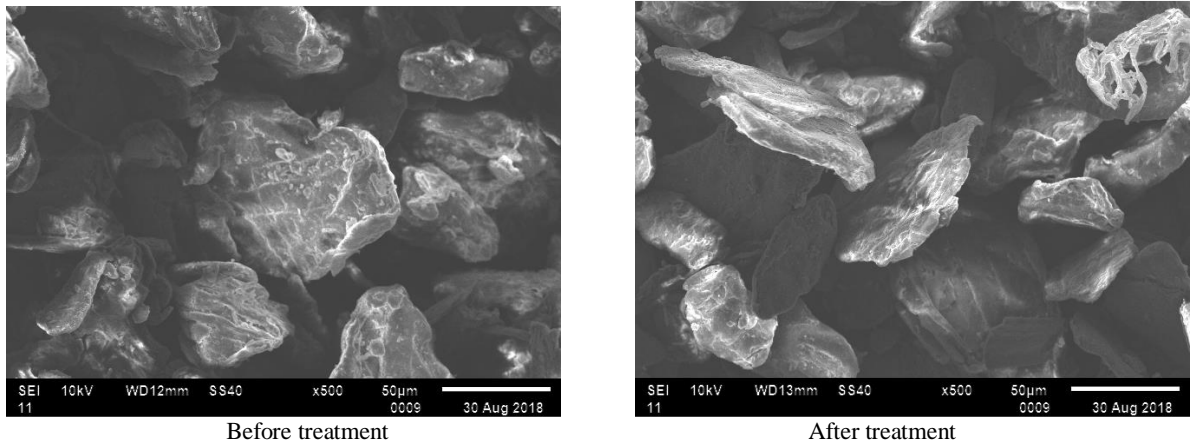


Fig 3: SEM images of biosorbent

3.2 Effect of Contact Time

The impact of contact time on biosorption of dye was investigated by adding known amount of Wild Tamarind Seeds powder (1g/100 mL) to conical flasks containing 50 mg/L concentration of Malachite Green dye with an underlying pH of 6 at a temperature of 303K. This solution is agitated in an Orbital Shaker at 180 rpm for 1min and then subjected to centrifugation. Post the agitation, the clear liquid is carefully decanted and subjected to analysis for residual dye concentration. Same procedure is repeated at different time intervals: 1,3,5,10,20,30,40,50,60,90,120,150 and 180 mins. From these intervals, equilibrium time is determined. From Fig 4. The percentage biosorption revealed that it increases with increase in agitation time and attained equilibrium at 50 mins and percentage of biosorption observed was 75.40%.

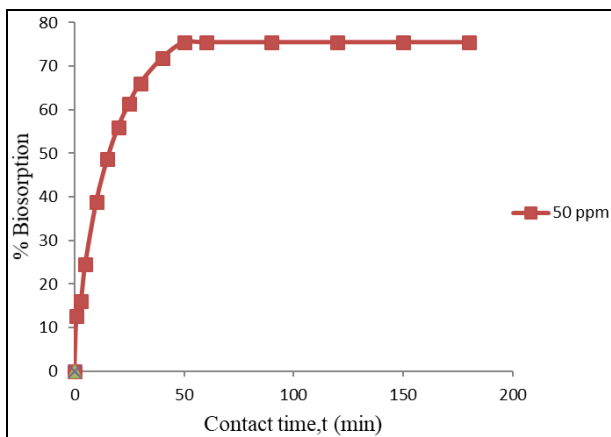


Fig 4: Effect of contact time on the adsorption of malachite green onto LL seeds (Experimental Data: Initial concentration = 50 mg/L, T=303K)

3.3 Effect of initial concentration

The effect of initial dye concentration was measured by varying concentrations of MG dye solution. For this, 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L initial concentration solutions were taken for the experimental purpose. The results obtained are shown in Fig. 5, shows that dye uptake increased and % biosorption of MG on to LL seeds decreased with increase in initial dye concentration in the studied range. This increase in dye uptake (1.68 to 10.5

mg/g) is probably due to higher interaction between dye ions and the biosorbent. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent [20]. Equilibriums have been established at 50 minutes for all concentrations. Fig. 4 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface.

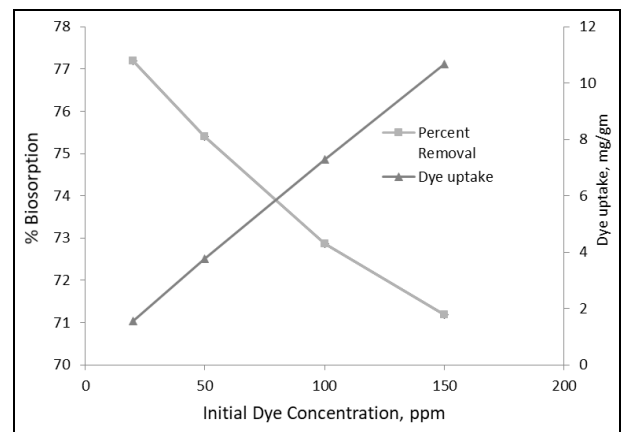


Fig 5: Effect of initial concentration on the adsorption of malachite green onto LL seeds. (Experimental Data: Adsorbent Dosage = 1g/100 mL, Contact time = 50mins, T=303K).

3.4 Effect of pH

The pH of the solution effects the charge on the surface of adsorbent and also degree of ionization of different components in the solution. The varying pH effects the adsorption process through the dissociation of functional groups onto the biosorbent surface active sites. The adsorption of MG is studied in the pH ranges of 2-9. As pH is increased from 2 to 6, the biosorption capacity of MG increased from 68 to 76.50% and later declined from 6 to 9. Low pH depresses the biosorption of dye, due to competition with H+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and dye ions replace H+ ions bound to the biosorbent. This indicates that biosorption of MG is favorable in acidic medium. The results are illustrated in Fig 6.

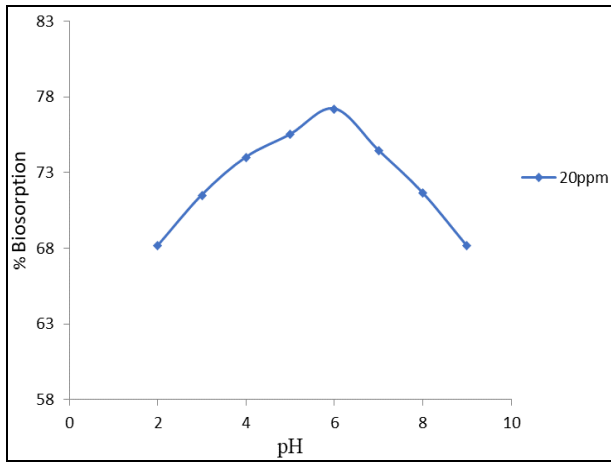


Fig 6: Effect of pH on the adsorption of malachite green onto LL seeds (Experimental Data: Adsorbent Dosage = 1g/100 mL, initial concentration = 20mg/L, Contact time = 50 mins, T=303K)

3.5 Effect of adsorbent dosage

The dosage of biosorbent is an essential parameter as it helps in determining the adsorption capacity of the biosorbent. Experimental results are represented in Fig 7. The biosorption yield increased from 71.65% to 85.1%, when biosorbent dosage was increased from 0.5g to 2.5g. This fluctuation could 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.

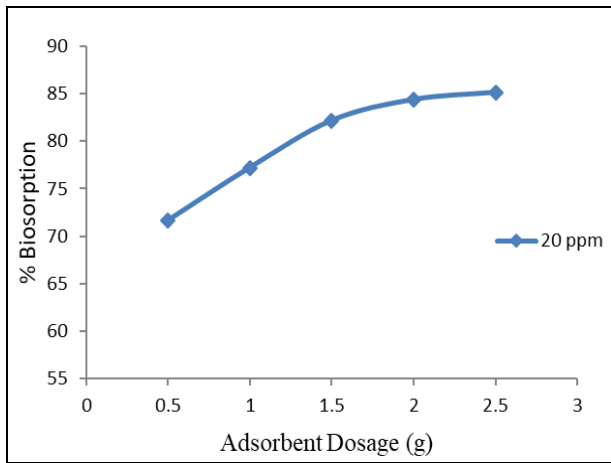


Fig 7: Effect of Adsorbent Dosage on the adsorption of malachite green onto LL seeds (Experimental data: Initial conc. = 20mg/L, Contact time = 50 mins, pH=6, T=303K)

3.6 Effect of Temperature

Temperature is one of the prime factors governing the process of adsorption. Equilibrium capacity of the adsorbent is affected by the changes in temperature. The adsorption rate constant of removal of MG with initial concentration of 20mg/L at pH 6 and temperatures 298K to 318K on *Lysiloma latissiliquum* seed powder has been studied for this purpose. The removal of MG increases from 76.8% to 85.65% by LL seeds powder with an increase in temperature from 298K to 318K. The results are illustrated in Fig 8. The rise in % biosorption may be due to the increase in chemical interaction between dye ions.

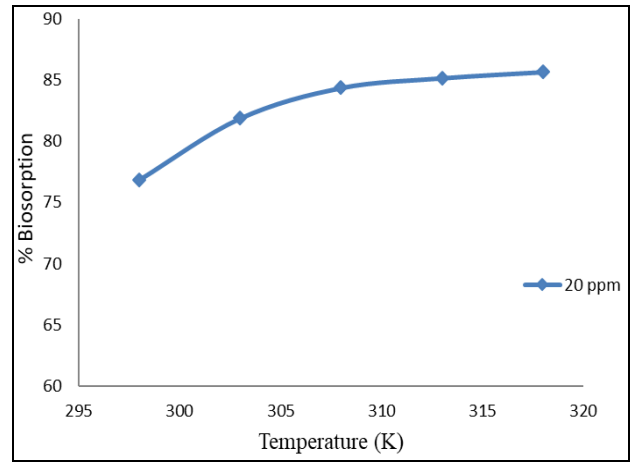


Fig 8: Effect of Temperature on the adsorption of malachite green onto LL seeds (Experimental Data: Adsorbent Dosage = 2g/100 mL, initial concentration = 20mg/L, Contact time = 50 mins, pH =6)

3.7 Biosorption Kinetics

Studying of kinetics plays a crucial role as it helps us analyze the reaction pathways and also the mechanism involved. Data on kinetics is required to obtain the optimum conditions for full-scale process. Kinetic studies were performed in conical flasks containing 100 mL MG solutions of 20 mg/L concentration. The flasks were shaken in an orbital shaker at constant rpm. Samples were taken at required intervals, centrifuged and analyzed for the residual MG concentrations. The Lagergren pseudo-first order rate equation and pseudo-second-order equations were used for modelling MG 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:

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

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

$$q = q_e(1 - e^{-K_1t})$$

$$\log(q_e - q) = \log q_e - K_1t/2.303$$

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.

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:

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

In linear form, this reduces to:

$$t/q = 1/K_2 q_e^2 + t/q_e$$

Where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption.

The experimental data and correlation coefficients are provided in Fig 8.1. 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.

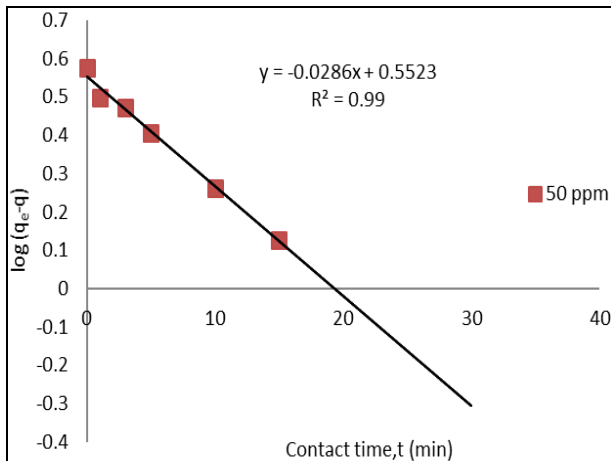


Fig 8.1: First order plots for the adsorption of MG onto LL seeds

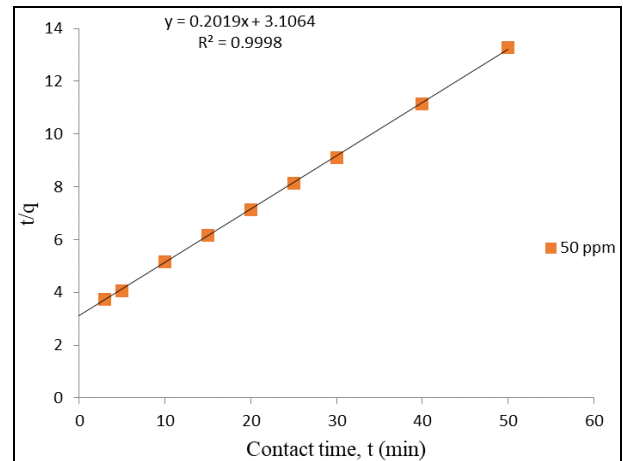


Fig 8.2: Pseudo second-order plots for the adsorption of MG onto LL seeds

Table 1: Kinetic Parameters for adsorption of MG onto *Lysiloma latisiliquum* 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	3.770	3.56	0.089587	0.99	4.95	0.0469	0.9993

3.8 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_e). 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 1g of LL Seeds powder with 100 mL MG solutions of 20 mg/L concentration at pH 5 and temperature of 303K. The solution is agitated using orbital shaker at constant rpm of 180 for equilibrium time. Entire procedure is repeated for temperatures in the range of 283K to 323K.

i) The Langmuir Model

This model was proposed by Irving Langmuir in 1916 for the adsorption of species onto simple surfaces. 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:

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

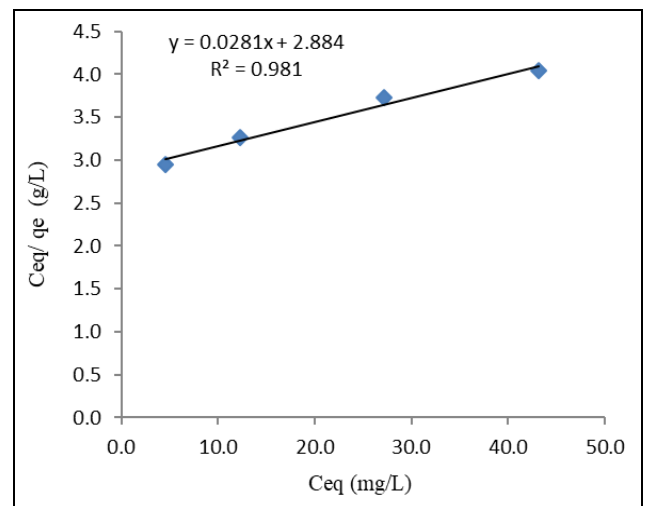


Fig 9: Langmuir adsorption isotherm for the adsorption of MG onto LL seeds

ii) The Freundlich Model

It was proposed by Boedeker in 1895 and later modified by Freundlich. It is an empirical equation based on sorption

onto a heterogeneous surface. Its equation is:

$$q_e = KC_e^{\frac{1}{n}}$$

The linearized form is:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Where ‘ q_e ’ is the equilibrium biosorption capacity (mg/g), C_e 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.

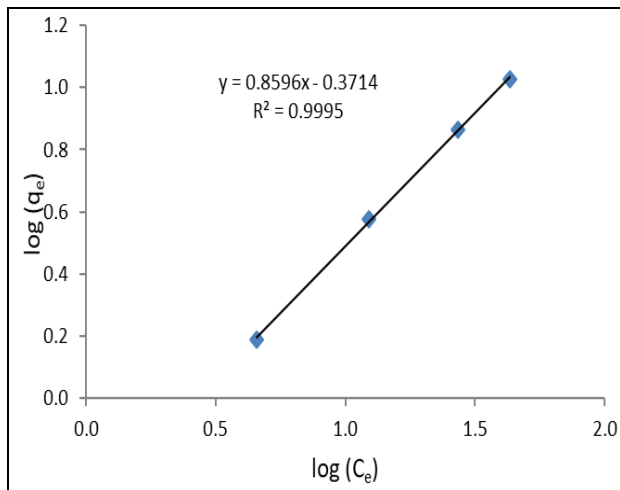


Fig 10: Freundlich adsorption isotherm for the adsorption of MG onto LL seeds

iii) **Tempkin Model**

It was proposed by Tempkin 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.

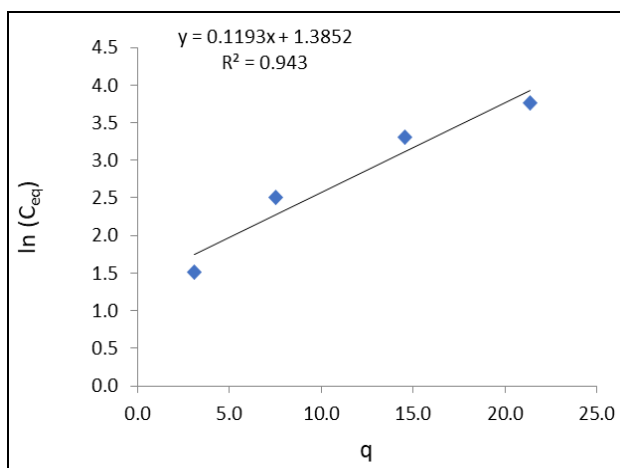


Fig 11: Tempkin adsorption isotherm for the adsorption of MG onto LL seeds

Table 2: Isotherm Parameters

Isotherm	Parameter	Values
Langmuir	q_{max} (mg/g)	35.5871
	K_a	0.01
	R^2	0.981
Freundlich	K	0.425
	n	1.16
	R^2	0.9995
Tempkin	A_T (L/g)	2.7831
	B (KJ/mg)	17.51
	R^2	0.943

4. **Conclusions**

Lysiloma latisiliquum seed powder was found to be very effective for removal of MG from aqueous solutions. The optimum pH for removal of MG was found to be 6. The adsorptive removal of MG follows Pseudo second order kinetics. Freundlich, Langmuir isotherm and Tempkin models were used to analyze equilibrium data. The Freundlich adsorption isotherm shows best fit with maximum removal capacity of 35.5871 mg/g. The studies reveal that *Lysiloma latisiliquum* seed powder can be used as a potential adsorbent for removal of MG.

5. **References**

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