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Kinetic and Equilibrium Studies of Biosorption of Methylene Blue and Crystal Violet Using Leaf Biomass (*Albizia saman)* as Adsorbent

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Abstract The essential objective of the present research work is removal of dye from industrial waste effluent using a plant leaf biomass (Albizia Saman). The Absorption process is found to be one of the effective and economic ways for the treatment of dye solution. Methylene Blue and Crystal Violet have been used as a sorbate for evaluating the potential of Albizia Saman as a biosorbent. Powdered biomass was used in this experiment. The experiments were carried out by varying different parameters like pH (5-8), adsorbent dosage (100-700 mg), concentration ratios of 30:30, 50:10, 10:50. Incubation was carried out at a temperature of 34°C and rotated at 130 RPM. Kinetic study shows that biosorption of methylene blue and crystal violet follows a pseudo second order kinetic model. It also validates the experimental dye removal capacity (R^2 =.99) with the calculated values. The equilibrium sorption data of methylene blue and crystal violet by *Albizia saman* were analysed by Langmuir isotherm model.

Keywords: *methylene blue, crystal violet, biosorption, Albizia saman*

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1. Introduction

Water pollution has always been a very challenging and a constant threat towards aquatic and non aquatic life forms especially in a densely populated country like India. According to the AQUASTAT database, the water consumption by the industrial sector contributes to 2.2% of the total water withdrawn in India. Studies conducted by the World Bank suggested that the textile industries are responsible for about 20% of the total global wastewater generation. The waste water generated from the textile industries typically comprises a mixture of dyes with other contaminants at varying concentrations [1]. The industrial effluents are quite harmful when under treated however in textile industries greater focus is towards the treatment of non biodegradable components which are often dyes [2].

Dyes are extensively used in textile and leather industries to impart colour [3]. They are mainly classified into three types which are anionic, cationic and non-ionic dyes [4]. The most important characteristic of any dye is its solubility in water, and their tendency to impart bright colour when they come in contact with water. Among all the dyes used in industries, textile industries use a huge amount of dyes every year to colour their products. Due to this the wastewater discharged from dyeing processes exhibit a higher BOD, COD, and high number of dissolved solids [3,5]. Effluents discharged from dyeing industries are highly coloured and are harmful for aquatic life.

The current techniques used for dye removal are classified into three major categories [6,7]:

(a) Physical methods (includes adsorption, ion exchange and coagulation-flocculation)

(b) Chemical methods (includes ozonation, photochemical and electrochemical process)

(c) Biological methods (includes standard biological degradation)

Out of the aforementioned methods, adsorption [7] is a well established technique for removal of dye components from the wastewater generated due to its affordability in comparison to other processes [8]. Adsorption is a surface-based process of accumulation of the molecular species at the surface rather than in the bulk of the solid or liquid. The substance that adsorbs on the surface is called 'Adsorbate', and the substance on which it adsorbs is called 'Adsorbent' [7]. Many research and investigations have been carried out in different parts of the world for the search of low-cost adsorbents suitable to remove dyes from waste water [3]. The adsorbents produced from the biomass will be a great economic alternative in comparison to the activated carbon adsorbent available commercially [9]. Such biomass based adsorbents may include coffee ground, tea leaves, wheat straw, rice husk etc. Various studies reveal that wastewater treatment is possible by using Albizia saman [8] as an adsorbent. The use of Albizia saman as an adsorbent will reduce solid waste in the environment by converting the waste to wealth. Methylene blue and crystal violet are very toxic when exposed to the environment, the hazards are mentioned below in Table 1 [7,10].

Table 1. Dye characteristics

Name of Dyes	Type	Appearance	Molecular Formula	Health Hazard
Methylene blue	Cationic	Blue	$C_{16}H_{18}ClN_3S$	Jaundice, shock, red blood cells breakdown.
Crystal violet	Cationic	Blue - Violet	$C_{25}H_{30}ClN_3$	Mitotic poison, carcinogen.

2. Experimental

2.1. Preparation of Biosorbent

The biosorbent was made from the leaves of Albizia saman (siris). The leaves were procured from the outskirts of Bilaspur city (Chhattisgarh, India). Then they were washed thoroughly with water and sun dried for 3 days at a temperature of 39°C. Then they were grounded mechanically and 1/32 mesh sieve was used for screening of leaf powder. Consequently it was stored in an airtight case away from the sunlight. In many other types of experimental setups reported elsewhere [4,6,7], the adsorbents were treated with an acid or an alkaline solution. Here in the present setup the leaves were not subjected to any kind of chemical treatment.

2.2. Preparing the Dye Solution

Methylene blue, also known as methylthioninium chloride chemical formula $C_{16}H_{18}ClN_3S$ and has a molecular weight of 319.85 g/mol. The structure of methylene blue is shown in Figure 1

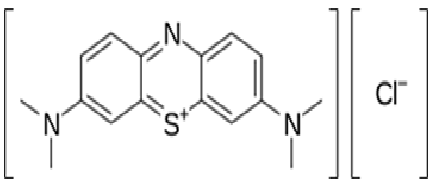

Figure 1. Methylene blue molecule

Crystal violet also known as methyl violet 10B or hexamethyl pararosaniline chloride and its chemical formula $C_{25}H_{30}ClN_3$ and has a molecular weight is 407.99 g/mol. The dye was bought from thermo fisher through an authorised retailer. The structure of crystal violet is shown in Figure 2.

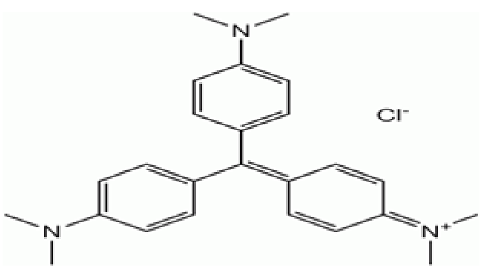

Figure 2. Crystal violet molecule

A stock solution of 1000 ppm was prepared using the dye powder and distilled water. Then from the stock solution experimental solution of different concentration 20 mg/L, 40 mg/L, 60 mg/L, and 80 mg/L and the experimental solution was made carefully based on the law of dilution.

3. Batch Biosorption Studies

This biosorption experiment was carried out in a rotatory incubator using four 250 ml conical flasks containing 100 ml of dye solution each, various parameters were optimised through this experiment such as sorbent dosage, initial pH and varying concentration ratios (methylene blue to crystal violet). The concentration of supernatant solution was found by measuring its absorbance in UV-visible spectrometers at a maximum wavelength of λ_{max} 665 nm for methylene blue and λ_{max} of 590 nm for crystal violet respectively. The amount of dye adsorbed (mg) per unit mass of adsorbent (g) is given by equation (1) and the dye removal percent (DRP) is determined from equation (2).

$$q_e = (C_o - C_e)V / W \quad (1)$$

$$DRP = \frac{(Co - Ce)}{Co} \times 100 \quad (2)$$

Where $C_e\left(\frac{mg}{L}\right)$ is the instantaneous concentration, $C_0\left(\frac{mg}{L}\right)$ is the initial concentration, *V(Litre)* is the volume of solution, $q_e\left(\frac{mg}{g}\right)$ is the instantaneous amount in milligram of dye adsorbed per gram of adsorbent and *W(g)* is the weight of adsorbent added.

4. Observation and Discussion

4.1. Optimising ph and Time of the Solution

The effect of initial pH for both the dye methylene blue and crystal violet was studied separately varying the pH from 5-8 for each dye contained in conical flasks 100 ml of 60 mg/L of dye solution. The pH range of this present work was decided from 5 to 8 because most of the dyes optimizing pH value tends to fall within this range. The sorbent dosage of 500 mg was added to each conical flask and placed in a rotatory incubator set at 34°C and 130 RPM. The supernatant was taken at particular intervals of time and centrifuged at 4000 RPM.

Further the supernatant concentration was determined and the equilibrium dye removal percent was observed. The pH was optimised for crystal violet at 6 pH and as for methylene blue at 8 pH. Along with this the time was also optimised with around 60 min as observed in Figure 3 and Figure 4. The results compiled from each dyes showed that if mixed concentration ratios were to be made, an optimising pH of 7 would be preferable as shown in Figure 5.

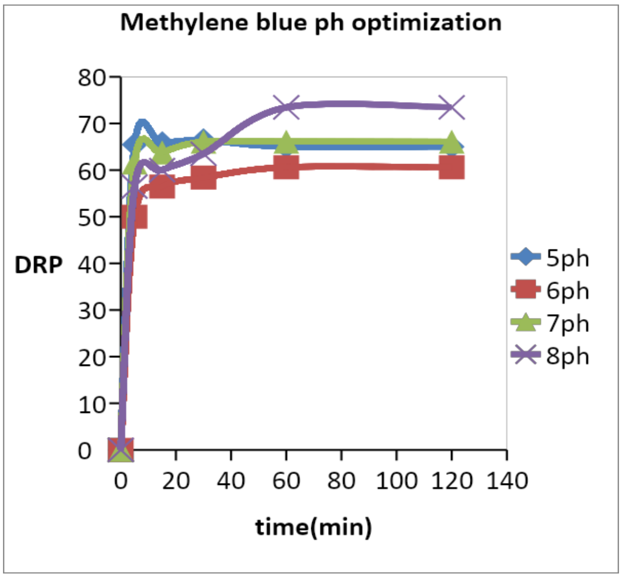

Figure 3. Plot between DRP and Time (Methylene blue)

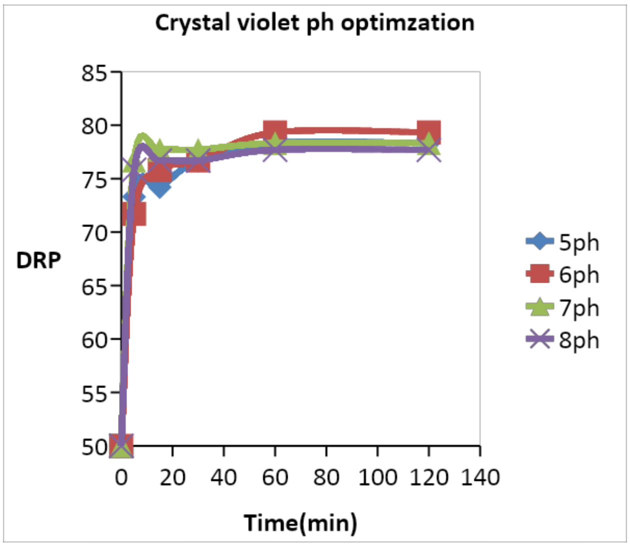

Figure 4. Plot between DRP and Time (Crystal Violet)

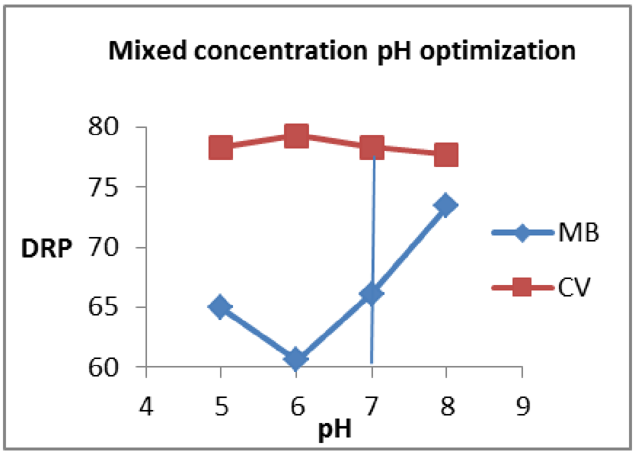

Figure 5. Plot between DRP and Time (Mixed concentration)

4.2. Optimising Adsorbent Dosage

The effect of initial sorbent dosage was studied varying the sorbent dosage 100, 300, 500 and 700mg. This was added to 4 conical flasks containing 100 ml of dye solution of concentration 60 mg/L for both methylene blue and crystal violet at 34°C and set at 130 RPM subsequently the supernatant was centrifuged at 4000 RPM for 4 min. Then the clear supernatant absorbance value was determined using the UV spectrometer. The pH was adjusted to 6 and 8 for crystal violet and methylene blue respectively using a pH meter. The corresponding dye removal percent was determined.

The dye removal percent was found to increase initially with increase in sorbent dosage but later on after reaching the dosage of 300 mg of adsorbent for crystal violet and 500 mg of adsorbent for methylene blue, the dye removal percent did not increase showing that the adsorbent had reached its saturation level of adsorbing the dye present in the solution. The optimized adsorbent dosage for crystal violet and methylene blue were 300 mg and 500 mg respectively (In case of mixed concentration ratios the adsorbent dosage of 500 mg will be considered). As indicated in Figure 6 and Figure 7.

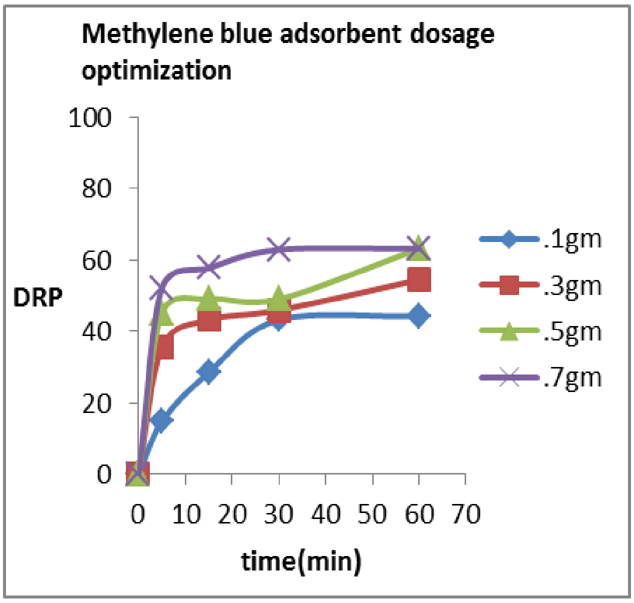

Figure 6. Plot between DPR and time (methylene blue adsorbent dosage)

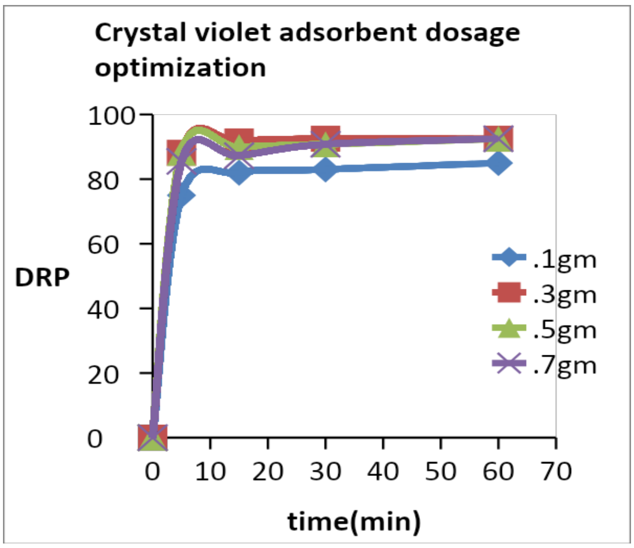

Figure 7. Plot between DRP and Time (crystal violet adsorbent dosages)

4.3. Studying at Various Concentration Ratios

The different concentration ratios were made with methylene blue to crystal violet in the ratio of 50 ppm: 10 ppm, 30 ppm:30 ppm and 10 ppm:50 ppm.

The pH was adjusted to 7 (refer Figure 5) for crystal violet and methylene blue using pH meter, adsorbent dosages were fixed at 500 mg for each conical flask containing different concentration ratios of methylene blue and crystal violet. The total concentration combined was fixed to 60 mg/L. The conical flasks were placed in a rotatory incubator at a temperature of 34^{o}C and set at 130 RPM. The supernatant was taken at particular intervals of time and centrifuged at 4000 RPM. Then the clear supernatant's absorbance value was determined. The equilibrium dye uptake capacity *q* was determined from Figure 8.

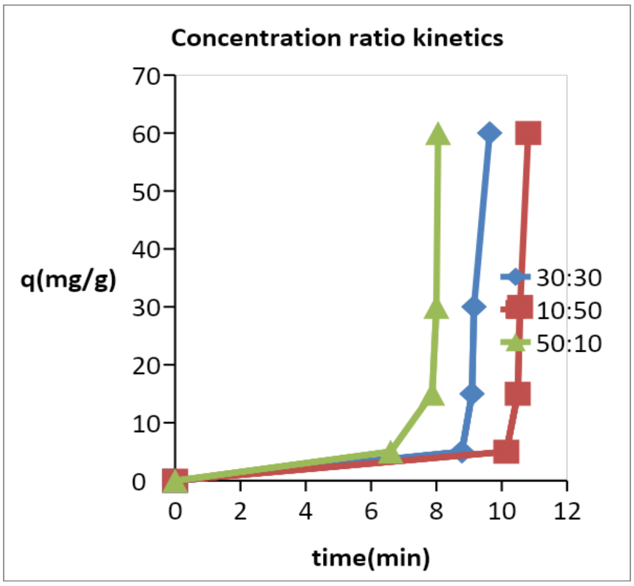

Figure 8. Plot between q and time (concentration ratio methylene blue : crystal violet)

5. Results

5.1. Equilibrium Isotherm Studies

For understanding equilibrium two most extensively used models have been taken. The model used here is Langmuir's adsorption isotherm, since the Freundlich isotherm model did not fit with the data collected experimentally. The isotherm parameters Q^o and b were found assuming the binary dye system as a single component system.

LANGMUIR ADSORPTION ISOTHERM

Langmuir's adsorption isotherm is given by

$$q_{eq} = \frac{Q^{\circ} b C_{eq}}{1 + b C_{eq}} \quad (3)$$

Where,

C_{eq} = Equilibrium dye concentration in the solution $\left(\frac{mg}{L}\right)$

q_{eq} = $equilibrium\ dye\ uptake\ capacity\ \left(\frac{mg}{g}\right)$.

Q° = Maximum quantity of dye adsorbed per unit weight of biosorbent to form a complete monolayer on the surface $\left(\frac{mg}{g}\right)$

b = constant related to the affinity of the binding site $\left(\frac{L}{mg}\right)$.

The plot between $1/q_{eq}$ and $1/C_{eq}$ was made to find the constant parameters such as Q° and b as shown in Figure 9.

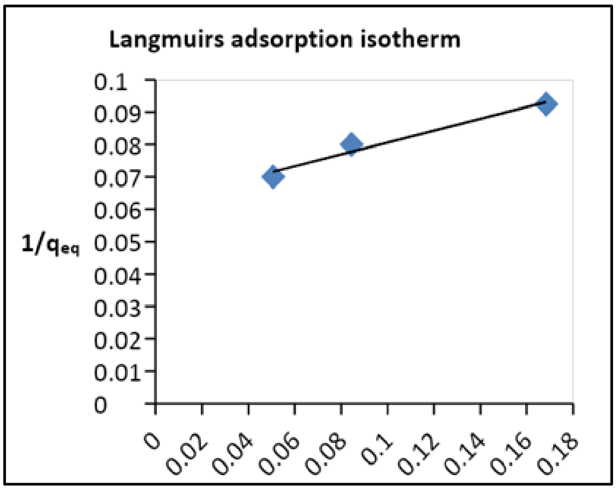

Figure 9. Plot between $1/q_{eq}$ and $1/C_e$

The calculated parameters are shown in the following Table 2. It has been observed that the langmuir's parameters showed a great fit with the experimental results indicating a regression coefficient value of 0.969 as indicated in the following table.

Table 2. Langmuir's isotherm parameters for adsorption methylene blue and crystal violet

LANGMUIR'S PARAMETERS	VALUES	UNIT
Q°	16.12	mg/g
b	0.3389	L/mg
R^2	0.969	-----

The exploration of adsorption using different biomass has been carried out to reduce the amount of waste generated, recycling, reusing and transitioning towards usage of biomass which are renewable resources. Here are a few untreated adsorbents presented in Table 3 used for carrying out adsorption studies using the dye/dyes which are used in the current studies.

Table 3. Langmuir's isotherm parameter Q^o for different adsorbent

Adsorbent	Adsorbate	Q^o (mg/g)
Rice husk (12)	Methylene blue and Crystal violet	24.48, 25.56
Rice husk ash (13)	Methylene blue	8.59
Sugarcane bagasse (14)	Methylene blue and Crystal violet	112.9, 107.5
Spent tea leaves (15)	Methylene blue	45.8
Clay soil (16)	Methylene blue and Crystal violet	47.82, 35.71

5.2. Studying the Kinetics

The kinetic studies were carried out by fitting the experimental data using pseudo first order and pseudo second order based models. The modelling and results obtained are discussed in subsequent sections, tables and figures in detail.

PSEUDO FIRST ORDER

Lagergren's pseudo first order equation is as follows

$$\frac{dq}{dt} = k_1\left(q_{eq} - q\right) \quad (5)$$

q_{eq} = equilibrium dye uptake capacity.
q = dye uptake capacity at any time.
k_1 = first order rate biosorption rate constant.

Integrating the above equation,

$$\log\left(q_{eq} - q\right) = \log q_{eq} - \frac{k_1 t}{2.303} \quad (6)$$

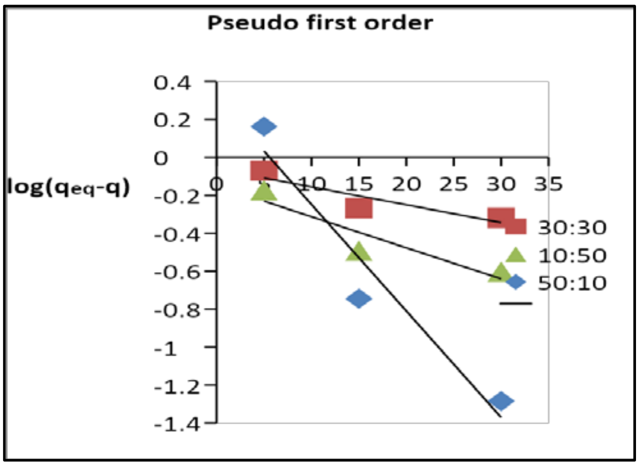

Figure 10. Plot between log(q_{eq}-q) and t

By plotting graph between $\log\left(q_{eq} - q\right)$ in the y-axis and t in the x-axis as indicated in Figure 10. The rate constant k_1 and q_{eq} (theoretical) values were determined graphically. It has been observed that the regression coefficients for the fitting of 30:30, 10:10 and 50:50 were 0.816, 0.815 and 0.933 for the pseudo first order respectively.

PSEUDO SECOND ORDER

Lagergren's pseudo second order equation is as follows

$$\frac{dq}{dt} = k_2\left(q_{eq} - q\right)^2 \quad (7)$$

Integrating the above equation, the resultant equation is

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (8)$$

By plotting graph between $\frac{t}{q}$ in y-axis and t in x-axis, the resultant graph's intercept and slope were determined. Using these data the value of q_{eq} (theoretical) and k_2 were further deduced and are reflected through Table 4. It has been observed that the regression coefficients for the fitting of 30:30, 10:10 and 50:50 were 0.999, 0.999 and 0.999 for the pseudo second order respectively. It has been further deduced that the pseudo second order model is a better fit than the first model to explain the kinetics.

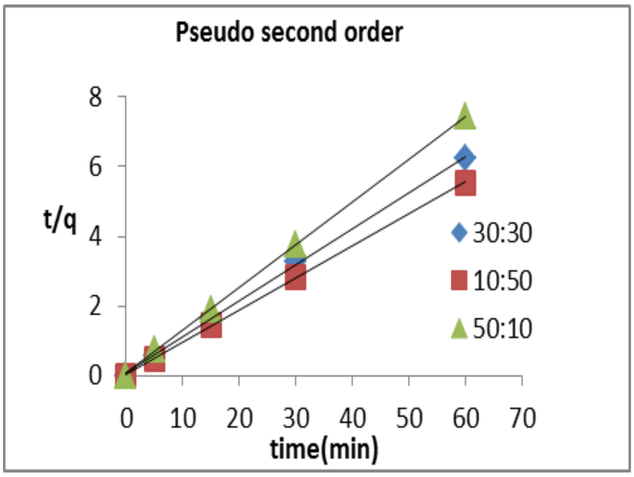

Figure 11. Plot between t/q and t

COMPARISON OF PSEUDO FIRST AND SECOND ORDER KINETIC MODEL

Table 4. Pseudo first and Second order kinetic parameter for the adsorption of methylene blue(mb): crystal violet(cv) on Albizia Saman

Concentration Ratio (mb:cv)	q_e (mg/L)	Pseudo First Order			Pseudo Second Order		
		k_1	q_{eq} (Theoretical)	R_2	k_2	q_{eq} (Theoretical)	R_2
30ppm:30ppm	9.630	0.2070	0.8689	0.819	0.0981	9.8039	0.999
10ppm:50ppm	10.812	0.0368	0.7095	0.855	0.1656	10.9890	0.999
50ppm:10ppm	8.052	0.1289	2.0510	0.933	0.1391	8.1967	0.999

6. Conclusion

From the experiments carried out it was found that *Albizia saman* leaf biomass can be used as an alternative low cost biosorbent, as Langmuir's parameters like Q° and b have reasonably higher values.

The sorbent dosage, pH, and initial dye concentration found to be affecting biosorption process and at optimised condition their adsorption got increased. The maximum sorption at equilibrium condition was obtained at an adsorbent quantity of 500 mg/100 ml of dye solution and at a pH of 7 for mixed concentration ratios of the two dyes namely methylene blue and crystal violet. Under all the parameters optimised, the dye removal percent reached above 90. Further it has been noted from the present work that by increasing the concentration of crystal violet, drastic improvement in the adsorption efficiency from 60 to 90%.

The biosorption process for this experimental setup can be explained through Lagergren's Isotherm and Pseudo second order kinetic equations.

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