Adsorptive Removal of dye from aqueous solution using Plumeria obtusa leaf powder

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Abstract- Pollution emanating from effluents containing residual dyes which are not biodegradable has become a serious environmental problem in the last decade due to the increasing and fast-growing usage of dyes in different applications. Even small amount of dye in water effects the aesthetic value and water transparency in water bodies therefore the contaminated dye in waste water needs to be removed before released to natural stream. The dye removal process which is the low cost of operation and occurred through the green reaction under the usage of the natural waste is the interested method. Biosorption is leaded to the decolorizing the waste water by using the agricultural waste through the adsorption technique. In this study the Malachite Green (MG) adsorption onto Plumeria obtusa leaf powder was investigated in terms of both adsorption efficiency and kinetic study. The effect of various parameters i.e. initial dye concentration, contact time, adsorbent dosage, pH and temperature were investigated. The adsorption data fitted the isotherm model such as Langmuir, Freundlich. Thermodynamic parameters (Such as $\Delta G0$, $\Delta H0$, $\Delta S0$) were also determined to find out the spontaneity of the adsorption process.

Index Terms—Biosorption, Malachite Green. Plumeria obtuse, Adsorption isotherm

I. INTRODUCTION

Dyes are extensively used in numerous industries like textile, plastic, dye, leather, paper, rubber, cosmetics, food, carpet and printing[1-2]. The waste water resulted from these industries contain residual dyes which are not bio-degradable and cause serious environmental problems, in general, and water pollution, in particular: visible pollution and damage on the aesthetic nature of effluent water, reduction in the sunlight penetration which affect photosynthesis and biota growth, ecotoxicity risk and bioaccumulation potential danger [1,3]

Malachite green (MG) was classified as a triarylmethane dye. MG is used for dyeing, in aquaculture to regulate the fish disease, as a fungicide and parasiticide. MG is applied in the cloth, leather and acrylic industries. When MG in the freshwater, the fish display a toxic disorder causing the mammalian cells toxic in nature and further affect the different body parts of fish. In humans, gastrointestinal irritation and irritation to the respiration if inhaled is caused. When MG exposed to the skin it results in tenderness and pain; simultaneous contact with eye causes permanent injury of human eyes [4].

Many conventional methods have been developed to remove dyes from wastewater: Coagulation, ion exchange, adsorption, chemical precipitation, membrane filtration, biodegradation. Adsorption process is preferred due to its high efficiency, low cost, flexibility, ease of operation, design simplicity and availability of adsorbents [3,5].

In this study, Plumeria obtusa leaf have been used as an adsorbent for the removal of Malachite green dye from aqueous solution. The biosorption performance of Plumeria obtusa leaf on various parameters was conducted and evaluated using adsorption equilibrium and isotherm data.

II. MATERIAL AND METHODS

A. Materials -

The Malachite Green (MG) dye used for the study was obtained from Fischer Scientific, India. The dye was used as supplied without any purification. All reagents such as hydrochloric acid, and sodium hydroxide were purchased from Qualigens, India and used as received. 1.0 g MG dye was dissolved in deionized water to get 1000 ml of stock solution which was further diluted to obtained working solutions of desired concentration.

B. Preparation of the Biosorbent -

The leaves of Plumeria obtusa were collected from the nearby garden. The leaves were washed with water subsequently with deionized water thoroughly so as to get rid of dirt and impurities and were dried at room temperature for few days and then kept in an oven at 105^0C overnight. Using a domestic mixer grinder, the leaves were powdered. To remove natural dyes/ pigments the POLP was dispersed in double distilled water. After drying in an oven at 105^0C overnight, the powder was sieved. The Plumeria obtuse leaf powder in the range of particle size 300 micron is used.

C. Batch Experiments -

The batch studies were preceded in 250ml glass-stoppered flasks with a working solution of 100 ml having 100 mg/L concentration. A quantity (1.0 g) of biosorbent was added to the solution. At a constant agitation of 120 rpm, the solution was rotated in an orbital shaker by maintaining the optimal pH required at a temperature of 303K for equilibrium contact time. At the equilibrium, the samples were centrifuged, filtered and interpreted for dye concentration. Similar studies were conducted for different process parameters. The influence of pH, dye concentration, biosorbent dosage, time interval and temperature were evaluated during this study. The dye concentrations were measured using UV spectrophotometer (Model UV-1800, Shimadzu, Japan) at 618 nm.

In each case, the equilibrium concentration of the dye adsorbed per gram of the adsorbent was calculated using equation (1)[6].

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where C_0 and Ce are the initial and equilibrium concentrations of the dye, V is the volume of the solution in litre and m is the mass of the adsorbent in gram. Effect of each of the response property on adsorption was investigated through maintenance of constancy of other functions but varying values of the investigated parameter.

The percent biosorption (%) of dye:

$$\%\ \text{Biosorption} = \frac{(C_0 - C_e) \times 100}{C_0} \qquad (2)$$

III. RESULTS AND DISCUSSION

A. Effect of Contact Time -

With respect to contact time, the % biosorption of MG dye on POLP biosorbent was represented in Fig.1. For a time period of 5 to 120 min, a number of free surface sites is applicable for biosorption and as time period increases, the surface sites are employed with the dye molecules [7-8]. In Fig 1, an equilibrium site which is attained at 60 min where biosorption will not alter much with contact time and remained nearly plateau is represented at a dye concentration of 100 mg/L. The biosorption efficiency is increased from 45.6% to 64.2 % with a contact time of 120 min at 100 mg/L dye concentration.

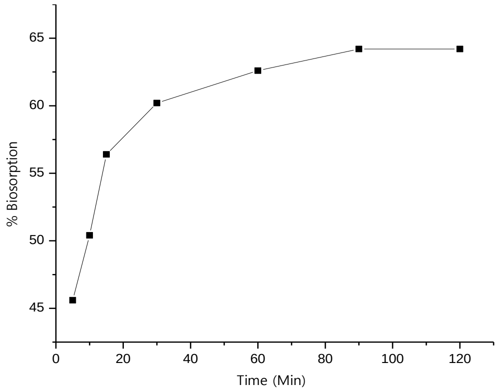

Fig.1: Effect of Contact Time on biosorption of MG dye on POLP

B. Effect of Solution pH -

MG in aqueous solution contains positively charged ions. For charged species, the degree of biosorption onto the biosorbent surface is mainly altered by the biosorbent, which consecutively has an impact on pH 10. Fig.2 represents the effect of pH on the biosorption of dye, where the MG removal increased with an increase in pH. The biosorption efficiency is influenced by the H^+ concentration [9]. As surface density decrease with an increment in the pH, the electrostatic repulsion between the positively charged MG and the surface of the POLP is low, that conclude that biosorption rate increases. 67.6 % of maximum biosorption was obtained at pH 10.

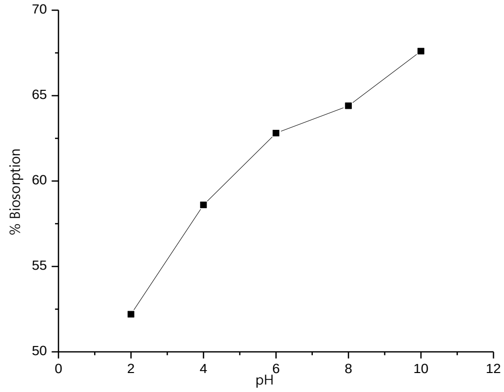

Figure 2: Effect of pH on biosorption of MG dye on POLP

C. Effect of Dye Concentration -

The biosorption rate is an objective of the concentration of the biosorbate, representing effective biosorption. The impacts of different concentrations are in the range of 20-150 mg/L on the biosorption of MG onto POLP. As depicted in fig 3 with an increment in dye concentration, the % biosorption was declined and dye uptake was inclined. At 303K, the dye uptake increased from 1.45 to 6.48 mg/g and % biosorption of dye concentration decreased from 72.8 to 64.8%.

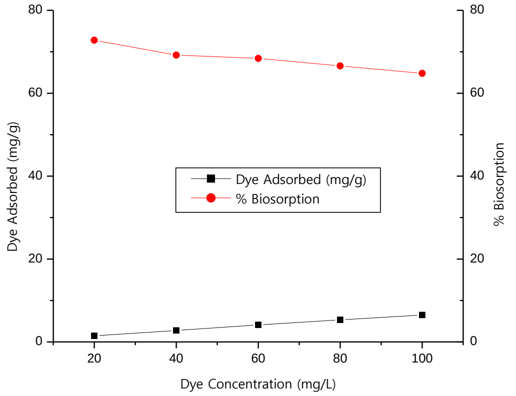

Figure 3: Effect of initial dye concentration of MG dye on POLP

D. Effect of Dosage of Biosorbent -

The dosage of biosorbent influences the process of biosorption. Therefore, the impact of biosorbate dosage on MG biosorption was identified in the range of 0.2 - 1.0 g. The % biosorption increased with an increment of dosage. Fig 4 shows that % biosorption increases with increasing biosorbent dosage for MG concentration (100 mg/L), more dosage will indicate more availability of biosorption sites and more will be the MG adsorbed [10]. For 0.2-1.0 g of increment in biosorbent dosage the percentage removal was increased from 57.2 % to 64.2 % at 100 mg/L of dye concentration.

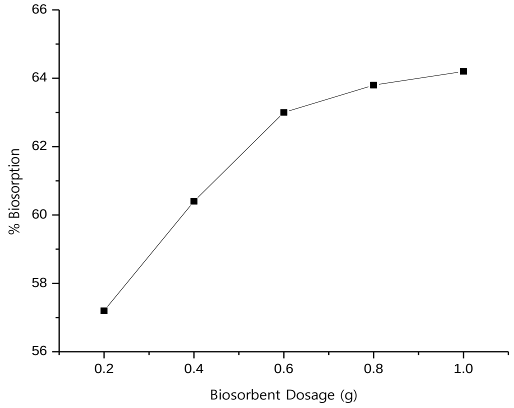

Figure 4: Biosorbent dosage effect on biosorption of MG dye on POLP

E. Effect of Temperature -

The temperature affects the biosorption capacity of the dye. Batch experiments of biosorption were performed at a temperature varying from 303K to 323K. Fig 5 shows a decrease in percentage biosorption with an increment in temperature. With an increase in temperature, the density decreases as dye transfer from the biosorbent surface to the solution phase [11]. The maximal biosorption is seen at 62.8% for a time interval of 120 min at 303K temperature, having 100 mg/L of dye concentration.

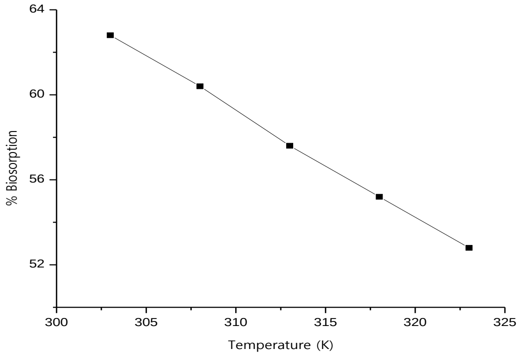

Figure 5: Effect of Temperature on biosorption of MG dye on POLP

F. Equilibrium Isotherm Study -

The isothermal study represents how the biosorption molecules attain a steady state between the liquid and solid phase. For the design purpose, isotherm models were analyzed and suitable model that can fit the data were obtained. Biosorption isotherm is mostly essential to find the interactions of solutes with biosorbents and optimize an effective biosorbent. At various temperatures, isotherm models were favorably adapted to the above system using linear regression analysis.

Langmuir Isotherm -

The Langmuir model assumes a monomolecular layer biosorption having a finite number of vacant sites of constant approach for biosorption with no transmigration of biosorbate in the uniform surface. The equation is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (3)$$

where Ce is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When Ce/q_e was plotted against Ce, a straight line with slope of $1/Q_0$ was obtained. The R^2 value is 0.9600 at a temperature of 303K and pH of 6. The Langmuir isotherm was fitted for the isotherm data. The Langmuir constants are represented in Table-1 that is calculated from eqn.-3.

Freundlich Isotherm -

The Freundlich isotherm model [12] considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented as equation (4)

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants. These constants were derived from the plot of log q_e vs log C_e and are presented in Table I. K_f can be defined as the adsorption capacity that represents the adsorbed quantity for a unit equilibrium concentration and value of n>1 giving an indication of favorability of the adsorption process. The values of K_f and n were found 0.099 and 0.8113 respectively.

Table I: Langmuir and Freundlich isotherm constants and best-fit coefficients for the adsorption of MG on POLP

Isotherm	Parameters
Langmuir	
Q_0 (mg/g)	18.9393
k_1 (L/mg)	0.0146
R^2	0.9600
Freundlich	
K_f (mg/g)	0.0992
1/n (g/L)	0.8113
R^2	0.9990

Thermodynamic Studies -

The effectiveness of the biosorption is given by thermodynamic studies. The Van’t Hoff equation is:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (5)$$

where, standard enthalpy (ΔH^o), standard entropy (ΔS^o) and Gibbs free energy (ΔG^o), K_D is constant, (R=8.314 J/mol K) and T is the temperature (K). The ΔH^o and ΔS^o were enumerated from the linear Van’t Hoff plot i.e. ln K_D vs. 1/T and computed using the eqn.-5.

$$\Delta G^0 = -RT \ln K_D \qquad (6)$$

The ΔG^0 is calculated from equation-6. The positive values of ΔG^0 represent the chemisorption. With a raise in temperature the positive values of ΔG^0 increases. The positive value of ΔH^0 represents biosorption mechanism to be endothermic. The decline in randomness between the solid-solute interface represents the negative value of ΔS^0. Table-II shows the thermodynamic parameters.

Table II: Thermodynamic parameters for MG on POLP

Temperature (K)	Malachite Green dye on POLP		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)
303	38.22	16.87	-70.45
313	38.57		
323	38.92		
333	39.27		
343	39.62		

CONCLUSION

The analyses were executed as components of contact time, pH, dye concentration, biosorbent dosage, average biosorbent size and temperature. Freundlich model best fit the isotherm data with R^2 value 0.9990. The positive value of ΔH^0 reveals the reaction is endothermic, ΔG^0 reveals the feasibility and spontaneity of process and ΔS^0 give the randomness of the reaction.

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