



# A KINETIC STUDY OF CATIONIC DYE REMOVAL FROM AQUEOUS MEDIUM USING BIOSORBENT

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**Abstract:** Biosorption of Malachite green dye using *Plumeria obtusa* leaf powder from an aqueous solution was studied using batch studies. The dye uptake on adsorbent was studied using initial dye concentration, agitation time, pH and biosorbent dosage. The kinetic studies were carried out by pseudo-first order and pseudo-second order kinetic models. The pseudo-second order kinetic model was best fitted with  $R^2$  value of 0.9990. The calculated and experimental values of equilibrium amount of dye adsorbed were showed better agreement.

**Index Terms - Biosorption, Cationic Dye, *Plumeria obtusa* leaf.**

## I. INTRODUCTION

One of the fundamental necessities for the continued existence of life on this Earth is water. Water pollution is the introduction of heavy metal ions, anions, organics, refractory, agro-chemicals etc., into fresh or ocean waters from domestic sewage, industrial effluent and agricultural discharges that affect quality of water and aquatic life<sup>1</sup>. Furthermore, 5-10 million people die annually due to various diseases caused by the consumption of contaminated water. It is not only the rising population adding to worldwide water stress, but also, industrialization will lead to greater demands for water, resulting in more water scarcity. Many industries already consume an abundance of water and pollute water sources that could have been directed to drinking and sanitary purposes<sup>2-3</sup>. Many countries use different types of dyes for various purposes which are common pollutants of effluents comes from textile industries<sup>3</sup>. Most of the dyes used in industries are mutagenic and carcinogenic to animal and aquatic organism.

The wastewater treatment is a great problem in developing countries due to financial constraints. The wastewater treatment is becoming costly as the environmental standards are becoming stricter. Use of partially treated wastewater for purposes other than drinking may reduce the depletion of fresh water natural resources having drinking quality water with it. Water can be reused at place after ensuring that it will not adversely affect the process for which it is to be used<sup>4</sup>.

Dyeing and printing industries are the major source of water pollution<sup>5</sup>. Dyes, although present in only small amounts is highly detectable and thereby capable of causing various problems of an aesthetic nature in receiving water bodies. Synthetic dyes can cause significant environmental issues and are serious health problems. Therefore, removal of dyes from waste water is most desirable.

Malachite green was recently nominated by the food and drug administration as a priority chemical for carcinogenicity testing by the National Toxicology Program<sup>6</sup>. The environmental pollution caused by the malachite green disposal creates a serious problem. Several methods have been applied with limited success to remove malachite green from wastewater, such as adsorption, chemical precipitation, photo degradation, osmosis and membrane filtration<sup>7-9</sup>. These methods were not only costly and inefficient, but also produce large

amounts of sludge. Therefore, the search for efficient, eco-friendly and cost-effective remedies for wastewater treatment has been started as research work.

The use of novel low cost biosorbents for waste water treatment through adsorption have a potential and cost-effective alternate to the conventional treatment methods and has led to the rapid growth of research interest. Adsorption is one of the processes that does not require energy and the amount of synthetic chemical. These processes can be carried out in situ at the contaminated site, and also, they are cost effective. Attempt have been made to search for novel adsorbent from plant sources to be used for removal of malachite green oxalate dye from aqueous solutions. In the present paper an attempt has been made to study the adsorption kinetics of malachite green onto plumeria obtusa leaf powder.

## II. MATERIAL AND METHODS -

The Malachite Green (MG) dye was obtained from Fischer Scientific, India and used as supplied without any purification. 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.

The leaves of Plumeria obtusa were collected locally during autumn and washed with water subsequently with distilled water thoroughly to remove dirt. The leaves were dried for few days at room temperature and then kept in an oven at 105°C for 12 h. The leaves were powdered using a domestic mixer grinder. The leaf powder was dispersed in double distilled water to remove natural dyes/ pigments. After drying in an oven at 105°C overnight, the powder was sieved to get desired particle size. 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 and temperature of 303K. 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)[10].

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

Where  $C_0$  and  $C_e$  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.

## III. RESULTS AND DISCUSSION -

### Adsorption Equilibrium Study:

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 20-100 mg/L on the biosorption of MG onto POLP. As depicted in fig 1 with an increment in dye concentration, the dye uptake was inclined. The biosorption efficiency is influenced by the  $H^+$  concentration [11]. Fig.2 represents the effect of pH on the biosorption of dye, where the MG removal increased with an increase in pH. 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. 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.

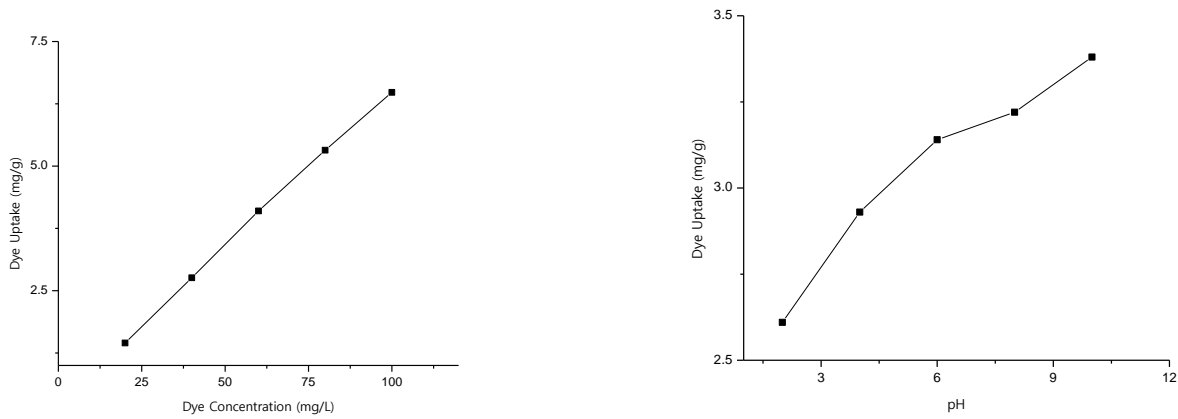


Fig.1: Initial dye concentration Vs  $q_e$  of MG dye on POLP Fig.2: pH Vs  $q_e$  of MG dye on POLP

With respect to contact time, the % biosorption of MG dye on POLP biosorbent was represented in Fig.3. The biosorption efficiency is increased with a contact time. 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 [12-13]. In Fig 3, 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 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 [14]. 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.

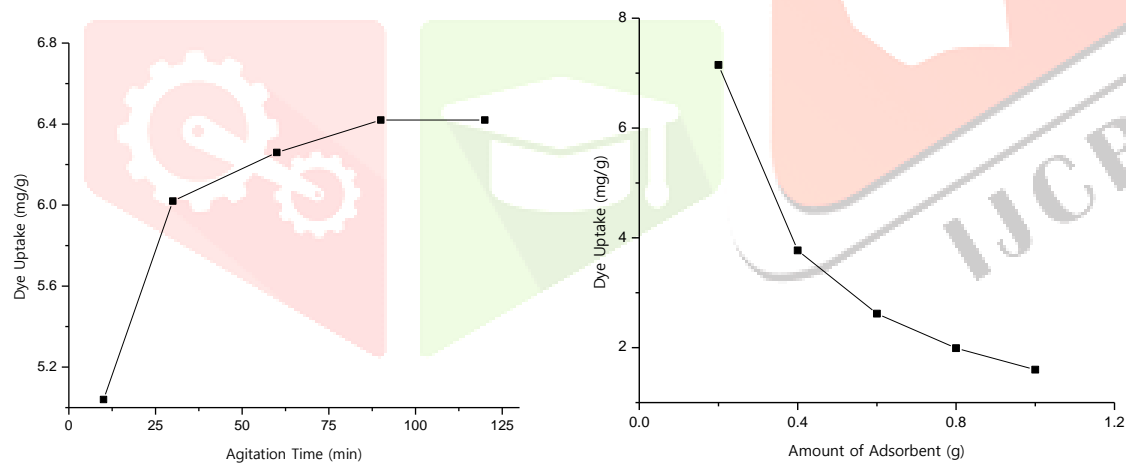


Fig.3: Contact Time Vs  $q_e$  of MG dye on POLP

Fig.4: Biosorbent dosage Vs  $q_e$  of MG dye on POLP

### Adsorption Kinetic Studies

Kinetics of solute uptake is used for optimum conditions of a batch process. The kinetic data was studied using two kinetic models:

#### Pseudo-First Order Model:

The kinetics of adsorption was analyzed by the pseudo-first order equation [15] as shown in equation (2).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where  $q_e$  and  $q_t$  are the amount of MG adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively, and  $k_1(\text{min}^{-1})$  is the rate constant the value of which obtained from the plot of  $\log(q_e - q_t)$  vs  $t$  for different initial concentrations of MG. The  $R^2$  value was 0.8674 for 100 mg/L of dye concentration. The pseudo-first-order kinetic model is mostly predicted for dye biosorption kinetics. The set of  $R^2$  values obtained were poor and the experimental  $q_e$  values did not agree with the calculated values obtained from the linear plots (Table 1).

### Pseudo-Second Order Model

The pseudo-second order equation based on equilibrium adsorption [16] is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $k_2$  (g/mg min) is the rate constant of second order adsorption. The linear plot of  $t/q_t$  vs  $t$  at constant temperature, yielded set of  $R^2$  value of 0.999 for 100 mg/L of dye concentration as shown in table 1. The values of calculated and experimental equilibrium amount of MG dye adsorbed on POLP are in better agreement with pseudo-second order kinetics. The calculated value of  $R^2$  confirms that the adsorption of MG on POLP favors pseudo-second order kinetic model.

**Table1:** Kinetics constants for MG on POLP

Initial Concentrations (mg/L)	Pseudo First Order Kinetic Model				Pseudo Second Order Kinetic Model		
	$q_e$ (mg/g) Exp	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g) Model	$R^2$	$k_2$ (g/mg. min)	$q_e$ (mg/g)	$R^2$
100	6.92	0.0136	1.8214	0.8674	0.0538	6.6181	0.9999

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