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Malachite green removal from aqueous solution using activated carbon prepared from tamarind stem charcoal

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ABSTRACT

In the present investigation, activated carbon prepared by physical activation method from tamarind stem charcoal has been used for the removal of malachite green dye from synthetic solution. Batch adsorption studies were conducted to study the influence of contact time, adsorbent dosage and initial dye concentration on the adsorption. Data analysis was done by different adsorption isotherms such as Langmuir, Freundlich and Temkin and the results showed Temkin isotherm as a suitable model to define the adsorption behaviour. kinetic study was carried out using pseudo - first order and pseudo- second order models and the pseudo-second order model described the MG adsorption process with a well-fitting ($R^2 = 1$) and the calculated value of q_e is very close to the experimental value.

Keywords: Tamarind stem charcoal, Malachite Green, Adsorption, kinetics, Isotherms

1. INTRODUCTION

Synthetic dyes utilization is increasing day to day and approximately 10-15% of these enter into natural environment during the production and utilization process (Vaidya and Datye, 1982). Nearly 66% of textile dyes belong to the category of azo dyes, malachite green (MG) is a cationic dye, a dark green and crystalline solid, which is extremely toxic and harmful for human [2]. MG is one of the significant pollutant sources of waste water and is come from vivid industries including textile, pigment, food, cosmetics manufacturing, rubber, leather, paper printing and cotton.[1].MG is used as an important topical antiphrastic and anti protozoan in aquaculture [3]. Study of MG properties led to the discovery of its harmful effect on liver, gills and kidney as well as irritation, redness and pain especially in eyes [4,5,6,7]. though its usage is prohibited in the world but still used a lot in aquaculture and industries due to lack of alternatives, availability and cost-effectiveness. Taking into account of these effects removal of MG from waste, surface and ground water is essential.Numerous methods have been used for the dye removal such as ozonation, chemical oxidation, biological treatments [8], irradiation, filtration, reverse osmosis and coagulation, membrane [9], micro extraction [10] and many others [11]. However the dyes are not completely removed by these methods because of the stability of the dyes [6].

Adsorption is a method that is considered simple, efficient, and economical for dye removal [19]. In this method variety of materials, either natural or synthetic, can be used as adsorbents [20]. However, carbon and its compounds are widely used adsorbents for purification of various water sources, as these have a vast network of internal pores with high surface. So these are considered as universal adsorbents [21].

This study explores the use of Tamarind (*Tamarindus indica*) stem charcoal, an abundant agricultural by-product, for activated carbon production via physical activation. Tamarind stem charcoal is locally available, not much explored, potential, and low-cost. The prepared charcoal activated carbon was characterized by FTIR and used in batch studies to assess its adsorption performance for Malachite Green dye under varied operating parameters, including contact time, adsorbent dosage, and initial dye concentrationn were examined. Kinetics data were fitted to pseudo- first order and pseudo-second order models, and isotherm data fitted to Langmuir, Freundlich and Temkin models.

2. MATERIALS AND METHODS

2.1. Materials

Tamarind stem charcoal was obtained from home. The malachite green dye was purchased from local vendor.

2.2. Methods

2.2.1. Preparation of activated carbon from tamarind stem(adsorbent)

Tamarind stem charcoal was collected and thoroughly washed with distilled water to remove ash content, dust and unwanted particles. Followed by oven drying at 100°C for two hours. The charcoal was then crushed using a ball mill to obtain charcoal in powdered form. Sieve analysis was performed on the resulting charcoal powder, which revealed a high yield of particles with a size of 125 µm. This specific particle size was selected for further processing due to its abundance.

2.2.2. *Preparation of Malachite Green dye stock solution (Adsorbate)*

A 1000 ppm stock solution of Malachite Green dye was prepared by dissolving 1 g of the dye in a 1000 ml volumetric flask and making up the volume to the mark with distilled water. Standard solutions of Malachite Green dye with concentrations of 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm, and 700 ppm were then prepared by serially diluting the stock solution.

2.2.3. Batch adsorption studies

Batch studies were conducted by mixing a measured quantity of adsorbent with 50 ml of dye solution. The samples were placed on a magnetic stirrer at 150 rpm at a constant temperature. The samples were withdrawn from the shaker at specified time intervals and filtered using What man No. 1 filter paper. The filtrates were analysed using a spectrophotometer to determine the absorbance and final concentration of the dye. The effects of contact time (15-180 minutes), adsorbent dosage (5 - 40 g), and initial dye concentration of 100-700 ppm on the adsorption process were investigated.

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

Where C_o is the initial concentration of adsorbate (mg/L), C_e is the final concentration of adsorbate (mg/L), 'm' is the mass of the adsorbent in gram (g) and 'v' is the volume of the adsorbate in liters (L).

The adsorption efficiency can be expressed as percentage adsorption of dye solution as;

$$\%\ \text{removal (R)} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

Where 'C_o' is the initial adsorbate concentration (mg/L) and 'C_e' is the final adsorbate concentration (mg/L).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Adsorbent

Fig. 3.1. Depicts the FT-IR spectrum of tamarind stem charcoal activated carbon(TSCAC), each peak in the spectrum corresponds to different bond of different functional group[12]. the absorption band near 1704 cm^{-1} can be assigned to C= O stretching vibrations of carbonyl

groups, possibly from carboxylic acids, ketones, or esters. This suggests partial oxidation of organic components during carbonization.

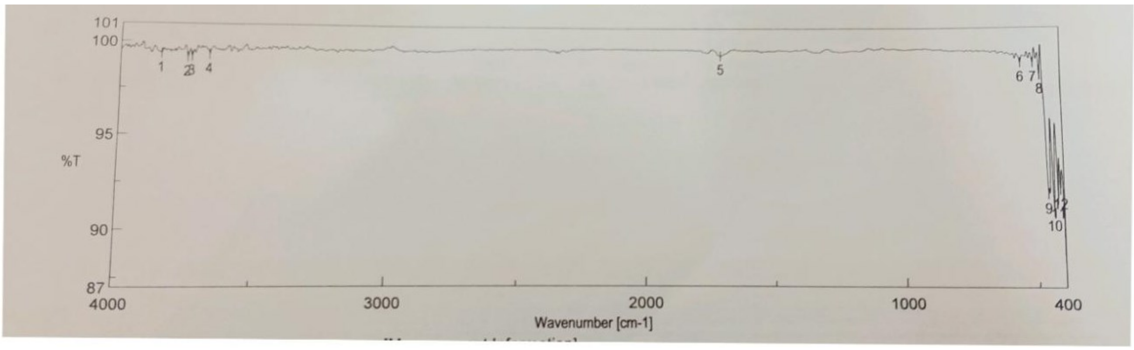

Fig. 3.1. FTIR Spectra of prepared activated carbon

3.2. Effect of contact time

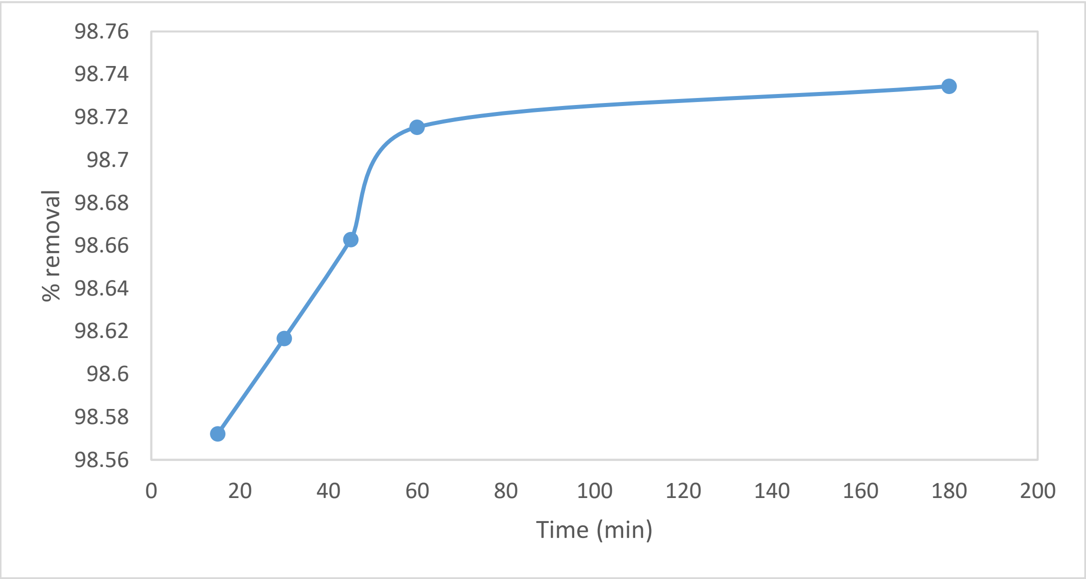

Fig. 3. 2. Effect of contact time

Effect of contact time on adsorption process helps in the determination of adsorption efficiency and equilibrium time. The above graph represents percent removal against contact time of the adsorption of dye on to Tamarind bark charcoal activated carbon shows that the maximum removal of dye has taken place during the first 15 mins and the equilibrium was reached around 60 minutes. At initial stages percentage removal and hence dye uptake is high compared to the end of the process. This is because initially the concentration difference (driving force) is maximum but it decreases with time, same was observed in previous work [12]. Further increase in contact time did not result in any significant adsorption and maximum adsorption was achieved at 60 minutes. The initial rapid removal of the dye and the establishment of equilibrium within a short time signifies the efficiency of the adsorbent for wastewater treatment [13].

3.3. *Effect of Adsorbent Dosage*

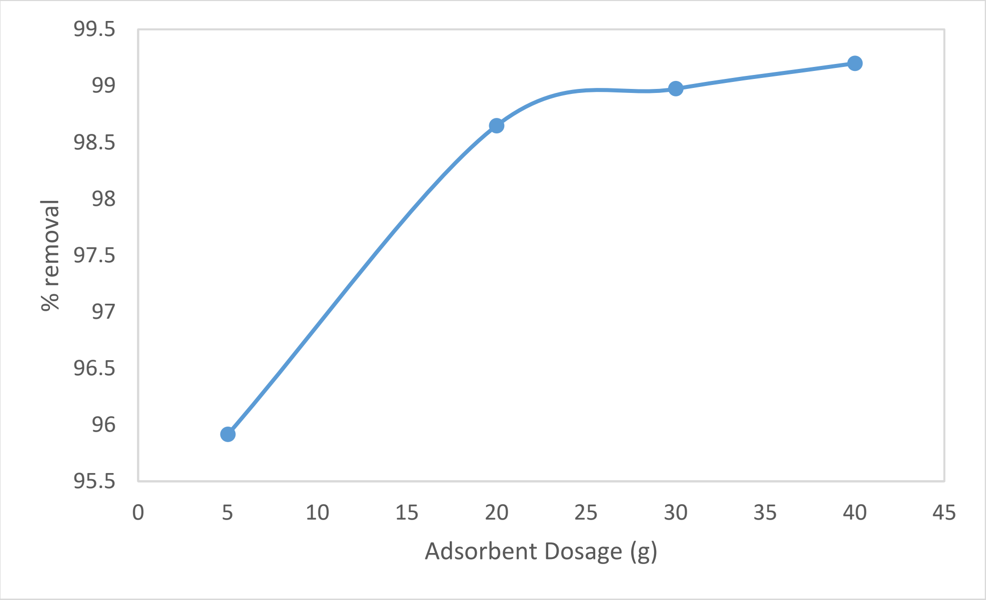

Fig. 3.3. Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of Malachite Green dye was studied between dose ranges 5 - 40 g as shown in Fig.3.3. It was observed that the adsorption of the dye increased with increasing adsorbent dosage as expected. This is principally due to increase in surface area of the adsorbent, which consequently increases the number of adsorption sites. The amount of dye adsorbed, however, decreased as the dosage increases as shown in figure) which could be attributed to the overlapping or aggregation of the active sites as the dosage increases which makes the sites inaccessible for the dye.

3.4. Effect of Initial Dye Concentration

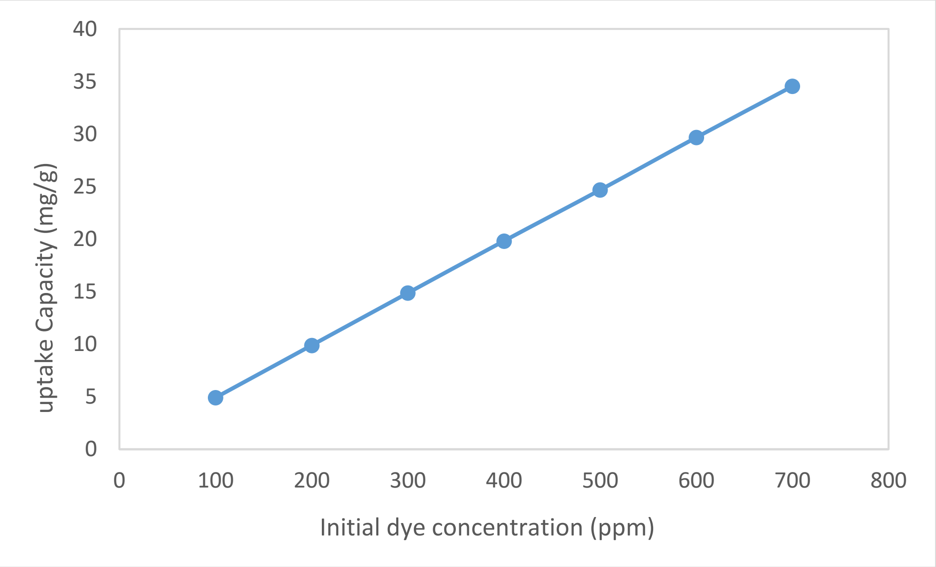

Fig.3.4 Effect of initial dye concentration

The above fig.3.4 represents the effect of initial dye concentration on the adsorption process. It was observed that adsorption capacity of the dye increases with an increase in initial dye concentration which implies that adsorption process depends on initial dye concentration. A higher concentration of dye provides a higher driving force for dye molecules to approach adsorption sites more rapidly [14]. The rate of diffusion of dye molecules at lower initial dye concentration is slow, hence few dye molecules reach adsorption sites.

3.5. Adsorption Kinetics

Kinetic studies are important to know the uptake rate of solute, to investigate this experimental data was analyzed firstly using pseudo first order model using the equation given below

$$\log(q_e - q) = \log q_e - ({}^{K_1 t}/_{2.303}) \qquad (3)$$

Where *q* is the amount of dye adsorbed (mg/g) at time *t* (min), *qe* is the amount of dye adsorbed at equilibrium (mg/g), and K_1 is the equilibrium rate constant of pseudo-first order adsorption. K_1 and q_e were obtained from the plot of $\log(q_e - q)$ against t. The R^2 obtained was high (0.9784) but the experimental and the calculated q_e values are very apart .

After the pseudo first order analysis the pseudo second order model was analysed using the below equation.

$$ {}^{t}/_{q} = {}^{1}/_{K_2 q_e^2} + {}^{t}/_{q_e} \qquad (4)$$

Where K_2 is the pseudo-second order rate constant.

The data was further analyzed using the intraparticle diffusion rate equation expressed below, to inquire the step thatat governs the overall rate of removal.

$$q = K_d t^{1/2} + C \qquad (5)$$

Where K_d (mg/g min$^{1/2)}$ is the intraparticle diffusion rate constant and C is the intercept.

Table. 3.1. Kinetic parameters

Kinetic Model	Parameter	Value
Pseudo-first order	Experimental q_e (mg/g)	24.67
	q_e (mg/g)	0.062
	K_1(min^{-1})	0.033
	R^2	0.9784
Pseudo- second order	q_e (mg/g)	24.69
	K_2 (g/mg min)	1.088
	R^2	**1**
Intraparticle diffusion rate	K_d (mg/g min$^{1/2}$)	0.009
	R^2	**0.9817**

Table. 3.1. Represents the kinetic parameters of Pseudo- first order, Pseudo-second order and intra particle diffusion rate. The correlation coefficient ($R^2 = 1$) shows a perfect fit of the data to Pseudo - second order model and the calculated q_e (24.69) is very close to the experimental value (24.67).Considering the correlation coefficient value and the closeness of experimental and calculated values of q_e the adsorption of MG dye onto the TSCAC can best described by the pseudo -second order model. The model assumes that the rate controlling step is chemisorption promoted by either valency or covalent forces [15]. The high value of R^2 (0.9817) for intra particle diffusion rate indicates that there was indeed intraparticle diffusion, but it is not the rate controlling step since the intercept C is not equal to zero [16]. Presence of the intercept shows that boundary layer diffusion occurs in the initial stages of the adsorption [17].

3.6. Adsorption Isotherms

The purpose of adsorption isotherm studies were to understand the interaction between the dye molecules and the activated carbon at equilibrium. This will give an indication of the practicability of using the activated carbon for removal of the Malachite green dye from wastewater. To come up with the most suitable equilibrium curve that can be used for design of adsorption system, the data was analyzed using three different isotherm models namely Langmuir, Freundlich, and Temkin. The isotherm parameters of the three models are calculated using Equations represented as below (6) to (9).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (6)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (7)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad (8)$$

Where C_e= any liquid phase concentration of the dye in equilibrium with the adsorbent, q_e = equilibrium adsorption capacity of the adsorbent, q_m = monolayer capacity, q_e = theoretical monolayer saturation capacity of adsorbent (mg/g), K_L = Langmuir adsorption constant, K_F = Freundlich constant for relative adsorption capacity of adsorbent, A_T = Temkin isotherm equilibrium binding constant (L/g), B_T = Temkin heat of adsorption [18].

Table. 3. 2. Isotherm coefficients for the MG dye adsorption

Isotherm Model	Parameter	Value
Langmuir	q_m (mg/g)	68.965
	K_L (L/mg)	0.111
	R^2	0.9934
Freundlich	K_F (mg/g)(mg/L)$^{1/n}$	8.343
	n	1.527
	R^2	0.9902
Temkin	B_T	15.412
	A_T	1.027
	R^2	**0.9997**

Table. 3.2 represents the isotherm coefficients of three different isotherm model such as Langmuir, Freundlich and Temkin. It was observed that the Temkin models fits well with R^2 =0.9997.

4. CONCLUSIONS

Tamarind bark charcoal activated carbon was prepared by physical activation. The functional groups on the adsorbent are given by FTIR. The percentage removal was observed to increase with increase in adsorbent dosage and contact time. The adsorption process was investigated by employing pseudo-first order, pseudo-second order and intra-particle diffusion models. The kinetic studies shows that the adsorption kinetics was more accurately described by pseudo second - order model. The equilibrium isotherm data were in best agreement with Temkin isotherm model, demonstrating the physicochemical nature of the sorption process. This study has shown the potential of tamarind stem charcoal activated carbon as an low cost adsorbent for the removal of color from malachite green dye solutions.

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