

Research Article

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Adsorption dynamics of Malachite green dye onto low cost *Pongamia pinnata* leaves carbon

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Abstract

Keywords

Malachite green,
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Adsorption,
Lagergren pseudo first
order,
Ho pseudo second
order kinetics,
Weber Morris,
pH.

In this paper activated carbon prepared from *Pongamia pinnata* leaves was utilized as low-cost adsorbent to remove basic dye Malachite green (MG) from aqueous solution by adsorption method. Batch mode experiments were conducted at 30 C to study the effects of initial concentration of Malachite green, contact time and pH on dye adsorption. The experimental data were analyzed using a pseudo first order and pseudo-second order kinetic and intraparticle diffusion equations. The experimental data fitted very well with the pseudo first order kinetic model. The *Pongamia pinnata* leaves carbon (PLC) was found to be very effective adsorbent for MG dye adsorption.

1. Introduction

Large numbers of dyes are discharged into waste stream by the textile industries. Many colour effluents are composed of non-biologically oxidisable organic compounds. As a dye imparts toxicity and upsets the biological activity of water, there is a necessity for the removal of dyes from effluents before they are mixed with water streams [1]. Dyes normally have a complex aromatic molecular structure which makes them more stable and more difficult to biodegrade [2]. Synthetic dyes are widely used in textile, paper, rubber, plastics, leather, cosmetics, pharmaceuticals and food industries. At present there are more than 10,000 dyes which are commercially available [3]. Widespread use of dyes often poses pollution problems in the form of coloured waste water discharged into environmental water bodies. It not only affects aesthetic merit but also reduces light penetration and photosynthesis. Also, some dyes are

either toxic or mutagenic and carcinogenic [4]. Dyes may enter into the food chain and could possibly cause carcinogenic, mutagenic, and teratogenic effects on humans [5,6].

Thus, the detection of malachite green in fishes, animal milk, and other foodstuff, destined for human consumption, alarm the health hazards against human being [7, 8]. Malachite green (MG) is a common basic dyestuff of triphenyl methane series used for dyeing silk and wool. The need for the treatment of dye contaminated waste water initiated a search for effective and economic treatment techniques to offer significant reduction in cost than other methods such as electrolysis, membrane filtration, chemical coagulation, oxidation, etc. Adsorption is one of the most effective and widely used techniques for the removal of dyes from aqueous

solutions. In recent years several investigators have concentrated their work on low-cost adsorbent materials to achieve the economically feasible and effective treatment of wastewaters containing dyes [9]

2. Materials and Methods

Preparation of Malachite green dye solution:

MG, a basic dye of triphenylmethane type (C.I. No. 42000, FW = 364.9, λ_{max} = 617 nm) in highest grade, was used without further purification. The experimental dye solutions were prepared by dissolving accurately weighted MG in distilled water to the concentration of 1g/L, then being diluted to different initial concentrations.

Preparation of adsorbent: The leaves of *Pongamia pinnata* were cut into smaller pieces and soaked in concentrated H_2SO_4 with 1:1 ratio (W/V) for 48 hour and activated at 160°C for 6 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water become neutral. The carbon obtained was dried at 110° C for nearly 2 h to remove the moisture. The above prepared carbon was designated as *Pongamia pinnata* Leaves Carbon there after referred to as PLC and it is kept in a desiccator.

Batchmode studies: A fixed amount of adsorbent (50 mg) was added into a set of each 250mL shaking flasks containing 50mL of different initial concentrations (20, 30, 40 and 50 mg/L) of dye solution. The flasks were agitated in an isothermal water bath shaker at 130 rpm for pre-determined time until equilibrium was reached. Dye concentrations were measured by a double beam UV/Visible spectrophotometer (Systronics 2202 make UV-Visible spectrophotometer at λ_{max} = 617 nm). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = (C_0 - C_e) \frac{V}{W}$$

where

' C_0 ' and ' C_e ' (mg/L) are the concentrations of dye solution at initial time and at equilibrium time respectively. V is the volume of the solution in litre, and W is the mass of adsorbent used in gram. The dye removal percentage can be calculated as follows:

$$\% \text{ of Removal} = (C_0 - C_t) / C_0 \times 100$$

Where C_t (mg/L) is the concentration of dye solution at time 't'.

3. Results and Discussion

Effect of pH:

Initial Solution pH is one of the most important parameters controlling the adsorption process. MG dye is yellow in colour when the solution pH is below 1.8 and it is colourless when the solution pH is above 13.2 [10]. Hence the effect of initial solution pH on the removal (%R) of MG dye was investigated by varying the solution pH from 2 to 11 by keeping all other factors constant as described in the Figure -1. At pH 2, the dye removal was minimum and it increased with the increase of initial pH which can be known from the Table -1. This can be explained on the basis of variation of charge density on the adsorbent and on the dye molecule. At lower pH, protonation on the dye molecule as well as on the adsorbent is high. Nitrogen atoms of the dye especially those not involved in aromatic systems are probable for protonation.[11]. pH_{zpc} of the PLC is 6.75. Below the solution pH 6.75, the adsorbent surface possess positive charge. The of positive charge at activated carbon surface, inhibits the adsorption of positively charged dye over it due to electrostatic repulsion. As the pH of the solution is increased, the dye and the adsorbent surface becomes more and more de-protonated due to decrease of proton density in the solution. [12]. When the pH of medium exceeds the pH_{zpc} of the adsorbent, the surface of the carbon acquires negative charge and hence the formation of electric double layer changes its polarity and consequently the dye uptake increases. A similar result was reported for adsorption of malachite green onto activated carbon prepared from lignite [13]. The increase of percentage of removal is mere 17 with the increase of solution pH 7 to 11. Hence further experiments are continued with solution pH 7 in order to avoid addition of base to the effluent and neutralising it later.

Table: 1- Effect of pH

C_i: 20 mg/L; Dose :50 mg/ 50 mL Time: 160 min.

pH	% R
2	28
3	36
4	51
5	56
6	59
7	64
8	71
9	74
10	78
11	81

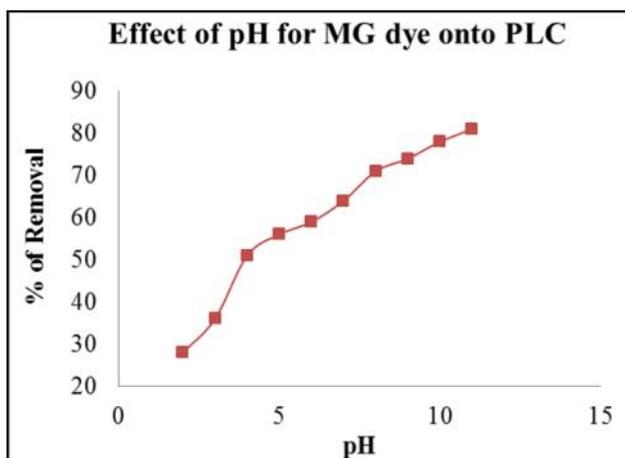


Fig 1: [MG dye]: 20 mg/L; Contact time: 160 min.

Effect of adsorbent dose: Along with increasing adsorbent dose from 10 to 100 mg/L, the percentage of removal of MG increased from 25.8 to 77.2%. The variation of percentage removal against adsorbent

dose is represented graphically in Figure-2. Increase in the MG adsorption with the increase in adsorbent dose could be attributed to increase of adsorbent surface area and availability of more adsorption sites [14]

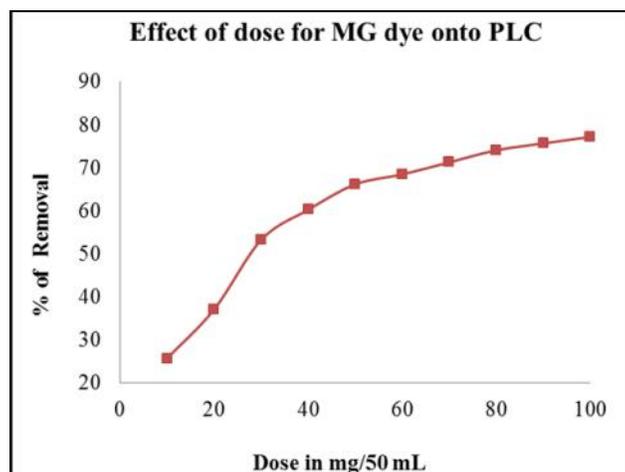


Fig 2: [MG dye]: 20 mg/L; Contact time: 160 min; pH: 7

Effect of contact time and initial dye concentration:

The experimental results of adsorptions of Malachite green dye on the activated carbon at various concentrations (20, 30, 40 and 50mg/L) with contact time are shown in Figure 3. The percentage removal decreased with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of the dye. It is

because, at lower concentration, the ratio of available adsorption site on the adsorbent to the initial number of dye molecules in the solution is high; therefore fractional adsorption becomes independent of initial concentration. However, at high concentration, the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration [15, 16]. Equilibrium was established around 80 minutes for the studied initial concentrations of dye solution.

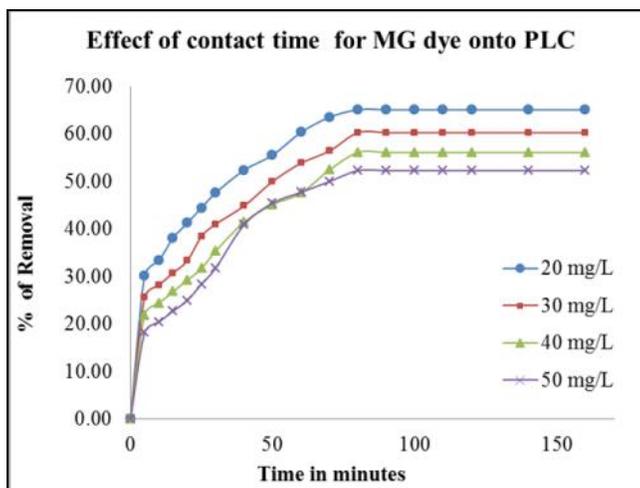


Fig 3: [MG]: 20-50 mg/L; Dose: 50 mg/L; pH: 7; T: 303K

Adsorption kinetic models:

Pseudo first order kinetic model : Pseudo first order and pseudo second order models were applied to test experimental data to elucidate the kinetic adsorption process. Pseudofirstorder kinetic equation proposed by Lagergren is in the form[17]:

$$\log(q_e - q_t) = \log q_e - k_1/2.303 \times t$$

Where k_1 (1/min), is the rate constant, q_e (mg/g) is the amount of solute adsorbed at equilibrium and q_t (mg/g) is the amount of solute adsorbed at any time. The value of k_1 for MG adsorption by PLC was determined from the plot of $\log(q_e - q_t)$ against t (Figure-4). The parameters of pseudo-first-order model are summarized in Table-2.

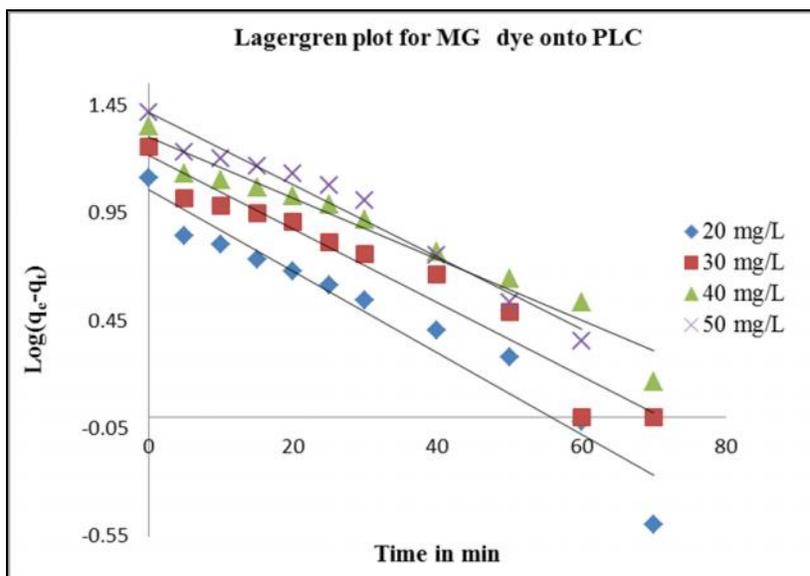


Fig-4: [MG]: 20-50 mg/L; Dose: 50 mg/L; pH: 7; T: 303K

Table:2 –Pseudo first order Kinetic results for MG dye onto PLC

Initial Concentration C_i (mg/L)	Pseudo First Order Kinetics					
	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e(\text{cal})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	q_e	R^2	MSSE
20	4.35	11.46	13.02	1.56	0.939	0.66
30	3.94	16.52	18.08	1.56	0.943	
40	3.27	19.99	22.44	2.45	0.955	
50	3.87	26.07	26.14	0.07	0.965	

Pseudo second order kinetic model:

The pseudo second order kinetic model proposed by Ho is in the form [18,19]:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e \times t$$

Where k_2 (g/mg min) is the second-order rate constant. The q_e and k_2 can be calculated from the slope and intercept of the plots t/q_t versus t .

The constant k_2 is used to calculate the initial sorption rate h (mg/g min), as $t \rightarrow 0$ as follows:

$$h = k_2 q_e^2$$

The results obtained from pseudo-second order kinetic models are presented in Figure-5 and Table-3. The increase of initial adsorption rate, 'h' with an increase in the initial dye concentration could be attributed to the increase in the driving force for mass transfer, allowing more dye molecules to reach the surface of the adsorbents in a shorter period of time [20,21]. The regression coefficient (R^2) values were ranged from 0.939 to 0.965 and 0.908 to 0.973 for the pseudo-first order and pseudo-second order kinetic models

respectively. The best fitting kinetic model is determined by comparing the calculated adsorption capacity ($q_{e(\text{cal})}$) values obtained from the respective kinetic models with the experimentally determined adsorption capacity ($q_{e(\text{exp})}$) at equilibrium. The kinetic model which gives the closer ' $q_{e(\text{cal})}$ ' values with the experimental ' $q_{e(\text{exp})}$ ' values is considered as the best fitting kinetic model. This can be known from the statistical tool 'Mean of Sum of Squared Error' (MSSE).

$$MSSE = \sqrt{\sum [(q_{e(\text{exp})} - q_{e(\text{cal})})^2] / N}$$

Where N is the number of data points, $q_{e(\text{exp})}$ is the experimental q_e and $q_{e(\text{cal})}$ is the calculated q_e . The kinetic model which gives lowest MSSE value is the best describing kinetic model.

Between the two studied kinetic models, the pseudo first order kinetic model seems to best describe the adsorption of MG dye as the MSSE value of pseudo first order model is smaller than the pseudo-second order kinetic model.

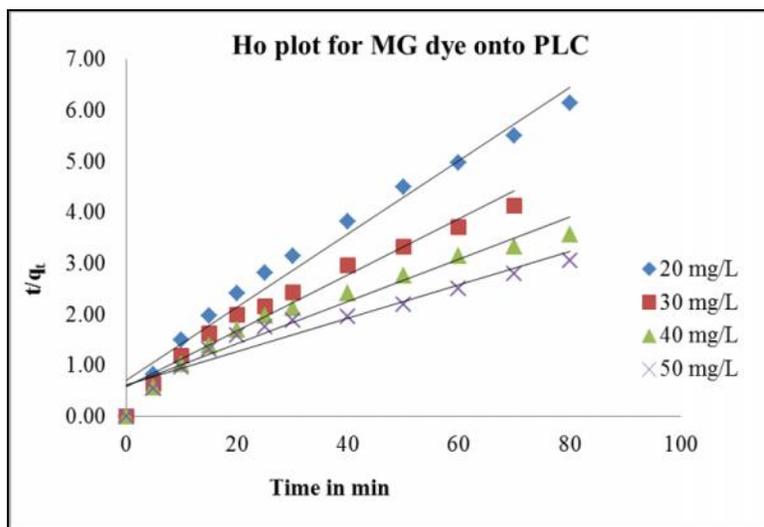


Fig-5: [MG]: 20-50 mg/L; Dose: 50 mg/L; pH: 7; T: 303K

Table: 3 –Pseudo second order Kinetics results for MG dye onto PLC

Initial Concentration C_i (mg/L)	Pseudo Second Order Kinetics						
	$k_2 \times 10^{-3}$ (g/mg.min)	h	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	q_e	R^2	SSE
20	7.2	1.40	13.94	13.02	0.93	0.973	0.98
30	5.2	1.72	18.25	18.08	0.17	0.954	
40	2.8	1.63	24.27	22.44	1.83	0.935	
50	1.7	1.63	30.58	26.14	4.44	0.908	

Intraparticle diffusion model: The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps control the overall rate of the process. Generally, pore and intra particle diffusion are often rate limiting in a batch reactor while for a continuous flow system, film diffusion is the rate limiting step [22]. Previous studies by various researchers [23,24, 25] showed that various steps involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process.

The results obtained from the effect of contact time experiments are used to study the rate limiting step in the adsorption process, as shown by Weber and Morris [26]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk solution to the particle external surface;

one might then postulate that the rate limiting step may be either film diffusion or intraparticle diffusion. As they act in series, the slower of the two will be the rate determining step. According to Weber and Morris [27], intra-particle diffusion co-efficient k_p is defined by the equation:

$$q_t = k_p t^{1/2} + C$$

Weber and Morris plot drawn between q_t and $t^{1/2}$, gave a straight line (Figure-6). Where k_p (mg/g/min^{0.5}) is the intra particle diffusion rate constant and C is the thickness of the boundary film [28]. The k_p values obtained from the slopes and intercepts were presented in Table-4.

The k_p values were found to increase with an increase of initial dye concentration which revealed the rate of adsorption governed by the diffusion of adsorbed dye within the pores of the adsorbent

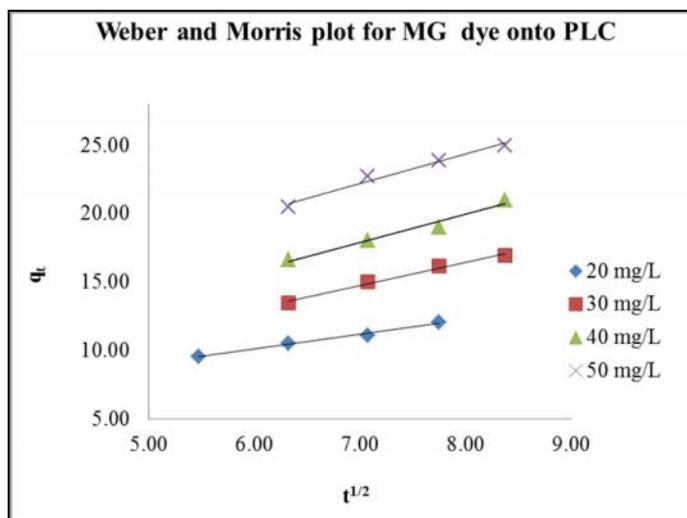
**Fig-6: [MG]: 20-50 mg/L; Dose: 50 mg/L; pH: 7; T: 303K**

Table-4: Intra Particle Diffusion results for MG dye on PLC

C_i (mg/L)	Intra Particle Diffusion	
	k_p (mg/g.min)	R^2
20	1.09	0.992
30	1.70	0.989
40	2.07	0.976
50	2.18	0.978

4. Conclusion

The present study shows that *Pongamia pinnata* leaves carbon (PLC) can be used as an adsorbent for the removal of MG dye from aqueous solutions. 77.2% removal of MG dye was observed at pH 7.0 for the dosage of 100mg/L for the initial concentration of 20 mg/L. The suitability of pseudo-first, pseudo-second order kinetic model was tested with statistical tool of Mean of Sum of squared Error (SSE) which revealed that the process of adsorption followed pseudo first order kinetic model and the Intraparticle diffusion model proved that pore diffusion played major role in the dye adsorption.

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