Research Article

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Kinetics of Malachite Green Adsorption Using A Low-Cost Activated Carbon Prepared From *Cassia Fistula*

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Abstract: The kinetics of the adsorption of a commonly used dye- malachite green onto activated carbon prepared from a economic source namely *Cassia fistula* has been discussed in this work. The percentage removal of malachite green increases from 24.05 to 28.81 in 180 minutes of contact time when the concentration of the dye solution was varied from 400 to 100 mg/L at pH 2.87 with 300 mg of the adsorbent used in this study. The adsorption of malachite green was found to be time and concentration dependent. The adsorption kinetics of malachite green onto the low-cost adsorbent used in this study followed first order Lagergren rate equation. The intraparticle diffusion study shows that the rate constants for intraparticle diffusion (K_p) increased with the increase in initial concentration of malachite green solution.

Keywords: kinetics, *Cassia fistula*, Lagergren, Intraparticle diffusion, adsorption

INTRODUCTION:

Most dyestuffs are designed to be resistant to environmental conditions like light, effect of pH and microbial attack. Hence their presence in waste water is unwarranted and it is desirable to remove colouring material from effluents before their discharge in their environment not only for aesthetic reasons [1]. The treatment of effluents containing dyes has been conventionally carried out to remove colour by physical or chemical methods such as adsorption, chemical precipitation, electrochemical treatment etc [2].

Adsorption has been found to be superior to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [3]. There are several reports on the colour removal of dyes [4,5]. This paper deals with the kinetics of the adsorption of a commonly used dye- malachite green onto activated carbon prepared from a economic source namely *Cassia fistula*. Several low cost materials [6] have been used in the removal of malachite green - ground nut shell [7], tamarind seed [3], rose apple carbon, coconut shell carbon and saw dust carbon[8], ginger waste [9] etc. The kinetics of malachite green sorption on rice-straw derived char followed the Lagergren's pseudo-first-order model and the overall rate of dye uptake was found to be controlled by external mass transfer at the beginning of adsorption, while intraparticle diffusion controlled the overall rate of adsorption at a later stage [10]. Alkali-treated fly ash is a potential low-cost adsorbent for removal of malachite green from an aqueous solution [11]. First order kinetics is reported for the adsorption of Malachite Green from wastewater utilizing hen feather as potential adsorbent . Decolourization of malachite green using tamarind seeds showed the process to follow first order pseudo kinetics with intraparticle diffusion as the rate controlling step. Citric acid modified rice straw was found to be effective in the removal of malachite green from aqueous solution. In this paper Lagergren's first order kinetic equation [15]and intraparticle diffusion equation[16] have been used to study the kinetics of the adsorption process of malachite green onto activated carbon from *Cassia fistula*.

MATERIALS AND METHOD:

Eco-friendly low-cost carbon adsorbent used in this study for the removal of Malachite green was prepared from the seeds of *Cassia fistula*. Batch studies were conducted owing to its simplicity and ease of evaluating some basic parameters which influence the adsorption process.

Preparation of the Adsorbent: Seeds of *Cassia fistula* were collected from Avinashilingam Deemed University campus, Coimbatore. The collected pods were cut into small pieces, dried in sunlight for 5 days and further dried in a hot air oven at 60^0C for 24 hours. The completely dried material was powdered well. The powdered raw material was chemically activated by treating with concentrated sulphuric acid with constant stirring and kept for 24 hours. The carbonized material was washed well with plenty of water several times to remove excess acid and dried at $105\text{-}110^0$C in a hot air oven.

Reagents: The dye solution was prepared by dissolving 5g of malachite green in distilled water and diluted to 1000 ml. The stock solution was diluted to appropriate concentration.

Equipment: Elico pH meter was used to measure pH.Photo colorimeter (model-1311) was used for spectro colorimetric work. Genuine equipment manufacturer's mechanical horizontal bench shaker was used for the shaking of solution containing adsorbent and adsorbate.

Effect of variation of contact time and initial concentration of the dye on the adsorption potential of activated carbon prepared from *Cassia fistula*.: The dye solution of different concentrations containing 10, 20, 30 and 40mg of dye in 100 ml was added with 300mg of the adsorbent taken in Pyrex bottles and shaken in a mechanical horizontal bench shaker for various time intervals (10, 20, 30, 40, 50, 60, 90, 120,150, and 180 minutes) at room temperature. The solutions were filtered and the dye concentrations of the filtrates were estimated colorimetrically at 620 nm.

Kinetic Modeling for Malachite Green Adsorption using Lagergren Equation: The chemical kinetics describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. In order to investigate the mechanism of adsorption various kinetic models have been suggested. In recent years, adsorption mechanisms involving kinetics - based models have been reported. Adsorption kinetic data of malachite green are analyzed using the Lagergren pseudo-first –order rate equation

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

where q_e and q_t are the amount of Malachite green adsorbed at time't' and at equilibrium time. K_a is the rate constant.

Intra Particle Diffusion Rate Equation for Adsorption of Malachite Green: Due to rapid stirring in batch reactors there is a possibility of transport of malachite green species from the bulk into pores of the adsorbent as well as adsorption at the outer surface of the adsorbent. 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. The possibility of malachite green species to diffuse into the interior sites of the particles of adsorbent was tested with Weber-Morris equation given as follows:

$$q = K_p t^{1/2}$$

where q is the amount of malachite green adsorbed in mg, K_p is the intraparticle diffusion rate constant and't' is the time (agitation time) in minutes.

RESULTS AND DISCUSSION:

Effect Of Contact Time On Adsorption Of Malachite Green: Effect of agitation time on adsorption is one of the factors affecting the adsorption potentials. It can be seen from the results (Table 1) of varying contact time, the percentage adsorption of malachite green increases with increase in contact time, when the initial concentration of the dye solution used was 100,200,300,400mg/L.. The malachite green removal curves were smooth and continuous indicating the formation of monolayer coverage of adsorbate on outer surface of adsorbent .The percentage of the dye removed by adsorption increased from 10.17 to 28.81%, when the contact time was varied from 10 to 180 minutes using 100ml of the dye solution of initial concentration 100mg/L with 300 mg adsorbent.

Kinetic Modelling For Malachite Green Adsorption Using Lagergren Equation: Adsorption kinetic data of malachite green was analyzed using the Lagergren pseudo-first -order rate equation:

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

where, q_e and q_t are the amount of Malachite green adsorbed at time't' and at equilibrium time. K_a is the rate constant. The rate constant K_a was calculated from the slopes of the linear plots of log $(q_e - q_t)$ Vs 't' (**Table 3**). The Lagergren plots of dye adsorption were linear (r>0.8). The rate constants K_a for different concentrations of dye solution is given in Table 2. The K_a value indicates that the adsorption of the dye followed first order Lagergren kinetics.

Intra Particle Diffusion Rate Equation For Adsorption of Malachite Green: The Weber-Morris equation $q = K_p t^{1/2}$ where q is the amount of malachite green adsorbed in mg, K_p is the intraparticle diffusion rate constant and't' is the time (agitation time) in minutes was used to interpret the results (Table 4).The rate constants (K_p) for intraparticle diffusion for various initial concentrations of malachite green solution was determined from the slope of respective plots drawn between square root of time ($t^{1/2}$) and the amount of adsorbate adsorbed (q). The plots were straight lines but not passing through the origin and thus indicating the intraparticle diffusion is not the sole rate limiting factor for the adsorption of malachite green [17].The values of K_p obtained in this study for the adsorption of malachite green is shown in Table 4.

CONCLUSION:

The percentage removal of malachite green increases from 24.05 to 28.81 in 180 minutes of contact time when the concentration of the dye solution was varied from 400 to 100 mg/L at pH 2.87

with 300 mg of the adsorbent used in this study. The adsorption of malachite green was found to be time and concentration dependent. The adsorption kinetics of malachite green onto the low-cost adsorbent used in this study followed first order Lagergren rate equation. The intraparticle diffusion study shows that the rate constants for intraparticle diffusion (K_p) increased with the increase in initial concentration of malachite green solution.

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Table 1: Adsorption of malachite green with variation off contact time and initial concentration of malachite green solution

Conditions: Adsorbent dosage : 300mg; pH : 2.87 Temperature : 37^0C;
Contact time : 10 to 180 minutes

Time in minutes	% Adsorption of Malachite green			
	Initial concentration of Malachite green			
	100 mg/L	200 mg/L	300 mg/L	400 mg/L
10	10.17	9.23	8.33	7.59
20	11.87	10.77	9.72	8.86
30	13.55	12.31	11.11	10.12
40	15.25	13.84	12.50	11.39
50	16.95	15.38	13.89	12.65
60	18.65	16.92	15.28	13.92
90	20.33	20.00	18.05	16.45
120	23.72	21.54	20.83	18.98

150	25.42	24.61	22.22	21.52
180	28.81	27.69	25.00	24.05

Table 2 Rate constant for the process of adsorption of malachite green onto activated carbon from *Cassia fistula*

Concentration of dye in mg/L	**Ka X 10 $^{-2}$minutes^{-1}**
100	0.7194
200	0.9682
300	1.1162
400	1.2137

Table 3 : Kinetic modelling for malachite green adsorption using Lagergren equation

Conditions: Adsorbent dosage : 300mg; pH : 2.87

Temperature : $37^{0}C$

Time in minutes	log (q_e-q)			
	100mg/L	200mg/L	300mg/L	400mg/L
10	0.2704	0.5671	0.6988	0.8184
20	0.2289	0.5294	0.6611	0.7836
30	0.1835	0.4879	0.6197	0.7458
40	0.1322	0.4423	0.5739	0.7044
50	0.0740	0.3911	0.5228	0.6587
60	0.0068	0.3330	0.4647	0.6075
90	-0.0716	0.1866	0.3186	0.4827
120	-0.2932	0.0899	0.0965	0.3066
150	-0.4698	-0.2111	-0.0793	-0.0056
Intercept log q_e	0.24041	0.59693	0.75120	0.90578
Slope –Ka/2.303x10^{-3}	-3.1241	-4.2041	-4.8470	-5.2702
Ka	0.71948	0.96820	1.11626	1.21372

Table 4: Intra particle diffusion rate equation for adsorption of malachite green

Conditions: Adsorbent dosage : 300mg; Temperature : 37^0C

pH : 2.87

Time in minutes	$t^{1/2}$	Initial concentration of Malachite green in mg/L — Amount of dye adsorbed (q) in mg			
		100	**200**	**300**	**400**
10	3.1622	10.17	9.23	8.33	7.59
20	4.4721	11.87	10.77	9.72	8.86
30	5.4772	13.55	12.35	11.11	10.12
40	6.3245	15.25	13.84	12.50	11.39
50	7.0711	16.95	15.38	13.89	12.65
60	7.7459	18.65	16.92	15.28	13.92
90	9.4868	20.33	20.00	18.05	16.45
120	10.9544	23.72	21.54	20.83	18.98
150	12.2474	25.42	24.61	22.22	21.52
180	13.4164	28.81	27.69	25.00	24.05
Intercept		9.7111	2.8859	2.4200	1.5179
Slope (Kp)x10^{-4}		1.1833	1.7853	1.6517	1.6221

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