IJEP 31 (10) : 850-854 (2011) (Received on June 25, 2011)

Kinetic Modeling of Adsorption of Malachite Green Using a Low-Cost Activated Carbon Obtained From *Caesalpinia Pulcherrima*

N.Renugadevi, R. Sumithra and P.Lalitha

Avinashilingam Deemed University for Women, Department of Chemistry, Coimbatore-641 043

Malachite green is traditionally used for dyeing cotton, jute, silk, wool leather, etc. Despite its industrial importance, malachite green poses several risks to the consumers. Therefore, effective removal of malachite green from wastewater is necessary. The present study involves kinetic modeling of the process of adsorption of malachite green from aqueous solution onto a low cost carbon adsorbent prepared from *Ceasalpinia.* With increase in contact time of adsorption from 10 to 180 min, the % adsorption was found to increase from ~8% to 29% with 100 mg/L at pH 2.87 with 300 mg of the adsorbent. The adsorption kinetics of malachite green onto the low-cost adsorbent used in this study followed first 'er Lagergren rate equation. The intraparticle diffusion study shows that the rate con-...nts for intraparticle diffusion (K_p) increased with the increase in initial concentration of malachite green solution. Intraparticle diffusion is not the sole rate limiting factor for the adsorption of malachite green.

KEYWORD

Caesalpinia pulcherrima, kinetic modeling, Lagergren, intraparticle diffusion, First order kinetics.

INTRODUCTION

The synthetic dyes are largely used in industries, like textiles, paints, pulp and paper, carpet and printing. Malachite green is traditionally used for dyeing cotton, jute, silk, wool leather and as an antifungal, antibacterial and antiparasitical therapeutic a nt (Gupta *et al.*, 2011). The reduced form of Malachite green persists in fish tissues for longer period of time and its consumption may alarm health hazards against human being (Pan and Zhang, *et al.* 2008). Despite its industrial importance, malachite green poses several risks to the consumers, including its effects on the immune system and reproductive system as well as its genotoxic and carcinogenic potentials. Therefore, effective removal of malachite green from wastewater is necessary (Srikhun *et al.*, 2009). Now-a-days numerous low cost adsorbents, such as coal, flyash, wood, silica gel, clay materials, agricultural wastes, cotton wastes and cellulose based wastes, such as orange, lemon, banana and lychee had been used for dye removed (Gupta *et al.*, 2011). The present study involves kinetic modeling of the process of adsorption of malachite green from aqueous solution onto a low cost carbon adsorbent prepared from *Ceasalpinia.*

MATERIAL AND METHOD

Eco-friendly low -cost carbon adsorbent used in this study for the removal of malachite green was prepared from the fruits of *Caesalpinia pulcherrima*. Batch studies were conducted owing to its simplicity and ease of evaluating some basic parameters which influence the adsorption process. The effect of variation in contact on the adsorption potential of activated carbon from *Caesalpinia pulcherrima* has been evaluated. Lagergren first order kinetic equation and

Table 1. *Adsorption of malachite green with variation of initial concentration of malachite green solution*

Conditions :
Adsorbent dosage : 300 mg
pH : 2.87
Temperature : 37°C
Contact time : 10 to 180 min

Time, min	% Adsorption of malachite green			
	Initial concentration of malachite green			
	100 mg/L	200 mg/L	300 mg/L	400 mg/L
10	8.47	7.69	6.94	6.32
20	10.17	9.23	8.33	7.59
30	11.86	10.77	9.72	8.86
40	13.56	12.31	11.11	10.12
50	15.25	13.84	12.50	11.39
60	16.95	15.38	13.89	12.65
90	20.34	18.46	15.28	13.92
120	22.03	21.53	19.44	16.45
150	23.73	23.07	22.22	20.25
180	28.81	27.69	25	24.05

Table 2. *Rate constants for adsorption of malachite green*

Concentrationof dye, mg/L	Ka x 10^{-2}min^{-1}
100	0.660
200	0.9334
300	1.132
400	1.090

intraparticle diffusion rate equation have been used to interpret the kinetics of the adsorption process.

Preparation of the adsorbent

Fruits of *Caesalpinia pulcherrima* were collected from Avinashilingam Deemed University Campus, Coimbatore. The collected pods were cut into small pieces, dried in sunlight for 5 day and further dried in a hot air oven at 60 °C for 24 hr.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 hr. The carbonized material was washed with plenty of water several times to remove excess acid and dried at 105-110 °C in a hot air ove for 24 hr. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in an air tight container for further use.

Reagent

The dye solution was prepared by dissolving 5 gm of malachite green in distilled water and diluted to 100 mL. The stock solution was diluted to appropriate concentration.

Equipment

1. Elico pH meter was used to measure pH.

2. Photo colourimeter was used for spectrocolourimetric work.

3. Genuine equipment manufacture's mechanical horizontal bench shaker was used for shaking of solution containing adsorbent and adsorbate.

Effect of variation of contact time on the adsorption

The dye solution of different concentrations

Table 3. *Kinetic modeling for malachite green adsorption using Lagergren's equation*

Conditions:
Adsorbent dosage : 300 mg
pH : 2.87
Temperature : 37 °C

Time, min	$\log(q_e - q)$			
	100 mg/L	200 mg/L	300 mg/L	400 mg/L
10	0.3083	0.602	0.7337	0.8505
20	0.270	0.567	0.698	0.8183
30	0.2291	0.529	0.661	0.7836
40	0.188	0.4881	0.619	0.7458
50	0.132	0.442	0.574	0.7044
60	0.0742	0.3911	0.522	0.6586
90	-0.0718	0.2662	0.464	0.6075
120	-0.1687	0.0901	0.2218	0.4825
150	-0.2937	-0.0347	-0.0794	0.1815
180	-	-	-	-
Intercept log qe	0.2814	0.6384	0.8105	0.9420
Slope-Ka/2.303 x 10^{-3}	-2.867	-4.056	-4.917	-4.735
Ka	0.660	0.934	1.132	1.090

Table 4. *Intraparticle diffusion rate equation for adsorption of malachite green*

Conditions:
Adsorbent dosage : 300 mg
pH : 2.87
Temperature : 37 °C

Time, min	$t^{1/2}$	*Initial concentration of malachite green, mg/L			
		Amount of dye adsorbed (q), mg			
		*100	*200	*300	*400
10	3.162	8.47	7.69	6.94	6.32
20	4.472	10.17	9.23	8.33	7.59
30	5.472	11.86	10.77	9.72	8.86
40	6.324	13.56	12.31	11.11	10.12
50	7.071	15.25	13.84	12.50	11.39
60	7.745	15.95	15.38	13.89	12.65
90	9.486	20.34	18.46	15.28	13.92
120	10.954	22.03	21.53	19.44	16.45
150	12.247	23.73	23.07	22.22	20.25
180	13.416	28.81	27.69	25	24.05
Intercept		1.8565	0.6633	0.299	0.0277
Slope (Kp)x 10^{-4})		1.8988	1.908	1.7602	1.6343

10,20,30 and 40 mg of dye/100 mL) was shaken with 300 mg of the adsorbent taken in a Pyrex bottles for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150 and

180 min) at room temperature. The solutions were filtered and the dye concentrations of the filtrates were estimated colourimetrically 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.

Intraparticle 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 min.

RESULT AND DISCUSSION

The experimental data obtained and the findings of the present study are presented and discussed in the light of the objectives set forth. Batch experiments were carried out for the removal of malachite green by adsorption. The results were used to evaluate the optimum conditions for the removal of the dye, malachite green and to examine the efficiency of the low-cost adsorbent prepared in this study for the treatment of aqueous solution containing malachite green. The parameters which influence the extent of adsorption, such as concentration of the adsorbate, contact time, pH and adsorbent dosage were investigated.

Effect of contact time on adsorption of malachite green

Effect of agitation time on adsorption is on of the factors affecting the adsorption pc tentials. It can be seen from the results 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, 400 mg/L. From the table 1, it is evident that for maximum removal of dye by the adsorbent, the solution should be equilibrated for 180 min or more. 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 8.47 to 28.81%, when the contact time was varied from 10 to 180 min using 100 mL of the dye solution of initial concentration 1(mg/L with 300 mg adsorbent.

Kinetic modelling for malachite green adsorption using Lagergren equation (variation of initial concentration of dye solution)

The adsorption kinetic data of malachite green analyzed using the Lagergren's 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 could be calculated from the slopes of the linear plots of log $(q_e - q_t)$

verses 't'. 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. Table 3 gives the kinetic modeling data for the adsorption of malachite green onto activated carbon.

Intraparticle diffusion rate equation for adsorption of malachite green

The results of study interpreted in terms of 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 min, is given in table 4. The rate constants (K_p) for intraparticle diffusion for various initial concentrations of malachite green solution was determined ʼom the slope of respective plots drawn ᴗetween 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 (Santhi *et al.*, 2009).The values of K_p obtained in this study for the adsorption of malachite green is shown in table 4.

CONCLUSION

The low-cost activated carbon derived from the fruit of *Caesalpinia pulcherrima* can be used as a resourceful adsorbent for the removal of a basic dye, malachite green from aqueous solution. The adsorption kinetics ᵒᶠ malachite green onto the low-cost ad- ·bent 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.

ACKNOWLEDGEMENT

The authors thank the concerned authorities of the Avinashilingam Deemed University for Women, Coimbatore for providing the necessary facilities to carry out this work..

REFERENCE

Gupta, Neha, Atul K. Kushwaha and M.C. Chattopadhyaya. 2011. Kinetics and thermodynamics of malachite green adsorption on banana pseudo-stem fibers. *J. Chem. Pharmaceutical Res.,* 3(1) : 284-296.

Pan, Xiangliang and Daoyong Zhang. 2008. Removal of malachite green from water by *Firmiana simplex* wood fiber. *Electronic J. Biotech.,* 12(4).

Santhi, T. Manonmani and S. Smitha. 2009. Removal of malachite green from aqueous solution by activated carbon prepared from the *Annona squmosa* seed by adsorption. *Electronic J. Chemistry.* 2(2).

Srikhun, Sarawut, Samoran Hirunpraditkun and Kamachai Nuithitikul. 2009. Adsorption of malachite green dye onto activated derived from durian peel. *J. Taiwan Inst. Chem. Eng.,* 41(5) : 591-598.

AUTHOR

1*. Dr.N.Renugadevi, Associate Professor, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.

2. Ms. R. Sumithra, M.Sc Student, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.

3. Dr.P.Lalitha, Assistant Professor, Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore-641 043.