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Kinetics of the adsorption of methylene blue from an industrial dyeing effluent onto activated carbon prepared from the fruits of *Mimusops Elengi*

N. Renugadevi, R. Sangeetha and P. Lalitha

Department of Chemistry, Avinashilingam Deemed University for Women, Coimbatore

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ABSTRACT

The present paper deals with the kinetics of the adsorption of methylene blue from an industrial effluent onto activated carbon prepared from a cheap source- fruits of Mimusops elengi. The rate constants for the adsorption of methylene blue dye were determined using Lagergren rate equation, Intraparticle diffusion rate equation and Elovich rate equation. Commercially available activated carbon was used for comparative purpose. The results of the study show that the adsorption process followed first order kinetics and that the economic adsorbent can be successfully employed in the removal of dyes from effluents. The applicability of the foresaid rate equations is also well evident.

Keywords: methylene blue, Adsorption, Lagergren, *Mimusops elengi*, kinetics, intraparticle diffusion, Elovich.

INTRODUCTION

Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually world wide of which about 20 – 30% are wasted in industrial effluents during the textile dyeing and finishing processes [1]**.** Methylene blue has long been used as a model for the adsorption of organic dye from aqueous solution. Methylene blue is one of the most commonly used thiazine dyes and various adsorbents have been reported for its removal from aqueous solutions[2]**.** The present paper deals with the kinetics of the adsorption of methylene blue from an industrial effluent onto activated carbon prepared from a cheap source- fruits of *Mimusops elengi.* The results of the variation of contact time of adsorbent with the industrial effluent, has been used to determine the rate constants using Lagergren rate equation, Intraparticle diffusion rate equation and Elovich rate equation. Commercially available activated carbon has been used for comparative purpose.

Kinetics is concerned fundamentally with the details of the process whereby a system gets from an initial state to final state and the time required for the transition, hence it gives ideal about the mechanism of adsorption[3].

MATERIALS AND METHODS

Preparation of the adsorbent

Fruits of *Mimusops Elengi* were collected from Avinashilingam University campus, Coimbatore. The pods of the *Mimusops Elengi* were cut into small pieces, dried in sunlight for 5 days and further dried in a hot air oven at 60°C 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 obtained was washed well with plenty of water several times to remove excess acid and dried at 105-110°C in a hot air oven for 24 hours. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in an airtight container for further use. This adsorbent has been given the acronym ACM and commercially available activated carbon designated as ACC and will be henceforth referred to as ACM and ACC.

Reagents

The dye solution was prepared by dissolving 5g of Methylene blue in distilled water and diluted to 1000ml. 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 mechanical horizontal bench shaker was used for the shaking of solution containing adsorbent and adsorbate.

Analytical Procedures

Characterization of the adsorbents

Physical characteristics namely ash content (%), moisture content (%), pH, surface area, bulk density, specific gravity and porosity (%) of the adsorbents used in this study were determined and are reported in our previous paper [4].

Batch Experiments

Batch mode experiments were carried out to study the adsorption capacities of the adsorbent ACM and commercial activated carbon adsorbent (ACC) used in this study. Though industrial operations are not carried out batch- wise, these are simple and effective in evaluating the basic parameters affecting adsorption process. In batch mode adsorption study, a very good contact occurs between the methylene blue species and carbon by shaking at 150rpm (rotation per minute) speed. Experiments were performed with 100mg of the adsorbent ACM with dyeing industrial effluent (600, 800and 1000mg/L). Similarly experiments were performed with 50mg of the adsorbent ACC. These solutions were taken in a temperature controlled horizontal electrical bench shaker and agitated for various time intervals (10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 minutes). The adsorbate and the adsorbents were separated and analyzed colorimetrically.

RESULTS AND DISCUSSION

Characteristics of the adsorbents

The results of the physical characteristics namely ash content, moisture content, pH, surface area, bulk density, specific gravity and porosity of the adsorbents used in this study are given in Table 1.

TABLE 1: Characteristics of the adsorbents

	Adsorbents	
	ACC	**ACM**
Ash content (%)	0.3860	6.32
Moisture content (%)	17.44	7.42
pH	6.57	3.60
Surface area (m^2/g)	710	340
Bulk density (g/cc)	0.2450	0.603
Specific gravity(g/cc)	0.9128	0.615
Porosity (%)	72.35	35.26

(Renugadevi et al,2010)

Kinetics of adsorption of methylene blue (Lagergren Rate Equation)

The study of adsorption kinetics is significant as it provides valuable insights into the reaction path ways and into the mechanism of the reactions. Any adsorption process is normally controlled by three steps:

1. Transport of the solute from bulk solution to the film surrounding the adsorbent.
2. From the film to the adsorbent surface.
3. From the surface to the internal sites followed by binding of the adsorbent species into the active sites [5]**.**

TABLE 2 Kinetic modelling for the adsorption of methylene blue onto acm using lagergren equation

Conditions: *Adsorbent dosage: 100mg ; pH: 6.7 ± 0.02* *Temperature: 32°C*

Time in seconds (t)	**Initial concentration of Methylene Blue 600mg/L**		**Initial concentration of Methylene Blue 800mg/L**		**Initial concentration of Methylene Blue 1000mg/L**	
	q(mg/g)	**log (q_e-q)**	**q(mg/g)**	**log (q_e-q)**	**q(mg/g)**	**log (q_e-q)**
10	28.7	0.9637	33.7	1.0086	21.4	1.1553
20	30.6	0.8633	35.7	0.9138	23.5	1.0863
30	31.2	0.8260	36.7	8573	24.5	1.0492
40	33.0	0.6902	37.7	0.7924	26.5	0.9637
50	34.3	0.5563	38.8	0.7075	27.6	0.9085
60	34.9	0.4771	39.8	0.6127	29.6	0.7853
90	36.7	0.0792	41.8	0.3222	31.6	0.6127
120	37.3	-0.2218	43.9	-	33.7	0.3010
150	37.9	-	43.9	-	34.7	0.0000
180	37.9	-	43.9	-	35.7	-
Intercept: log q_e	1.1122		1.1057		1.2813	
Slope: (-Ka/2.303) ×10^{-3}	-11.10		-8.42		-8.19	
K_a×10^{-2}	25.563		19.391		18.861	
Correlation coefficient (r)	-0.9970		-0.9957		-0.9950	

The slowest of these steps determines the overall rate of the adsorption processes and usually it is thought that the step 2 leads to surface adsorption and the step 3 leads to intra particle adsorption. Intra particle transport from bulk fluid to the external surface of the porous adsorbent may also have an effect on the overall rate of adsorption under some circumstances. The rate constant for the adsorption of methylene blue from dyeing effluents onto adsorbents namely ACM and ACC was determined using Lagergren equation [6].

$$\log (q_e - q) = \log q_e - K_a / 2.303 \times t$$

where,
q and q_e = amount of Methylene blue adsorbed at time 't' and at equilibrium time.
K_a = rate constant of adsorption in time^{-1}. The data are given in tables 2 and 3. Lagergren plots of log (q_e - q) vs 't' were linear showing the applicability of the equation to the adsorption process.

TABLE 3 Kinetic modelling for the adsorption of methylene blue onto acc using lagergren equation

Conditions: *Adsorbent dosage: 50mg ; pH:6.7 ±0.02* *Temperature : 32^oC*

Time in seconds (t)	Initial concentration of Methylene Blue 600mg/L		Initial concentration of Methylene Blue 800mg/L		Initial concentration of Methylene Blue 1000mg/L	
	q(mg/g)	log (q_e-q)	q(mg/g)	log (q_e-q)	q(mg/g)	log (q_e-q)
10	47.0	1.0086	51.2	1.1732	61.2	1.2380
20	48.9	0.9190	54.4	1.0682	64.3	1.1523
30	49.8	0.8692	56.5	0.9822	66.3	1.0863
40	51.6	0.7482	58.6	0.8750	68.4	1.0043
50	53.5	0.5682	59.7	0.8061	71.4	0.8512
60	54.4	0.4471	61.8	0.6334	72.4	0.7853
90	55.3	0.2787	64.0	0.3222	73.4	0.7075
120	57.2	-	65.0	0.0414	76.5	0.3010
150	57.2	-	66.1	-	77.5	0.0000
180	57.2	-	66.1	-	78.5	
Intercept: log q_e	1.1116		1.2874		1.3323	
Slope: (-Ka/2.303) ×10^{-3}	-9.81		-10.47		-8.54	
K_a×10^{-2}	22.592		24.112		19.667	
Correlation coefficient (r)	-0.9829		-0.9984		-0.9895	

Elovich Equation

The Elovich equation was developed to describe the kinetics of chemisorption of gases onto solids [7] and it is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where,

q_t = Amount of adsorbate adsorbed at time't',
α = Initial adsorption rate (mg g^{-1}min^{-1}) and
B = Desorption constant (g mg^{-1}) during any experiment.

Assuming the initial boundary condition[8], q = 0 at t = 0, equation (1) on integration becomes

$$\frac{1}{q_t} = \frac{1}{\beta} \ln(1+\alpha\beta t) \quad \ldots\ldots\ldots\ldots\ldots (2)$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta >> 1$ and applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t=t, equation (2) becomes

$$q_t = \beta \ln (\alpha\beta) + \ln t \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

Equation 3 is commonly used in the kinetics of chemisorption of gases on solids. **Taylor *et al.*,** [9] successfully used the Elovich equation for the sorption of zinc ions onto soils and **Juang and Chen** [10] studied the sorption kinetics of metal ions from sulphate solutions onto solvent impregnated resins. Elovich plots of "ln t Vs q_t" (amount of dye adsorbed) gives a linear relationship. The high correlation coefficient (r) shows the successfulness of the Elovich model. The Elovich eqation data obtained in this study for methylene blue adsorption with ACM is summarized in Table 4 . The general explanations for this form of kinetic equation involves a variation of the energetic of chemisorption with the active sites are heterogeneous in ACM. This supports that the heterogeneous sorption mechanism likely to be responsible for the dye uptake. Elovich model basically supports chemisorptions [11].

TABLE – 4 Elovich equation for the adsorption of methylene blue onto ACM
Condition: Adsorbent dosage: 100mg ; pH : 7.4 ±0.02

Time in minutes	In(t)	Initial concentration of Methylene blue in mg/L		
		600(mg)	800 (mg)	1000(mg)
10	2.3025	28.7	33.7	21.4
20	2.9957	30.6	35.7	23.5
30	3.4012	31.2	36.7	24.5
40	3.6889	33.0	37.7	26.5
50	3.9120	34.3	38.8	27.6
60	4.0943	34.9	39.8	29.6
90	4.4998	36.7	41.8	31.6
120	4.7875	37.3	43.9	33.7
150	5.0106	37.9	43.9	34.7
180	5.1929	37.9	43.9	35.7
Intercept: 1/β lnα β		20.2042	23.8394	7.6686
Slope: 1/ β		3.5215	3.9489	5.3181
Initial adsorption rate α		2.7589	2.9734	2.7166
Desorption constant β		0.2839	0.2532	0.1880
Correlation Coefficient (r)		0.9887	0.9863	0.9867

Intra particle diffusion rate equation for the adsorption of methylene blue

Due to rapid stirring in batch reactors there is a possibility of transport of methylene blue 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 methylene blue species to diffuse into the interior sites of the particles of adsorbent was tested with Weber-Morris equation given as follows:

$$q = K_p t^{1/2} \quad \text{where,}$$

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

The results of the study were interpreted in terms of the above equation and data is given in the Tables 5 and 6.

TABLE – 5 Intra particle diffusion rate equation for the adsorption of methylene blue onto ACM

Conditions: Adsorbent dosage =100mg pH =6.7± 0.02 Temperature =32^{o}C

Time in minutes	**√t**	**Initial concentration of Methylene blue in mg/L**		
		Amount of dye adsorbed (q) in mg		
		600 (mg)	**800 (mg)**	**1000 (mg)**
10	3.1622	28.7	33.7	21.4
20	4.4721	30.6	35.7	23.5
30	5.4772	31.2	36.7	24.5
40	6.3245	33.0	37.7	26.5
50	7.0711	34.3	38.8	27.6
60	7.7459	34.9	39.8	29.6
90	9.4868	36.7	41.8	31.6
120	10.9544	37.3	43.9	33.7
150	12.2474	37.9	43.9	34.7
180	13.4164	37.9	43.9	35.7
Intercept		26.7555	31.0321	17.2291
Slope (Kp) x 10^{-4}		0.9326	1.0649	1.4498
Correlation coefficient (r)		0.9650	0.9803	0.9915

TABLE – 6 Intra particle diffusion rate equation for the adsorption of methylene blue onto ACC

Conditions: Adsorbent dosage =100mg pH =6.7± 0.02 Temperature =32^{o}C

Time in minutes	**√t**	***Initial concentration of Methylene blue in mg/L**		
		Amount of dye adsorbed (q) in mg		
		***600**	***800**	***1000**
10	3.1622	47.0	51.2	61.2
20	4.4721	48.9	54.4	64.3
30	5.4772	49.8	56.5	66.3
40	6.3245	51.6	58.6	68.4
50	7.0711	53.5	59.7	71.4
60	7.7459	54.4	61.8	72.4
90	9.4868	55.3	64.0	73.4
120	10.9544	57.2	65.0	76.5
150	12.2474	57.2	66.1	77.5
180	13.4164	57.2	66.1	78.5
Intercept		44.7751	48.5567	57.5330
Slope (Kp) x 10^{-4}		1.0496	1.4663	1.6746
Correlation Coefficient (r)		0.9586	0.9652	0.9768

The rate constant K_p for intraparticle diffusion for various initial concentrations of methylene blue adsorption using a dying industrial effluent for both the adsorbents were determined from the slope of respective plots drawn between square root of time (√t) and amount of adsorbent adsorbed (q). The plots are straight lines (for both the adsorbents) but not passing through the origin and thus indicating that intra particle diffusion is not the sole rate-limiting factor for the adsorption of methylene blue. The values of K_p obtained in this study for the adsorption of

methylene blue is shown in Tables 5 and 6 and this study indicates, increase in K_p with increase in methylene blue initial concentration.

Based on the correlation co-efficient values of the three equations, the kinetics of methylene blue adsorption was best described by Lagergren equation. All the models fit progressively well with increasing sorbate concentration.

CONCLUSION

The adsorption of methylene blue from industrial effluent was found to be dependent on contact time and the initial concentration of the adsorbate. The data was found to fit well to Lagergren and Elovich equation. All the models fit progressively well with increasing sorbate concentration. The process of adsorption was found to follow first order kinetics.

The successful use of a cost-effective adsorbent in the removal of methylene blue from aqueous solution is well apparent from the study.

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