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Kinetic Modelling of the Adsorption of Methylene Blue onto Blue Green Algae

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Abstract

The present paper deals with the kinetics of the adsorption of Methylene Blue dye from the aqueous solution using dried Blue Green Algae as an adsorbent. The rate constants for the adsorption of Methylene Blue dye were determined using Lagergren rate equation, Intraparticle diffusion rate equation and Elovich rate equation.

Keywords: Methylene Blue, Lagergren, Intraparticle diffusion, Elovich, Blue Green Algae (BGA).

Introduction

Dye wastes are usually discharged into water with or without processing. Aesthetic merit, gas solubility and water transparency are affected by the presence of dyes even in small amounts. Among many classes of synthetic dyes used in the textiles and dye industries, triphenyl methane group of dyes such as Methylene Blue, Crystal Violet and Malachite Green are the largest, most versatile and play a predominant role in almost every type of application^{1,2}.

Novel procedures for the decolourisation of different dyes by various low cost adsorbent have been developed. Adsorption has been recognized as an effective method for the removal of dye effluents from water^{3,4}.

The present study is an effort to develop the kinetics of the adsorption of Methylene Blue dye from the aqueous solution by using dried Blue Green Algae. The results of the variation of initial concentration of Methylene Blue dye solution using Blue Green Algae adsorbent have been used to determine the rate constants using Lagergren rate equation, Intraparticle diffusion rate equation and Elovich rate equation.

Material and Methods

Preparation of adsorbent: The adsorbent used in this work, Blue Green Algae was collected and was washed with distilled water to remove the impurities and contaminants. It was then dried for 30 days to remove the moisture. The dried algae were milled and sieved by 250-mesh wire sieve.

Batch mode experiments: The stock solution of 1000 mg/L of Methylene Blue dye solution was prepared. Batch adsorption experiments were carried out at 32°C by varying the contact time from 10 to 180 minutes, at pH 7 with 500mg of the adsorbent and shaken at a constant agitation speed (200rpm). The initial concentration of Methylene

Blue dye solution used in this study is 60, 80,100 and 120 mg/L.

Results and Discussion

The kinetics for the adsorption of Methylene Blue dye using Blue Green Algae as an adsorbent follows Lagergren rate equation, Intraparticle diffusion rate equation and Elovich rate equation.

Lagergren rate equation: The kinetics of adsorption may be described by Lagergren equation^{5,6} is generally expressed as:

$$dq/dt = K_a(q_e - q_t)$$

where q_e and q_t are the amount of dye adsorbed on adsorbent at equilibrium and at time t respectively (mg/g) and K_a is the rate constant of first order adsorption (min^{-1}). After integration and applying initial conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, the integrated form of the equation becomes:

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

The first-order rate expression was described as the chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces and ion exchange⁷.

Lagergren plots of $\log (q_e - q_t)$ versus t (time in minutes) were linear showing the applicability of the first order equation to the adsorption process shown in figure 1. The rate constant K_a for different concentration was calculated from the slope of the plots given in table 1. Based on the correlation coefficient value $R^2 \approx 0.90 - 0.98$ and the rate constant K_a , it was concluded that the adsorption of MB on BGA follows the first order kinetic model such a kinetic equation was suggested by Sadhasivam et al⁸.

Intraparticle diffusion rate equation: Due to rapid stirring in batch reactors,⁹ there is a possibility of transport of Methylene Blue dye from the bulk solution 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 Intraparticle (pore) diffusion was explored by using the Intraparticle diffusion model:

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

where q is the amount of dye adsorbed on adsorbent at time

t , K_p is the intraparticle diffusion rate constant ($\text{mg/g}\cdot\text{min}^{1/2}$) and I is an intercept. The value of intercept gave an idea about the boundary layer thickness that the large is the intercept, the greater is the boundary layer effect.

The rate constant K_p for intra particle diffusion for the various initial concentration of Methylene Blue adsorption from aqueous solution using BGA adsorbents was determined from the slope of respective plots drawn between \sqrt{t} and q (amount of dye adsorbed).

The value of K_p obtained was increase in K_p with increase of initial dye concentration of MB which also indicated the increase of the thickness of the boundary layer. The linearity obtained from the plots (Figure 2) shows the validity of Intraparticle diffusion process for the adsorption of Methylene Blue dye onto BGA and also the applicability of the first order kinetic equation. The results of the study were interpreted in terms of the above equation and the data obtained are given in the table 2.

Elovich's equation: Elovich's model equation is generally expressed as:

$$dq_t/dt = \alpha \exp(-\beta q_t)$$

where q_t is the amount of dye adsorbed at time t , α is the initial adsorption rate ($\text{mg/g}\cdot\text{min}$) and β is the desorption constant (g/mg). Assuming the initial boundary condition, $q=0$ at $t=0$. On integration the above equations becomes:

$$1/q_t = 1/\beta \ln(1 - \alpha\beta t)$$

To simplify the Elovich's equation, it was assumed that $\alpha\beta \gg 1$ and integrating by applying the boundary conditions t

$= 0$ to t and $q = 0$ to q_t , then the above equation becomes :

$$q_t = 1/\beta \ln(\alpha\beta) + \ln t$$

If the removal of Methylene Blue dye from aqueous solution using BGA by adsorption process fits the Elovich's model, a plot of q_t versus $\ln t$ should yield a linear relationship which confirmed the applicability of the Elovich's equation. From the plot, the slope ($1/\beta$) and an intercept of $1/\beta \ln(\alpha\beta)$ can be calculated and are shown in table 3. The ' α ' value increases with the decrease of ' β ' value which indicates the reduction of adsorption reaction rate. The general explanation for this form of kinetic equation involves a variation of the energetic of chemisorptions with the active sites which are heterogeneous in Blue Green Algae adsorbent. This supports that the heterogeneous adsorption mechanism likely to be responsible for the dye uptake. Elovich's model basically supports chemisorptions¹⁰. The high correlation coefficient (R^2) shows the successfulness of the Elovich model.

Conclusion

The adsorption of Methylene Blue dye from aqueous solution was found to be dependent on contact time and the initial dye concentration of the dye solution. The effect of dye concentration on rate constants helped to describe the mechanism of removal of dye. From the calculated kinetic parameters, the experimental data were also fitted to the Lagergren, Intraparticle diffusion and Elovich's first order kinetic model. Thus it is concluded that BGA has an ability to adsorb the dyestuffs from aqueous solution and it could be used as a cheap substitute of commercially available adsorbents for the removal of dye from the dyeing industrial effluents.

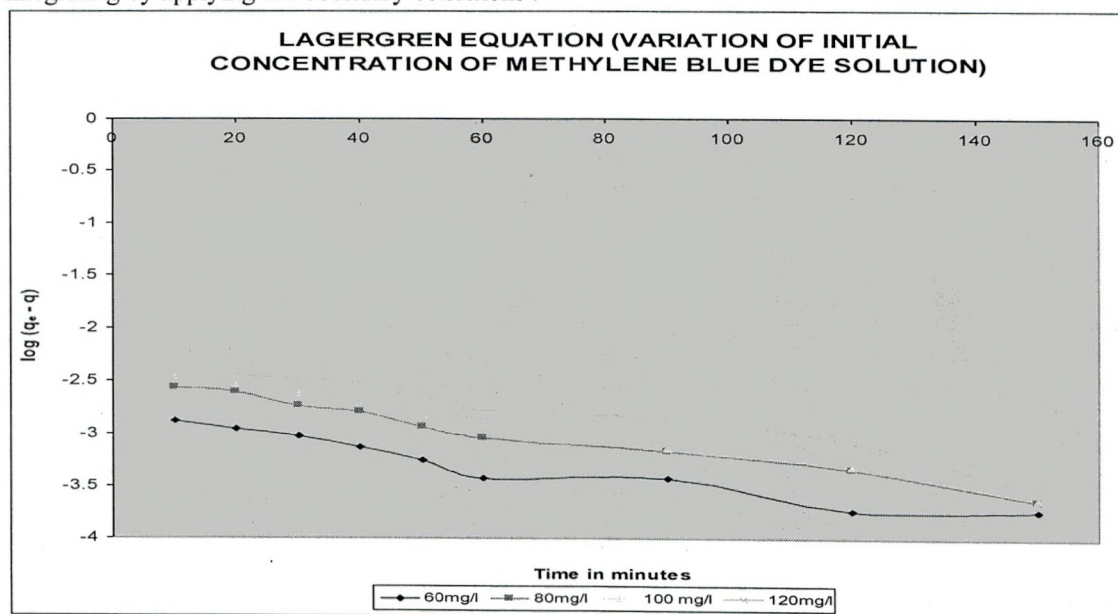


Figure 1

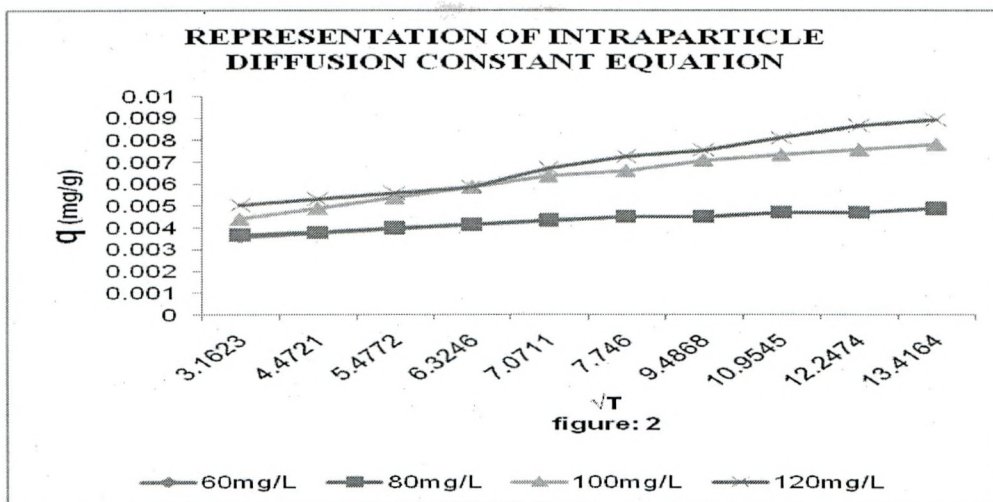


Figure 2

Table 1
Kinetic Modelling of Lagergren rate equation for Methylene Blue Dye Adsorption onto BGA
Conditions: Adsorbent Dosage 500mg, pH 7.00 ± 0.02, Temperature: 32° C

Time in minutes	log (q _e - q)			
	60mg/L	80mg/L	100mg/L	120mg/L
10	-2.177	-1.745	-1.7902	-1.4634
20	-2.387	-1.9523	-1.8480	-1.5385
30	-2.445	-2.0035	-2.0241	-1.5604
40	-2.519	-2.2534	-2.2676	-1.6542
50	-2.688	-2.4295	-2.3925	-1.7187
60	-2.8125	-2.5086	-2.3925	-1.7943
90	-2.8125	-2.6055	-2.4711	-1.9123
120	-2.9914	-2.7305	-2.8697	-2.1618
150	-3.292	-2.7305	-3.1739	-2.8153
180	-	-	-	-
Intercept log q _e	-2.2414	-1.89574	-1.7685	-1.3073
Slope (-K _a /2.303) × 10 ⁻³	6.93	6.84	9.32	8.51
K _a in inutes × 10 ⁻²	1.595	1.58	2.15	1.96
Correlation Coefficient (R ²)	0.9661	0.9013	0.9750	0.9580

References

1. Bumpus J. A. and Aust S. D., Biodegradation of environmental pollutants by the white rot fungus *P. chrysosporium*: involvement of the lignin degrading system, *Bio Assays*, **6**, 166-170, (1987)

2. Bumpus J. A. and Brock B. J., Biodegradation of crystal violet by white rot fungus *Phanerochaete chrysosporium*, *Applied Environmental Microbiology*, **54**, 1143-1150 (1988)

3. Ho Y.S., Bibliometric analysis of adsorption technology in environmental science, *Journal of Environmental Protection Science*, **1**, 1-11, (2007)

4. Ho Y.S., Bibliometric analysis of biosorption technology in water treatment research from 1991 to 2004, *International Journal of Environment and Pollution*, **33**, 1-13, (2008)

Table 2

Kinetic Modelling of Intraparticle diffusion rate equation for Methylene Blue Dye Adsorption onto BGA
 Conditions: Adsorbent Dosage 500mg, pH 7.00 ± 0.02, Temperature: 32° C,

Time in minutes	\sqrt{t}	Initial concentration of Methylene Blue dye in mg/L			
		Amount of Dye adsorbed (q) in mg			
		60mg	80mg	100mg	120mg
10	3.1623	5.026	5.643	7.568	6.191
20	4.4721	5.282	6.326	7.770	6.726
30	5.4772	5.333	6.450	8.243	6.879
40	6.3246	5.385	6.884	8.649	7.414
50	7.0711	5.487	7.070	8.784	7.720
60	7.7460	5.538	7.132	8.784	8.025
90	9.4868	5.538	7.194	8.851	8.408
120	10.9545	5.590	7.256	9.054	8.942
150	12.2474	5.641	7.256	9.122	9.478
180	13.4164	5.692	7.442	9.189	9.631
Intercept		4.9893	5.6159	7.2845	5.0987
Slope $-K_p \times 10^{-3}$		5.85	1.59	1.6883	3.569
Correlation Coefficient (R^2)		0.9177	0.8691	0.9115	0.9956

Table 3

Elovich equation for Methylene Blue Dye Adsorption onto BGA
 Conditions: Adsorbent Dosage 500mg, pH 7.00 ± 0.02, Temperature: 32° C

Time in minutes	Int	Initial Concentration of the dye in mg/ litre			
		Amount of dye adsorbed (q) in mg			
		60mg	80mg	100mg	120mg
10	2.3030	50.26	56.43	75.68	61.91
20	2.996	52.82	63.26	77.70	67.26
30	3.4012	53.33	64.50	82.43	68.79
40	3.6889	53.85	68.84	86.49	74.14
50	3.9120	54.87	70.70	87.84	77.20
60	4.0943	55.38	71.32	87.84	80.25
90	4.4998	55.38	71.94	88.51	84.08
120	4.7875	55.90	72.56	90.54	89.42
150	5.0106	56.41	72.56	91.22	94.78
180	5.1930	56.92	74.42	91.89	96.31
Intercept $(1/\beta) \times \ln \beta$		45.994	44.807	61.758	29.469
Slope $(1/\beta)$		0.2140	0.60197	0.6123	1.2522
Initial adsorption rate constant (α)		6.57	12.09	14.1579	16.718
Desorption constant(β)		4.6729	1.6612	1.6331	0.7986
Correlation Coefficient R^2 2222)		0.9736	0.9474	0.9618	0.9835

5. Lagergren S., Zur theorie dersogenannten adsorption geloster stoffe kungliga svenska vetenskapsakademiens, *Handlingar*, **24**, 1-39, (1898)
6. Annadurai G. and Krishnan M.R.V., Kinetic of adsorption on carbon from solution, *Journal of Sanitary Engineering*, **89**, 31 – 59 (1996)
7. Ho Y.S., Review of second-order models for adsorption systems, *Journal of Hazardous Material*, **136**, 681-689, (2006)
8. Sadhasivam S., Savitha S. and Swaminathan K., Exploitation of *Trichoderma harzianum* mycelial waste for the removal of Rhodamine 6G from aqueous solution, *J. Environ. Manage*, **85(1)**, 155-161 (2007)
9. Renugadevi N., Sangeetha R. and Lalitha P., Kinetics of the adsorption of methylene blue from an industrial dyeing effluent onto activated carbon prepared from the fruits of *Mimusops Elengi*, *Archives of Applied Science Research*, **3(3)**, 492-498 (2011)
10. Senthilkumar S., Krishna S. K., Kalaamani P., Subburamaan C.V., Ganapathy Subramaniam N. and TwKang, *E- Journal of Chemistry*, **7(S1)**, S511 – S519 (2010).

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