Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 11	No. 1	pp. 113-116	2012

Original Research Paper

Adsorptive Treatment of Methylene Blue Dye from Aqueous Solution Using *Moringa Oleifera* as an Adsorbent

Bhanupriya Mordhiya, Kailash Daga, Suresh Chandra and Sonia Aggarwal
Environ-Industrial Laboratory, Department of Chemistry, J.N.V. University, Jodhpur-342 001, Rajasthan, India

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 25/7/2011
Accepted: 24/9/2011

Key Words:
Methylene blue adsorption
Activated carbon
Moringa oleifera
Adsorption isotherms

ABSTRACT

The adsorption of methylene blue dye in aqueous solution on low cost adsorbent, prepared from barks of *Moringa oleifera,* was studied. The adsorption equilibrium isotherms have been reported. The effect of pH, contact time, adsorbent dose and initial dye concentration on adsorption process was investigated. The adsorption equilibrium data fitted both Freundlich and Langmuir isotherm equally well. Experiment was done using batch process.

INTRODUCTION

Most industries use dyes to colour their products. More than 8000 chemically different types of dyes are being manufactured, and the colour and dye bearing wastewater is discharged into water streams leading to water pollution and disrupting aquatic life. Such dye effluents are toxic and difficult to be removed by conventional wastewater treatment methods like filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems (Garg et al. 2003). The removal of colour and dyes by adsorption using low cost adsorbent has recently become the subject of considerable interest (Namasivayam & Kadirvelu 1994). Adsorption has evolved into one of the most effective physical processes for removal of dyes (APHA 1990). The adsorption of dyes by charcoal obtained from local plant material was studied and found to be very effective. The most commonly used adsorbent for the dye removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbates (Aurelia et al 1989). The study includes the contact time, pH, dose and concentration on the adsorption.

MATERIALS AND METHODS

Preparation of activated carbon from *Moringa oleifera*: The activated carbon was prepared from the naturally dried barks of the plant *Moringa oleifera*. The barks were cut into small pieces and treated with 2% v/v sulphuric acid in 1:1 ratio, kept in oven at 150°C for 24 hours, filtered and washed with distilled water repeatedly to remove sulphuric acid, and finally dried and powdered. Chemical activation of carbon using sulphuric acid produces a high surface area and high degree of microporosity. The adsorbent was sieved to 40-60 mesh size and heated at 150°C for 2 hours. This powder was used as an adsorbing material.

Dye solution preparation: Methylene blue, a cationic dye is used for direct dyeing wool and silk.

A stock solution of 500 mg/L methylene blue was prepared in distilled water. Experimental solutions of the desired concentration were obtained by successive dilution.

Batch adsorption studies: Batch adsorption studies were carried out to study the effect of pH (4, 5, 6, 7, 8, 9), contact time (15-120 min), adsorbent dose (3-7 g/L) and initial dye concentration (50-250 mg/L) at room temperature using stopperred bottles (U.S. EPA 1988). The initial pH of the solution was adjusted by using 0.1 M sodium hydroxide or 0.1 M nitric acid without changing volume of the sample. The contants were centrifuged for the required contact time and filtered through Whatman No. 41 filter paper and untreated dye in the filtrate was analysed. All the measurements were made at a wavelength corresponding to the maximum absorbance of 655 nm. The effect of pH, time of contact and amount of adsorbent on the adsorption process were studied.

The removal efficiency (E) of the adsorbent was calculated as:

$$E (\%) = [(C_o - C_e)/C_o] \times 100$$

Where C_o and C_e are the initial and and equilibrium concentrations of dye solution (mg/L) respectively.

Freundlich adsorption isotherm: Freundlich isotherm is represented by the following equation.

$$\text{Log } q_e = \log K_f + 1/n \text{ Log } C_e$$

Where,

q_e = Amount of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent)

K_f = Adsorption capacity

n = Empirical constant

C_e = Equilibrium concentration of adsorbate (mg/L)

Langmuir adsorption isotherm: Langmuir isotherm is represented by the following equation.

$$C_e/q_e = 1/Q_m b + C_e/Q_m$$

Q_m and b are Langmuir constants related to adsorption capacity (maximum specific uptake corresponding to the site saturation) and energy (intensity) of adsorption (L of adsorbent/mg of adsorbate) respectively. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter R_L that is defined as:

$$R_L = 1/(1+ bC_o)$$

Where, b is the Langmuir constant and C_o is the initial concentration of the dye. Values of dimensionless equilibrium parameter R_L show the adsorption to be favourable if $(0 < R_L < 1)$.

Adsorption kinetics: To describe the adsorption kinetics, a pseudo-second order rate model reported in the literature was applied in the following form (Senthikumaar et al 2005).

$$t/q_t = 1/h_o + 1/(q_e)t$$

Where,

h_o = Initial adsorption rate (mg/g min)

q_e = Amount of the dye adsorbed at equilibrium (mg/g)

q_t = Adsorbed at time t (mg/g)

The initial adsorption rate, h_o at $t = 0$ is defined as:

$$h_o = K_2 q_e^2$$

Where, K_2 is the pseudo second order rate constant for the adsorption process (g/mg min). The initial adsorption rate h_o, the equilibrium adsorption capacity, and the rate constant K_2 were determined from the slope and intercept of the plot of t/q_t against t.

RESULTS AND DISCUSSION

Effect of contact time: In adsorption system, the contact time plays a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Fig. 1 shows that increasing contact time increased dye uptake and remained constant after 90 minutes, thus the effective contact time (equilibrium time) is 90 min.

Effect of pH: The adsorption of dye was found to be strongly dependent on pH of the solution. At lower pH values, the large number of H^+ ions neutralize the negatively charged adsorbent surfaces, thereby reducing hindrance of the dye. At the high pH values, the reduction in adsorption may be due to the abundance of OH^- ions causing increased hindrance to diffusion of dye. With the pH 7, the percent removal of methylene blue dye increases sharply for AC-MO (Fig. 2).

Effect of initial dye concentration: The increase in initial dye concentration decreased the percent adsorption (Fig. 3). The adsorption efficiency decreased with increasing the initial dye concentration. These results may be explained on the basis that the increase in the number of dye molecules compete for the available binding sites and also because of the lack of the active sites on the adsorbent at higher concentrations. Therefore, more dye molecules were left unadsorbed in solution at higher concentration levels.

Effect of adsorbent dose: The effect of adsorbent dose on percent removal of methylene blue dye is shown in Fig. 4. Adsorbent dose was varied (3, 4, 5, 6 and 7 g/L) and studies were performed at pH 7. The study indicated that the amount of dye adsorbed increase with increase in the AC-MO dose up to 6 g/L, but thereafter with further increase in dose, the increase in removal was very small. Thus, the optimal dose is 6 g/L.

Results of adsorption isotherms: Langmuir and Freundlich isotherms for adsorption of methylene blue by AC-MO were found to be linear showing the applicability of the isotherms (Figs. 5 and 6). The linear regression data for Langmuir and Freundlich adsorption isotherms are given in Table 1. The values of Langmuir and Freundlich constants calculated from the graph are summarized in Table 2 for methylene blue adsorption by AC-MO. Values of *n* for methylene blue was 1.6638 at effective dose and contact time, indicates good adsorption potential of the adsorbent.

Kinetic study: Based on linear regression (R^2) values, the kinetics of methylene blue adsorption onto AC-MO for 50 mg/L solution described well by pseudo second order (R^2 = 0.9934) equation (Fig. 7). The values of K_2 for methylene blue are 9.2×10^{-3}, 4.7×10^{-3}, 3.1×10^{-3}, 2.3×10^{-3} and 1.7×10^{-3} for 50, 100, 150, 200 and 250mg/L respectively. The results clearly indicate that this model fits progressively well with increasing adsorbate concentration (Table 3).

CONCLUSION

The present investigation indicates that activated carbon of *Moringa oleifera* has rapid adsorption rate for methylene

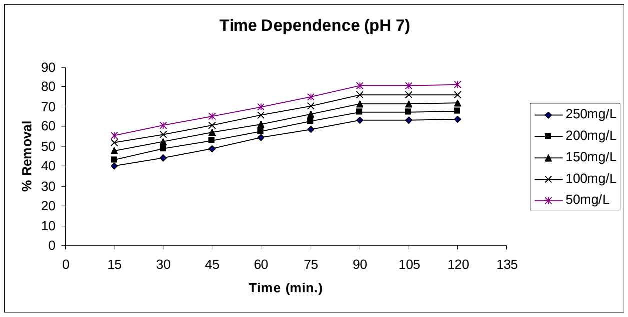

Fig. 1: Effect of contact time on removal of methylene blue at different concentrations by AC-MO at pH 7.

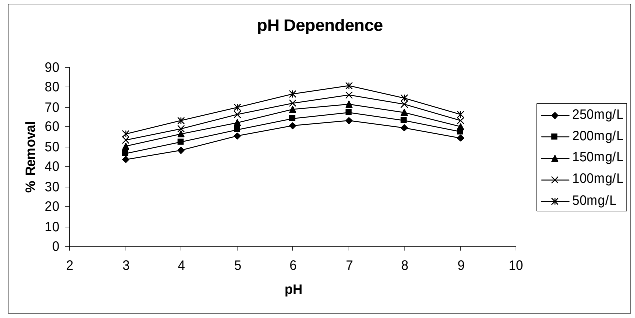

Fig. 2: Effect of pH on removal of methylene blue at different concentrations by 6g/L of AC-MO at constant contact time of 120 min.

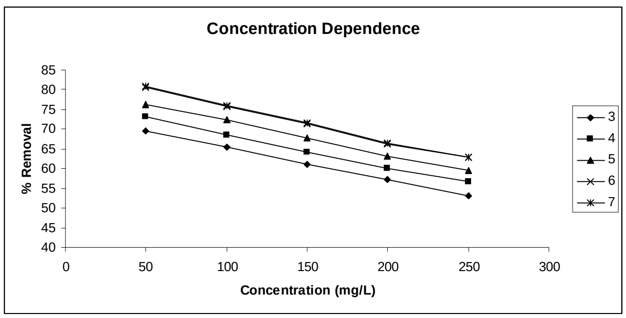

Fig. 3: Effect of initial concentration of methylene blue on percent removal by 6g/L of AC-MO at equilibrium contact time 90 min at pH 7.

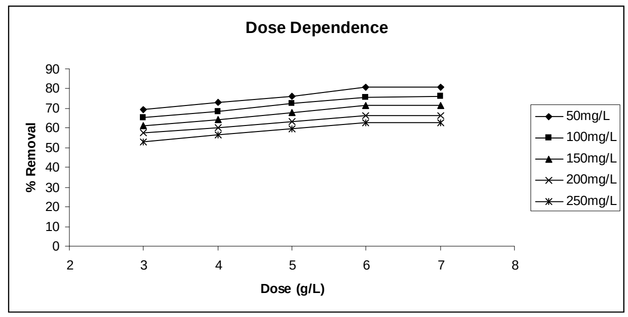

Fig. 4: Effect of AC-MO dose on percent removal of methylene blue at equilibrium contact time of 90 min at effective pH 7.

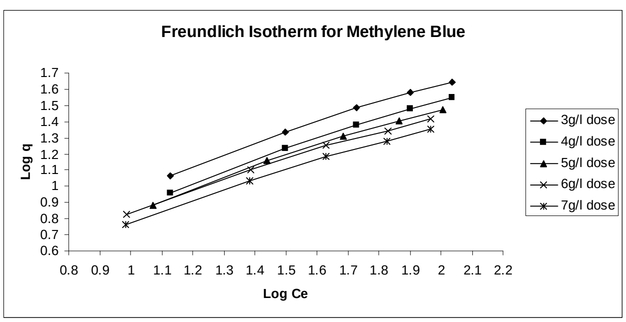

Fig. 5: Freundlich isotherm plot for methylene blue adsorption by AC-MO at optimum conditions.

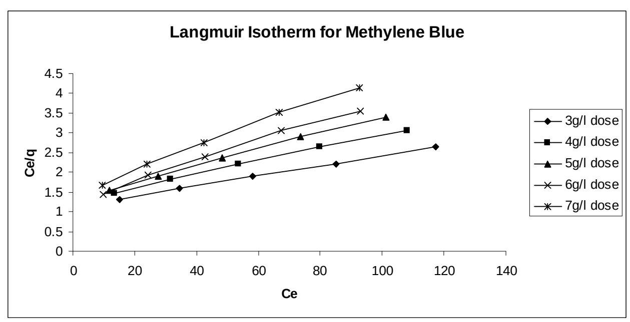

Fig. 6: Langmuir isotherm plot for methylene blue adsorption by AC-MO at optimum conditions.

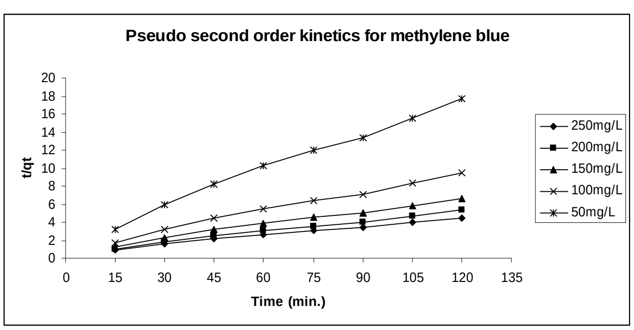

Fig. 7: Pseudo second order kinetic model plot for methylene blue.

blue dye. The dye adsorption was found to be dependent on initial dye concentration, contact time, pH and amount of adsorbent. The Freundlich and Langmuir adsorption models was used to represent the experimental data, and equilibrium data fitted very well to both the Freundlich and Langmuir isotherm models. Kinetics of dye adsorption obeyed the pseudo-second order model, which suggests chemisorption as the rate-determining step in adsorption process. Maximum adsorption of 80.8% of methylene blue dye was occurred at pH 7. Since *Moringa oleifera* plant is abundant and its activated carbon can be easily synthesized at relatively low cost, the adsorbent could be applied for the

Table 1: Linear regression data for Langmuir and Freundlich adsorption isotherms for adsorption of methylene blue by AC-MO.

Adsorbent dose (g/L)	Langmuir isotherm (Linear equation)	Freundlich isotherm (Linear equation)
3	y = 0.0129 x + 1.1313	y = 0.6455 x + 0.3533
4	y = 0.0167 x + 1.2873	y = 0.6487 x + 0.2455
5	y = 0.0208 x + 1.3352	y = 0.6328 x + 0.2241
6	y = 0.0253 x + 1.2742	y = 0.601 x + 0.2509
7	y = 0.0295 x + 1.4663	y = 0.5997 x + 0.1892

Table 2: Values of Langmuir and Freundlich adsorption constants for adsorption of methylene blue by AC-MO.

Adsrbent dose (g/L)	Langmuir constants Qm (mg/g)	b (L/mg)	R_L	R^2	Freundlich constants Kf	n	R^2
3	77.51	0.0114	0.6368	0.9993	2.2557	1.5491	0.9937
4	59.88	0.0129	0.6065	0.9957	1.7599	1.5415	0.9953
5	48.07	0.0155	0.5621	0.9975	1.6753	1.5802	0.9918
6	39.52	0.0198	0.5018	0.9935	1.7819	1.6638	0.994
7	33.89	0.0201	0.4985	0.9943	1.5459	1.6675	0.9938

Table 3: Pseudo second order parameters for methylene blue at pH 7.

Parameters	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
K_2	9.2 × 10-3	4.7 × 10-3	3.1 × 10-3	2.3 × 10-3	1.7 × 10-3
R^2	0.9934	0.9934	0.9925	0.9927	0.9921
qe	7.56	14.2	20.32	25.77	30.67
h	0.5303	0.9744	1.2966	1.537	1.6869

removal of dye from wastewaters.

ACKNOWLEDGEMENT

The authors are grateful to Council of Scintific and Industrial Research Institute, New Delhi for financial assistance.

REFERENCES

Garg, V.K., Gupta Renuka, Yadav Anu Bala and Kumar Rakesh 2003. Dye Removal from aqueous solution by adsorption on treated sawdust. Bioresource Technol., 89: 121-124.

Namasivayam, C. and Kadirvelu 1994. Coir pitch, an agricultural waste byproduct, for the treatment of dyeing wastewater. Bioresource Technology, 48: 79-81.

APHA 1990. Standard Methods for the Examination of Water and Wastewater, 17th edition. Washington DC.

Aurelia Meghea, Mihaela Draganoiu, Margareta Nicolau and Agenta Liebman 1989. Removal of organic impurieties from saline wastewater by adsorption. Rev Chim., 40(5): 441-445.

U.S.EPA. 1988. Reporting Guidance: Estimating Chemical from Textile Dying, Title II, Section 313 Release, Office of Pesticides and Toxic Substances.

Senthikumaar, S., Varadarajan, P.R., Porkadi, K., Subbhuraam, C.V. 2005. Adsortion of methylene blue onto jute fiber carbon: Kinetics and equilibrium studies. J. Colloid Interf. Sci., 284: 78-82.