Jr. of Industrial Pollution Control 26 (2) (2010) pp 19-22

METHYLENE BLUE REMOVAL USING A LOW–COST ACTIVATED CARBON ADSORBENT FROM *MIMUSOPS ELENGI*

N. RENUGADEVI, M. SANGEETHA AND B. KAVITHA

Department of Chemistry, Avinashilingam University for Women, Coimbatore 641 043, T.N, India

Key words : Activated carbon, Methylene blue and Adsorption.

ABSTRACT

The present study deals with the removal of Methylene blue from aqueous solution using a low-cost activated carbon prepared from fruits of *Mimusops* Elengi. Batch adsorption studies were conducted by varying the initial concentration of the adsorbate, adsorbent dosage, contact time and pH. The experimental adsorption data obtained in this study fitted with Lagergren, Intra-particle kinetic equations and as well as Langmuir and Freundlich adsorption isotherms.

INTRODUCTION

Dyes are used to colour paper, fabrics, carpets, rubbers, plastics, cosmetics and food (Mehmet *et al.* 2008). Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually world wide and of which about 20-30% are wasted in industrial effluents during the textile dyeing and finishing processes (Chaurasia and Shashikant, 2007). The dyestuffs are water-soluble dispersable organic colourants, having high potential use in various industrial applications. Most of the aromatic dyestuffs are fused with inorganic metals. Dye-bearing wastes impose a serious threat to the surrounding environment matrix by creating imbalance in the aquatic ecosystem by disturbing the symbiotic equilibrium (Venkatamohan and Karthikeyan, 2003). Effluents with dye pollutants discharged are highly coloured due to the residual dyes and when they are disposed to the natural water sources, they pollute water (Jothirekha *et al.* 2008). Many dyes have toxic effect as well as carcinogenic and also have mutagenic effects on aquatic life. It caused many significant problems such as increasing the chemical oxygen demand (COD) of the effluent and also reducing light penetration, which has a derogatory effect on photosynthetic phenomena (Mehmet *et al.* 2008). Even a very small amount of dye in water is visible and thus reduces photosynthesis in aquatic plants, affect their growth and decreases gas solubility, interfering with the natural purification process. Many physical and chemical methods, such as coagulation, floatation, chemical oxidation, solvent extraction, hyper filtration etc have been tried in order to remove colour from wastewater (Jyotirekha *et al.* 2008). However all of these methods suffer from one or another limitation and none of them were successful in completely removing the colour from wastewater. Although biological treatment processes remove BOD, COD and suspended solids to some extent, they are largely ineffective in removing colour from waste water as most dyes are toxic to the organisms used in such processes (Mohan *et al.* 2002). In this study a low-cost, eco-friendly adsorbent prepared from fruits of Mimusops Elengi was used to remove Methylene blue dye from aqueous solution. The objectives of this in-

Address for correspondence : **Email** : punitaparikh@gmail.com

vestigation is to study the effect of initial concentration of Methylene blue solution, contact time, pH and adsorbent dosage on the extent of Methylene blue removal by adsorption and fit the adsorption data to Lagergren, Intra-particle kinetic equations and as well as Langmuir and Freundlich adsorption isotherms.

MATERIALS AND METHODS

Preparation of the adsorbent

Fruits of *Mimusops* Elengi were collected from Avinashilingam University campus, Coimbatore. Pods were cut into small pieces and dried. The completely dried material was powdered well and chemically activated using concentrated sulphuric acid.

Batch experiments

Varying initial concentration of Methylene blue solution, adsorbent dose, contact time and pH batch experiments were performed. The adsorbent and adsorbate were separated by filtration and the filtrate was analysed for Methylene blue concentration spectro colorimetrically at 520nm. The pH was adjusted using 2N sulphuric acid.

RESULTS & DISCUSSION

Effect of variation of initial concentration of Methylene blue solution on adsorption of Methylene blue from aqueous solution

The adsorbate concentrations were varied from 400 to 1000mg/L and batch experiments were performed to optimize the initial concentration of the adsorbate. An increase in percentage removal (31.6 to 56 %) of Methylene blue noticed when the initial concentration of adsorbate was varied from 1000 to 400mg/L (Table 1). This may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of Methylene blue causing a decrease in percentage removal of Methylene blue corresponding to an increased initial concentration of the dye solution.

Effect of contact time on adsorption of Methylene blue

The percentage adsorption of Methylene blue increases with increase in contact time and the equilibrium was obtained after agitating for 180 minutes. The percentage of the dye removed by adsorption increased from 37.25 to 56%, when the contact time was varied from 10 to 150 minutes at pH 4 using 100ml of the dye solution of initial concentration 400mg/L with 100mg adsorbent.

Effect of pH variation on adsorption of Methylene blue

In order to optimize the pH for maximum Methylene blue removal, experiments were conducted with 100ml of aqueous solution of Methylene blue containing 100mg of the dye with 100mg adsorbent by varying the pH from 2 to 6 at various contact time. The results indicated a maximum adsorption of dye (≈ 46%) at pH 6.0 (Figure 1).

Effect of adsorbent dosage on adsorption on Methylene blue

The effect of variation of adsorbent dosage was determined by varying the adsorbent dosage from 100 to 400mg (Table 2). It is evident from the table that the adsorption potential of the adsorbent increases with increasing the dosage of the adsorbent. The dye adsorbed increased from 38.3 to 99.1% when the adsorbent dose was varied from 100 to 400mg in 180 minutes of contact time. The increase in percent adsorption of dye with increase in the adsorbent dosage may be due to the availability of more surface area of the adsorbent for adsorption for more number of Methylene blue species.

Lagergren kinetic modeling for Methylene blue removal by adsorption technique

The rate constant of dye adsorption was calculated (Table 3) using the following Lagergren first order kinetic rate equation.

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

Where,

Ka = rate constant of adsorption (sec^{-1})

q and q_e = amount of Methylene blue adsorbed at time 't' and at equilibrium time

t = time (agitation time or contact time) in minutes.

The Lagergren plots obtained by plotting of log (q_e-q) Vs 't' are linear showing the validity of Lagergren equation for the removal of Methylene blue by adsorption from aqueous solution. The rate constant K_a values (Table 3) indicate that the adsorption of the dye followed First order Legergren kinetics (Renugadevi *et al.* 2009).

Intra particle diffusion rate equation for 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: (Sahmoune *et al*. 2009).

$q = Kp\, t^{1/2}$

Where,

q = amount of Methylene blue adsorbed in mg,
K_p = intra-particle diffusion rate constant
t = time (agitation time or contact time) in minutes.

The rate constants for intra particle diffusion (Kp) for various initial concentrations of Methylene blue solution was determined from the slope of respective plots drawn between square root of time(vt) and amount of adsorbate adsorbed(q). The plots are straight lines 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 (Sahmoune *et al*. 2009). The values of K_p obtained in this study for the adsorption of Methylene blue are shown in Table3. An increase in Kp with increase in Methylene blue initial concentration was noted.

Langmuir adsorption isotherms

Langmuir adsorption isotherm is based on the assumption that points of valency exist on the surface of the adsorbent and that each of this site is capable of adsorbing one molecule. Thus the adsorbed layer will be one molecule thick. Further, it is assumed that all the adsorption sites have equal affinities for the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

The Langmuir adsorption isotherm is commonly given by,

$$x / m = (k_1^1 C_e / 1 + k_1 C_e)$$

Where,

x - Amount of Methylene blue adsorbed (mg)
m - Weight of adsorbent (mg)
C_e - Concentration of Methylene blue at equilibrium
k^1_1 - Adsorption capacity
k1 - Energy of adsorption

The linear plots of $1/C_e$ Vs m/x shows the applicability of Langmuir adsorption isotherm model for the present system indicating the formation of monolayer coverage of adsorbate on the surface of the adsorbent.

Separation factor – RL

The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'RL'which is defined by,

$$RL = 1/\ (1+b\, C_i)$$

where, C_i = initial concentration of the dye in mg/L
b = Langmuir constant (k_1^1)

R_L value Type of isotherm
$R^L > 1$ Unfavourable
$R_L = 1$ Linear
$R_L < 1$ Favourable

The RL values obtained in this study was below one and this shows the feasibility of the adsorption process at all initial concentrations of Methylene blue used in this study.

Freundlich adsorption isotherm

The linear form of Freundlich adsorption isotherm equation (Renugadevi et al., 2009) is represented as,

$$x/m = KF\, C_e^{\ 1/n}$$
$$\log x/m = \log KF + 1/n \log C_e$$

Where,

x/m = Amount of Methylene blue adsorbed on unit weight of adsorbent at equilibrium
C_e= Concentration of solute in aqueous solution.

The Freundlich parameters KF and 1/n are indicators of adsorption capacity and adsorption intensity respectively. The linear form of Freundlich adsorption isotherm at room temperature is plotted between log x/m Vs log Ce for different initial concentrations of the aqueous solution of Methylene blue solution. KF and 1/n values are evaluated from the slope and the intercept respectively.

The 'n' value range between 2-10 indicates favourable adsorption (Jambulingam *et al*. 2005). The 'n' values of Metyhlene blue adsorption onto the low-cost activated carbon used in this study is between 2-10 indicating adsorption is favourable in the case of Methylene blue.

CONCLUTION

The low-cost activated carbon prepared from the fruits of Mimusops Elengi is an efficient adsorbent for the removal of Methylene blue from aqueous so-

Table 1. Adsorption of Methylene blue with variation of initial concentration of Methylene blue solution

Conditions	
Adsorbent dosage	- 100mg
pH	- 4.0
Temperature	- 32°C
Contact time	- 10 to180 minutes

Time in minutes	Initial concentration of Methylene blue			
	% Adsorption of Methylene blue			
	400 mg/L	600 mg/L	800 mg/L	1000 mg/L
10	37.25	30.7	25.5	21.7
20	40.75	33.3	27.75	22.5
30	44.0	36.0	28.75	23.5
40	45.75	37.3	29.75	24.4
50	47.5	38.7	30.87	25.6
60	49.25	40.0	32.0	27.1
90	50.75	41.3	33.0	28.0
120	52.5	42.7	34.0	28.9
150	56.0	45.3	34.0	30.7
180	56.0	45.3	34.0	31.6

Table 2. Adsorption of Methylene blue with variation of adsorbent dosage

Conditions	
Concentration of dye solution	- 1000 mg/L
Temperature	- 32°C
pH	- 6.0
Contact time	- 10 to180 minutes

Time in minutes	Adsorbent dosage			
	% Adsorption of Methylene blue			
	100 mg	200 mg	300 mg	400 mg
10	21.1	28.0	37.8	59.5
20	23.2	30.7	41.5	64.2
30	25.1	33.4	44.4	71.7
40	27..3	35.2	49.1	77.4
50	29.4	37.9	51.9	83.1
60	30.9	38.8	55.7	88.7
90	31.8	41.5	58.5	92.5
120	33.0	43.3	61.4	93.5
150	35.1	45.1	64.2	96.3
180	38.3	46.0	67.0	99.1

Table 3. Kinetic rate constants for Methylene blue adsorption

Kinetic rate constants	Concentration of dye			
	400 mg/L	600 mg/L	800 mg/L	1000 mg/L
Lagergren rate constant (K_a x 10^{-2} in minutes^{-1})	1.222	1.378	1.336	1.471
Intraparticle diffusion rate constant (K_p x 10^{-4})	7.148	8.091	8.302	9.998

lution. Maximum Methylene blue removal (99.1%) in this study achieved in 180 minutes of contact time at pH 6 with 400mg of low-cost adsorbent using the 100mL dye solution containing 100mg of the dye.

REFERENCES

Dinesh Mohan, Kunwar P. Singh, Gurdeep Singh and Kundan Kumar, 2002. Removal of dyes from wastewater using Flyash, a low- cost adsorbent. *Ind. Eng. Chem. Res*. 41 (15) : 3688-3695.

Jambulingam, M. Renugadevi, N. Karthikeyan, S. Kiruthika, J. and Patabhi, S. 2005. Adsorption of Cr (VI) from aqueous solution using a low-cost activated carbon. *IJEP*. 25 (5) : 458-463.

Jothirekha Sarma, Arunima Sarma and Krishna, G. Bhattacharya, 2008. Biosorption of commercial dyes on Azadirachta indica leaf powder: A case study with a basic dye Rhodamine B. *Ind.Eng.Chem.Res*. 47 (15) : 5433 - 5440.

Mehmet Dogan, Harun Abak and Mahir Alkan, 2008. Biosorption of Methylene blue from aqueous solutions by hazelnut shells: Equilibrium, Parameters and Isotherms. *Water, Air & Soil Pollution*. 192 (1-4) : 141-153.

Renugadevi, N. Archana, B. and Sreeja, M. 2008. Conversion of the Rind of Crescentia Cujeta L into an Effective Adsorbent for the Removal of Cr (VI) From Aqueous solution. *I.J.E.P*. 28 (6) : 540-546.

Sahmoune,M.N. Louhab, K. and Boukhiar, A. 2009. Biosorption of Cr (III) from aqueous solution using bacterium biomass Streptomyces rimosus. *Int. J. Environ. Res*. 3 (2) : 1735-6865.

Shri Ram Chaurasia and Shashikant. 2007. Removal of basic dye from aqueous solution using natural adsorbents: Kinetic studies. *I.J.E.P*. 27 (9) : 782-788.

Venkatamohan, S. and Karthikeyan, J. 2003. Adsorptive removal of reactive azo dye from an aqueous phase onto charfines and activated carbon. *Journal of Environmental Management*. 84 (4) : 390-400.