REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION BY BIOADSORPTION ONTO *Ricinus communis* EPICARP ACTIVATED CARBON

T. Santhi*[,1], S. Manonmani[2]

[1]*Department of Chemistry, Karpagam University, Coimbatore-641021, India*
[2]*Department of Chemistry, PSG College of Arts and Science, Coimbatore-641014, India*

Received 19 May 2009; received in revised form 22 July 2009

Abstract: Carbon prepared from the epicarp of *Ricinus communis* was used to remove a textile dye (methylene blue (MB)) from an aqueous solution by adsorption technique under varying conditions of agitation time, dye concentration, adsorbent dose and pH. Adsorption depended on solution pH, dye concentration, carbon concentration and contact time. Adsorption followed both Langmuir and Freundlich isotherm models. The adsorption capacity was found to be 62.5 mg/g at a neutral pH of 7 for the adsorbent size of 125-250 μm at room temperature (32±2°C). The kinetics of adsorption of MB obeys Pseudo-first order. The results in this study indicated that activated carbon from *Ricinus communis* was an attractive candidate for removing cationic dyes from the dye wastewater.

Keywords: *Epicarp, Ricinus communis, Adsorption, Methylene blue, Kinetics*

DOI:*10.3329/cerb.v13i1.2518*

1. Introduction

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries[1]. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the water and affecting aquatic ecosystem [2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities [3].

There are various conventional methods of removing dyes from aqueous solutions. Among these methods, adsorption is by far the most versatile and widely used method because of its low cost and ease of operation. A number of agricultural waste and by-products of cellulosic origin have been studied for their capacity to remove dyes from aqueous solutions, such as peanut hulls [4], maize bran [5], sawdust [6], sugar beet pulp [7], crab shell [8], cornstarch [9], rice husk [10], chitin [11], orange waste [12], lemon peel [13], granular kohlrabi peel [14],raw barley straw [15] and eggshell [16].

Therefore, there is the need to look for low cost alternatives in easily available bio-materials, which can adsorb dyes from wastewaters. In this paper, we attempt to use activated carbon developed from *Ricinus communis*, as an adsorbent for the removal of dyes from water. Annual production of *Ricinus communis* is estimated to be more than 1.0 tons globally, of which India accounts for 60% of the production. The epicarp of Ricinus is a segregated waste by-product (35% of production) during segregation of *Ricinus Communis* seed. Since the epicarp of Ricinus is available free of cost, only the carbonization of its involved for the wastewater treatment. Therefore the main objective of this study was to evaluate the possibility of using dried epicarp of Ricinus to develop a new low-cost activated carbon and study its application to remove methylene blue from simulated wastewater. The various parameters such as pH, adsorbent dose, initial dye concentration, adsorbent particle size were investigated.

2. Experimental

2.1. Preparation of the epicarp of Ricinus communis adsorbent

The epicarp of *Ricinus communis* was obtained from an agricultural farm in Coimbatore District, Tamil Nadu, India. It was air-dried and powdered in a grinder. The powder was then soaked in concentrated H_2SO_4 for 12 hours and washed thoroughly with distilled water till it attained neutral pH and then soaked in two percent $NaHCO_3$ overnight in order to remove any excess acid present. Then the material was washed again with distilled water and dried at 110±2°C. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in a desiccator for use.

*Corresponding author Email: ssnilasri@yahoo.co.in

2.2. *Preparation of cationic dye solutions*

Methylene blue in commercial purity obtained from Fluka was used without further purification. A stock solution of 1000 mg/L of the MB dye was prepared by dissolving 1 g of the dye in 1 liter double distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

2.3. *Experimental methods and measurements*

Bioadsorption experiments were carried out in a rotary shaker at 150 rpm using 250mL-shaking flasks containing 50 mL of dye solutions at different concentrations and initial pH values. The initial pH values of the solutions were previously adjusted with 0.1 M HCl or NaOH using a DEEP VERSION model (EI) pH meter. The adsorbent (0.1g) was added to each flask, and then the flasks were sealed to prevent any change in volume during the experiments. After shaking the flasks for a predetermined time interval, the samples were withdrawn from the flasks and the dye solutions were separated from the adsorbent by filtration after centrifugation. The pH values of the separated dye solutions were again measured for estimating their change. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dye with a Systronics Spectrophotometer-104. The experiment was carried out at 480nm; throughout the experiment the wavelength was constant.

The amount of dye adsorbed by the biomass was calculated using the following equation:

$$q = C_0 - C_e V/W \quad (1)$$

Where q (mg/g) is the amount of dye adsorbed by the biomass, C_0 and C_e (mg/L) are the initial and equilibrium liquid phase concentration of dye. V (L) the initial volume of dye solution, and W (g) the weight of the biomass. All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than 2%.

Influence of each parameter (pH, initial dye concentration, adsorbent particle size and carbon concentration) were evaluated in an experiment by varying the parameter under evaluation, while all other parameters in the experiment were maintained as constant. The experiments were conducted with duplicate and the negative controls (with no adsorbent) to ensure that adsorption was by the epicarp of Ricinus Commnis biomass and not by the container. The surface morphology of activated carbon (activated carbon from Ricinus communis) was visualized via scanning electron microscopy(SEM).

3. Results and Discussion

3.1. *Influence of initial pH*

The effect of initial pH on bioadsorption percentage of dye was examined over a range of pH values from 2 to 10 and the results are presented in Figure 1. As elucidated in Figure 1, the dye removal was minimum at the initial pH 2. The dye adsorbed increased as the pH was increased from pH 2 to 7. Incremental dye removal was not significant beyond pH 7. For this reason, pH 7 was selected for future experiments.

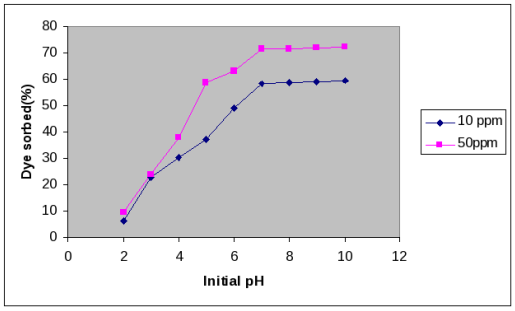

Figure 1: Influence of initial pH on bioadsorption of MB by carbon of the epicarp of *Ricinus communis* (adsorbent dose: 100mg/50mL; particle size: 125-250μm; contact time: 2 h)

After adsorption experiments, it was found that at low pH, the dyes become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent.

3.2. *Influence of initial dye concentration*

The influence of dye concentration on bioadsorption of dye is shown in Figure 2. When the dye concentration was increased from 10 to 50 mg/L, the percentage of dye adsorbed increased from 75.2% to 91.2%.

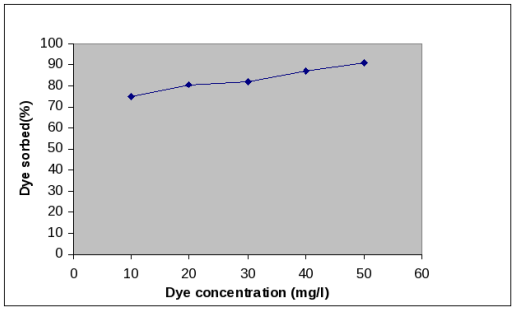

Figure 2: Influence of dye concentration on bioadsorption of MB by carbon of the epicarp of *Ricinus communis* (adsorbent dose: 100mg/50mL; particle size: 125-250 μm; contact time: 3 h; pH: 7.0)

3.3. Adsorption Isotherm

The Langmuir and Freundlich equation were employed to study the adsorption isotherms of dye.

The linearised form of the Langmuir equation [17] is as follows

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \quad (2)$$

where C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, Q_m is the maximum adsorption capacity and represents a practical limiting adsorption capacity when the adsorbent surface is fully covered with monolayer adsorbent molecule and a is Langmuir constant. The Q_m and a values are calculated from the slopes $(1/Q_m)$ and intercepts $(1/aQ_m)$ of linear plots of C_e/q_e versus C_e.

The linearised form of the Freundlich equation [18] is as follows:

$$\ln Q_e = \ln K + (1/n) \ln C_e \quad (3)$$

where Q_e is the amount of dye adsorbed at equilibrium, C_e is the concentration of the dye solution at equilibrium and $1/n$ is empirical constant and indicate adsorption capacity and intensity, respectively. Their values were obtained from the intercepts $(\ln K)$ and slope $(1/n)$ of linear plots of $\ln Q_e$ versus $\ln C_e$.

The Q_m and a values in the Langmuir equation, the K and $1/n$ values in the Freundlich equation are given in the Table 1. From the results in Table 1, it could be concluded that the adsorption of MB followed the Langmuir and Freundlich model.

Table 1: The Q_m, a values in the Langmuir equation, the K and $1/n$ values in Freundlich equation

Langmuir		Freundlich	
Q_m (mg/g)	a	K	$1/n$
62.5	0.7273	1.0715	1.1001

3.4. Effect of adsorbent particle size

The effect of adsorbent particle size on bioadsorption of dyes is shown in Figure 3. The dyes adsorbed increased as the adsorbent particle size decreased. This fact is explainable as smaller particles have a large surface area than larger particles and hence adsorbe more dye during the initial stages of adsorption [19]. For this reason, adsorbent particle sizes of 125-250 μm have been selected for all the batch experiements.

3.5. Effect of carbon concentration

The adsorption of the dyes on carbon was studied by varying the carbon concentration (50- 300 mg/mL). The percentage of adsorption increased as the carbon concentration increased shown in Figure 4. This is attributed to increased carbon surface area and availability of more adsorption sites.

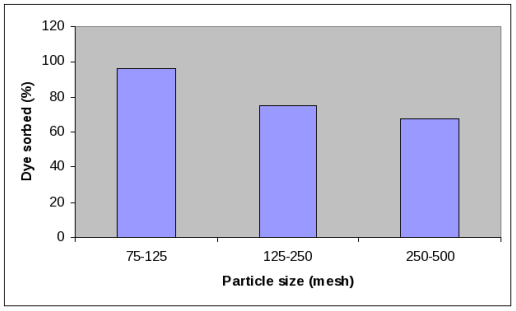

Figure 3: Effect of particle size on bioadsorption of MB by carbon of the epicarp of *Ricinus communis* (dye concentration: 10mg/50mL; adsorbent dose: 100mg/50mL; contact time: 2 h; pH: 7.0)

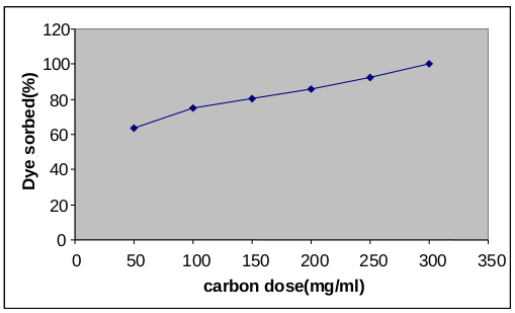

Figure 4: Effect of carbon dosage on bioadsorption of MB by carbon of the epicarp of *Ricinus communis* (dye concentration: 10mg/50mL; ; contact time: 2 h; pH: 7.0)

3.6. Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dyes. The effect of pH on desorption of methylene blue is shown in Figure 5. When pH was varied from 2 to 9, the percentage desorption was found to be decrease from 75.00 to 12.50. Further increase in the pH of the solution did not show any significant increase in the percentage of desorption. From the results, it can be concluded that the adsorption mechanism was complex and dominated by both physisorption and chemisorptions.

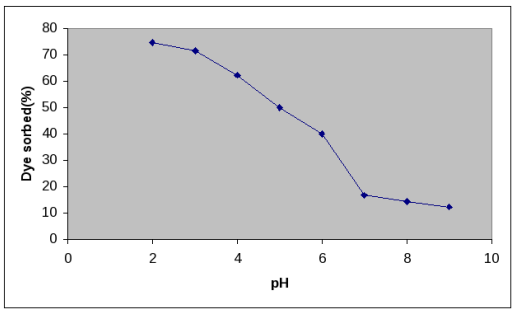

Figure 5: Effect of pH on desorption of MB by carbon of the epicarp of *Ricinus communis* (dye concentration: 10mg/50mL; adsorbent dose: 100mg/50mL; contact time: 2 h)

3.7. Adsorption kinetics

The bioadsorption kinetics of dyes is illustrated in Figure 6. The removal rates of dyes from solution were very rapid during the initial stages of the bioadsorption process. After a very rapid biosorption, dye uptake capacities increased with time and reached equilibrium values in approximately 2 h. The three phases of dye adsorptions could be attributed to boundary layer sorption, intraparticle diffusion and sorption equilibrium, respectively.

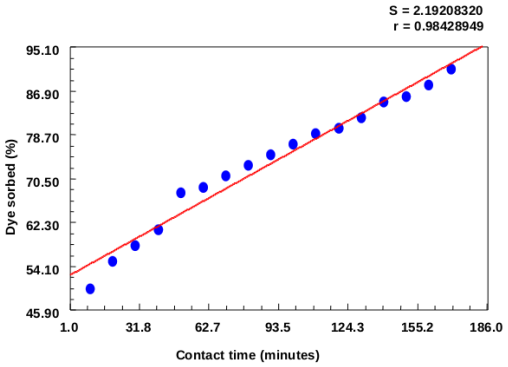

Figure 6: Bioadsorbtion kinetics of MB by carbon of the epicarp of *Ricinus communis* (dye concentration: 50mg/50mL; adsorbent dose: 100mg/50mL; particle size: 125-250 μm:pH ;7)

The kinetic data were treated with the following Lagergren's pseudo-first order rate equation:

$$\log(q_e - q_t) = \log q_e - k_{\text{ad}} t/2.303 \qquad (4)$$

where q_e and q_t (mg /g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constant k_{ad} could be calculated from the slopes of the linear plots of $\log(q_e - q_t)$ verses t. The Lagergren plots of dye bioadsorption are shown in Figure 7. The high values of correlation coefficients showed that the data conformed well to the pseudo-first-order rate kinetic model.

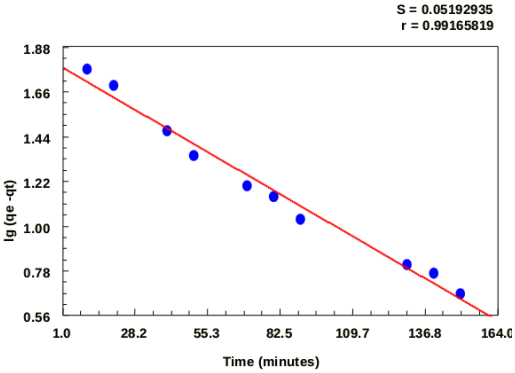

Figure 7: Lagergren plots for bioadsorbtion of MB by carbon of the epicarp of *Ricinus communis*

3.8. Spectrochemical Characterization

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM) at different magnification; the results are shown in Fig. 8. and Fig. 9. It was evident that the surface morphology of the activated carbon was different before and after adsorption.

4. Conclusion

This study confirmed that the bioadsorbent prepared from epicarp of *Ricinus communis*, a low cost agricultural waste, could effectively remove MB from an aqueous solution. The optimal pH for favorable adsorption of dye was 7. The change of particle size had an effect on the bioadsorption of dye. The adsorption equilibrium was reached in approximately 2 h. The isothermal data fitted the Langmuir and Freundlich model.So, the adsorbtion was physisorbtion. The bioadsorption processes followed the pseudo- first-order rate kinetics.

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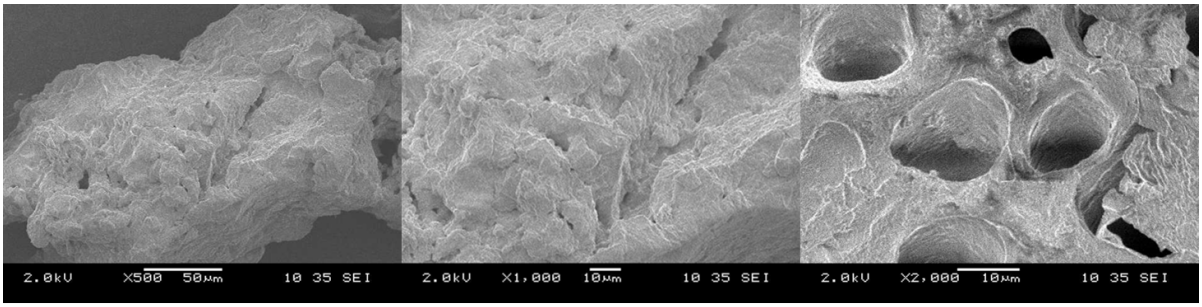

Figure 8: Cross section of activated carbon (Before adsorption)

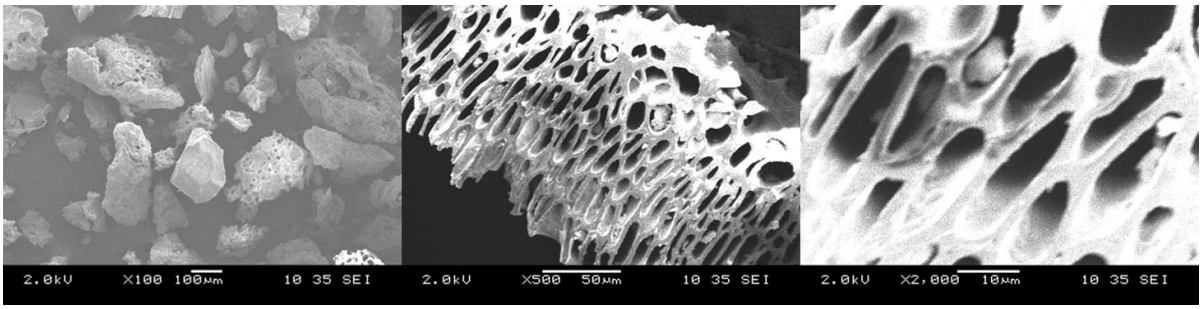

Figure 9: Cross section of activated carbon (After adsorption)

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