



## EQUILIBRIUM ISOTHERM STUDIES OF METHYLENE BLUE FROM AQUEOUS SOLUTION UNTO ACTIVATED CARBON PREPARED FROM STRYCHNOS POTATORUM SEED

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**ABSTRACT:** Methylene blue adsorption from aqueous solution onto activated carbon prepared from strychnos potatorum seed was investigated under various experimental conditions. Batch mode experiments and equilibrium isotherm studies were conducted to assess the potential of the above activated carbon for the removal of Methylene blue from aqueous solution by varying the following three parameters: initial concentration of Methylene blue dye solution, adsorbent dose on the uptake of dye from the solution, and  $p^H$ . The equilibrium data obtained were fitted to Langmuir and Freundlich isotherm models.

**Keywords:** Sorption, Isotherms, Activated carbon, carbonization, Methylene blue, Langmuir model, Freundlich model

### INTRODUCTION

Dyes are organic compounds used as coloring agents in chemical, textile, paper, printing, cosmetics, leather, coloring industries. Many treatment methods have been used to remove the dyes from wastewater. These can be divided into physical, chemical, and biological methods. Among the various methods, adsorption is an effective separation process for a wide variety of applications. It is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewaters. The most widely used adsorbent is an activated carbon because of its high surface area due to the presence of micro and meso pores. India produces more than 400 million tonnes (MT) of agricultural waste annually which include a very large percentage of the total world production of rice husk, bagasse, jute, stalk and coconut fiber. A number of studies have also been performed using activated carbon prepared from agricultural wastes for the removal of dyes from aqueous solution. The waste materials include coconut tree flower and Jute fiber (Senthilkumar et al., 2006), oil palm fiber (Tan et al., 2007), palm kernel shell (Jumasiah et al., 2005), corncob (Preethi et al., 2006), Wood apple outer rind (Malarvizhi and Sulochana 2008) and bagasse pith (Amin 2008). Basic dyes are the brightest class of water soluble dyes used by the textile industries, and Methylene blue is one of the most frequently used dyes in all industries. Presence of this dye in water leads to various health effects like eye burns, and irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea (Ghosh and Bhattacharyya 2002). In this study, we have used strychnos potatorum seed activated carbon. The carbon was prepared through carbonization and activation processes using concentrated sulphuric acid. The removal of Methylene blue by the above activated carbon was analyzed under the three different conditions initial concentration of Methylene blue dye solution, adsorbent dose on the uptake of dye from the solution, and  $p^H$ . The suitable isotherm model that explains the adsorption process is given separately and the combined effect on the isotherm model is also discussed later.

## MATERIALS AND METHODS

### Methylene Blue

Methylene blue (MB) supplied by Merck (AR), was used as an adsorbate and was not purified prior to use. Double distilled water was employed for preparing all the solutions and reagents. The chemical structure of the dye is shown in Appendix A.

### Preparation and characterization of adsorbent

Strychnos potatorum seed collected were thoroughly washed with water, air dried. Strychnos potatorum seed were then carbonised in muffle furnace at 300°C for period of one hour. The carbonized strychnos potatorum seed were then digested in 4N sulphuric acid(1:2, Carbon : acid w/v ratio) for half an hour. After the digestion period, excess sulphuric acid was removed and the adsorbed acid was removed by repeated washings with distilled water. Acid free shells were then dried in an air oven at 120°C for 24 hours, cooled and sieved to get particles in the size 150-250 $\mu$ .

### Experimental conditions

The stock solution of 1000 mg/dm<sup>3</sup> Methylene blue was prepared using distilled water. Solutions of desired concentration were prepared by diluting the stock solution stepwise. A calibration graph of absorbance versus concentration was constructed using systronics spectrophotometer at maximum wavelength of 665 nm. Batch mode experiments were conducted using 100 ml capacity closed containers using shaker at 150 rpm. For isotherm studies, initial concentration of Methylene blue dye solution, adsorbent dose on the uptake of dye from the solution, adsorption duration and pH were carried out at room temperature. Based on the preliminary studies and for less electrical power consumption, the following experimental conditions were fixed for the following studies. The influence of carbon dose on dye adsorption was determined by taking 50 ml of 50 mg/dm<sup>3</sup> of MB dye solutions and shaking with varying amounts of adsorbents ranging from 0.1g to 1g for 2 h at room temperature and solution p<sup>H</sup>. Effect of initial dye concentration was studied using 500 mg of activated carbon and 50 ml of different concentrations of dye solution in the range of 10 to 100 mg/dm<sup>3</sup> in the screw capped containers and shaken for 2 h. Effect of p<sup>H</sup> dye solution was carried by taking different p<sup>H</sup> of 4, 9 by taking 50ml of 50mg/dm<sup>3</sup> MB dye solutions of using 500 mg of carbon for 2 h shaking. After equilibrium time, the activated carbon was separated by using filters and the absorbance of the clear liquid was analyzed using spectrophotometer at a wavelength of 665 nm. All of the experiments were carried out at 25°C.

## RESULTS AND DISCUSSION

### Effect of initial concentration of the dye solution

The initial concentration of methylene blue solution was varied from 10 to 100mg/dm<sup>3</sup> and batch experiments were carried out with 500mg of the adsorbent at 25°C and at solution p<sup>H</sup>. An decreased percentage removal of MB observed with 500mg of the adsorbent in agitation time 2 hrs and the results are shown in Figure 1. In order to establish equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of MB on adsorbent was studied as a function of contact time. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration.

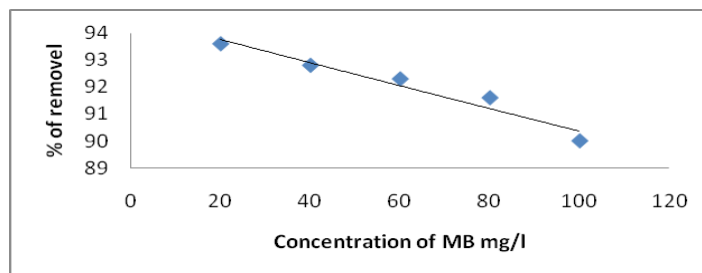
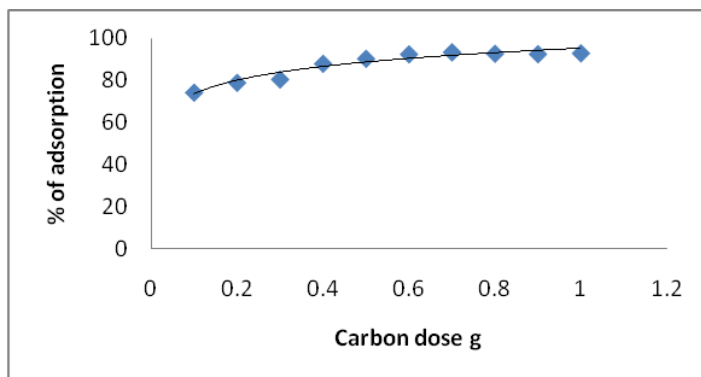


Figure 1: Effect of initial dye concentration on adsorption of MB

**Effect of adsorbent dosage**

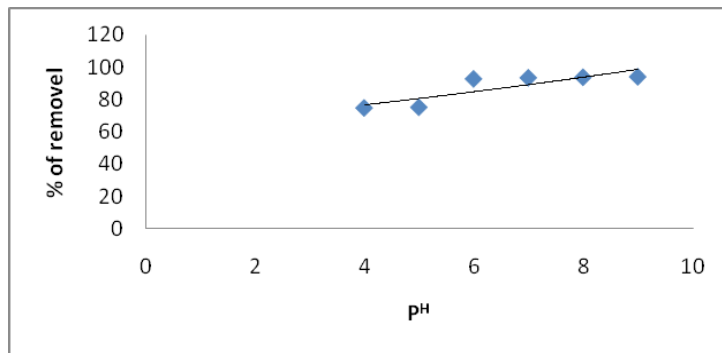
The adsorption of MB on strychnos potatorum seed carbon was studied by varying the adsorbent dosage from 0.1g to 1g. The amount of MB adsorption increased with increase in dosage of adsorbent. Figure 2. This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of adsorbent.



**Figure 2: Effect of adsorbent dosage and initial dye concentration on adsorption of MB**

**Effect of pH**

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of MB on strychnos potatorum seed carbon was studied by varying the pH from 4 to 9. The amount of dye adsorbed per unit mass of adsorbent at equilibrium increased by variation in pH from 4 to 9, Figure 3.



**Figure 3: Effect of pH on adsorption of MB**

**Adsorption isotherm**

Adsorption isotherm study provides fundamental physiochemical data for evaluating the adsorption capacities of an adsorbent, one of the most important criteria in selecting a suitable adsorbent. In the present investigation, the isotherm data were analyzed using the Langmuir and Freundlich isotherm equations (Figs. 4 and 5). The Langmuir sorption isotherm (Langmuir 1918) is the best and the Freundlich isotherm (Freundlich 1906) is an empirical equation most frequently used to describe the adsorption of inorganic and organic components in solution, respectively expressed as:

$$q_e = (C_0 - C_e) V / W \tag{1}$$

$$\text{Langmuir : } q_e = q_m K_L C_e / 1 + K_L C_e \tag{2}$$

$$\text{Freundlich : } q_e = K_f \times C_e^{1/n} \tag{3}$$

The linearized form of above equations can be written as follows:

$$1/q_e = 1/ q_m K_L C_e + 1/ q_m \tag{4}$$

$$\ln q_e = \ln K_f + 1/n \cdot \ln C_e \tag{5}$$

If the adsorption follows the Langmuir equation, a plot of  $1/q_e$  versus  $1/C_e$  should be a straight line.  $q_m$  and  $K_L$  can be determined from the intercept and slope. Similarly, from a plot of  $\ln q_e$  against  $\ln C_e$ ,  $K_f$  and  $n$  can be computed. Figure 4 and 5 shows the results of the Langmuir and Freundlich isotherm, indicating the reasonably good correlation between the experiment and both the two models, as reflected by correlation coefficients ( $R^2$ ) in the value of 0.977 and 0.975. The fact that the Langmuir isotherm fits the experimental data well may be due to the homogenous distribution of active sites on strychnos potatorum seed activated carbon.

Table 1 : parameter valules from fitting the adsorption equilibrium data with isotherm models					
Langmuir			Freundlich		
$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_f$ (mg/g)(L/mg) <sup>1/n</sup>	$n$	$R^2$
100	0.010	0.977	0.961	0.9784	0.975

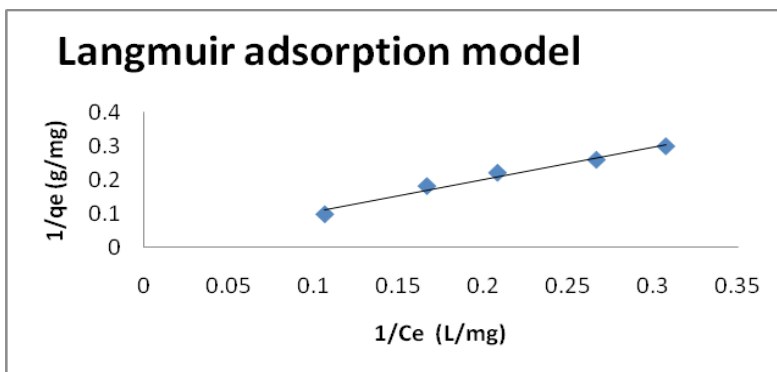


Figure 4: Experimental data and predicted Langmuir adsorption Isotherm

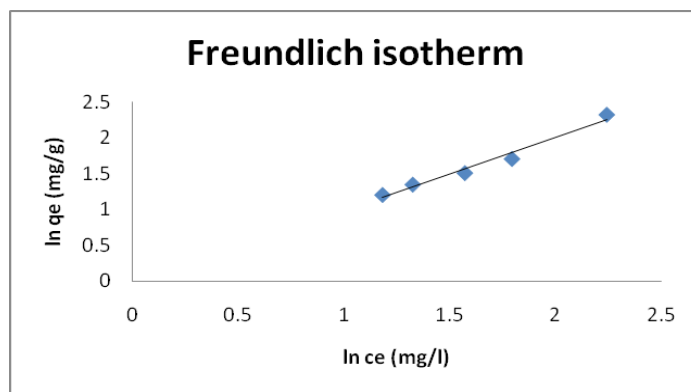
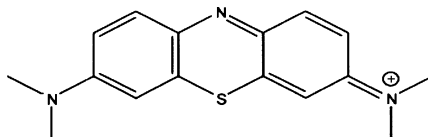


Figure 4: Experimental data and predicted Freundlich adsorption Isotherm

## CONCLUSION

The present investigation showed that strychnos potatorum seed can be effectively used as a raw material for the preparation of activated carbon for the removal of methylene blue dye from aqueous solution over a wide range of concentration. Methylene blue is found to adsorb strongly on the surface of activated carbon. Adsorption behaviour is described by a monolayer Langmuir type isotherm. This model could be used to describe the Methylene blue/ strychnos potatorum seed carbon adsorption system very well.

### Appendix A. Chemical structure of Methylene Blue dye



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