MAHOGANI (*SWIETENIA MAHOGANI*) LEAF POWDER: STUDY OF ADSORPTION PROPERTIES FOR REMOVAL OF REACTIVE BLUE P3R DYE FROM AQUEOUS SOLUTIONS

Md. Mizanur Rahman Badal[*], Md. Easin Ali, Meghla Akter, Gazi Jahirul Islam and Parbhej Ahamed

Department of Chemistry, Khulna University of Engineering & Technology, Khulna 9203, Bangladesh

ABSTRACT

In the present work, the Mahogani (Switenia Mahogani) leafs treated with sulphuric acid and formaldehyde were used as an adsorbent for the removal of reactive blue P3R dye from aqueous solution. The adsorption characteristics of reactive dye on activated Mahogani leaf powder (MLP) were evaluated as a function of pH, adsorbent dose and initial concentration of adsorbate. The amount of dye adsorbed per unit weight of the adsorbent increased with the increase of concentration and contact time but significantly increased with the decrease of pH. Therefore, adsorption of reactive blue dye was found highly pH dependent. The pH at the point of zero charge (pH_{PZC}) of the adsorbent was found to be 4.6. The equilibrium data were well represented by both Langmuir and Freundlich isotherms.

Keywords: *Adsorption isotherms, Freundlich isotherm. Langmuir isotherm, Mahogani leaf powder, Reactive dye.*

1.   INTRODUCTION

Pigments and dyes are widely used in the textile and leather dyeing, paper, printing, pharmaceutical, and cosmetic industries because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes (Garg, 2004; Sarma, 2005; Garg, 2003 and Gupta, 2003). Colour is a visible pollutant. Most of dyes are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin (Yener, 2006; Tsai, 2001; Liu, 2006 and Strikland, 1995). The release of the colored dyes into the ecosystem is a dramatic source of esthetic pollution, of eutrophication, and of perturbations in aquatic life (Wang, 2005). In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic adverse effect of dyes on environment and human such as skin, lung and other respiratory disorders are also reported[9]. Therefore, the removal of such dye from effluents becomes environmentally important.

There are several reported methods for the removal of dyes from effluents. The technologies can be divided into three categories: biological, chemical and physical. Biological treatment requires large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation (Krishna, 2003). Although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Kumar, 1998). On the other hand chemical methods use huge amount of chemical and produce large volume of sludge which itself requires treatment. These methods are very expensive too. Different physical methods such as membrane filtration processes (Nakao, 1994 and Zhou, 2001) (nanofiltration, reverseosmosis, electrodialysis etc.) and adsorption techniques (Crini, 2006; Guptta 2009 and Singh, 2011) are widely used. The major disadvantage of the membrane processes is that they have a limited life time before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. Due to its effectiveness and versatility, activated carbon (AC) is widely in used in water and wastewater treatment but commercially available activated carbons are very expensive (Singh, 1994 and Khare, 1987). Consequently, many investigators have studied feasibility of using low cost substances such as rice husk (Kalderis, 2008), coconut coir (Kavitha, 2007), banana pith (Sivakumar, 2010), baggase (Mohan, 2002), olive stone (El-Sheikh, 2004), sawdust (Jadhav, 2004), orange peel (Namasivayam, 1996), and corn cob (Amphol, 2009) for removal of dyes.

The main objective of the present work is to investigate the adsorption properties of Mahogani leaf powder (MLP) for the removal of reactive blue P3R dyes as a model experiment. The study includes adsorption as a function of time, adsorbent dose, concentration of dye solution, pH of the dye solution and adsorption isotherms.

2.   EXPERIMENTAL SECTION

2.1   Preparation of Adsorbent

The mature mahogani (*Swietenia Mahogani*) leaves used in the present investigation were collected from the trees in the area of Khulna University of Engineering and Technology. The leaves were washed twice with water to remove dust and water soluble impurities and were dried until the leaves become crisp. The dried leaves were grinded into powder and were boiled in distilled water to remove lignin and colouring components about one hour and filtered. The residue left was treated with formaldehyde and finally with very dilute solution of sulphuric acid, stirred for 30 minutes vigorously using magnetic stirrer at room temperature, it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment residue were dried first in air and finally in oven at 105°C for 24 hours. The homogeneous powder was then passed through mesh for desired particle size. The adsorbent once prepared were used throughout the experimental work.

2.2   Preparation of Adsorbate Solution

The reactive blue P3R dye was used without further purification. A stock solution of strength 800 mg/L was made by dissolving 800 mg in 1 L double distilled water. The pH of the dye solution was 4.8. All other solutions of various concentrations were made from this solution.

2.3   Batch Adsorption Experiments

The adsorption experiments were done in a batch process. The batch experiments were carried out in 250 mL stopper plastic bottle by mixing a pre-weighed amount of activated powder and 50 mL of aqueous dye solution of fixed concentration. The bottles were then kept in shaker (Gemmy orbit shaker, VRN-480) at constant oscillation of 180 osc/min. The samples were agitated for a predetermined time interval. The parameters such as pH, time of contact, adsorbent amount and dye concentration were varied during different sets of batch experiments. The pH was maintained at different values either by addition of a few drops of dilute hydrochloric acid or sodium hydroxide. After adsorption, the mixtures were allowed to settle, and portions of supernatant liquids were centrifuged. The supernatant solutions were analyzed using a UV-Visible spectrometry (Helios Gamma Spectrophotometer, UVG-152411) by monitoring the absorbance changes at a wavelength of maximum absorbance 589 nm.

2.4   Adsorption Isotherm Studies

The adsorption data for a wide range of adsorbate concentration and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of dye adsorbate.

2.5   The Method Of PH_{pzc} Determination

The pH at the point of zero charge (pH_{PZC}) of the adsorbent was evaluated with changing the pH values by using the titration method[27]. 0.1 g adsorbent was taken in a 250 mL conical flask and add into it 50 mL of 0.1M KNO_3 solution and agitated with magnetic stirrer. Then the pH of the solution was measured after an equilibrium time of 30 minutes. The titration was carried out with 0.1 M NaOH and 0.1 M HCl, respectively.

3.   RESULTS AND DISCUSSION

3.1   Determination of PH_{pzc} of Adsorbent

The surface charge Q of the adsorbent was calculated from the experimental titration data according to Eq. [1] (Kiefer, 1997).

$$Q = \frac{1}{w}(C_A - C_B - [H^+] + [OH^-]) \tag{1}$$

where, w is the dry weight of adsorbent in aqueous system (g/L); C_A is the concentration of added acid in aqueous system (mol/L); C_B is the concentration of added base in aqueous system (mol/L); $[H^+]$ is the concentration of H^+(mol/L); $[OH^-]$ is the concentration of OH^- (mol/L). The pH value at the point of zero charge was then determined by plotting Q versus pH.
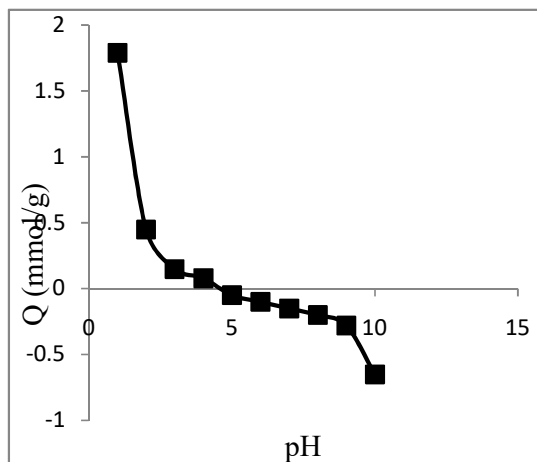
Figure 1: Surface charge of adsorbent as a function of pH

Figure 1: Shows the surface charge of the adsorbent as a function of pH. From Figure 1 it is obvious that the surface charge of the adsorbent (MLP) around pH 4.6 is zero. Hence the pH_{PZC} at point of zero charge of the Mahogani leaf adsorbent is 4.6.

3.2   Effect of PH

It was observed that λ_{max} for the dye changed very little in the studied pH range 2.0-9.0. The initial pH value of the solution can significantly influence the adsorption of dyes. In the present study the effect of pH on the amount of dye removal was analyzed over the pH range from 2.0 to 9.0. This result is shown in figure 2.
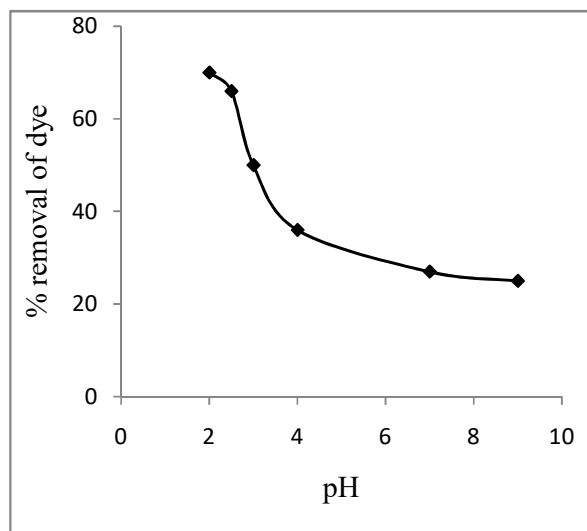

Figure 2: Effect of pH on removal of reactive blue P3R dye

The figure 2 showed that the removal of reactive blue P3R dye favored at lower pH may be attributed to the increase in the concentration of hydrogen ion in dye solution which neutralizes some of the anionic functional groups present on the surface of the adsorbent powder making the surface either positively charged or less negative. Under these conditions, the diffusion rate of dye molecules enhance towards the surface of adsorbent attributing the higher adsorption. Similarly decreasing adsorption at higher pH which may be due to the availability of large number of anionic functional group (hydroxyl group) and consequently the diffusion barrier is increased which results in poor adsorption. This result consistent with the pH_{PZC} of the biosorbent determined, whose value was 4.6. At pH values lower than pH_{PZC} the surface of MLP is positively charged, facilitating the electrostatic attraction of dye, a anionic dye. On the other hand, for pH values higher than pH_{PZC}, the surface of the adsorbent becomes negatively charged and precluding the electrostatic attraction of dye and hence the dye adsorption was decreased.

3.3   Effect of Adsorbent Dose

Effect of adsorbent dose plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. In our present investigation with increase in the amount of MLP adsorbent i.e. from 0.5 g to 1.0 g the removal efficiency of dyes increase rapidly which may be attributed to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent. It is shown in figure 3.
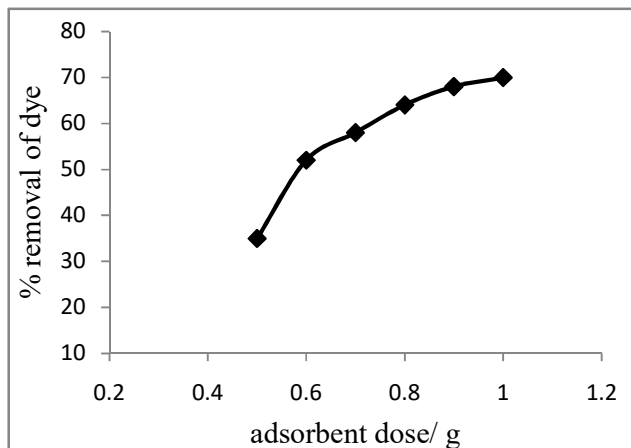

Figure 3: Effect of adsorbent dose on removal of reactive blue P3R dye

3.4   Effect of Initial Concentration and Contact Time

To determine proper dye adsorption and equilibrium time, initial concentrations of dye solutions were changed and time intervals were evaluated until no adsorption of adsorbate onto MLP took place. The adsorption data for the removal of dye versus contact time at different concentrations were shown in Figure 4. This indicates that the capacity of removal of dye increased with increase in dye concentration. This is due to increase in the driving force of the concentration gradient, as an increase in the initial dye concentration. The surface of MLP may contain a large number of active sites and the dye uptake can be related to the active sites on equilibrium time. The higher sorption rate at the initial period may be due to an increased number of vacant sites available at the initial stage, as a result there are increased concentration gradients between adsorbate in solution and adsorbate in adsorbent surface. These increased concentration gradients tend to increase in dye sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of dye particles in the vacant sites leading to a decrease in the sorption rate.
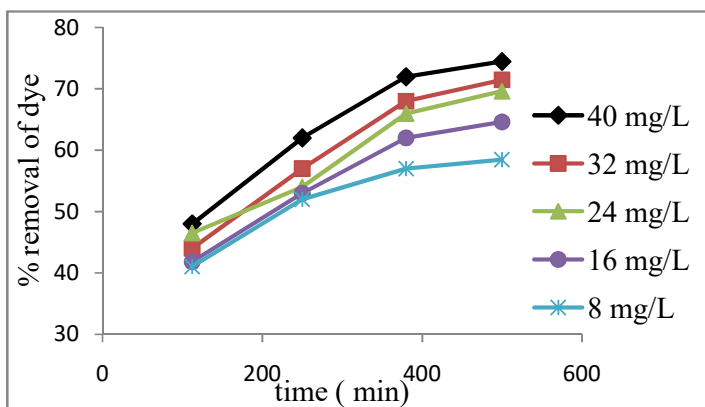

Figure 4: Effect of contact time and initial concentrations on the adsorption of reactive blue P3R dye onto MLP.

3.5   Morphological Studies

The surface studies of adsorbent were also done before and after adsorption by taking images through scanning electron microscope (SEM) shown in figure 5. It was showed the surface of adsorbent which was unsaturated before adsorption (a) and saturated after adsorption (b).
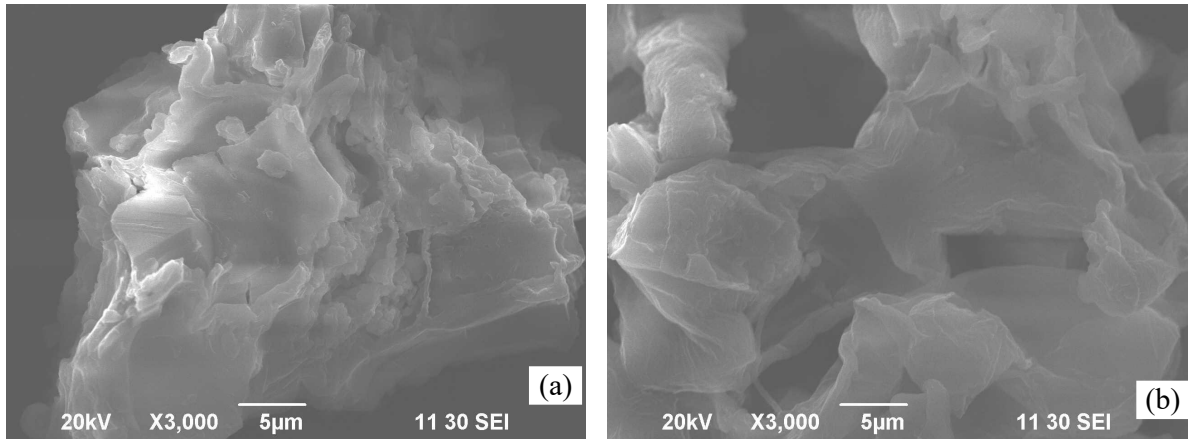

Figure 5: a) SEM of adsorbate before adsorption and **b)** SEM of adsorbate after adsorption.

3.6   Adsorption Isotherms

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution (Collin, 2007).

3.6.1   Langmuir Isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing   a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Webber, 1974).The linear form of Langmuir isotherm equation (2) is given as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad - - - - - - - - - - (2)$$

 Where C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g) and Q_o and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms and a representative plot is given in figure 6.
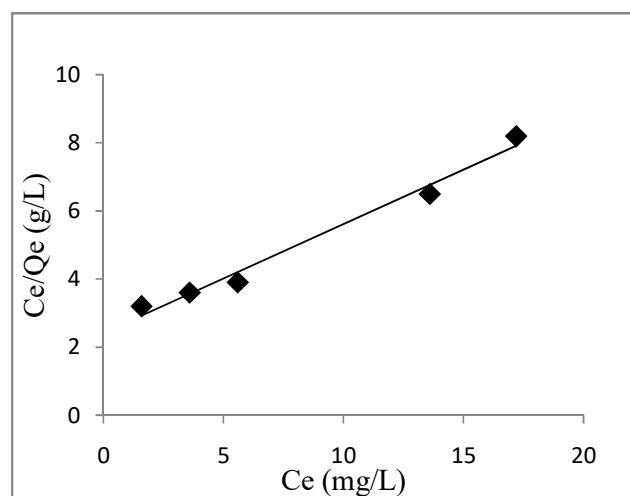

Figure 6: Langmuir isotherm for dye adsorption onto MLP

The correlation (R^2) for reactive blue dye was found 0.983. The values of Q_o and b were determined from the slope and intercept of the plot (Q_o = 3.13, b=0.132). The observed b values suggest the endothermic nature of the process involved in the system. To confirm the favourability of the adsorption process, the separation factor R_L = $1/(1+bC_o)$ has been calculated and the values were found to be between 0 and 1 which confirms that the ongoing adsorption process is favourable.

3.6.2   Freundlich Isotherm

The Freundlich isotherm, in the following form, was also employed for the adsorption of the dyes on the adsorbent.

$$log Q_e = log K_f + 1/n\, log C_e \quad ----------- (3)$$

Where Q_e and C_e have usual meanings, and K_f and *n* are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $log Q_e$ versus $log C_e$ shows that the adsorption of dyes follows the freundlich isotherm and a representative plot is given in figure7. The correlation (R^2) for reactive blue dye was found 0.987. The values of K_f and *n* were determined from the slope and intercept of the plot (K_f =0.104 , *n* =1.53). The values of intensity of adsorption, *n*, are greater than unity indicating that the adsorption is favourable
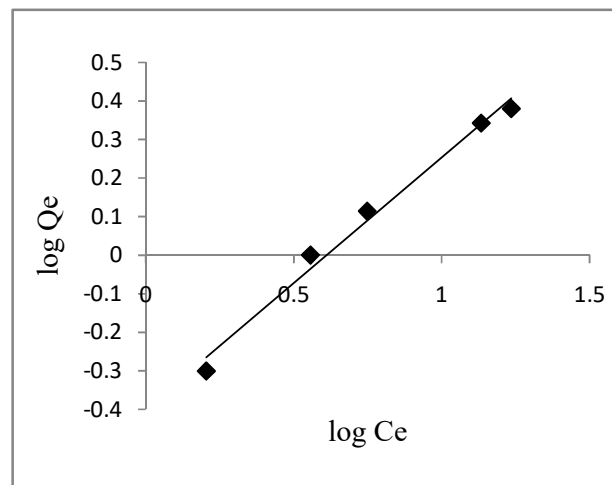

Figure 7: Freundlich isotherm for dye adsorption onto MLP

4.   CONCLUSIONS

From the results of the study it can be concluded that MLP could be used effectively for the removal of reactive blue P3R dye from aqueous solutions. The amount of dye adsorbed per unit mass of MLP was found to increase with increase in contact time and adsorbent dosages but significantly increase with decrease of pH. The Langmuir and Freundlich isotherm parameters showed that the adsorption of dye on MLP was favourable.

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