Asian Journal of Water, Environment and Pollution, Vol. 10, No. 2 (2013), pp. 59–64.

Effect of Operating Variables on the Batch Removal of a Dye Using Activated Plant Biomass

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Received November 17, 2012; revised and accepted January 29, 2013

Abstract: Acid activated date palm tree powder is proposed as an adsorbent for the removal of acid dye, Acid Blue 92, in this study. The influence of operating variables like solution pH, adsorbent dosage and initial dye concentration are studied thoroughly to evaluate the optimum conditions. Maximum adsorption was found to take place at pH 2.0 while equilibrium was achieved in 6 h. The mechanism of adsorption was explored by Pseudo-second order and Elovich models and it was found that this sorption process is well represented by Elovich model with a higher value of $R^2 = 0.997$. The physicochemical properties of the adsorbent are also studied.

Key words: Dye, sorption, date palm, kinetics.

Introduction

The waste water from textile dyeing industries is one of the most difficult industrial effluents to be treated because of the presence of synthetic dyes which are highly resistant to biodegradation due to their complex aromatic structure (Srinivasan and Viraraghavan, 2010; Forgacs et al., 2004; Rai et al., 2005). Textile industries are characterized by the consumption of large volumes of water and chemicals for wet processing of textiles (Thinakaran et al., 2008). The chemical reagents used are very diverse in composition, ranging from inorganic compounds to polymers and organic products. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Robinson et al., 2001). Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. An indication of the scale of the problem is given by the fact that two per cent of dyes that are produced are discharged directly in aqueous effluent (Pearce et al., 2003; Robinson et al., 2001). However, waste water containing trace amount of dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and is stable to light, heat and oxidizing agents.

Textile dye wastewater is usually treated by a number of physical and chemical methods like flotation, flocculation, coagulation, membrane filtration, electrochemical destruction, ion-exchange, irradiation, precipitation and ozonation (Gercel et al., 2008; Rajeshkannan et al., 2011). Adsorption has been observed to be a popular technique and more effective for the removal of dyes. Even though activated carbon is a well-known adsorbent, it suffers from demerits like expensive replacement cost and poor regeneration. This has led to the search of low cost naturally available adsorbents which can be used for efficient removal of dyes. Many studies have been reported on the application of low-cost adsorbents like peat, bentonite, fly ash, china clay, maize cob and silica for colour removal (Gupta and Suhas, 2009). However, these low cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents (Srinivasan and Viraraghavan, 2010; Ponraj et al., 2011).

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Therefore, there is a need to identify a new, economical and highly effective adsorbent for the removal of dyes. In this research work, we have tried to utilize date palm tree powder after acid activation for the removal of an acid dye, Acid blue 92, from its aqueous solution. The effect of operating parameters like pH, adsorbent dosage and initial dye concentration on the percentage dye removal under batch conditions for the removal of Acid blue 92 was studied. Also, the kinetic studies were conducted to determine the mechanism of removal.

Materials and Methods

Adsorbate

The adsorbate used in this study is an acid dye named Acid blue 92 (AB 92) which is purchased from Sigma-Aldrich and used without any purification. All other reagents were of analytical reagent grade and were obtained from Merck chemicals. The dye stock solution was prepared by dissolving a calculated amount of the dye in 1 L of deionized water and was kept in dark colored glass bottles.

Adsorbent—Preparation and Activation

The adsorbent used in this study was obtained from the barks of *Phoenix dactylifera* (date palm) tree. The tree barks were cut into pieces and washed with tap water to remove soil and dust and dried in sun for 72 h. The dried tree barks were ground into fine powder and sieved to the desired size range. The waste material was washed with tap water to remove soil and dust, sprayed with distilled water, and air dried. Finely powdered adsorbent was acid activated by soaking it in 0.1 M H_2SO_4 for 4 h in order to protonate it. The activated adsorbent was then washed in distilled water and dried at 60º C overnight. A weight loss of approximately 12% was observed. The acid activated adsorbent is termed as "Acid Activated Date palm Powder (AADP)". The surface area of the *Phoenix dactylifera* tree powder was determined by a three-point N_2 gas adsorption method using a Smart Sorb Surface Area Analyzer (model 92/93; Smart Instruments, India). The bulk density of the sorbent was determined by densitometer. Porosity of the biosorbent was determined by porositometer (model H; M7V, NGRI, India). The physicochemical properties of the sorbent are given in Table 1.

Table 1: Physicochemical properties of the adsorbent

Property	*Value*
Bulk density (g/cc)	0.53
Specific gravity	0.66
Porosity (%)	71
Average particle size	97.6 µm
Surface area (m^2/g)	32.6
Moisture content (%)	56
Loss on ignition (*w/w*, %)	93.1

Batch Experiments

The effect of operating variables like pH, adsorbent dosage and initial concentration of the dye for the removal of colour in AB 92 was studied by conducting the experiments in batch mode using an orbital shaker with temperature control at a fixed speed of 200 rpm. After agitation, the dye solutions were centrifuged for 10 min and the absorbance of the supernatant solution was analyzed using UV-double beam spectrophotometer (Shimadzu, Japan). The influence of initial pH of the dye solution on the percentage colour removal was studied over a pH range of 2-10. The adjustment of pH of the samples were done by adding either 0.1N HCl or NaOH as the buffering agent. To determine the optimal sorbent dosage per unit mass of the adsorbate, the dye solution was contacted with different amounts of AADP (0.5 to 4 g L^{-1}) till equilibrium is attained. The effect of various initial dye concentrations on the percentage colour removal was studied in the range of 50-200 mg L^{-1} at optimal pH and sorbent dosage. The amount of dye uptake was calculated by using the following equation:

$$q = (C_o - C_e)V/W \tag{1}$$

where q is the amount of dye adsorbed by adsorbent (mg g^{-1}); C_o and C_e are the initial and final dye concentrations (mg L^{-1}), respectively, V is the volume of sample solution (L) and W is the adsorbent dosage (g).

The percentage colour (or dye) removal is defined as

$$\text{\% colour (or dye) removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Kinetic Studies

In order to express and investigate the mechanism of sorbate sorption onto a sorbent, two kinetic models, namely pseudo-second order and Elovich equations were employed and their characteristic constants were determined using linearized plots**.**

Pseudo-second Order Model

The Pseudo-second order model (Ho and McKay, 1998) can be represented in the following form:

$$\frac{t}{q_t} = \frac{1}{\left(k_2 q_e^2\right)} + \frac{t}{q_e} \tag{3}$$

where, q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), and the pseudo-second order constant k_2 (g mg^{-1} min^{-1}) can be determ ined experimentally from the slope and intercept of plot $\frac{t}{q_t}$ versus t.

The Elovich Equation

The Elovich equation (Ozacar and Sengil, 2005) in its linear form is generally expressed as:

$$q_t = \frac{\ln \alpha\beta}{\beta} + \frac{1}{\beta}\ln (t) \quad (4)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}).

If the dye adsorption fits the Elovich model, a plot of q_t versus ln(t) should yield a linear relationship with a slope of $\frac{1}{\beta}$ and an intercept of $\frac{\ln \alpha\beta}{\beta}$.

Results and Discussion

Effect of pH

The effect of initial pH on the adsorption of dye by AADP was studied by varying the initial pH of the dye solution from 2 to 10 under constant experimental conditions like initial concentration C_0, 50 mg L^{-1}, and adsorbent dosage, m, 0.2 g/50 ml, as shown in Figure 1. The adsorbent showed better adsorption capacity at the initial pH of 2 with the maximum dye removal percentage of 79% with AB 92. The electrostatic attraction, as well as the organic properties of the activated date palm and structure of dye molecules, could play a very important role in the dye adsorption on the adsorbent. At pH 2, there is high electrostatic attraction existing between the positively charged surfaces of the adsorbent, due to the ionization of functional groups of adsorbent, and the negatively charged anionic dye molecules. As the pH of the system increases, the number of negatively charged sites is increased. A negatively charged site on the adsorbent does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion. It is known that acid dyes, on dissolution, release coloured dye anions into solution. The adsorption of these anionic charged groups onto the adsorbent surface is primarily influenced by the surface functional groups on the adsorbent, which in turn is influenced by the solution pH (Arami et al., 2006; Namasivayam et al., 2002).

Effect of Adsorbent Dosage

The effect of AADP dosages on the adsorption rate of AB 92 was studied by varying the concentration of the adsorbent from 0.5 to 4 g/L while keeping the other experimental conditions constant with initial dye concentration (C_o) of 50 mg/L, room temperature of 30°C for 2 h. From Figure 2, it was observed that the percentage of colour removal increased (from 35 to 90%) when there is a corresponding increase in the adsorbent dosage (0.5 to 4 g/L). This was due to the availability of more surface functional groups at higher concentrations of adsorbents (Arami et al., 2006; Shafique et al., 2012).

Effect of Initial Concentration

The effect of initial dye concentration, C_0, on the removal of AB 92 was studied by varying the dye concentration in the range of 50-200 mg/L. From Figure 3, it is evident that the percent AB 92 removal decreased with the increase in C_o. At lower concentrations, all AB92

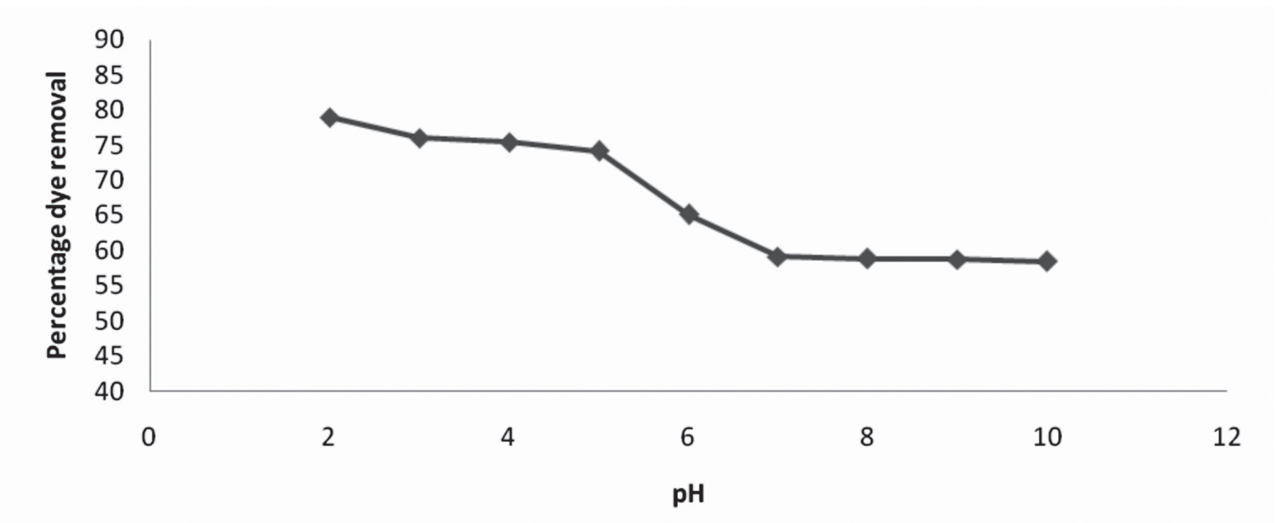

Figure 1: Effect of pH (t = 6 h, C_0 = 50 mg/L, m = 0.2 g/50 mL) on the removal of AB 92 by AADP.

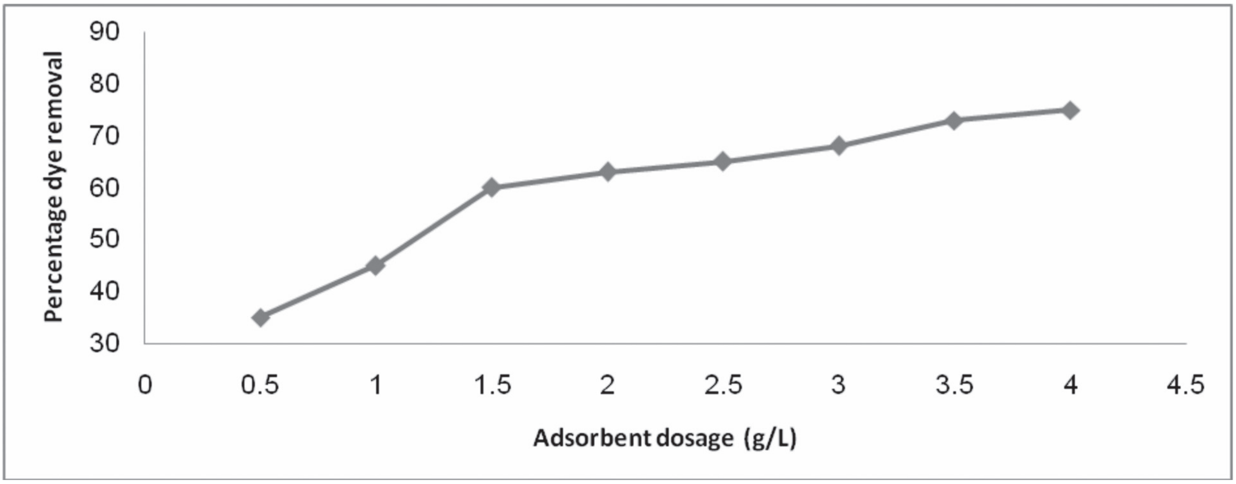

Figure 2: Effect of adsorbent dosage on the removal of AB 92 by AADP (t = 6 h, C_0 = 50 mg/L, T = 30 °C).

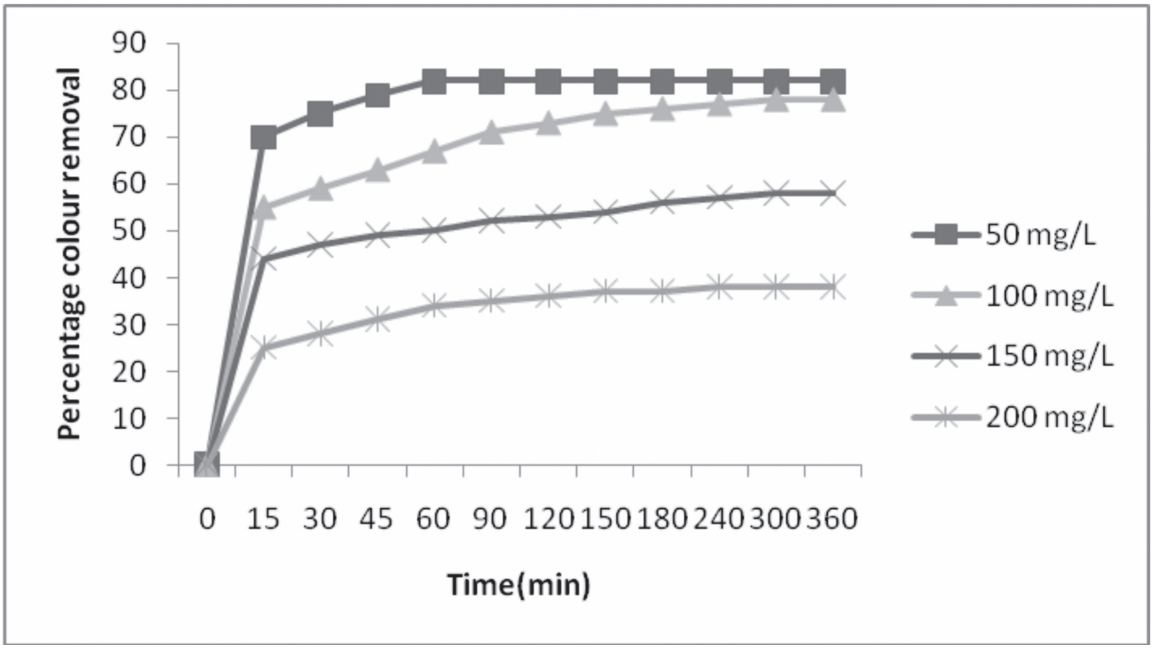

Figure 3: Effect of initial concentration on the removal of AB 92 (t = 6 h, pH = 2.0, T = 30 °C).

present in the adsorption medium could interact with the binding sites resulting in higher percentage removals. At higher concentrations, lower removal percentage was observed because of the saturation of the adsorption sites (Thinakaran et al., 2008).

Adsorption Kinetics

The mechanism of solute sorption onto the adsorbent has been explained by various models. In order to investigate the mechanism of sorption of AB 92 on AADP, two kinetic models, namely pseudo-second order model and Elovich equation, has been employed in this study.The kinetic data were analyzed using the linearized models presented in Eqs (3) and (4) and are represented in Figures 4 and 5. The parameters of the models are listed in Table 2. The highest regression coefficient (R^2 = 0.997) was obtained for Elovich model. The Elovich equation assumes that the active sites of the adsorbent are heterogeneous and therefore exhibit different activation energies for chemisorption (Ozacar and Sengil, 2005). When increasing the concentration of AB 92, it was observed that the constant α (related to the rate of chemisorption) increased and the constant β (related to the surface coverage) decreased, which is due to the decrease in the available adsorption surface for the adsorbents. Therefore, by increasing the concentration, within the range studied, the rate of chemisorption can be increased.

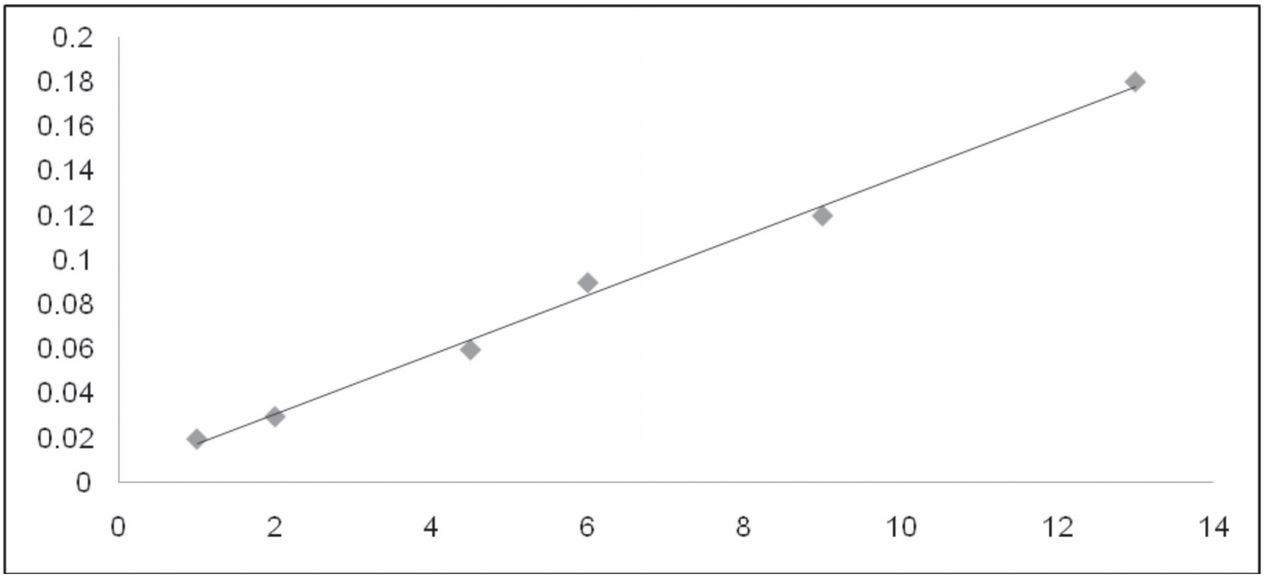

Figure 4: Pseudo-second order sorption kinetics of AB 92 onto AADP. Conditions: pH = 2, T = 30 °C and C_0 = 50 mg/l.

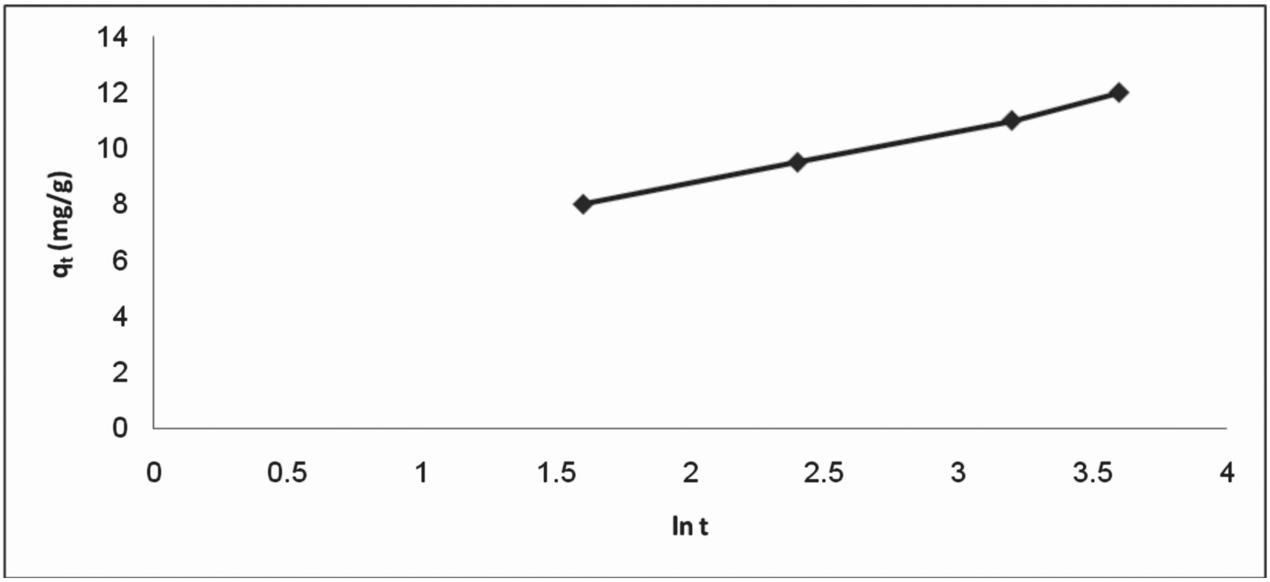

Figure 5: Plot of Elovich equation for sorption of AB 92 onto AADP. Conditions: pH = 2, T = 30 °C and C_0 = 50 mg/l.

Table 2: Kinetics constants for pseudo-second order and Elovich model

Dye type	*Pseudo-second order model*			*Elovich model*		
	k_2 g mg^{-1}min^{-1}	q_e mg g^{-1}	R^2	α mg g^{-1} min^{-1}	β g mg^{-1}	R^2
AB 92	0.0423	76.92	0.995	122.1	0.508	0.997

Conclusion

Adsorption of the acid dye, Acid Blue 92, onto acid activated date palm tree powder has been studied in detail. It was found that the maximum dye removal has taken place at pH 2.0 at an initial concentration of 50 mg L^{-1} and adsorbent dosage of 0.2 g/50 ml of dye solution. Also, the effect of adsorbent dosage and initial dye concentration was studied. The mechanism of solute sorption onto the adsorbent has been explained using pseudo-second order and Elovich models. The order of fit in relation to coefficient of correlation was Elovich > pseudo-second order.

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