Belpatra (Aegel Marmelos) Bark Powder as an Adsorbent for the Color Removal of Textile Dye "Torque Blue"

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Abstract—Adsorption is used as a potential method for the removal of color (dye) from industrial waste water. In this paper an easily available low cost Belpatra (Aegel marmelos) bark powder was used as an adsorbent for the removal of textile dye Torque Blue. For the present work several experiments were conducted at different adsorbent dosage, pH, temperature, dye concentration, particle size, and contact time in a batch adsorption mode. The experimental results revealed that maximum adsorption capacity of Belpatra bark powder on Torque blue dye was found to be 98% at an adsorbent dosage of 0.7gm in 100 ml dye solution having 15mg/L concentration at a temperature 310K and pH 7.5. The equilibrium data was fitted well in Langmuir isotherm model. The values of the Langmuir constants for adsorption capacity (Q^0) of Torque Blue on the adsorbent were 4.73, 4.13 and 3.74 at temperature 300,310 and 320K respectively. Kinetic studies showed that adsorption followed first order rate law. Thermodynamic parameters such as standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy changes (ΔS^0) were calculated for the interpretation of the adsorption process. The negative values of ΔH^0 and ΔG^0 showed that adsorption was exothermic and spontaneous in nature.

Keywords— Industry effluent, adsorption, low cost adsorbent, Belpatra bark.

I. Introduction

Various industries such as plastic, paper, textile and cosmetics use dyes to color their product. The textile industry is the largest consumer of dye stuffs. During the coloration process a large percentage of synthetic dye does not bind and is lost in waste streams[1]. The waste water (effluents) released from these industries contains dyes in trace quantities. The discharge of highly colored effluents into natural water bodies is not aesthetically unpleasant[2] but it may be carcinogens and toxic to mammals[3, 4]. The removal of dyes from textile effluents is of great concern because such discharge may render water harmful and injurious to public health as far as domestic, commercial, industrial and agricultural life is concerned[5]. Textile waste water is difficult to treat because it contains suspended solids, weakly biodegradable substances like additives, detergents, surfactants etc[6]. Among various treatment options available for the removal of dye from colored waste water; adsorption is the particularly competitive, economically cost effective and the most suitable method since proper design of the adsorption process will produce a high-quality treated effluent.

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate on the adsorbent surface. Adsorption is operational in most natural physical, biological and chemical systems and is widely used in industrial application such as activated charcoal, synthetic resins and water purification. Literature survey shows that various bio adsorbents have been used by researchers such as Sagaun sawdust[6], Mango and Neem bark[7], Neem leaf powder[8], Coconut leaves[9], Spent Tea leaves[10], Banana leaves[11], Eucalyptus bark powder [12], Rice husk ash[13], Orange peel[14] etc.

In the present work adsorption capacity of the Belpatra bark powder was studied for the removal of Torque blue (textile dye) at different dye concentration, contact time, pH, temperature, and adsorbent dosage and particle size. The adsorption dynamics and thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) for such systems have been evaluated.

II. Materials and Methods

Preparation of Adsorbent

The bio-adsorbent Belpatra Bark was collected from local areas of Ghaziabad. Belpatra bark was firstly washed several times with distilled water and then soaked in water for 5-6 hours to remove all the coloring and fine dust particles.

The sample was finally filtered and then dried in sunlight for 8-10 hours and then again dried in an oven at 150^0C for 24 hours. After drying it was grounded and sieved into different particle sizes of 75 µm, 150 µm, and 300 µm. After sieving, the powders were again washed, dried and stored in air tight containers for further use.

Collection and preparation of dye solution

Torque blue was used as an adsorbate in the present study. It is a basic dye and it was collected from the Rituraj textile industry Mohan Nagar, Ghaziabad. A predetermined quantity of dye was dissolved in 100 ml of distilled water to prepare a stock solution. Desired concentration of dye solution was obtained by diluting this stock solution. Concentration of dye solution was measured by Shimadzu UV-1800 spectrophotometer.

Absorption and Calibration curve of Torque blue dye

The value of λ_{max} for Torque blue dye was obtained from absorption curve. Figure 1 shows absorbance curve of torque blue at different wavelengths. It was observed that up to some wavelength absorbance increased by increasing wavelength, beyond which the absorbance decreased. The point at which the absorbance decreased is called the point of deflection and the wavelength corresponding to this is called maximum absorbance wavelength[14]. It was found at wavelength of 665 nm for torque blue dye.

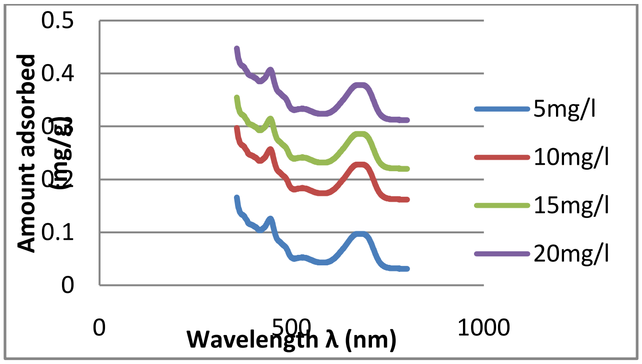

Figure 1. Absorbance curve of Torque blue at different wavelengths

Calibration curve is used for color removal capacities of various adsorbents. Figure 2 indicated calibration curve for torque blue dye at wavelength of 665 nm with R^2 value of 0.977. It was noticed that absorbance decreased on increasing dilution.

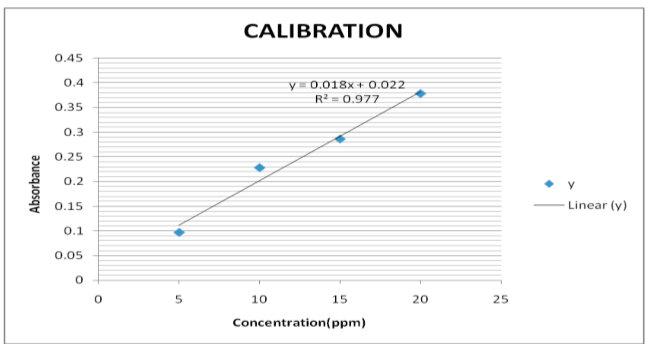

Figure 2. Calibration curve of Torque blue at wavelength of 665nm

Adsorption experiments

For each batch experiment, 100 ml dye solution of different concentration (10, 15, 20 mg/L) was stirred with different dosages (0.3, 0.5, 0.7gm) of Belpatra bark powder at different pH (4.5, 6.0, 7.5) and at different temperatures (300, 310, 320 K). After every 15 minutes of time interval, samples were withdrawn from the solution using a syringe and filtered through Whatman filter paper (size 0.45µm PES, filter media). The remaining concentration of dye solution was measured using Shimadzu UV 1800 spectrophotometer. The effect of contact time, concentration of dye, temperature, pH, adsorbent dosage, and particle size were investigated. The adsorption dynamics and thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) for such system have been calculated.

III. Results and Discussions

Effect of initial concentration and contact time

The effect of initial concentration and contact time was studied by agitating 0.5 gm of Belpatra bark powder having particle size of 150 µm in 100 ml dye solution of different concentration (10, 15 and 20 mg/L) over a time period of 15, 30, 45, 60, 75 and 90 minutes at a temperature of 310 K and pH7.5.

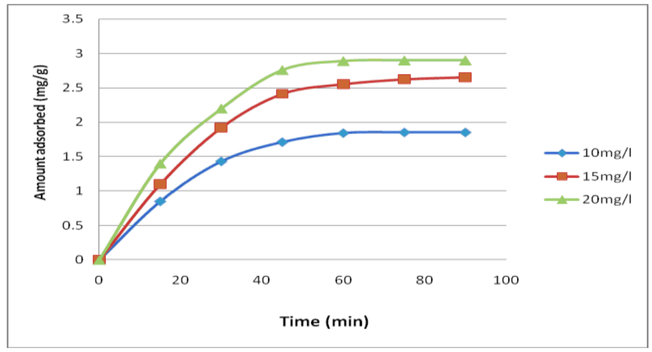

Figure 3. Effect of concentration and contact time of Torque blue by Belpatra bark

Figure 3 showed rapid uptake of dye during the first 20 minutes, after which the rate of adsorption became slower, attaining equilibrium in 60 minutes. This was due to the fact that most of the binding sites on adsorbent were free which allowed quick binding of the dye on the adsorbent surface. As the binding sites become exhausted, the uptake rate slowed down due to competition for decreasing availability of actives sites by adsorbent[15]. These curves are smooth and continuous indicating the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent[16]. The removal of dye by Belpatra bark was increased from 1.85 mg/g to 2.90 mg/g when the dye concentration increased from 10 to 20 mg/L at the temperature of 310 K and pH 7.5. However the percentage of the amount of dye adsorbed decreased from 92.5% to 72.5%, while the concentration of the dye increased from 10 to 20 mg/L. This was due to the fact that as the dye concentration increased, the dye/adsorbent ratio gets increased, therefore less adsorption sites were available in Belpatra bark powder since most of the adsorption site were saturated resulting a decrease in adsorption[7].

Effect of Particle size

The effect of different particle size of adsorbent (75, 150 and 300 µm) on removal of dye was studied at an adsorbent dosage of 0.5 gm/100 ml dye solution at 15 mg/L dye concentration at the temperature of 310 K and pH 7.5.

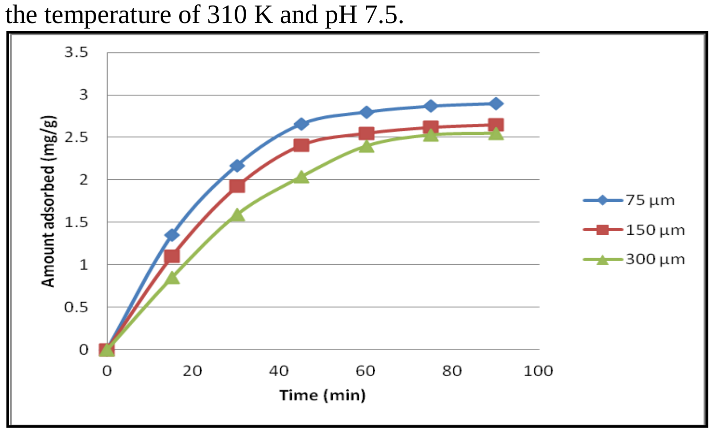

Figure 4. Effect of particle size and contact time of Torque blue by Belpatra bark

From Figure 4 it was shown that the amount of dye adsorbed increased from 2.55 mg/g to 2.90 mg/g while decreasing the particle size from 300 µm to 75 µm. Similarly the percentage of the amount of dye adsorbed increased from 85% to 96.6%, while the particle size of the adsorbent decreased from 300 µm to 75 µm. It was observed that the amount of dye adsorbed increased up to the saturation level as the particle size of the adsorbent decreased. The high uptake with decreasing particle size was attributed to the fact that smaller particles had a larger external surface area compared to larger particles, hence more binding sites were exposed on the surface and thus, leading to higher adsorption capacity since adsorption is a surface process. Apart from that, particles with smaller size also moved faster in the solution compared to larger particles, consequently, the absorption rate was faster[15].

Effect of Adsorbent dosage

The color removal efficiency of Belpatra bark powder at various adsorbent dosages 0.3 gm, 0.5 gm and 0.7 gm was studied in 100 ml dye solution of 15 mg/L concentration at a temperature of 310 K and pH 7.5. It was found that the amount of dye adsorbed increased from 2.21 mg/g to 3.13 mg/g when the adsorbent dosage decreased from 0.7 gm to 0.3 gm while the percentage of the amount of dye adsorbed increased from 62% to 98% when the adsorbent dosage increased from 0.3 gm to 0.7 gm. This was due to increased adsorbent surface area and availability of more adsorption sites resulting from the increased dosage of the adsorbent[7]

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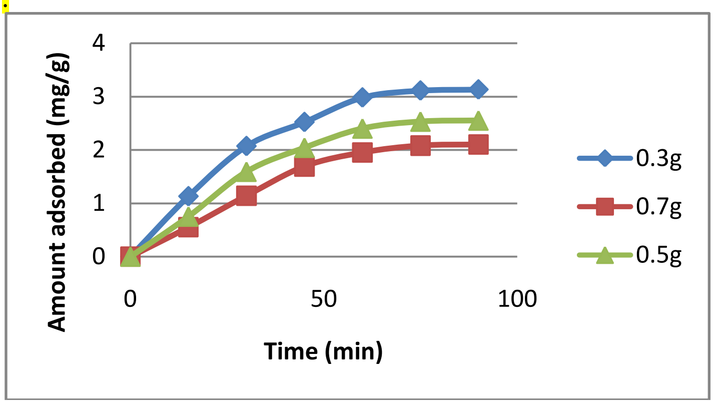

Figure 5. Effect of adsorbent dosage and contact time of Torque blue by Belpatra bark

Effect of pH

The effect of different pH (4.5, 6.0 and 7.5) on the removal of dye was studied at an adsorbent dosage of 0.5gm/100ml dye solution in 15mg/L dye concentration at the temperature of 310 K and at the particle size of 150 µm. It was observed that as the pH of the dye solution increased; the amount of dye adsorbed also increased. It was found that the amount of dye adsorbed increased from 1.65 mg/g (55%) to 2.55 mg/g (85%) when the pH of the dye solution increased from 4.5 to 7.5.

This was due to the fact that in the acidic medium (pH is 4.5 and 6.0), the electrostatic repulsion between protonated adsorbate (dye) species and positive surface charges of adsorbent occurred. So that the adsorption rate was decreased in lower pH. When the pH was increased (pH is 8.0) i.e. In the alkaline medium the adsorbent surface was negatively charged while the adsorbate species were still positively charged, the electrostatic attraction increased and the absorption rate gets increased[17, 18].

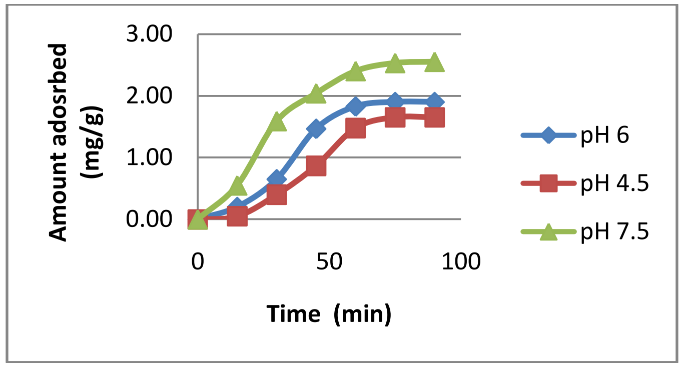

Figure 6. Effect of pH and contact time of Torque blue by Belpatra bark

Effect of temperature

The effect of temperature is studied for the color removal of torque blue dye on Belpatra bark at a temperature from 300 K to 320 K with an increment of 10 K and at an adsorbent dosage of 0.5 gm, adsorbate concentration of 15 mg/L in 100ml solution and pH of 7.5. From figure 7, it was observed that the amount of dye adsorbed decreased from 2.738 mg/g (91.27%) to 2.175 mg/g (72.5%) with the rise in the temperature of dye solutions from 300 K to 320 K. This was due to the fact that the solubility of the adsorbent increased with increase in temperature, the chemical potential decreased and then both effects worked in the same direction resulting a decrease in adsorption.

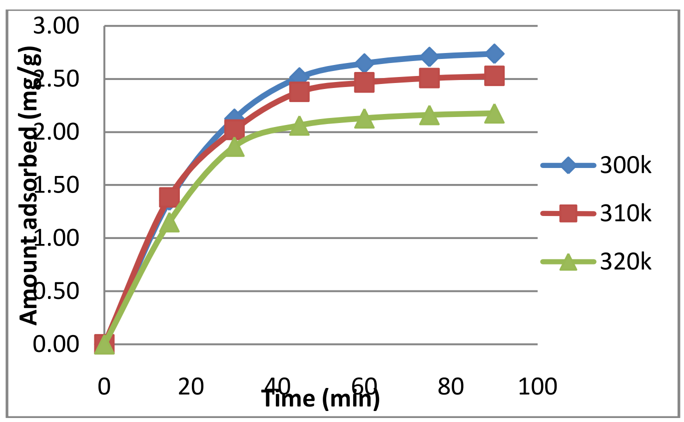

Figure 7. Effect of temperature and contact time of Torque blue by Belpatra bark

Estimation of thermodynamic parameters

The thermodynamic parameters, e.g. the changes in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) at different temperatures (300, 310, and 320 K) were calculated by following equations 1, 2, 3 and shown in Table 1.

$$\Delta G^0 = -RT \ln K \quad (1)$$

$$\Delta H^0 = R\left[\frac{T_2 T_1}{T_2 - T_1}\right] \ln\left(\frac{K_2}{K_1}\right) \quad (2)$$

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T} \right) \quad (3)$$

Where R is the gas constant and K, K_1, K_2 are equilibrium constant at temperature T (300 K), T_1 (310 K), T_2 (320 K) respectively. The equilibrium constant (K) can be calculated by following equation 4

$$K = \frac{\text{concentration of dye present on the adsorbent surface}}{\text{remaining concentration of dye in solution}}$$

(4)

Table1. Thermodynamic parameters for Torque blue dye

Temperature (K)	Thermodynamic Parameters		
	$-\Delta H^0$ [kJ/mol]	$-\Delta G^0$ [kJ/mol]	$-\Delta S^0$ [J/(Kmol)]
300	5.85	58.301	174.83
310	4.32	51.804	153.17
320	2.58	–	–

Adsorption Dynamics

The kinetics of adsorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction[19]. It determines the efficiency of adsorption.

The adsorption rate constant (k_{ad}) study was carried out with the famous Lagergren rate equation 5.

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t \quad (5)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g); q is the amount of dye adsorbed at the time t (mg/g); k_{ad} is the rate constant of first order adsorption. Straight lines were obtained by plotting log (q_e – q) versus t, as shown in Figure 8. The values of k_{ad} at different temperatures were calculated from the slope of the respective linear plots and are given in Table 2.It is clear from the values of k_{ad} that the system favors first order kinetics.

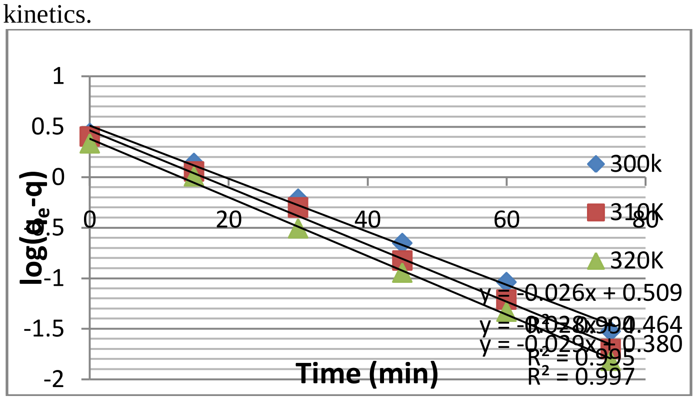

Figure 8. Lagergren plot for the adsorption of Torque blue on to Belpatra bark

Table 2. Adsorption constant at different temperatures for Torque blue

Temperature (K)	Adsorption constant (k_{ad})
300	5.98 x 10^{-2}
310	6.44 x 10^{-2}
320	6.67 x 10^{-2}

Adsorption Isotherm

The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium in waste water treatment applications. The linearised form of Langmuir isotherm is given by the following equation 6:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (6)$$

Where C_e is the equilibrium concentration (mg/L); q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q^0 (mg/g) and b (L/mg); the Langmuir constants related to adsorption capacity and energy of adsorption respectively. Straight lines were obtained by plotting C_e/q_e against C_e as shown in the figure 9. It indicates the applicability of the Langmuir isotherm over the entire concentration range studied with R^2 value of 0.985, 0.995 and 0.998 for temperature 320 K, 310 K and 300 K respectively.

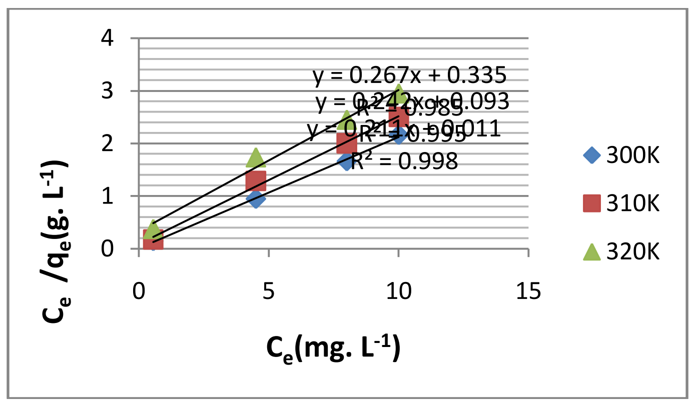

Figure 9. Langmuir plot for the adsorption of Torque blue on to Belpatra bark
at various temperatures

Table 3. Langmuir constants and equilibrium parameter at different temperatures for Torque Blue

Temperature (K)	Langmuir constants Q^0 (mg.g^{-1})	b (L.mg^{-1})	R_L
300	4.7393	0.0521	0.5613
310	4.1322	0.3842	0.1478
320	3.7453	1.2546	0.0504

The values of Q^0 and b were determined from the slopes and intercepts of linear plots and listed in Table 3.The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by the following equation 7[20].

$$R_L = \frac{1}{1+bC_0} \quad (7)$$

Where C_0 is the initial concentration of dye (mg/L) and b is the Langmuir constant (L/mg). The parameter R_L is related to the shape of the isotherm according to the following adsorption characteristics. $R_L > 1$ represents unfavourable adsorption. $R_L=1$ represents linear adsorption; $R_L = 0$ represents irreversible adsorption and $0 < R_L < 1$ represents favourable adsorption[21]. The values of R_L listed in Table 3 indicate that the adsorption of torque blue on to Belpatra bark was a favourable process since the R_L values lies between 0 and 1.

IV. Conclusions

In this paper a batch adsorption study was conducted to determine the suitability of bio-adsorbent Belpatra bark powder to remove Torque blue dye from textile effluents. The following conclusions can be drawn from the present work.

1. The adsorption of Torque Blue dye increased while decreasing temperature indicating that the adsorption is exothermic in nature. This is also confirmed by the negative value of enthalpy (ΔH^0). The negative value of ΔG^0 showed that adsorption is spontaneous.
2. The adsorption data described well linear Langmuir isotherm equation indicating monolayer coverage of the dye molecules on the outer surface of the adsorbent. The value of R_L (equilibrium parameter) was found between 0 and 1 which confirmed that adsorption is favorable.
3. The adsorption kinetics followed the first order rate law.
4. The adsorption was found to be pH dependent and the maximum adsorption was occurred at pH 7.5.

Thus, from the results of adsorption data, it was concluded that the Belpatra bark powder was found to be excellent adsorbent for the adsorption of Torque blue dye from industrial waste water.

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