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Adsorption of Textile Dye onto Activated Carbon Prepared from Industrial Waste by $ZnCl_2$ Activation[#]

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Abstract: *Activated carbon was prepared from hazelnut bagasse by chemical activation with $ZnCl_2$ as activating agent at 600 ^oC and 3/1 impregnation ratio. Bagasse was obtained from oil factory in Karadeniz Region. The surface area of activated carbon was 1489 m^2/g. Prepared activated carbon was used to remove Acid blue 350 (Sandolan Blue) from aqueous solutions and adsorption behaviour of dye onto the porous carbon was studied by varying the parameters such as pH, agitation time, dye concentration and temperature. Acidic pH was favourable for the adsorption of Sandolan Blue. The amounts of dye adsorbed increased with increase in both dye concentration and temperature. The kinetic data and equilibrium data on batch adsorption studies were carried out to understand the adsorption process. To investigate the mechanism of dye adsorption characteristic, adsorption constants were determined using pseudo first-order, pseudo second-order and intraparticle diffusion model. Adsorption isotherms of Acid blue 350 (Sandolan blue) on activated carbon were determined and correlated with common isotherms equations. It was found that the Langmuir model appears to fit the isotherm data better than the Freundlich model. The maximum adsorption capacity of dye was 450 mg/g at temperature of 45 ^oC and pH value of 2. The present study shows that the activated carbon derived from hazelnut bagasse is an effective low-cost adsorbent for the removal of Sandolan Blue from aqueous solution.*

Keywords: *Adsorption; acid blue 350; activated carbon; hazelnut bagasse.*

Introduction

The textile dyeing industry consumes large quantities of water at its different steps of dyeing, finishing etc. processes. Due to the large volume of water consumption, the production of huge volume of wastewaters is inevitable. Generally, the wastewater from printing and dyeing units in a textile plant contain residue of dyes and chemicals (Arami *et al*., 2008). The release of colored wastewater may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain (Lin et al., 2008).

Because of this, it is necessary to remove organic pollutants by proper treatment method. The various treatment methods for the removal of color and dye have been proposed such as coagulation, filtration, sedimentation, oxidation, membrane separation process, adsorption and so on (Namane *et al*., 2005; Senthilkumaar et al., 2006). In these techniques, adsorption has been found to be an efficient process to remove dye (Jumasiah *et al*., 2005; Vadivelan & Kumar, 2005).

Activated carbons are the most widely used adsorbents in industry. Powdered and granular activated carbons are used in waste and potable water treatment, in system of air emission cleaning, in chemical processes such as solvent recovery and decolorizing, in general domestic applications such as odor and smell removal (Kavitha & Namasivayam, 2008). Activated carbons can be prepared from a large variety of carbon containing feedstocks. The most common feedstocks for the commercial production of activated carbons are anthracite and bituminous coal, lignite, peat, wood and coconut shells. Agricultural by-products and wastes may offer an inexpensive and renewable additional source of activated carbons (Ahmedna et al., 2000).

In recent years, condensed research on the production of low cost activated carbon from agricultural residues has been reported such as, corn cob (Tsai et al.,1998), coir pith (Namasivayam & Sangeetha, 2006), palm shells (Guo *et al*., 2005), rice husk (Guo *et al*., 2003), apricot stone (Kobya *et al*., 2005).

Hazelnut is Turkey's most important agricultural crop since Turkey is one of the main producers of hazelnuts in the world. Turkey has the largest hazelnut production area with 550-600 thousand

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hectare that includes the 83% of total world area (Demiral & Şensöz, 2006). In Turkey, 661,000 tonnes of hazelnut were produced in 2006 (www.turkstat. gov.tr). Although hazelnut is being raised mainly for its fruit and oil, hazelnut bagasse and hazelnut shells have a great importance as a source of energy.

In this study, the ability of hazelnut bagasse carbon to remove Acid Blue 350 by adsorption has been studied. The adsorption capacity of dye was also examined using the adsorption isotherm technique. The Langmuir and Freundlich isotherms were used to fit the equilibrium data. Pseudo first-order, pseudo second-order and intraparticle diffusion models were used to fit the experimental data.

Materials and Method

Materials

Acid blue 350 was supplied from a textile plant in Turkey. 1000 mg/L stock solution was prepared by dissolving the required amount of dye in distilled water. Working solutions of the desired concentrations were obtained by successive dilutions. 0.1 N HCl and 0.1 N NaOH solutions were used for pH adjustment. The hazelnut bagasse sample investigated in this study was taken from hazelnut oil factory around the city of Ordu located in the Black Sea region, in the northern part of Turkey.

Preparation of activated carbon

Activated carbon was produced from hazelnut bagasse by chemical activation using $ZnCl_2$ as chemical agent. $ZnCl_2$ were dissolved in water and then impregnated into the bagasse in the ratio of 3/1 (g $ZnCl_2$/ g bagasse). Chemical impregnated bagasse was carbonized at 600 ^oC under the nitrogen flow. Preparation details and characteristics of activated carbon from hazelnut bagasse was reported elsewhere (Demiral *et al*., 2008).

Batch adsorption studies

To study the effect of parameters such as pH, agitation time, dye concentration and temperature for the removal of acid blue 350, batch adsorption experiments were carried out. The effect of initial pH on dye removal was studied over the pH range of 2-11. The initial pH of the dye solution was adjusted by the addition of 0.1N solution of HCl and NaOH. 50 mL of dye solution (C_o=300 mg/L) was agitated with 0.1 g of activated carbon using water bath shaker (Memmert) at 25 ^oC. Agitation was made for 24 h. The adsorption isotherm experiments were carried out by agitating 50 mL dye solutions of various concentrations. Equal mass of (0.1 g) activated carbon was added to each flask and kept in an isothermal shaker (25, 35, 45 ^oC). After agitation, the dye solutions were separated from the adsorbent, and the dye concentrations in the supernatant solutions were measured. Langmuir and Freundlich equations were employed to study the adsorption equilibrium. Adsorption kinetics experiments were carried out by agitating of dye solution (250 mL) of known initial concentration with 0.5 g of activated carbon at 25 ^oC. Samples were pipetted out at different time intervals and the concentrations of the solutions were determined. The kinetic data were analyzed using three kinetic models: pseudo first order kinetic model, pseudo second order kinetic model and intraparticle diffusion model. Dye concentrations in the supernatant solutions were measured using a UV/VIS spectrophotometer (Thermo Electron Corp.- Aquamate) at 625 nm.

Results and Discussion

Characterization of the activated carbon

The textural properties of the activated carbon which was determined by N_2 adsorption method were given in Table 1.

Table 1: Textural properties of the activated carbon (Demiral et al., 2008)

S_{BET} m^2/g	S_{Micro} m^2/g	V_{Micro} cm^3/g	V_{Total} cm^3/g
1489	983	0,454	0,932

Pore size distribution of the activated carbon is shown in Figure 1. As can be seen from Table 1 and Figure 1, activated carbons include both micropores and mesopores.

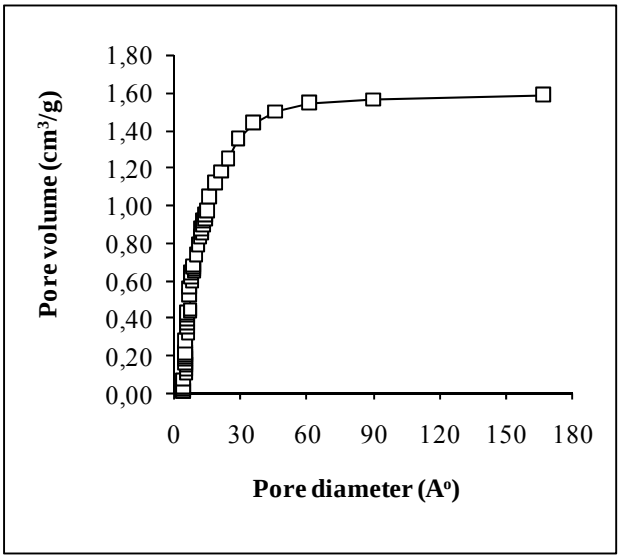

Figure 1: Pore size distribution of the activated carbon.

Adsorption studies

Effect of initial pH

The effect of initial pH on the adsorption of acid blue 350 is shown in Figure 2. The pH of the dye solutions was not change significantly during the experiments. This observation proved that there is not occurred any chemical structural change of dye molecules at this range of pH. As the initial pH is decreased from 11 to 2, the removal of dye is increased from 70% to %97. Maximum adsorption of acid dye occurs at acidic pH of 2.

Several reasons may be attributed to dye adsorption behavior of the adsorbent relative to solution pH. The electrostatic attraction as well as the organic properties of the activated carbon and structure of dye molecules could play important roles in dye adsorption. At pH=2, there is high electrostatic attraction existing between the positively charged surfaces of the adsorbent and the negatively charged anionic dye molecules. A negatively charged site on the adsorbent does not favour the adsorption of anionic dyes molecules due to the electrostatic repulsion. It is known that acid dyes 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 (Thinakaran et al., 2008). Similar results were observed for the adsorption of acid red 183 by shells of bittim (Aydın and Baysal, 2006) and acid brilliant blue by activated carbon (Kavitha and Namasivayam, 2008). Because of the solution at a pH value about 2 is an optimal condition for the adsorption of acid blue 350, following studies were carried out at initial pH of 2.

Adsorption is a physiochemical process that involves the mass transfer of a solute from the fluid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption (Aydın and Baysal, 2006).

The transient behaviour of the dye adsorption process was analyzed by using
pseudo first order, pseudo second order, and intraparticle diffusion models. A linear form of pseudo first order model was described by Lagergren (Aydın and Baysal, 2006).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium q_t is the amount adsorbed at time t (mg/g), and k_1 (h^{-1}). is the equilibrium rate constant of pseudo first order adsorption. The values of k_1 and q_e can be obtained from the slope and intercept of the plot $\log(q_e-q_t)$ vs. time (Figure 3). The

calculated k_1 value and the corresponding linear regression correlation coefficient (R^2) are shown in Table 2.

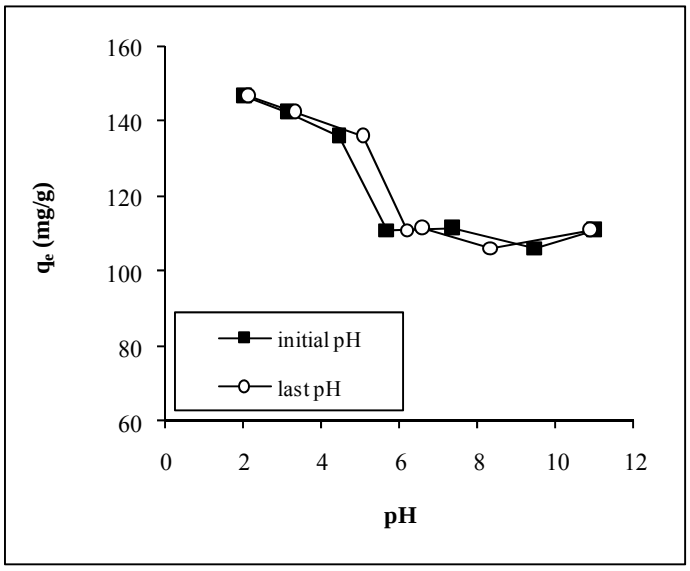

Figure 2: Effect of intial pH (C_0=300 mg/L; V=50 mL; m=0,1g; T=25 ^oC)

Adsorption kinetics

Adsorption kinetic was explained by the pseudo-second order model developed by Ho and McKay (Amin, 2008).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \qquad (2)$$

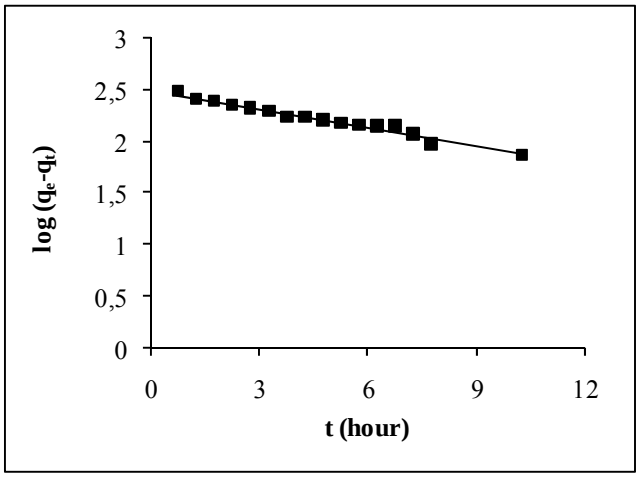

Figure 3: Pseudo first-order kinetic model

where k_2 is the equilibrium rate constant (g/mg h). The equilibrium adsorption capacity (q_e), and the second order constants (k_2) can be determined from the slope and intercept of plot t/q versus t (Figure 4). The calculated q_e, k_2 and the corresponding linear regression correlation coefficient values are summarized in Table 2. The possibility of intraparticle diffusion resistance affecting adsorption was explored by using intraparticle diffusion model as

$$q_t = k_p t^{1/2} + C \qquad (3)$$

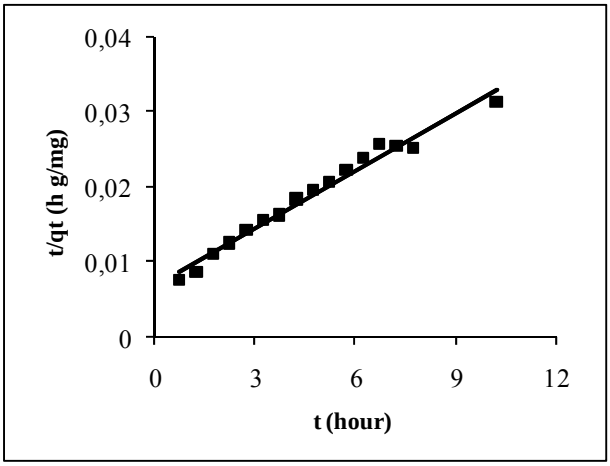

Figure 4: Pseudo second-order kinetic model

where k_p is the intraparticle diffusion rate constant (mg/g $h^{1/2}$) and C is a constant that gives idea about the thickness of the boundary layer (mg/g). According to Eq (3), a plot of q_t versus $t^{1/2}$ (Figure 5). should be a straight line with a slope k_p and intercept C when adsorption mechanism follows the intraparticle diffusion process.

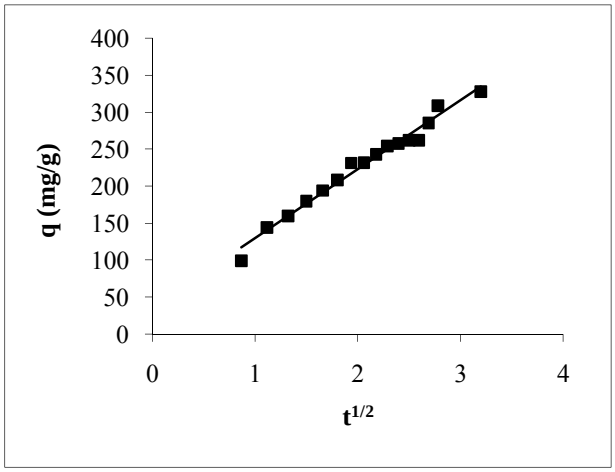

Figure 5: Intraparticle diffusion model.

Table 2 summarizes the rate constants and correlation coefficients (R^2) of the three kinetic models. The linearity of the plots indicates the applicability of the three models.
The correlation coefficient values of pseudo first order kinetic model (R^2=0.972), pseudo second order kinetic model (R^2=0.988) and intarparticle diffusion model (R^2=0.979) are almost same. But the experimental q_e value did not agree with the calculated value obtained from pseudo first order kinetic model. This shows that pseudo second order kinetic model fits better than pseudo first order kinetic model. Similar results were obtained in the adsorption of acid blue 45, acid blue 92, acid blue 120 and acid blue 129 (Hoda et al., 2006)

According to intraparticle diffusion model, the plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process, and if this line passes through the origin then intarparticle diffusion is the rate controlling step. When the plot doesn't pass through the origin, this is indicative of some degree of boundary layer control. This shows that the intraparticle diffusion is not the only rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously (Arami et al., 2008).

Adsorption isotherms

The adsorption isotherm indicates how the molecules distribute between the liquid phase and the solid phase when the adsorption process reaches equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes. Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents (Tan et al., 2008a). Figure 6 shows equilibrium adsorption isotherms of acid blue 350 on to the prepared activated carbon at different temperatures

Table 2: Kinetic constants for pseudo first order, pseudo second order and intraparticle diffusion (C_o=1000 mg/L, m=0.5 g, T=25 ^oC, q_e=401 mg/g)

Kinetic model	Constants		
Pseudo first order	q_e (mg/g)	k_1 (h^{-1})	R^2
	310.74	0.138	0.972
Pseudo second order	q_e (mg/g)	k_2 (g/ mg h)	R^2
	384	6.7 10^{-4}	0.988
Intraparticle diffusion	k_p	C	R^2
	93.23	36.31	0.979

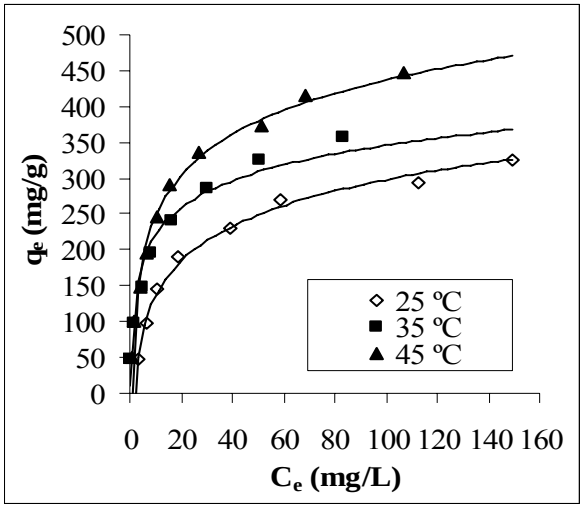

Figure 6: Adsorption isotherms of acid blue 350 on activated carbon at different temperatures (C_0=100-800 mg/L; V=50 mL; m=0.1g; pH=2)

The adsorption equilibrium increased with increase in temperature. This suggests that the adsorption process is endothermic in nature when temperature was increased from 25 to 45 ^oC. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of dye molecules into the pores of the activated carbon at higher temperatures (Tan *et al.,* 2008a). Similar results were obtained in the literature (Wang *et al*., 2005; Tan *et al*., 2008b).

Various isotherm equations have been used to describe the equilibrium nature of adsorption. Two well known isotherm equations, the Langmuir and Freundlich, have been applied for acid blue adsorption.

The linearized Langmuir equation is represented as follows (Bulut & Aydın, 2006),

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \qquad (4)$$

where C_e is the concentration of dye solution (mg/L) at equilibrium b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L/mg) and Q_o signifies the adsorption capacity (mg/g). Q_o and b were calculated from the slope and intercept of the straight lines of the plot C_e/q_e versus C_e (Figure 7). The adsorption capacity can be correlated with the variation of surface area and porosity of the adsorbent. Higher surface area and pore volume will result in higher adsorption capacity.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L (Kavitha and Namasivayam., 2007). R_L indicates the shape of isotherm as follows

$$R_L=1/(1+bC_o) \qquad (5)$$

where b is the Langmuir constant and C_o is the initial dye concentration (mg/L). If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates favorable adsorption.

As seen from Table 3 the Langmuir equation represents the adsorption process very well. The correlation coefficients (R^2) were found to be higher than 0.99 at all temperatures. In all of the temperatures, the values of R_L were calculated between 0 and 1. This confirmed that the Langmuir isotherm was favorable for adsorption of acid blue on activated carbon derived from hazelnut bagasse. The maximum adsorption capacities were found to be 357.14, 370.37 and 450.25 mg/g at 25, 35 and 45 ^oC, respectively. Maximum adsorption capacities of activated carbon increased with increased temperature. Conformation of the experimental data into Langmuir isotherm equation indicated the homogeneous nature of the surfaces of the activated carbon. The results also demonstrated the formation of monolayer coverage of dye molecules at the outer surface of the activated carbon.

Table 3: Langmuir parameters for acid blue 350 adsorption

T (^oC)	Q_o (mg/g)	b (L/mg)	R^2	R_L
25	357.14	0.054	0.9965	0.057
35	370.37	0.16	0.9912	0.020
45	450.25	0.11	0.9953	0.035

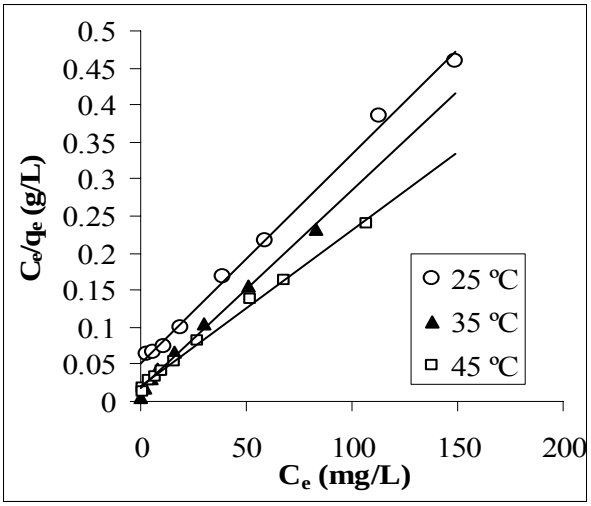

Figure 7: Langmuir plots for adsorption of acid blue 350 at different temperatures.

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. The Freundlich isotherm is given in logarithmic form as (Bulut and Aydın, 2006),

$$\log q_e = \log k_f + (1/n)\log C_e \qquad (6)$$

where k_f is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent $(mg/g)(L/mg)^{1/n}$ and 1/n is the adsorption intensity. k_f and 1/n can be determined from the linear plot of log q_e vs. log C_e (Figure 8). The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. 1/n values indicate the type of isotherm to be irreversible (1/n=0), favorable (0<1/n<1), unfavorable (1/n>1). The values of 1/n were found to be between 0 and 1, indicating favourable adsorption of acid blue 350 on activated carbon at all temperatures. The correlation coefficients for Freundlich isotherm were found to be less than 0.99 (Table 4). Therefore, the equilibrium data were best represented by Langmuir isotherm as compared to the Freundlich model Similar results were obtained in the literature (Arami *et al*., 2008).

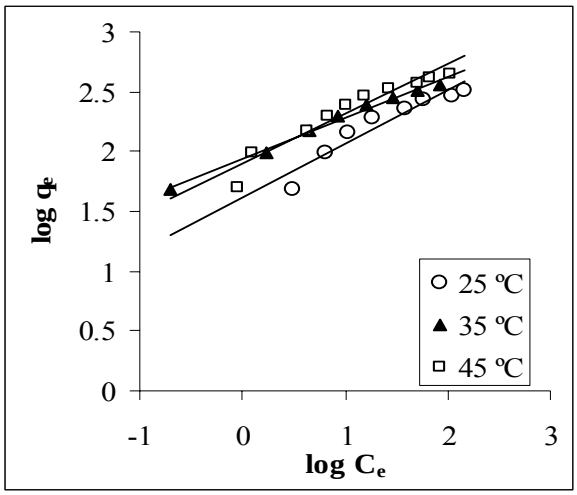

Figure 8: Freundlich plots for adsorption of acid blue 350 at different temperatures.

Table 4. Freundlich parameters for acid blue 350 adsorption

T (°C)	k_f	1/n	R^2
25	40.62	0.448	0.9093
35	87.13	0.341	0.9815
45	77.03	0.425	0.9243

Conclusion

In this study, activated carbon was produced from hazelnut bagasse by chemical activation and used for the removal of acid blue 350 from aqueous solutions. Adsorption was influenced by various parameters such as initial pH and temperature. The maximum adsorption of acid blue 350 dye by activated carbon occurred at an initial pH of 2. The adsorption increased with increasing temperature. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium. The equilibrium data were best described by the Langmuir isotherm model with maximum adsorption capacity of 476 mg/g at 45 °C. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. The studies presented were indicated that the derived activated carbon could be employed as an adsorbent for dye removal.

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