Research Article

Biosorption of Acid Green 25 from Textile dye effluent using Barley husk

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ABSTRACT:

This paper presents the performance of the low cost adsorbent Barley husk in removing the acid green 25 (AG25) such from textile dye effluent. Biosorption studies were carried out for various parameters such as adsorbent dosage, initial AG 25 concentration and contact time. Adsorption of AG25 onto Barley husk increased with the increase in the adsorbent dosage and the optimum adsorbent dosage was found to be 3 g/L. The equilibrium between the dye and the adsorbent in the solution was established within 75 min. The pseudo-second-order kinetic model agrees very well with the experimental results. Thermodynamic parameters such as Gibb's free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated. The positive values of $\Delta H°$ and negative values of $\Delta G°$ indicates that the AG25 adsorption process is endohermic and spontaneous in nature. The results indicate that Barley husk is a suitable adsorbent for the adsorption of textile dyes.

Keywords: Acid Green 25, Barley husk, Adsorption, kinetics, thermodynamics

INTRODUCTION:

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from Industrial are a large amount of suspended organic solid(1,2). Dyes are widely used in industries such as textile, rubber, paper, plastics and cosmetics to color the products(3,4). These dyes are invariably left as industrial wastes into the environment without pretreatment. Dyes, even in low concentration, affect the aquatic life through food web due to the large degree of toxic compounds presents(5,6). The discharge dyes into aquatic ecosystems constitute a severe health hazard to aquatic biotic systems, mainly due to their non-degradability and toxicity(7,8).

In recent decade, many researchers have focused their interest on dyes due to their known toxicity and carcinogenicity(9,10). SO dyes is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies(11,12). The removal of the dye ions from water is very difficult due to the high cost of treatment methods(13,14). There exist several methods for the removal of toxic metal ions dye ions from dye effluent such as reverse osmosis, ion exchange, chemical precipitation, electrodialysis and lime coagulation(15,16). These techniques are not only expensive but also inefficient in complete removal, high reagent and energy requirements and generation of toxic sludge(17,18).

Adsorption is a procedure of choice for the removal of dyes from wastewater(19,20). The major advantages of this technique are its low generation of residues and the possibility of its

adsorbent being recycled and reused(21,22). Several effective, selective, and cheaper adsorbent materials were developed such as waste orange peel, banana pith, rice husk, azolla filiculoides, clay, lemna minor, powdered activated sludge, and activated carbon/charcoal(23,24). Recently, conducting polymer was tested in the adsorption of dye effluent.

In this study Barley husk were used and evaluated as a possible sorbent for the removal of a acidic dye (acid green 25) from aqueous solution. The objective of this study is to investigate the effect of AG 25 concentration, adsorbent dosage and contact time on the adsorption process. kinetics and thermodynamics studies have been performed and the results have been analyzed by applying conventional theoretical methods.

Materials and Methods:

Acid green 25 (AG 25) is an acidic dye with molecular weight 622.58 g/mol and maximum adsorption 608 nm. The AG 25 ($C_{28}H_{20}N_2Na_2O_8S_2$) dye used in this work was the analytical grade (merck, Germany). For treatment experiments, the dye solutions with concentration in the range 10-200 mg/L were prepared by sucessive dilution of the stock solution (1000 mg/L) with distilled water. All other chemicals used in the study were of analytical grade.
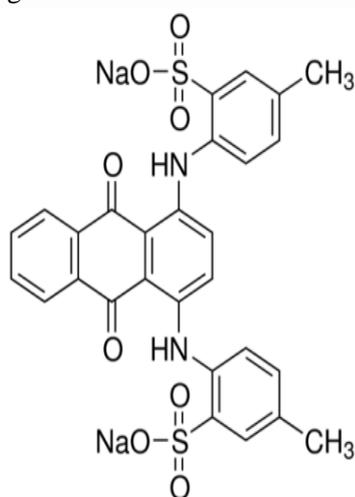
Preparation of Adsorbent: The stalks of Barley husk (C) were collected from research farm of

Tabriz agricultural school. Barley husk were washed with distilled water and dried in a drier for 5h at 105 ◦C until a constant weight was reached. It was then ground in a ball mill and sieved to particle sizes ranging from 1 to 2 mm. The sieved raw material was then activated by chemical treatment. The activation was carried out by 0.5M HCL for 3 h. After activated, the sample was washed with distilled water several times and then dried in an oven at temperature of 105 ◦C overnight. The activated biomass was kept in a closed container till use.

Batch adsorption experiments: Batch studies were carried out at the temperature of 30 ◦C. In the adsorption experiment, weighed quantity of Barley husk was taken in a standard-joint pyrex glass stoppered bottle (250 ml) containing 100 ml wastewater sample. The pH of the system was adjusted to the desired value and the mixture was shaken for a predetermined period using a thermostated horizontal shaker operated at 180 rpm. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye colour at different time intervals. Independent bottles containing 100 ml wastewater sample and 3 g Barley husk were used during the kinetic studies to get accurate results for each point on the graph. Isothermal studies were conducted with different doses of adsorbent (0.5-5 g) and 100 ml sample by shaking the reaction mixture for equilibrium time. The residual dye colour in the reaction mixture was analyzed by centrifuging the reaction mixture and then measuring the absorbance of the supernatant at the wavelength that correspond to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated from the calibration curve. The amount of dye adsorbed onto the biomass, q_e (mg/g), was calculated by the following mass balance relationship(25,26):

$$q_e = (C_0 - C_e) \frac{V}{M}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye, respectively (mg/l), V the volume of the solution (L), and M is the weight of the biomass used (g).

RESULTS AND DISCUSSION:

Effect of Initial Dye Concentration and Contact Time

The experimental results of adsorptions of AG25 on the Barley husk at various initial concentrations (10, 25, 50, 75 and 100 mg/L) with contact time are shown in the Figure 2 and 3. The percentage adsorption decreased with increase in initial dye concentration, but the actual amount of dyes adsorbed per unit mass of biomass increased with increase in dye concentration. The amount of dye adsorbed increased from 3.29 mg/g to 28.48 mg/g for AG25 , revealed that the adsorption is highly dependent on initial concentration of dye. This is because that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low(27). However, at high concentration the available sites of adsorption becomes lesser and hence the percentage removal of dye gets decreased with increase in initial concentration(28,29). Further in Figures 2 and 3, the curves are single and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the biomass surface.

Effect of adsorbent dose

The influence of adsorbent dosage on AG25 removal by Barley husk in individual dyes is presented in Fig 4. The percentage of removal of the dye increased from 33.4% to 82.2% as the Barley husk dose was increased from 0.5 to 5 g/L. The increased removal at high dosages is expected, because of the increased adsorbent surface area and availability of more adsorption sites(30,31).

Effect of Stirring rate

The effect of agitation speed on the dye adsorption (Fig. 5) at the adsorbent dosage of 3 g/L, initial dye concentration of 50 mg/L, pH 7. This effect can be attributed to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing. This result also indicates that external mass transfer was the rate limiting step(32).
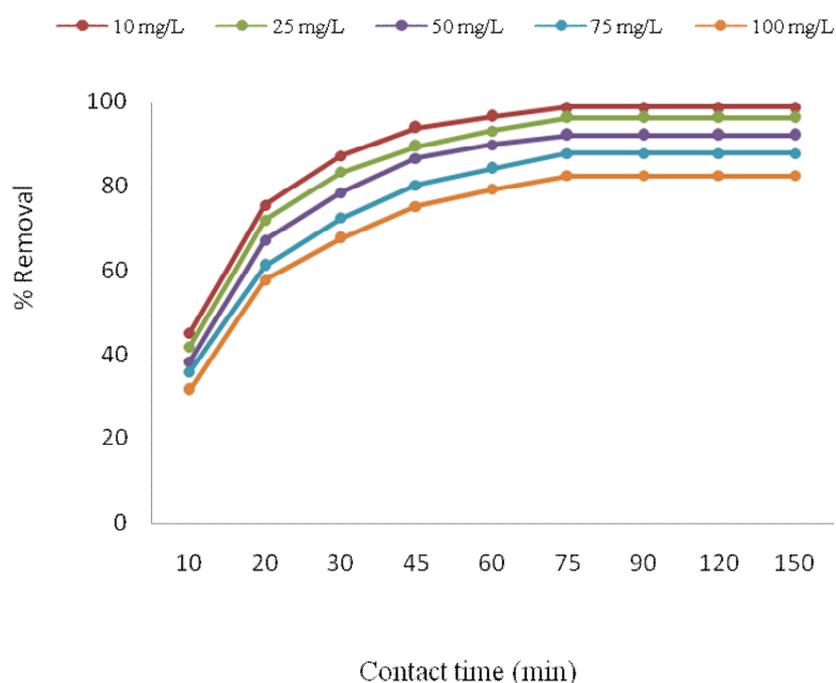

Fig 2. Effect of contact time and concentration on AG25 removal (pH =7, Adsorbent dosage 3 g/L and temperature = 28 ± 2^0C)
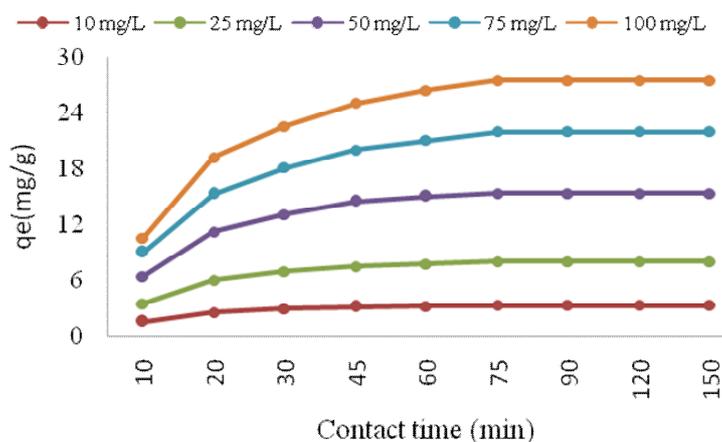
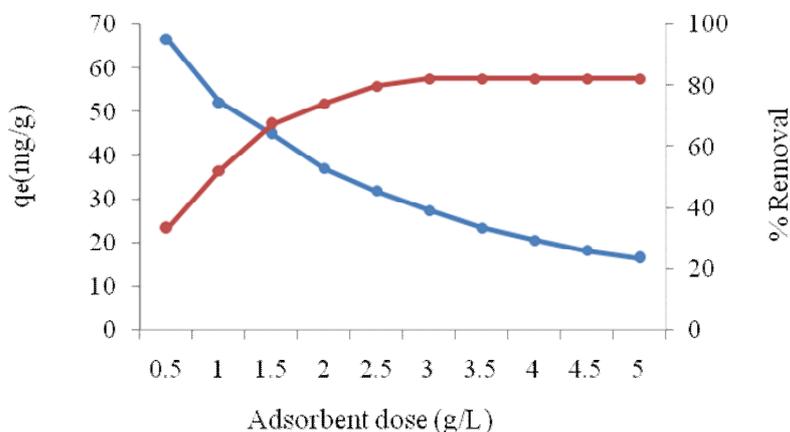**Fig 3.** Effect of contact time on adsorption capacity (pH =7, Adsorbent dosage 3 g/L and temperature = 28± 2^{0}C)

Fig 4: Effect of adsorbent dosage on AG25 adsorption. (C_0 = 100 mg/L, time = 75 min, pH = 7, temp= 28 ± 2^{0}C)
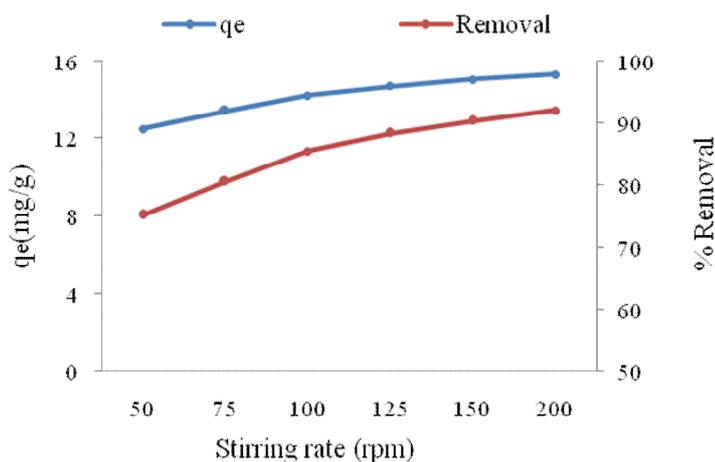

Fig 5. Effect of Stirring rate on AG25 removal (pH =7, dose= 3 g/L, C_0 = 50 mg/L, time 90 min, temp= 28 ± 2^{0}C)

Adsorption kinetics

The adsorption kinetic shows the evolution of the adsorption capacity with time. To examine the potential rate controlling step several kinetic models were used to test the experimental data.

The pseudo first order equation is expressed as[33,34]:

$$Log\ (q_e - q_t) = \log q_e - \frac{K_1}{2303}t$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (mg/g), k_1 is the first-order rate constant (min^{-1}) and t is time (min).

The results of pseudo first-order for the adsorption of AG25 by Barley husk are given in table 1. The pseudo first-order rate constant ranged between 0.0185 to 0.0391 min^{-1}. The correlation coefficient R^2 found to range from 0.912 to 0.958. The calculated and experimental q_e values shows a reasonable correlation in the case pseudo first-order kinetics. Even though q_e cal (calculated value) and q_e exp (experimental value) are closer, the R^2 values suggests that the adsorption data fitted poor to pseudo first-order kinetics. Hence, the adsorption AG25 onto Barley husk does not follow the pseudo first-order rate

The Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as[37-39]:

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

The results of Elovich for the adsorption of AG25 by Barley husk at various initial dye concentrations are given in table 1. The correlation coefficients for the Elovich model are greater than 0.9 and experimental q_e values agree with the calculated ones indicating the applicability of this kinetic equation. The initial adsorption rate, a, increases from 7.841 to 11.65 mg/g min while increasing the initial dye concentration from 25 to 100 mg/L.

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent.

Table 1: kinetic parameters for AG25 adsorption onto Barley husk

C$_o$ (mg/L)	Pseudo second order			Pseudo first order			Elovich			Intraparticle diffusion	
	k$_2$	R^2	q$_e$	K$_1$	R^2	q$_e$	α	R^2	β	K	R^2
25	0.0012	0.997	8.112	0.0185	0.912	6.851	7.841	0.916	0.0771	2.862	0.845
50	0.0038	0.998	15.49	0.0274	0.936	12.89	9.254	0.934	0.0552	6.341	0.836
100	0.0059	0.999	26.74	0.0391	0.958	25.34	11.65	0.947	0.0348	10.47	0.802

expression.

The adsorption may also be described by pseudo second-order kinetic model, if the adsorption does not follows the first order kinetics. The linearized form of the pseudo second-order model is[34-36]:

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

Where k_2 are constants of adsorption rate, q_t is adsorption capacity at time t, q_e is adsorption capacity at equilibrium condition. The pseudo second-order parameters is given in Table 2. The pseudo second-order rate constant decreases from 0.0012 to 0.0059 (g/mgmin) with increases in initial dye concentration. The correlation coefficient R^2 ranges from 0.997 to 0.999, which is higher than pseudo first-order values. From the results it can be suggested that pseudo second-order describes the adsorption of AG25 by Barley husk much better than pseudo first-order model.

Weber and morris suggested the following kinetic model to investigate the adsorption is intra-particle diffusion or not. The is intra-particle diffusion model is generally expressed as[40,41]:

$$q_t = K\ t^{1/2}$$

Where, K is the intraparticle diffusion rate constant and the results are given in table 1. The set of R^2 values obtained were poor. From the R^2 it can be seen that the Pseudo second order equation fits the experimental appreciably when compared to the other equations.

Thermodynamic parameters

The adsorption capacity of the biomass increased with increase in the temperature of the system from 0° to 60°C. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined using the following equations[42-43]:

$K = C_{solid}/C_{liquid}$

$\Delta G° = -RT \ln K$

$\ln (K) = \dfrac{\Delta S^0}{R} - \dfrac{\Delta H^0}{RT}$

Where, K is the equilibrium constant, C solid is the solid phase concentration at equilibrium (mg/L), C liquid is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. Table 2 presented the thermodynamic parameters at various temperatures. The increase in surface coverage with increasing temperature may be attributed to increased penetration of AG25 dye inside micropores at higher temperatures or to the creation of new active sites.

As shown in table 2, The positive values of $\Delta H°$ show the endothermic nature of adsorption and it governs the possibility of physical adsorption. $\Delta H°$ value suggests that adsorption process is physisorbed onto Barley husk. The enthalpy of adsorption of organic molecules from aqueous solution on Barley husk is usually within the range 8-80 kJ/mol. Enhancement of the adsorption capacity of the Barley husk at higher temperatures has been attributed to the enlargement of pore size and activation of the adsorbent surface.

Table 4: Thermodynamic parameters for the adsorption of AG25 on Barley husk			
T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
273	−1.124		
288	−1.946		
303	−2.278	21.76	49.83
318	-2.763		
333	-3.384		

CONCLUSION

The results of different experiments showed that Barley husk has an ability to adsorb AG25 dye from aqueous solution. Different variables, such as contact time, adsorbent dose, initial AG25 concentration and temperature influenced the adsorptive quantity. The adsorption has nearly reached equilibrium in 75 min and adsorbent dose 3 g/L. The best correlation was obtained using the pseudo-second-order kinetic model. The adsorptive process is endothermic and spontaneous. These values obtained from thermodynamic parameters demonstrated that adsorption process is physical in nature and the adsorption process is endothermic and spontaneous.

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