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Research Article

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Adsorption Behavior of Acid Red 97 Dye on Canola Stalks

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Abstract In this investigation, the mechanism of the adsorption of Acid Red 97 dye (AR97) from aqueous solution using an Canola stalks was studied. Different parameters affecting dye removal were studied. These parameters include contact time, initial dye concentration, adsorbent dose, stirring rate and adsorbent particle size. Langmuir and Freundlich isotherm models were applied to the equilibrium data. Equilibrium data fitted well with the Langmuir model and adsorption capacity (qmax) obtained from the Langmuir isotherm was 19.8 mg/g at initial pH 7. The optimum conditions for the removal of BPA within the experiment range of variables studies were 10 mg/L of initial dye concentration, 3.5 g/L of adsorbent dose, stirring rate 180 rpm, adsorbent particle size 20 mesh and 75 min of contact time. Under these conditions the maximum removal efficiency was 96.4%.

Keywords Acid Red 97 dye, Adsorption, Canola stalks, Isotherms

Introduction

Common pollutants in textile effluents are dyes which are toxic, non- degradable due to their complex structure [1, 2]. As a result, the toxic effluents pose a huge risk to the environment if discharged untreated [3, 4]. Dyes are synthetic aromatic water soluble dispersible organic colorants, having potential application in various industries [5, 6]. The dyestuff usage has been increased day by day due to tremendous increase of industrialization and human desire for colour [7, 8]. It is estimated that there are currently more than 10,000 commercially available dyes with an annual production of over 0.7 million tons worldwide, of which 10 to 15% is lost in industrial effluents during manufacture and processing operations [9, 10]. The presence of very small amounts of dye in water (<1ppm for some dyes) causes aesthetic deterioration and diminishes the solubility of dissolved oxygen, water transparency, and sunlight permeability, affecting aquatic life and the food chain [11, 12].

There are several methods to remove dyes such as physical and chemical processes to treat wastewaters including organic pollutant and dyes [13, 14]. The most commonly used methods for color removal are biological oxidation and chemical precipitation [15, 16]. However, these processes are effective and economic only in the case where the solute concentrations are relatively high [17, 18]. The adsorption technique has proven to be an effective and attractive process for the treatment of these dye-bearing wastewaters [19, 20]. The adsorption characteristics of dyes on various adsorbents have been extensively investigated for many purposes involving separation and purification [21, 22]. Adsorption potential of selected activated carbons were tested and found that dye was effectively removed from aqueous solution [23]. However, the problem associated with the activated carbon decrease the attraction of its application [24]. Therefore, the researchers are trying to find a low-cost and effective adsorbent. Recently, the various natural material such as Red mud, Banana peel, Apple residues, Orange peel, Azolla and etc have been used as effective adsorbents to remove the dyes [25-27].

The canola stalk is one of lignocellulosic wastes that are widely produced in Iran and all of the world due to the growth of the production and consumption of vegetable oils; therefore, the Canola stalk is easily available and due to its characteristics has been used in several studies to remove the pollutants [28, 29]. The aim of the study was: (1) investigation of Canola ability to remove the AR97 dye from aqueous solution, (2) determination of adsorption behavior of AR97, (3) determination of impact of stirring rate, contact time, initial dye concentration, adsorbent particle size and biomass dosage on sorption.

Materials and Methods

In this study, the Canola was used as low cost natural or agricultural wastes for AR97 dye removal from aqueous solutions. The stalks of Canola were collected from research farm of Tabriz (Iran) agricultural school. Canola stalks were washed with distilled water and dried in a drier for 2 h at 105 ◦C until a constant weight was reached. It was then ground in a ball mill and sieved to particle sizes ranging from 10 to 100 mesh. The biomass were then treated with 0.5 M HCL for 2 h followed by the washing with distilled water and then was oven dried at 105℃ for 3 h.

The AR97 dye was purchased from Alvan sabet Company (Iran). The stock solution of AR97 was prepared by dissolving 1 g of dye in 1000 ml of distilled water. The experimental solution say (10 to 200 mg/L) from stock solution by diluting to desired concentrations in accurate proportion. The chemical structure and some properties of the AR97 dye are presented in Table 1 and fig 1.

Table 1: Characteristics of Acid Red 97

Molecular Formula	CAS Number	Colour Index Number	λ_{max} (nm)	Molecular Weight
$C_{32}H_{20}N_4Na_2O_8S_2$	10169-02-5	22890	630 nm	698.63

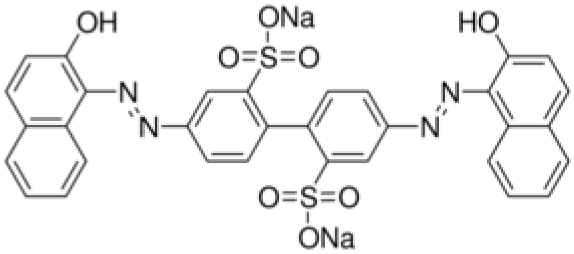

Figure 1: Structure of Acid Red 97

Adsorption studies

Batch adsorption experiments were carried out at room temperature (27°C±1). Exactly 100 ml of dye solution of known initial concentration (50 mg/L) was stirred at a constant stirring rate (200 rpm) with a required dose of adsorbents (0.5-5 g/L) for a specific period of contact time (5–120 min) using a magnetic stirrer, at fixed pH=7. The pH of the solutions were adjusted to the required value by adding either 0.1 M HCl or 0.1 M NaOH solution. After equilibrium, the final concentration (C_e) were measured using absorbance values with a spectrophotometer (UV-Vis-DR 5000) and compared with the absorbance values of the initial solutions. The absorbance was measured at 630 nm. Experiments were carried out in duplicate and mean values are presented. The percentage removal of dye were calculated using the following relationship [30]:

$$R = \frac{(Co - Ce)}{C_0} \times 100$$

Where C_0 and C_e are the initial and final (equilibrium) concentrations of dye (mg/L), respectively. Blanks containing second distilled water were used for each series of experiments as controls. The amount of dye adsorption per unit mass of Canola stalks at equilibrium, *q*e (mg/g) was calculated by the following equation [31]:

$$q_e = \frac{(Co - Ce) \times V}{M}$$

Where C_0 and C_e are the initial and equilibrium dye concentrations in solution, respectively (mg/L), V the volume of the solution (L) and m is the mass (g) of the adsorbent used.

Results and Discussion

Effect of contact time and initial dye concentration: The effect of contact time on the percentage removal of the dye was investigated at initial dye concentration 50 mg/l as shown in Fig. 2. The percentage removal of dye by different Canola stalks was rapid in the beginning due to larger surface area available of adsorbent but it gradually decreased with time until it reached equilibrium. The plots reveal that maximum percent removal of the dye after about 1 h of continuous stirring [13, 32]. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles.

Fig. 2. shows the effect of contact time on the removal of disperse dye by Canola stalk for different initial dye concentrations. The adsorption amount increased with an increase in initial dye concentration. This is because a higher initial concentration enhanced the driving force between the aqueous and solid phases and increased the number of collisions between dye ions and adsorbents [33].

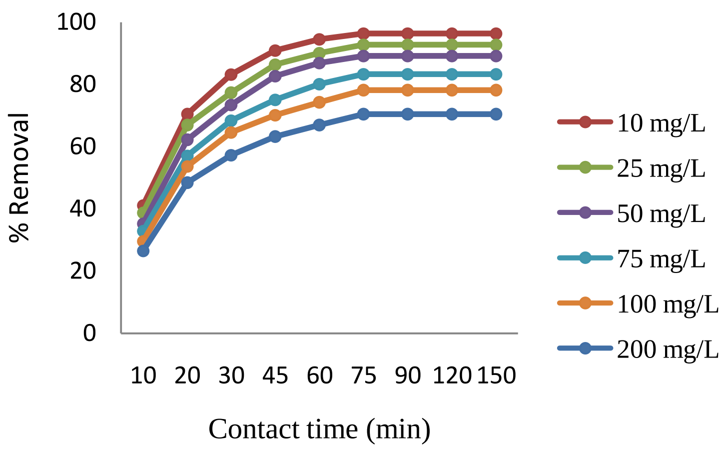

Figure 2: Effect of contact time and initial dye concentration (Stirring rate=200 rpm, pH=7, Temp: 27 °C, adsorbent size =10 mesh and adsorbent dose =3.5 g/L)

Effect of Stirring rate: The effect of agitation speed on the dye adsorption (Fig. 3) at the adsorbent dosage of 3.5 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 [34].

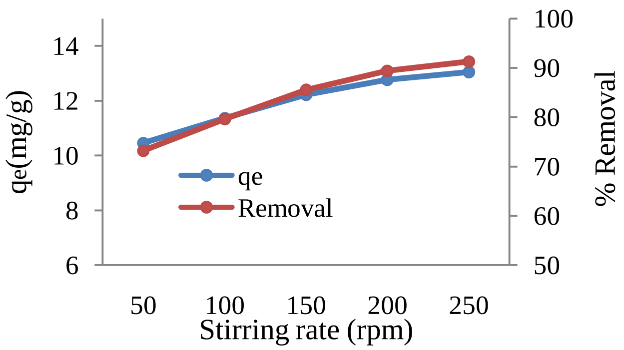

Figure 3: Effect of Stirring rate (C_0 = 50 mg/L, pH=7, Contact time=75 min and Temp: 27 °C, adsorbent size =10 mesh and adsorbent dose =3.5 g/L)

Effect of adsorbent dose: The influence of adsorbent dosage on dye removal by Canola stalk in individual dyes is presented in Fig. 4. The percentage of removal of the dye increased from 32.4% to 89.2% as the Canola stalk 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 [35].

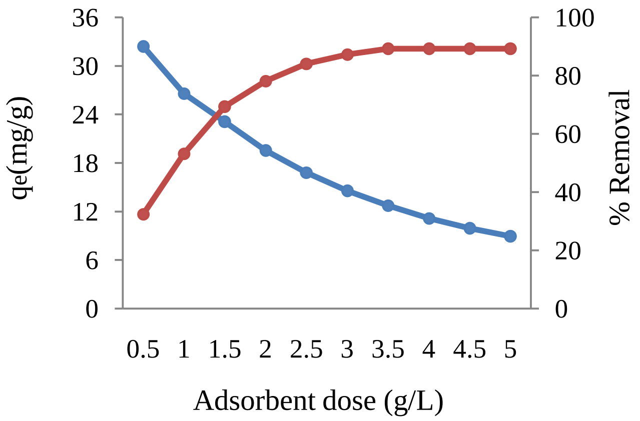

Figure 4: Effect of adsorbent dose (C_0 = 50 mg/L, pH=7, Contact time=75 min and Temp: 27 °C, adsorbent size =10 mesh and Stirring rate=200 rpm)

Effect of adsorbent particle size: The effect of different adsorbent particle sizes on percentage removal of dye is investigated and showed in Fig 5. It reveals that the adsorption of dye on tea powder decrease from 96.4 to 66.9% on coffee powder with the increased particle size from 10 mesh to 100 mesh at an initial concentration of 50 mg/L. The smallest size obtained was 10 mesh due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity [36].

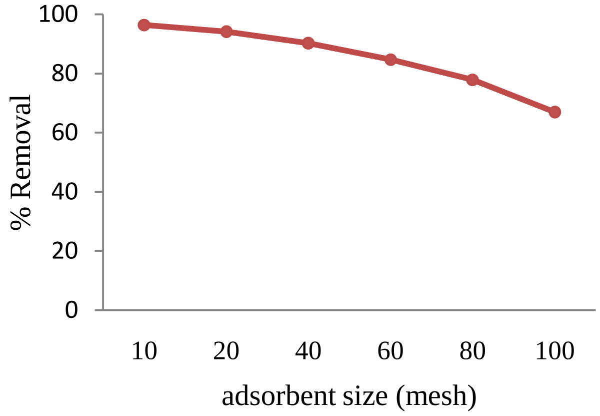

Figure 5: Effect of adsorbent particle size (C_0 = 50 mg/L, pH=7, Contact time=75 min and Temp: 27 °C, Stirring rate=200 rpm and adsorbent dose =3.5 g/L)

Adsorption isotherms

The adsorption data were analyzed using adsorption isotherm models, Langmuir and Freundlich.

The Langmuir model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The expression of the Langmuir model is given by the following equation [37, 38]:

$$q_e = \frac{q_{\max}\ b\ C_e}{1+bC_e}$$

Where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit mass of sorbent and dye concentration in solution at equilibrium, respectively. q_{max} is the maximum amount of the adsorbed dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e (mg/g), and *b* (L/mg) is a constant related to the affinity of the binding sites on the adsorbent surface.

The linear form of the Langmuir equation is written as follows [39,40]:

$$\frac{Ce}{qe} = \frac{1}{q_{\max}\ b} + \frac{Ce}{q_m}$$

A plot of (C_e/q_e) versus C_e should be a straight line with a slope of $1/q_{max}$ and intercept $1/q_{max}$ b (fig 6). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [41,42]:

$$R_L = \frac{1}{1+bC_0}$$

Where C_0 represents the initial concentration (mg/L) and b the Langmuir constant related to adsorption energy (l/mg). R_L value implies the shape of the isotherms to be either unfavorable (R_L), linear (R_L=1), favorable (O<R_L<1) or irreversible (R_L=0). As can be seen in Table 2, for the sorption system, R_L values at different temperatures are between 0 and 1, showing favorable adsorption (C_0=50 mg/L). All R_L values at different temperatures and concentrations were between 0 and 1.

The Freundlich model assumes heterogeneous adsorption due to the diversity of active sites on the surface. The Freundlich equation is expressed as [43,44]:

$$q_e = K_F\, C_e^{1/n}$$

Where K_F (mg/g) is an indicator of the biosorption capacity and 1/n (l/mg) is the biosorption intensity. A value for 1/n below one indicates a normal Frendlich isotherm while 1/n above one is an indicative of cooperative adsorption.

The linear form of the Freundlich equation is written as follows [45,46]:

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

Where the values of K_F and 1/n are determined from the intercept and slope of the linear regressions (Table 2). As seen, a very high regression correlation coefficient was shown by the Langmuir model. This indicates that the Langmuir model was very suitable for describing the sorption of disperse AR97 dye on Canola stalks.
The maximum capacity q_{max} determined from the Langmuir isotherm defines the total capacity of the Canola stalks for the dye as 19.8 mg/g sorbent. The fact that the Langmuir isotherm fits the experimental data compared to Freundlich isotherm may be due to the homogeneous distribution of active sites on the surface of sorbent.

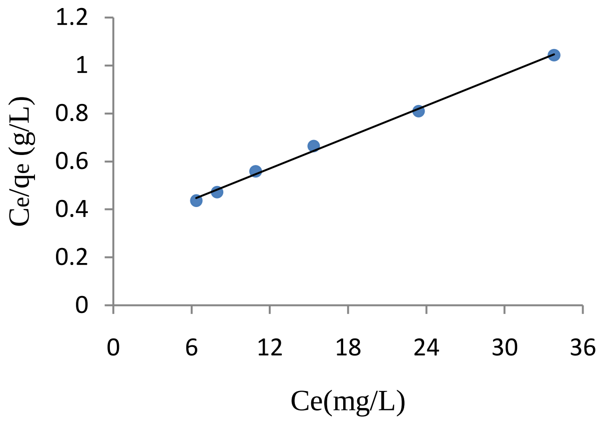

Table 2: Isotherms constants for the removal AR97 on Canola stalks

Langmuir model				**Freundlich model**		
q_m	R_L	b	R^2	n	K_F	R^2
19.8	0.594	0.028	0.992	3.44	1.086	0.934

Conclusion

The results of different experiments showed that Canola stalks has an ability to adsorb disperse AR97 dye from aqueous solutions. Different variables, such as contact time, adsorbent dose, adsorbent particle size, initial dye concentration and stirring rate influenced the adsorptive quantity. The sorption process was found to be adsorbent particle size and stirring rate dependent. The adsorption process has nearly reached equilibrium in 75 min. The experimental data ofadsorbing disperse AR97 dye are fit well to Langmuir isotherm model more than Freunlich model and the maximum adsorptive quantity of Canola stalks was 19.8 mg/g according to Langmuir model.

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