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Removal of dye from synthetic textile wastewater using agricultural wastes and determination of adsorption isotherm

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ABSTRACT

Reactive dyes have been applying extensively in textile industries. The treatment of textile industry waste waters is one of the main concerns of environmental health experts due to having excessive dyes and pollution. The aim of this study was to remove the Reactive Black 5 (RB5) dye from synthetic textile waste waters using agricultural wastes and determination of adsorption isotherm. In this research, *Glycyrrhiza glabra* root ash was prepared in laboratory condition and graded by standard sieve. The reactive Black 5 dye removals from textile synthetic wastewater using this adsorbent were tested. The effect of some parameters such as contact time (10–180 min), initial dye concentration (20, 40 and 60 mg/g) adsorbent dosage (0.2–2 g) and pH (2–12) were evaluated. Measurements were performed using an ultra violet-visible spectrophotometer at a wavelength of 597 nm and adsorption isotherm analyses were carried out. The results showed that data follow better the Langmuir adsorption model and the R_L = 0.1123 was in the range of 0 to 1. Adsorption efficiency was reduced with increasing initial dye concentration and decreasing the adsorbent dosage. According to the results, the remaining root as an agricultural waste showed proper efficiency economically for the removal of dyes from textile industry wastewater.

Keywords: Reactive dye; Adsorption isotherm; Agricultural waste; Synthetic; Textile industry

1. Introduction

Nowadays textile industries have expanded throughout the world so that produce about 10,000 different dyes with a global production of more than 700,000 tons per year consuming thousand types of chemical dyes [1]. The textile industry is one of the major consumers of water for various production processes between 25 and 250 m³ per ton of product based on the type of product [2]. According to the application, the dyes are divided into vat, reactive, direct, acidity, disperse and cationic. Azo reactive dyes are among the largest and most extensive water-soluble synthetic dyes that are most diverse in terms of type and structure [3]. The dyes in wastewater of these industries are usually resistant to biodegradation and are sustainable in the environment [4]. In addition, the dyes have adverse effects on aquatic organisms because of their toxicity [5]. They have been also considered as one of the most important threats to public and environmental health thorough the world due to their negative aesthetic impacts on drinking water quality, reducing the penetration of light into water and subse-

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quently causing disruption in the photosynthesis process in water resources and genetic mutations in human beings [6,7]. The reactive dyes have low affinity to be absorbed on the biomass in biological treatment because of the presence of sulfate compounds and their hydrophilic properties. These dyes have high molecular weight and aromatic rings and because of good flexibility, high reactivity, acceptable transparency, easy to use techniques and low energy consumption, used widely [8,9]. The reactive black 5 dye has four phenolic groups [10]. It is applied in industries such as textiles, paper, leather, printing of colored papers, plastics, pharmaceuticals and chemicals. The dyes are resistant to light, heat, biodegradation and conventional wastewater treatment methods because of their molecular structure[11]. Common methods of these treatments include ion exchange membrane, adsorption, coagulation-flocculation, electro dialysis, advanced oxidation, ultra filtration, photo catalytic decomposition and reverse osmosis [12,13].

The coagulation-flocculation technique is used to improve the removal of dye from industrial wastewater, but this method involves the production of large amount of sludge, which is difficult to disposal regarding the environmental standards [11]. Chemical methods are effective techniques for removal of dyes, but they lack economic justification and often produce unwanted side effects [14]. In addition, chemical processes have limited application in eliminating all types of dye, and the advanced oxidation process has high cost problems [15]. The adsorption process is favorable due to easy use, initial cost and non-sensitivity to toxic substances. Active carbon is the most commonly used adsorbent in absorbing organic compounds and heavy metals from aqueous solutions [16]. However, production of activated carbon has been reduced because of high costs and problems associated with the resuscitation of saturated adsorbents; the use of inexpensive adsorbents with high adsorption capacity has been developed in recent years [7]. Adsorbents containing natural, industrial and agricultural wastes such as corn, peat, chitin, fly ash, banana peel, orange peel and so on have been considered as useful adsorbents [12,14,17]. In the current study, *glycyrrhiza glabra* (licorice) root extract was used as adsorbent. Ash of this plant root was prepared in laboratory condition. This plant is found in East Azerbaijan, West Azerbaijan, Zanjan, Golestan, Kurdistan, North Khorasan, Fars and other provinces in Iran [18]. Remaining licorice after extraction is discarded as agricultural waste in industries [19,20]. In this study, this agricultural waste ash was evaluated as a low-cost adsorbent for the removal of reactive black 5 dye from synthetic wastewater in the textile industry.

2. Materials and methods

To prepare the adsorbent, *Glycyrrhiza glabra* root extract was initially prepared from the Rishmak Plant in Shiraz, washed with urban tap water to remove impurities and then rinsed with distilled water, and dried at 103°C for 2 h. Next, the dried material in the absence of oxygen was burned at 500°C for 2 h and subsequently passed through standard 60–200-mesh sieves for gradation. The adsorbent was stored in a sealed container until testing [12]. The reactive black 5 dye, which its characteristics are presented in Table 1, was used to provide a stock sample. One gram of this dye was weighed and transferred to a 1000-ml volumetric flask that was reached the volume with distilled water while stirring [20]. In the present study, each test included the preparation of 100-ml dye solution with initial concentrations (20, 40 and 60 mg/l) and certain pH values (2, 5, 7, 9 and 12). The 1N HCl and NaOH solutions were used to adjust the sample pH, and pH meter was utilized to measure the pH. Then, a certain amount of *Glycyrrhiza glabra* root ash (0.3, 0.5, 0.7, 1 and 2 g per 100 ml) was added to the solution and then was placed on a magnetic stirrer for mixing at 120 rpm for specified periods (10, 30, 60, 120, 180 min). A vacuum pump, buccaneer funnel and 0.45-µcellulose acetate filter were used to separate the adsorbent particles from the aqueous solution [21]. The final concentration of reactive black 5 dye was measured by the UV-2100 spectrophotometer at 597 nm. The dye removal percentage was calculated using the Eq. (1):

$$\text{Up} = \frac{\left(C_o - C_e\right)}{C_o} \times 100 \quad (1)$$

where C_0 and C_e are respectively the initial and final (after adsorption) concentrations. The concentration of RB5 dye absorbed at equilibrium was also determined using Eq. (2):

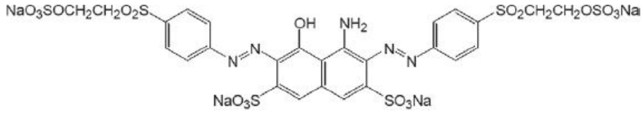
$$q_e = \frac{\left(C_o - C_e\right) \times V}{M} \quad (2)$$

where V is the volume of solution (l), and M is the used adsorbent dosage (g) [22].

The statistical method used in this study is Taguchi method. Linear regression analysis was also used to determine the adsorption isothermal equations.

The study of isotherms can describe how the adsorbent-adsorbate reaction can occur. In fact, isotherm provides the relationship between the dye concentration in the solution and the amount of absorbed dye at the solid-phase surface in condition that both phases be in equilibrium [7]. In this study, Langmuir and Freundlich

Table 1
Physicochemical characteristics of RB5 dye

Dye	Chemical formula	Maximum wavelength (nm)	Chemical structure	Molecular weight (g/mol)
Reactive black 5 dye	$C_{26}H_{21}N_5Na_4O_{19}S_6$	597		991.82

adsorption models were used to analyze the data consistency. Langmuir adsorption model suggests mono layer and uniform adsorption and the elimination of interactions between absorbed molecules. The linear Langmuir equation is as Eq. (3):

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3)$$

where the Langmuir constant of q_m and K_L are respectively the maximum adsorption capacity (mg/g) and adsorption intensity of adsorbent, which are obtained from the equation of $1/q_e$ vs $1/C_e$ diagram and relevant correlation coefficient (Fig. 5a).

Freundlich isotherm is obtained by assuming a heterogeneous surface with no uniform distribution of the adsorption heat on the surface; the linear Freundlich equation is Eq. (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where Freundlich coefficient (K_f) and Freundlich constant (n) depend on the capacity and intensity of the adsorption, which is determined by the linear log q_e vs. log C_e along with relevant correlation coefficient (Fig. 5b). The value of $1/n$ in the Freundlich equation describes the type of Freundlich isotherm. The type of relationship is given in Table 2 [23].

The values of the R_L dimensionless factor, which is called the separation coefficient, can be used to determine the validity of Langmuir isotherms. This relationship describes the type and shape of the adsorption isotherm, presented in Eq. (5) [24] The relationship between R_L and the Langmuir adsorption isotherm is given in Table 3.

$$R_L = \frac{1}{1 + \left(K_L C_0\right)} \quad (5)$$

Table 2
Relationship between the value of $1/n$ and the type of Freundlich isotherm

Isotherm type	Value
Optimal	$1/n$
Irreversible	$1/n = 0$
Non optimal	$1 < 1/n < 0$

Table 3
Relationship between the value of R_L and type of Langmuir isotherm

Isotherm type	Value
Non optimal Linear	$R_L > 1$
Optimal	$R_L = 1$
Reversible	$0 < R_L < 1$
	$R_L = 0$

3. Results and discussion

The assessment of initial dye concentration effect is given in Fig. 1. According to the obtained data, the dye removal efficiency using agricultural wastes was reduced by increasing the initial concentration from 20 to 60 mg/l in optimal values of pH = 2, adsorbent dosage of 2 g and contact time of 60 min. The highest efficiency (98.48%) occurred in 20 mg/l. Given the fact that the adsorption sites are constant for a certain level of adsorbent, the dye removal efficiency is decreased by increasing initial dye concentration. Amin (2009) also achieved the same result in removal of direct blue-106 dye from aqueous solution using activated carbons developed from pomegranate peel [25]. Jaafari et al. conducted a similar study entitled "Removal of Reactive Black 5 (RB5) dye from aqueous solution using adsorption onto activated red mud", and concluded that the dye removal efficiency is decreased by increasing pH and initial dye concentration [26]. Gök et al. in 2010 observed that the adsorption of the Reactive Blue 19 dye from aqueous solutions could be improved with increasing the adsorbent dosage [27].

Based on the results of this study, the dye removal efficiency is elevated with an increase in the adsorbent dosage from 0.2 to 2 g/100 ml, as shown in Fig. 2. The reason for such a phenomenon is the unsaturated active sites in the pollutant adsorption. In other words, some adsorption sites remain unsaturated during the adsorption process. Zhenget al. reported such results in 2007 [28]. In a study conducted by Wang et al. they have achieved the same results in this regard [29].

According to the results of this study, the dye removal efficiency was improved by prolonging the contact time, and the highest dye removal efficiency at different dye concentrations was observed in the first 60 min, then the adsorption efficiency became milder (Fig. 3). This phenomenon is due to the fact that in the early stages of adsorption, the dye molecules can be quickly absorbed on adsorbent surface, but the velocity of the pollutant adsorption as the initial adsorption phenomenon is vigorous which slows down as the process proceeds. Within the pores is decreased due to the repulsive force between the negative charges absorbed on the adsorbent surface and the negative charges in the fluid mass. Bazrafshan et al. obtained the same result in the removal of Reactive Red 198 using pistachio-nut shell ash, and the highest removal efficiency was achieved at the first 60 min [12]. Amin in 2009 also reported the consistent results [25].

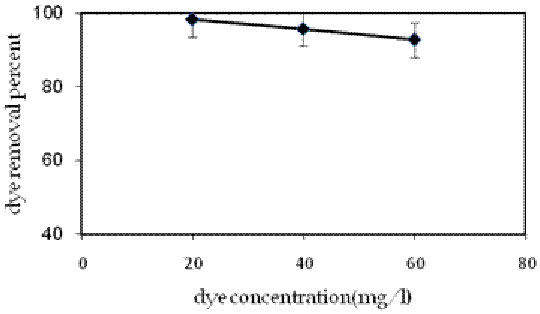


Fig. 1. The effect of initial dye concentrations from 20 to 60 mg/l on the dye removal efficiency.

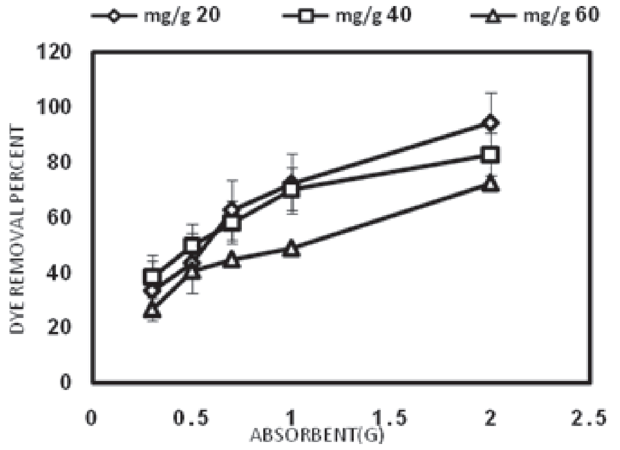


Fig. 2. The effect of adsorbent dosage from 0.2 to 2 g/100 ml on the dye removal efficiency at different dye concentrations.

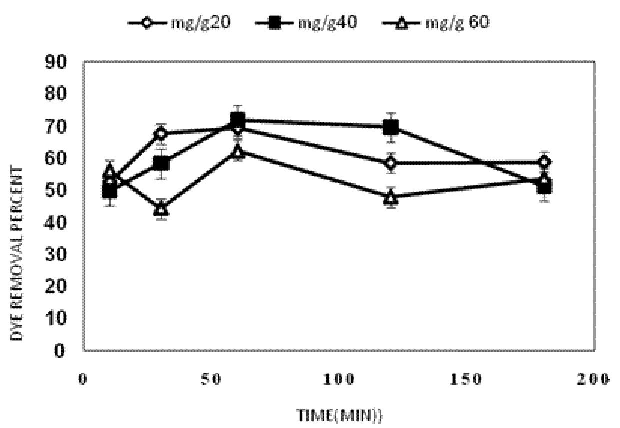


Fig. 3. The effect of contact time (min) on the dye removal efficiency at different dye. concentrations.

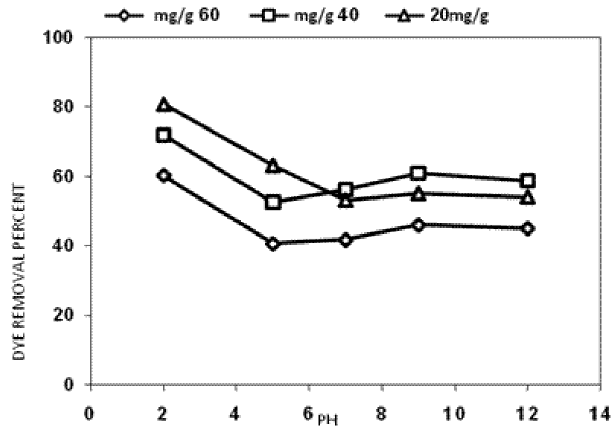


Fig. 4. The effect of pH on the dye removal efficiency at different dye concentrations.

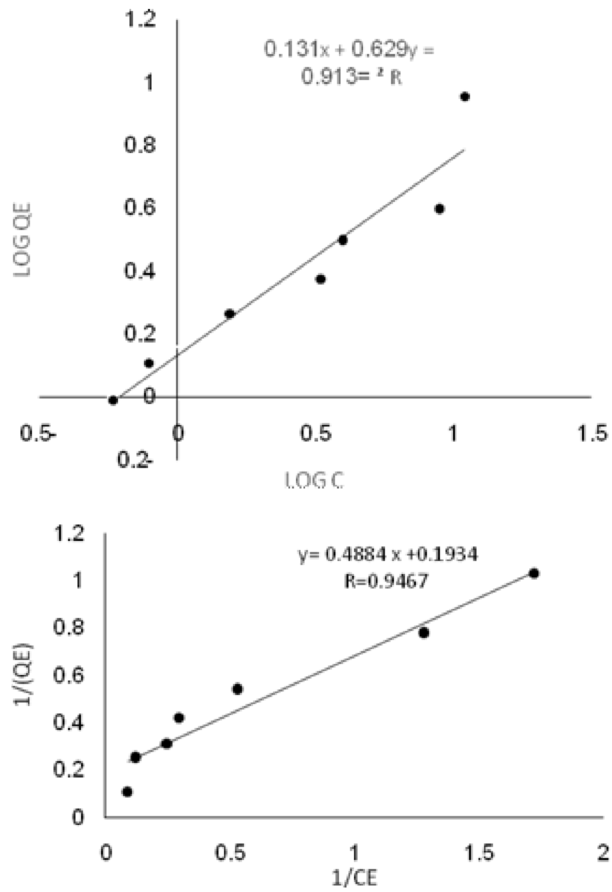


Fig. 5. Langmuir (a) and Freundlich (B) isotherm models.

pH is one of the important factors affecting adsorption process through influencing the dye structure. The results indicate that the dye removal efficacy at all three studied concentrations is reduced by increasing the pH values from 2 to 12 so that the highest removal efficiency at all concentrations occurred in the pH of 2 (Fig. 4). In fact, the solution pH is an important parameter in the adsorption process because can affect the adsorbent superficial charge, the ionization degree of various pollutants, the separation of functional groups on adsorbent active sites and the dye molecular structure. In acidic pH, adsorption bond sites involve with hydrogen ions acting as a bridge between the adsorbent surface and the dye molecules. The lower pH results in optimal conditions for the adsorption of reactive dye. Bouberka et al. reported in line results so that adsorption of acid orange 7 dye had been occurred in acidic pH [30].

The results of isothermal studies indicate high R^2 values in both the Freundlich and Langmuir equations, as seen in Fig. 5. These values reveal that the Langmuir model has a better fit with the removal of the Reactive Black 5 dye ($R^2 = 0.9467$), indicating the mono layer dye adsorption on the homogeneous surface of adsorbent. In the current study, according to the Langmuir model, the maximum adsorption capacity (q_m) for RB5 dye was calculated 5.17 mg dye per gram of the respective adsorbent. In this study, According to Eq. (5), the adsorption of RB5 dye on the adsorbent was calculated 0.1123. As seen in Table 3, this suggests the optimal adsorption of RB5 on the *Glycyrrhiza glabra* root ash. As shown in Table 4, 1/n is 0.6292 close to unit value that indicates the adsorption process in appropriate experimental conditions. The results of each isotherm are presented in Table 4. The studies of Gulnaz

Table 4
Equations, constant coefficients and correlation coefficients of isotherms in RB5 dye removal using *Glycyrrhiza glabra* root ash

Adsorption isotherm	Adsorption equations	Isothermal constant and correlation coefficients		
Langmuir	$\frac{1}{q_e}=\frac{1}{q_m K_L C_e}+\frac{1}{q_m}$	$q_m(mg/g)$	K_L	R^2
		5.17	0.395	0.9467
Freundlich	$\text{Log } q_m = \text{Log } K_f$	K_f	$1/n$	R^2
	$\frac{1}{n}\log C_e$	0.1315	0.6292	0.9131

et al., Yousefi et al. and Mesdaghinia et al. confirm a better fit of results with Langmuir isotherm [31,32].

4. Conclusion

The results obtained from the present study demonstrated that the increased adsorbent dosage can improve the dye removal efficiency, and the change in the initial pollutant concentration is one of the other factors affecting the adsorption efficiency. Based on the results, the dye removal efficiency was decreased with increasing the initial dye concentration from 20 to 60 mg/l. The pH = 2 showed the maximum removal efficiency at all three selected concentrations. The data of the RB5 dye adsorption on the industrial products and agricultural wastes indicated that the dye adsorption follows the Langmuir isotherm. The optimal dye removal efficiency (98.48%) was obtained at pH of 2, the adsorbent dosage of 2 g and the initial dye concentration of 20 mg/l. In the present study, the use of this adsorbent as an agricultural or industrial waste was evaluated suitable, novel and in expensive adsorbent for the removal of textile dyes. This adsorbent was able to remove optimally the polluting dyes and other water-soluble contaminants from synthetic textile wastewater and aqueous solutions. Due to the ease of adsorbent preparation and the proper efficiency of this process in reactive dye removal from synthetic textile wastewater, this method can be employed in large scale of water and wastewater treatment.

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