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Original Article

Application of Licorice-derived Activated Carbon in Tannery Wastewater Treatment

Toktam Shahriari*, Hojat Kangazian and Behnoush Aminzadeh Goharrizi

Department of Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran

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***Corresponding author**
tshshahriari@ut.ac.ir,
ORCID: 0000-0001-9568-1731

ABSTRACT

This study used licorice-derived activated carbon to absorb chromium and COD from tannery wastewater. Wastewater used in this research was prepared from Charm Shahr Industrial Estate. First, licorice was converted into activated carbon using zinc chloride as an activator. The licorice-derived activated carbon was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) analysis. Licorice-derived activated carbon was then used to adsorb Cr and COD from tannery wastewater. Factors affecting the adsorption rate, including pH, adsorbent dosage, contact time, and temperature, were investigated. The optimal conditions were pH=7 and adsorbent dosage of 2 g/100 ml. Also, the test time of 30 minutes was determined as the optimal time. Licorice-derived activated carbon adsorbed 99.93% and 99.22% of Cr (III) and COD, respectively. According to the results, Cr and COD adsorption by licorice-derived activated carbon followed the Freundlich isotherm. In addition, Cr and COD adsorption by licorice-derived activated carbon followed the pseudo-second-order kinetic model.

INTRODUCTION

Leather industries always discharge large volumes of wastewater into the environment because of high water consumption in the tanning operation, considerably contaminating surface and underground water resources, changing water's physical and chemical quality, and disturbing the water ecosystem [1]. Discharging large amounts of heavy metals to the environment through industrial wastewater seriously threatens water ecosystems. Chromium is a heavy toxic metal in relatively stable and almost dominant three- and six-valent oxidation states [2]. The difference in the oxidation state of chromium affects its chemical properties and toxicity in water [3]. Several methods are available to remove chromium species from wastewater [4]. Among these methods, adsorption [5-7] is very important due to its simplicity and low cost. Numerous studies have been conducted on using various natural materials for the removal of chromium, such as modified potato starch [8], chitosan [9], shrimp shell [10], and polymeric nanofibers [11]. This study investigated pollutant adsorption by licorice-derived activated carbon. Licorice is a traditional medicinal plant that grows in various world regions. It is particularly important due to its root and rhizome's vital nutritional and medicinal compounds. Glycyrrhizin is the main substance found in licorice roots, causing the sweetness of its roots.

The therapeutic value of licorice is related to its anti-cough, anti-diabetes, and antiviral properties. Moreover, some compounds in licorice have anticancer properties, and some inhibit enzymes [12]. Fat-reducing compounds and flavonoids with strong antioxidant activity have been found in licorice [13]. This research used licorice-derived activated carbon to remove chromium and COD from tannery wastewater. The effects of pH, adsorbent dosage, contact time, and temperature to achieve maximum removal were investigated.

MATERIALS AND METHDOS

Wastewater used in this research was prepared from Charm Shahr Industrial Estate. The chromium concentration in the wastewater was determined by ICP-OES. Table 1 reports the analysis results for the heavy metal and other parameters. Licorice stems and leaves were prepared and washed several times to prepare activated carbon.

Table 1 Tannery wastewater characteristics

Parameter	Amount
Cr^{3+} (mg/l)	4664.2
COD (mg/l)	5400
pH	3.25

The stems and leaves were dried at ambient temperature for one week. After that, the licorice stems and leaves were crushed, and 500 g of crushed licorice stems and leaves were placed in $ZnCl_2$ solution (weight ratio: 1:2) for 24 h, then dried in an oven at 110 °C for 24 h. The prepared sample was carbonized in a furnace under N_2 gas flow for 1 h. The resulting product was washed with distilled water and soaked in a 3 M HCl solution for 2 h to remove residual Zn from carbon pores. After separating the solution, the activated carbon was washed with distilled water. The obtained activated carbon was dried in an oven at 110 °C, and mesh #500 was used for particle sizing [14]. Carbonization was performed at the Central Laboratory of Isfahan University.

The specific surface area of the produced activated carbon was measured by BET analysis. The licorice-derived activated carbon showed a specific surface of 1.0585 m^2/g before activation. Table 2 shows its characteristics after activation. The BET analysis was performed at the Basic Science Lab of Tarbiat Modarres University.

Table 2 Characteristics of licorice-derived activated carbon

Activated carbon	Density (g/cm^3)	Specific surface area (m^2/g)	Pore volume (cm^3/g)
-	1000	144.3774	0.003139

Figure 1 shows the porous structure of licorice resulting from its cellular structure and activation by zinc chloride. The pores in this figure allow adsorbates to access the internal surfaces of the adsorbent.

This study investigated Cr and COD adsorption from wastewater by licorice-derived activated carbon. The experiments were repeated three times to ensure their accuracy and precision.

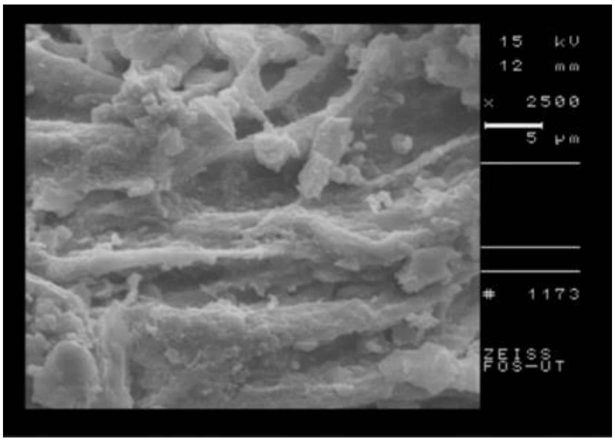

Fig. 1 SEM image of licorice-derived activated carbon

RESULTS AND DISCUSSIONS

The adsorption experiments were carried out at different pHs to determine the optimal pH for maximum adsorption. After that, the effects of adsorbent dosage, temperature, and contact time were examined.

In pH experiments, 1 g adsorbent was used in 100 ml wastewater at 25 °C for 60 min (contact time). As shown in Fig. 2, the adsorption rate increases with increasing pH. Hydroxide ions on the adsorbent surface cause attractive electrostatic interactions between the positive ions and negative ions.

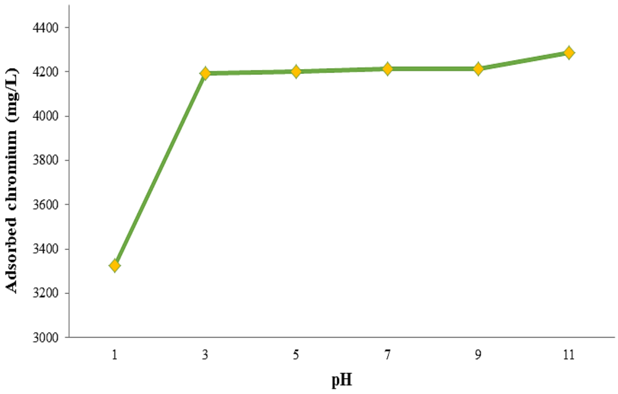

Fig. 2 Effect of pH on Cr adsorption by licorice-derived activated carbon

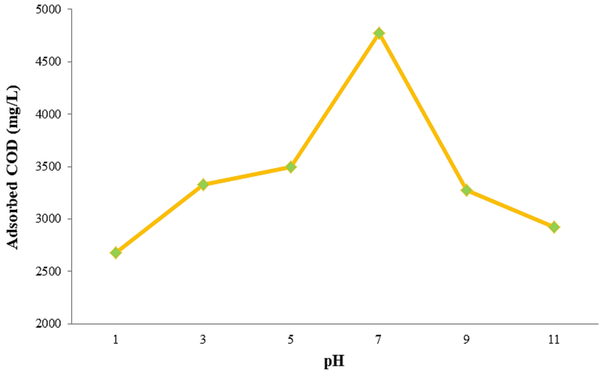

Fig. 3 Effect of pH on COD removal by licorice-derived activated carbon

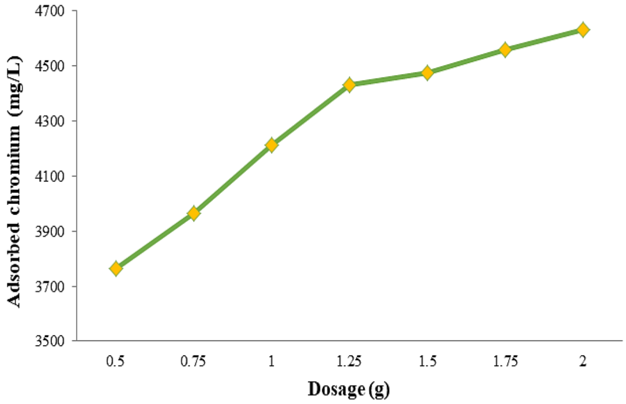

Fig. 4 Effect of adsorbent dosage on Cr adsorption by licorice-derived activated carbon

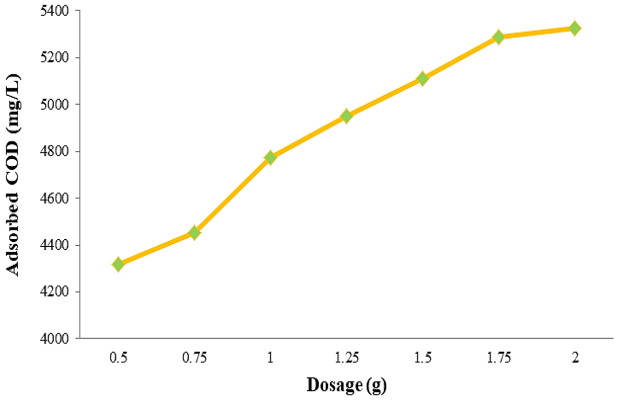

Fig. 5 Effect of adsorbent dosage on COD removal by licorice-derived activated carbon

The results show that pH variation affects Cr adsorption as it determines the ionic type of Cr and adsorbent surface charge. It also affects the reaction between the adsorbent and adsorbate [15].

pH is a critical factor in degrading organic matter in tannery wastewater [16]. As shown in Fig. 3, COD removal first increases with increasing pH and then decreases at high pHs, which depends on the nature of organic compounds in the wastewater.

Considering the optimal pH for Cr adsorption and the nature of wastewater, COD removal, and discharge standard, a pH of 7 was considered for the rest of the experiments.

The experiments were performed at pH=7 and 25 °C for a contact time of 60 min in 100 ml wastewater to study the effect of adsorbent dosage. As shown in Fig. 4, Cr adsorption efficiency increases with increased adsorbent dosage (activated carbon) due to increased surface area. Figure 5 shows an increase in COD removal with increasing the adsorbent dosage.

Generally, the results of other studies show that the removal percentage increases with increasing the adsorbent dosage due to increased adsorption surface area and binding sites [17].

Due to the large amounts of pollutants in the studied wastewater, 2 g of the adsorbent was used for the rest of the experiments. Solution temperature is among the factors affecting the adsorption process. This parameter affects physical adsorption further and changes interactions. In this stage, experiments were carried out at pH=7 using 2 g adsorbent in 100 ml wastewater for a contact time of 60 min.

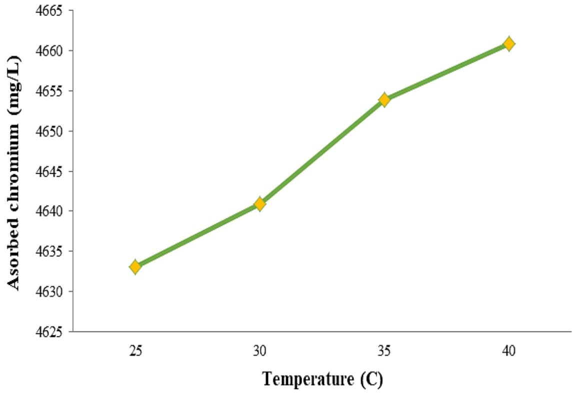

Fig. 6 Effect of temperature on Cr adsorption by licorice-derived activated carbon

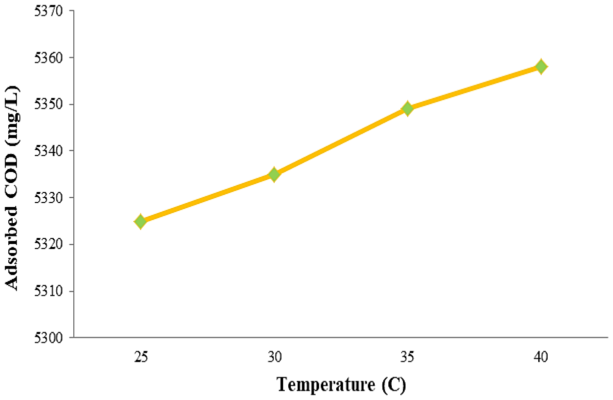

Fig. 7 Effect of temperature on COD removal by licorice-derived activated carbon

As shown in Figs. 6 and 7, adsorption is an endothermic process and increases with increasing temperature.

Ahsan *et al.* studied the effect of temperature in a wastewater treatment with natural materials and wastes on removing suspended solids, phosphate, nitrate, ammonium, and COD. According to their results, the removal of suspended solids and COD increased when the temperature increased from 20 to 50 °C [18].

Temperature rise in discharging wastewater to the environment is considered a pollutant that consumes energy. Accordingly, experiments were carried out at 25 °C to examine the effect of contact time on adsorption.

The experiments were performed at pH=7, adsorbent dosage of 2 g in 100 ml wastewater and 25 °C to determine the optimal contact time. According to the results, the pollutant was first removed quickly but decreased with time and reached equilibrium. This phenomenon can be due to the large number of vacant sites available at the early stages of adsorption.

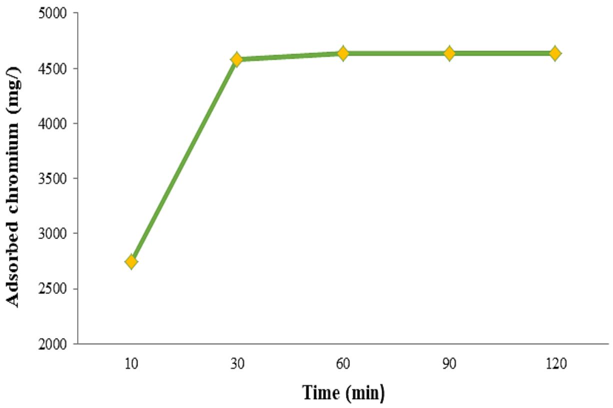

Fig. 8 Effect of contact time on Cr adsorption by licorice-derived activated carbon

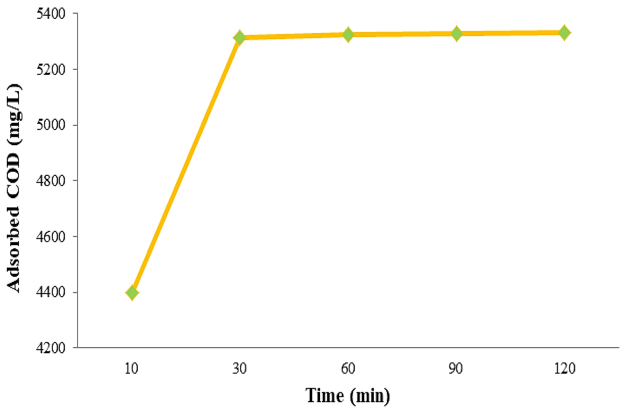

Fig. 9 Effect of contact time on COD removal by licorice-derived activated carbon

As shown in Figs. 8 and 9, pollutant adsorption by licorice-derived activated carbon reaches equilibrium after 30 min.

The adsorption kinetics was studied by linear analysis using pseudo-first and second-order equations.

The pseudo-first and second-order models are as follows:

Equations 1 and 2 show the pseudo-first and second-order equations, respectively.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (1)$$

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

Where q_e and q_t represent adsorbed pollutants at equilibrium and time t, and k_1 and k_2 are the constants of the pseudo-first and second-order reactions, respectively [19]. Figures 10 and 11 show the pseudo-first and second-order adsorption kinetics for Cr, respectively. Figures 12 and 13 show the pseudo-first and second-order adsorption kinetics for COD adsorption by licorice-derived activated carbon.

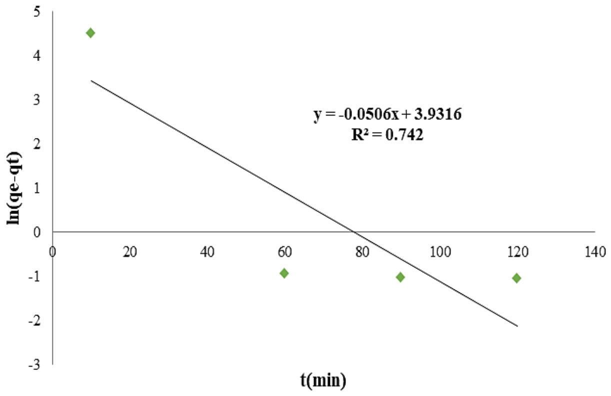

Fig. 10 Pseudo-first-order kinetics of Cr adsorption by licorice-derived activated carbon

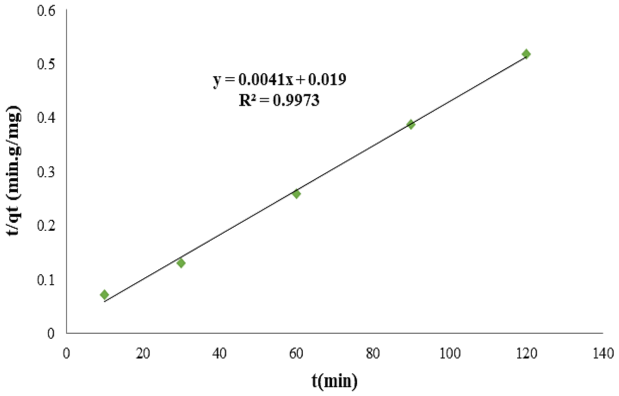

Fig. 11 Pseudo-second-order kinetics of Cr adsorption by licorice-derived activated carbon

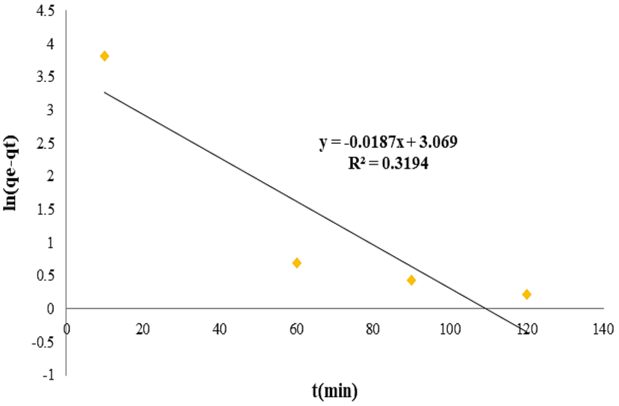

Fig. 12. Pseudo-first-order kinetics of COD adsorption by licorice-derived activated carbon

As shown in Figs. 10-13, the Cr and COD adsorption kinetics by licorice-derived activated carbon follow the pseudo-second-order model.

Langmuir and Freundlich isotherms were used to better understand data obtained from adsorption experiments.

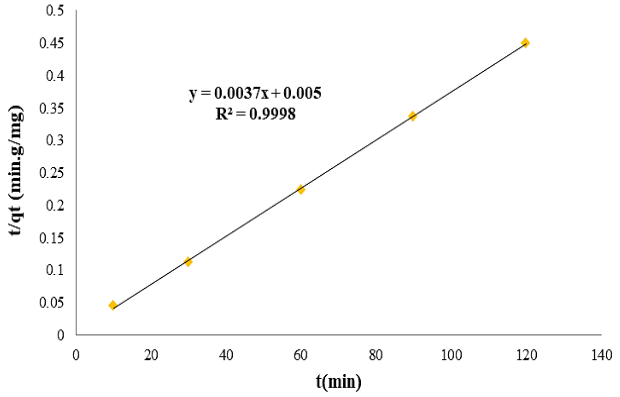

Fig. 13 Pseudo-second-order kinetics of COD adsorption by licorice-derived activated carbon

These isotherms can evaluate the relationship between adsorption capacity and adsorbent concentration at equilibrium [20, 21]. Equation 3 shows the linear form of Langmuir isotherm.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{b.q_m}\right)\frac{1}{C_e} \qquad (3)$$

Equation 4 shows the linear form of Freundlich equation.

$$q_e = K\,C_e^{\frac{1}{n}} \qquad (4)$$

Where q_e is the ratio of adsorbate to adsorbent mass at equilibrium, q_m is the maximum adsorption rate, C_e shows the adsorbate concentration at equilibrium, b is Langmuir constant, and K and n are Freundlich constants [19].

Figures 14 to 17 show the Langmuir and Freundlich isotherms for Cr and COD adsorption by licorice-derived activated carbon. Comparing Figs. 14 to 17 show that Cr and COD adsorption by licorice-derived activated carbon follows the Freundlich isotherm. Comparing Cr adsorption by licorice-derived activated carbon and eggshell [22] shows the high adsorption capacity of licorice-derived activated carbon.

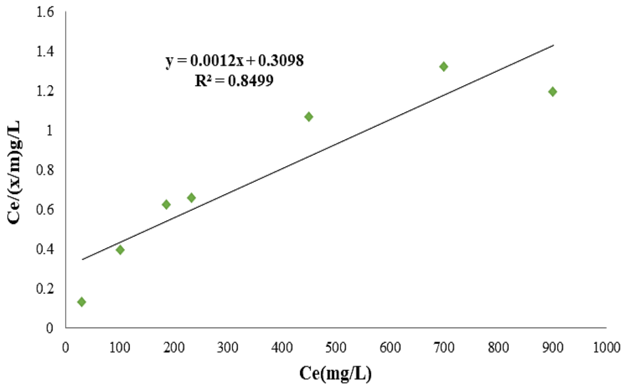

Fig. 14 Langmuir isotherm for Cr adsorption by licorice-derived activated carbon

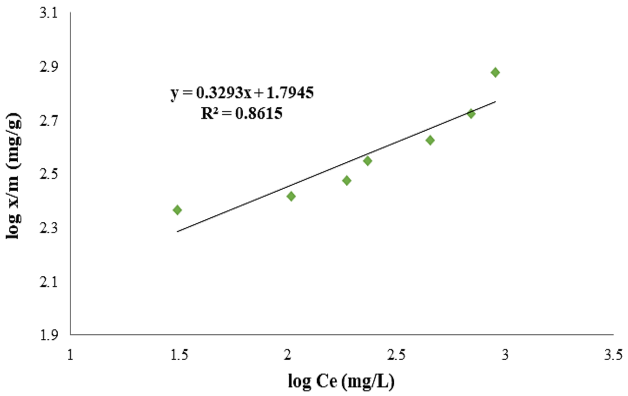

Fig. 15 Freundlich isotherm for Cr adsorption by licorice-derived activated carbon

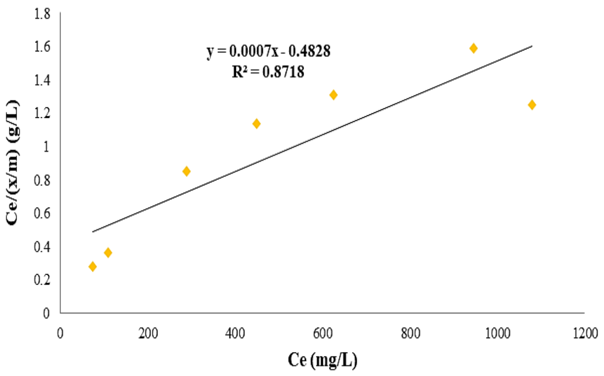

Fig. 16 Langmuir isotherm for COD adsorption by licorice-derived activated carbon

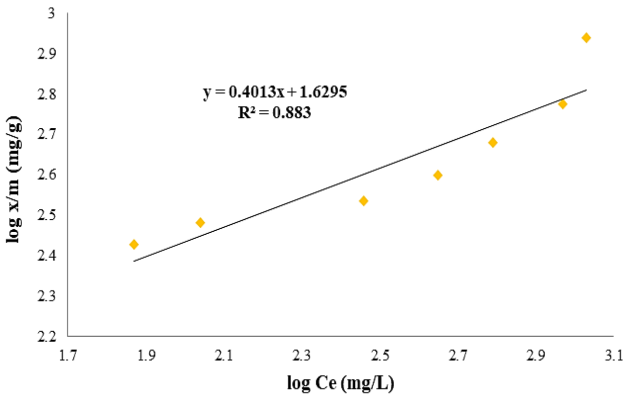

Fig. 17 Freundlich isotherm for COD adsorption by licorice-derived activated carbon

Moreover, COD removal by activated carbon derived from palm wastes [23] compared to licorice-derived activated carbon indicates that licorice-derived activated carbon is a good adsorbent for pollutants.

CONCLUSION

Licorice is a medicinal plant that grows in various regions of the world, including Iran. Glycyrrhizin is the main substance found in licorice roots, causing the sweetness of its roots. Licorice roots have therapeutic properties due to the presence of various compounds. Activated carbon was prepared from licorice stems and leaves to manage the environment and used as an adsorbent to remove pollutants in tannery wastewater. Among the factors affecting pollutant adsorption are pH, adsorption dosage, and contact time. The experiments also showed that the adsorption reaction was endothermic. Generally, the results showed the high adsorption capacity of licorice-derived activated carbon in removing pollutants from tannery wastewater. It is suggested to use licorice-derived activated carbon in other industrial wastewater treatments in future research.

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