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Cr(VI) adsorption on a thermoplastic feather keratin film

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ABSTRACT

Feather is a kind of waste and hardly to be degraded in the environment. Thermoplastic film was made from feather by mechanical method with enhancing the temperature and pressure to 160˚C, 5 MPa, respectively. Glycerol was added as plasticizer in various amounts in mass ratio of 10, 20, 40, 60, and 80%, respectively. During film preparation, influence glycerol content on film's mechanical property was studied, and 40% was chosen as the best ratio. Film with the best mechanical property was used to adsorb Cr(VI) in aqueous solution. Effects of temperature, adsorbent dosage, initial concentration, and pH on adsorption were studied. The adsorption was endothermic and fitted to both Langmuir and Freundlich models, and the process contained both physical and chemical adsorptions. The biggest removal rate was 99.1%, and the best absorption capacity was 75.45 mg/g at 60˚C. After adsorption, there appeared many particles on the surface of the film that can be seen in SEM. FT-IR was used to study the chemical group changes between the films before and after adsorption.

Keywords: Feather; Wastewater; Cr(VI); Adsorption

1. Introduction

Adsorption method is the most commonly used method in pollutant removal from wastewater. Chromium (Cr) was ranked as the top 16th most toxic pollutants as its mutagenic and carcinogenic effects which mainly come from metal finishing industry and steel industry [1,2]. Chromium has been exist in two forms in water, which is Cr(III) and Cr(VI), and Cr(VI) has higher toxicity than Cr(III). Nowadays, there is an increasing interest in utilizing agriculture wastes for adsorption as they are renewable resource. Adsorption pollutants especially heavy metals and organics in water based on feather has plenty of developments, such as adsorption for brilliant blue [3], phenol [4], Cu^{2+}, Cr^{6+} [5], and As^{3+} [6]. Raw feathers can be used to adsorb organic pollutants in wastewaters [7], and moreover, in our previous studies, keratin film made from feather by chemical reduction method showed good adsorption capability for Cr(VI) of 148.8 mg/g [8].

Feather wastes are hardly to be degraded in the environment and their pollution is more serious with poultry production increased these years, and they are composed basically of keratins and contain abundant disulfide linkage [9]. However, there are short of effective ways to depose it [10]. Methods for

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abstracting keratin from feathers are mechanical methods, chemical methods, and biological methods. The end products in biological methods are mainly amino acids and are applied to feed addition which cannot create much value. The warm points are abstracting protein of higher molecules through chemical method, and the protein can be used in high-tech and biotechnology area. Mechanical method is the simplest among the three methods, which made feathers into films through warming and forcing, as feathers contain abundant keratins they have great ability to from films, but the investigations are mainly focus on the mechanical behavior of the thermoplastic keratin film, rarely research reports the film's adsorption property.

To deal with the feather's dispersity, we use the thermoplastic keratin film from mechanical method for the adsorption of Cr(VI) in the water, which has rarely been investigated around the world yet. Influence of glycerol content on the film's mechanical character was investigated, and the film with the best glycerol content was used as the adsorbent for Cr(VI) adsorption. Important factors for adsorption, such as temperature, initial concentration, and adsorbent dosage, were studied. The adsorption process was fitted with the most typical adsorption isotherms models—Langmuir model and Freundlich model. Scanning electron microscopy (SEM) and Nicolet fourier transform-infrared spectroscopy (FT-IR) spectrometer were used to investigate the physical and chemical changes of the film before and after adsorption.

2. Materials and methods

Feather powders were purchased from a local feather powder processing company. All the chemicals were analytic pure.

2.1. Film preparation

Feather powder and glycerol were mixed together and put in semi-automatic pressure molding machine (YX-25(O)) for 3 min under 160℃ 5 MPa. Mechanical character of the film was tested by Fiber strong stretch instrument XQ-1. Thickness was tested by thickness tester YG 141N.

2.2. Adsorption experiment

About 0.5658 g potassium dichromate ($K_2Cr_2O_7$) was dissolved in distilled water to 1 L and got a 200 mg/L Cr(VI) solution for dilution. Cut the film into pieces of corresponding qualities, put each piece into each 100 -mL flask contained 40 mL Cr(VI) solution of corresponding concentration. Adsorption experiments were conducted on a shaker with setting temperature at 80 rpm for 5 h, then vacuum filtration the solution for solid–liquid separation. Changes of the film before and after adsorption were tested by Nicolet fourier transform-infrared spectroscopy (FT-IR) spectrometer and JSM-5600 LV SEM. Cr(VI) concentration was detected by UNICO UV-2802-PCS spectrophotometer using diphenylcarbazide spectrophotometry method (National standard of the People's Republic of China: GB 7467-1987).

Remove rate and adsorption capacity were calculated according to the following equations:

$$\text{Remove rate} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$\text{Adsorption capacity } (q_e) = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 the initial concentration, C_e the equilibrium concentration, W adsorbent dosage, V the solution volume.

3. Results and discussion

3.1. Mechanical character of the film

The feather powders were mixed with glycerol of mass ratio 10, 20, 40, 60, and 80%, respectively, the mixtures were put semi-automatic pressure molding machine under 160℃ 5 MPa for 3 min, and the thermoplastic keratin film can be obtained. The film with 80% glycerol was very dense in the end and form fragments after 5 min and were not able to test the mechanical character. From the result of glycerol content on the film's breaking strength in Fig. 1, we can see that film with glycerol of 40% content had the

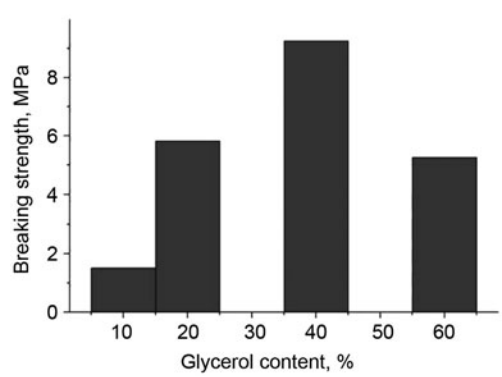

Fig. 1. Effect of glycerol content on breaking strength (glycerol content 160℃, 5 MPa, 3 min).

highest breaking strength, and we chose films under this condition to operate the adsorption experiment. Thickness of the film was 2.032 mm, and we cut the film into chips of specific mass.

3.2. Effect of temperature on uptake of Cr(VI)

Effect of temperature on the film was operated with initial concentration 100 mg/L, solid to liquid ratio 12.5 mg/L, and from the result of effect of temperature on adsorption in Fig. 2, it can be seen that removal rate was increased firstly and then decreased with temperature rising and the highest removal rate emerged at 60℃. We also found that at 100℃, the film was softer after the adsorption process which may destroy the surface adsorption function and desorption. As the film was mainly consist of keratin and high temperature may cause protein denaturation, 60℃ was the best temperature for this process which can keep the film's structure stable and ensure the removal rate at the same time.

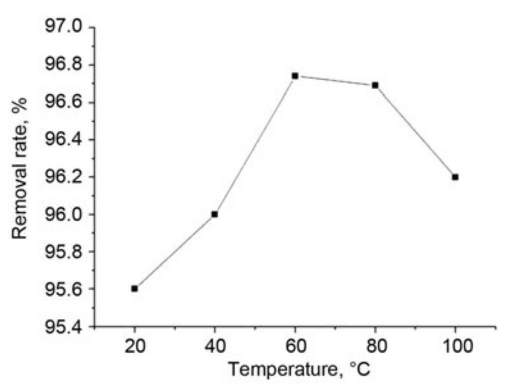

Fig. 2. Effect of temperature on adsorption (initial concentration 100 mg/L, solid to liquid ratio 12.5 mg/L, pH 7).

3.3. Effect of adsorbent dosage on uptake of Cr(VI)

The effect of adsorbent dosage on adsorption was operated in initial concentration 100 mg/L, 60℃ in 40 mL solution. Adsorbent dosages were 0.05, 0.1, 0.2, and 0.5 g. From the result, we can see that with the adsorbent dosage rising, removal rate increased as in Fig. 3(a) and the adsorption capacity decreased as in Fig. 3(b). It was because more adsorbent addition created more adsorption points for Cr(VI) which was good for the total removal result, but the adsorption chance for unit area reduced which was bad for the adsorption capacity. What is more, more adsorbent can larger the resistance in the transportation process between adsorbent and adsorbents and the electrostatic repulsion between them also enhanced [11,12]. Under this condition, the highest removal rate was 99.1%, and the highest adsorbent capacity was 75.45 mg/g which indicated the film can be a potential adsorbent for Cr(VI) in wastewater. The result showed that after 0.1 g the removal rate increased slower and the adsorption capacity decreased obviously, so that 0.1 g was the most economic additive amount under this condition in 40 mL solution.

3.4. Effect of initial concentration on uptake of Cr(VI)

The effect of initial concentration was studied in 60℃, solid to liquid ratio 2.5 mg/L, pH 7, from the result in Fig. 4 stated that the removal rate increased with the initial concentration increased, indicating that the adsorbent has higher potential to treat high concentration Cr(VI) wastewater, as the industrial wastewaters always have high concentrations, the film has large potency to be used in practical application.

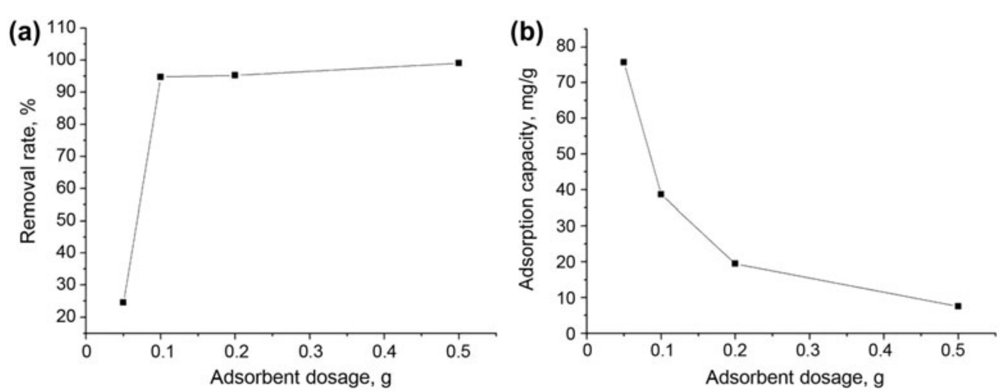

Fig. 3. Effect of adsorbent dosage on adsorption (initial concentration 100 mg/L, 60℃, 40 mL, pH 7): (a) effect of adsorbent dosage on removal rate; (b) effect of adsorbent dosage on removal rate.

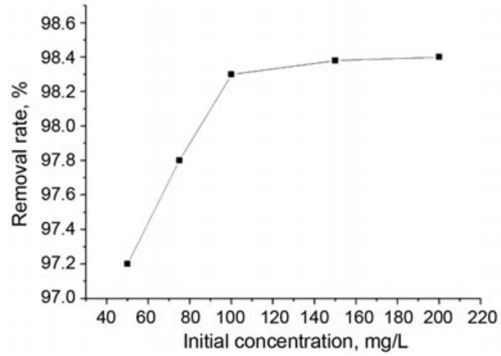

Fig. 4. Effect of initial concentration on adsorption (solid to liquid ratio 2.5 mg/L, 60℃, pH 7).

3.5. Effect of pH on uptake of Cr(VI)

The effect of pH was studied in 60℃, solid to liquid ratio 2.5 mg/L, initial concentration 100 mg/L, from the result in Fig. 5, we can see that the removal rate increased with pH increased before pH 7 and decreased in higher pH, this may be related to the protein degeneration besides neutral condition, and the surface adsorption was destroyed to some extent. From the result, we can also see that the removal rate in acid condition was better than alkalinity condition, it was related to the Cr existence form changes in this process, the film's surface was less positive in higher pH and the binding of anionic Cr(VI) ion species was weaken and lead to a lower removal rate [13]. So the best pH was neutral.

3.6. Adsorption isotherms

Adsorption was correlated with Langmuir and Freundlich isotherms that are commonly used for describing adsorption, which are given by the following equations:

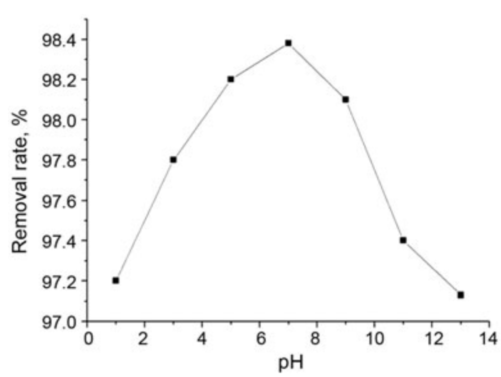

Fig. 5. Effect of pH on adsorption (solid to liquid ratio 2.5 mg/L, 60℃, 100 mg/L).

$$\frac{c_e}{q_e} = \frac{1}{q^0} + \frac{c_e}{q^0} \tag{3}$$

$$\lg q_e = \lg k + \frac{1}{n} \lg c_e \tag{4}$$

In the model, q^0, k, b, n are constants, q_e is adsorption capacity (mg/g), C_e is equilibrium concentration (mg/L).

From the result shown in Fig. 6, we can see that this adsorption process satisfied both isotherms with correlation coefficient 0.9631 and 0.9074, the better imitative effect with Langmuir isotherm had been reported by many other investigations on Cr(VI) adsorbent made from agriculture waste [14–16].

From the Freundlich isotherm fitting result, it can be calculated that n^{-1} was 0.3777 which accounted for that this adsorption was easy to go on [17]. From the result that the process fitted Langmuir isotherm, we can come to the conclusion that this process was monolayer adsorption and also indicated that the sponge surface had good homogeneity.

3.7. Microstructure changes before and after adsorption

Changes of the film's microstructure before and after adsorption were tested by SEM as in Fig. 7, it can be seen that after adsorption there appeared many particles on the surface of the film, and the film turned to be smoother after adsorption, indicating

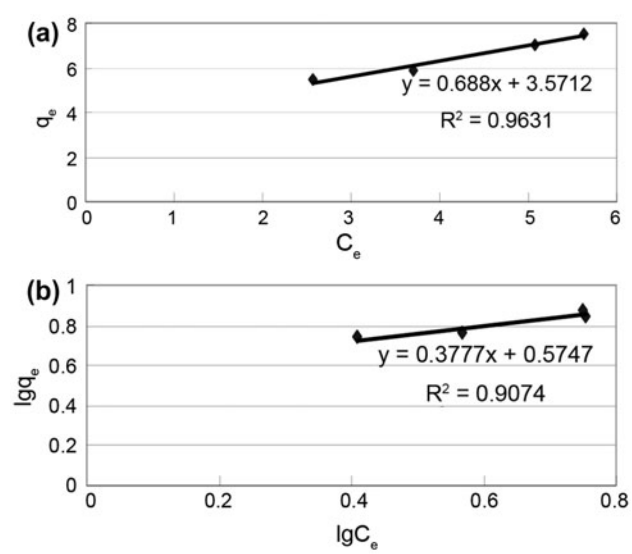

Fig. 6. Adsorption isotherm fitting (60℃, 5 h, solid to liquid ratio 2.5 g/L): (a) Langmuir model; (b) Freundlich model.

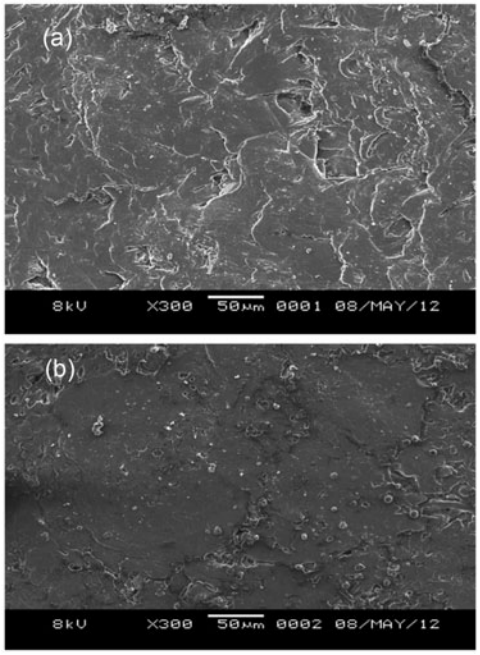

Fig. 7. SEM pictures of keratin film (a) before and (b) after adsorption.

chemical changes took place in this adsorption process. As it was known that proteins can occur complex reaction with heavy metals, the chemical changes may be the oxidation of keratin by Cr(VI) [18].

3.8. Changes of functional groups before and after adsorption

It can be seen from FT-IR pictures as in Fig. 8 that after adsorption many peaks weakened clearly

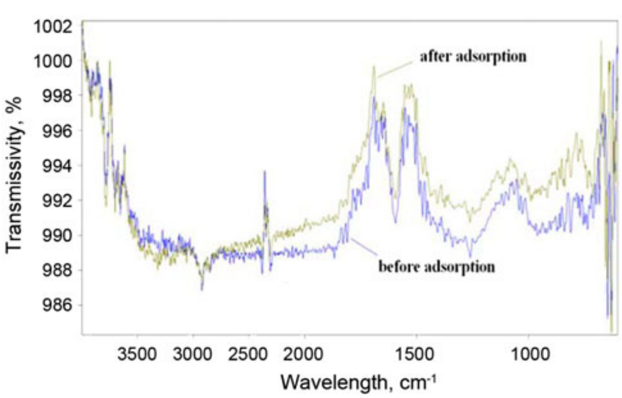

Fig. 8. FT-IR pictures of keratin film before and after adsorption.

demonstrated that chemical reaction occurred in this process, but the position of the peaks had little change indicated that physical reaction was in dominate. Peaks around 1,600 cm^{-1} were C=O stretching vibration and peaks around 1,300 cm^{-1} were O–H bending vibration, they all got slacker after adsorption, the reason may be they were oxidized by Cr(VI) in adsorption process.

4. Conclusions

Feather wastes were successfully made into thermoplastic feather keratin film and applied in Cr(VI) adsorption. Film with 40% glycerol content had the best mechanical character in 160℃. Various parameters were evaluated on the Cr(VI) removal by the film with the best mechanical character. The best pH was neutral, and acid condition was better than alkalinity condition, removal rate increased with temperature rising and the best temperature was 60℃, under higher temperature the film became soft which indicating the destruction of the protein structure. Under the best condition, highest removal rate was 99.1%, and the highest adsorbent capacity was 75.45 mg/g which indicated the film can be a potential adsorbent for Cr(VI) in wastewater. The results fitted to Langmuir model and Freundlich model, and the result with Freundlich was better, reaction in the adsorption contained both physical and chemical process and physical was in dominant, indicating that sponge surface had good homogeneity and complex reaction played important role in the adsorption. After adsorption, there appeared many particles on the surface of the film, and the film turned to be smoother after adsorption. Chemical bonds such as C=O and O–H got slacker after adsorption. Therefore, feathers, which were a wastes but also an abundant protein resource, may be a good choice of low-cost material for Cr(VI) adsorption, and using film for adsorption was easier for solid–liquid separation.

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