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Adsorption Behaviors of Cr(III) on Carboxylated Collagen Fiber

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ABSTRACT: Carboxylated collagen fiber (CCF) was prepared by modifying collagen fiber with glyoxylic acid. The structure of CCF was characterized and analyzed by scanning electron microscopy and Fourier transform infrared spectroscopy. CCF was an effective adsorbent for the removal of Cr(III) from aqueous solutions, and the adsorption capacity of Cr(III) increased by 74.13% after modification. The adsorption isotherm, as well as the kinetics of the adsorption of Cr(III) on CCF, was studied. The results showed that the adsorption isotherm of Cr(III) could be well described by the Freundlich equation, and the adsorption capacity increased slightly with increasing temperature, but the influence was not so obvious. The adsorption kinetic investigations indicated that the adsorption rate of Cr(III) on CCF could be well described by the pseudo-second-order rate model, and that the adsorption capacity calculated using the pseudo-second-order rate model was close to that from actual measurements. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40285.

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INTRODUCTION

The current treatment methods for wastewater containing Cr(III) mainly include alkaline precipitation, electrolysis, ion exchange, chemical flocculation, adsorption, etc.[1–3] However, the most commonly used method is the adsorption method because of its simple operations and mild conditions.[4] Activated carbon and resins, which have a high adsorption capacity for Cr(III), are the most popular adsorbents for wastewater containing Cr(III).[5–7] However, activated carbon and resins are usually very expensive, and their regeneration costs are high because the desorption of Cr(III) is complex,[8,9] so the biomass adsorption materials attract more and more researcher's attention.[10–12] The collagen fiber (CF) extracted from solid leather waste is a kind of structural protein, which is water-insoluble but hydrophilic in nature, and can maintain a decentralized state after swelling in water. However, CF contains numerous functional groups, such as -NH$_2$, -COOH, and -OH. The I-style collagen molecule, which is the main composition of CF, consists of three polypeptide chains with triple-helical structures and is easily biodegraded. The structure and characteristics of CF show that it is a potential biomass adsorbent and is appropriate for industrial wastewater treatment.[13] On the other hand, compared with some biomass adsorption materials such as buckwheat husks, peanut hulls and plant stalks, CF not only has advantages of widely distributed, low price, high adsorption capacity, mild adsorption conditions, and simple work-up procedure, but also it can realize the recycling use of solid leather wastes and reduce environmental pollution. Moreover, some previous studies reported that CF has a high adsorption capacity for metal ions and dyes in water, and strong adsorptive specificity.[14–16] Thus, the use of CF as adsorbents in Cr(III) removal from industrial wastewater can be a significant and effective method of recycling leather wastes, and can be beneficial to the environment and the economy.

Considering the environmental and economic benefits, combined with the mechanisms of aldehyde and chrome tanning, the adsorbent carboxylated collagen fiber (CCF) was prepared by modifying CF with glyoxylic acid. The adsorption behaviors of Cr(III) on CCF were also determined in this study.

EXPERIMENTAL SECTION

Materials and Devices

Acetic acid, sodium hydroxide, sodium carbonate, etc. were all of analytical grade. Glyoxylic acid (40%) was supplied by Hao-Chem Industry (Shanghai, China). Chromium powder (Cr(OH)SO$_4$) was purchased from Sisecam Company (Turkey).

The JJ-2 tissue-mashing machine was supplied by the Xi'an Bilang Biological Technology (China). The DSX-90 digital mixer was supplied by the Hangzhou Electronic Instrument (China). The thermostatic water bath was purchased from the YuHua

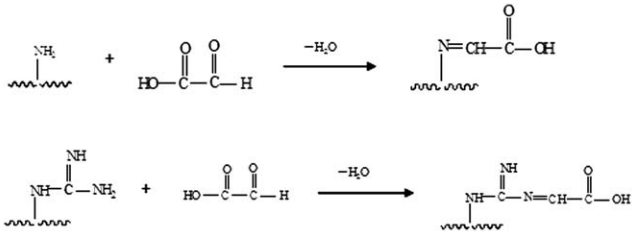

Figure 1. Reaction synthesis for CCF.

Instrument (China). The UV-1009 spectrophotometer was supplied by Lab Tech (China). The THZ-82A constant-temperature bath oscillator was supplied by the PuDong Physical Optical Instrument Factory (China) and the 905 Titrando potentiometric titration was purchased from the Metrohm (Switzerland). The instrument used for scanning electron microscopy (SEM) was X-650 SEM, which was supplied by Hitachi (Japan). The instrument used for Fourier transform infrared spectroscopy (FT-IR) was FT-Raman FT-IR, which was purchased from Nicolet Instrument (USA).

Preparation of CF. With solid leather wastes as raw material, CF was prepared using the acetic acid relaxation method according to a previous study.[17]

Preparation of CCF. Approximately 2.5 g of CF was placed in a three-necked flask containing 30 mL of distilled water. The mixture was stirred until the fibers were fully swollen. After diluting with 40 mL of water, 2 g of glyoxylic acid (40%) was slowly added to the filtrate. Then, the pH was adjusted to 6.5 using 0.1*M* NaOH, and the reaction was conducted in a water bath at 308 K for 5 h. The CF was filtered through a nylon cloth and repeatedly washed with distilled water to remove the unreacted glyoxylic acid. Finally, CCF was prepared. The reaction synthesis for CCF is shown in Figure 1.

Methods

Effect of pH on Adsorption. To study the effect of pH on adsorption, 0.1 g of adsorbent CCF was suspended in 100 mL of chrome solution containing 100 mg/L Cr(III). The initial pH values of the solutions were adjusted to 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, and 6.5 using either 0.1*M* NaOH or 0.1*M* HCl. The adsorption experiments were conducted at 308 K for 4 h under constant shaking. After adsorption, the Cr(III) concentration of the solutions was determined using the UV-1009 spectrophotometer at a wavelength of 540 nm. Finally, the effect of pH on adsorption was analyzed using the adsorption capacity as the reference index.[18]

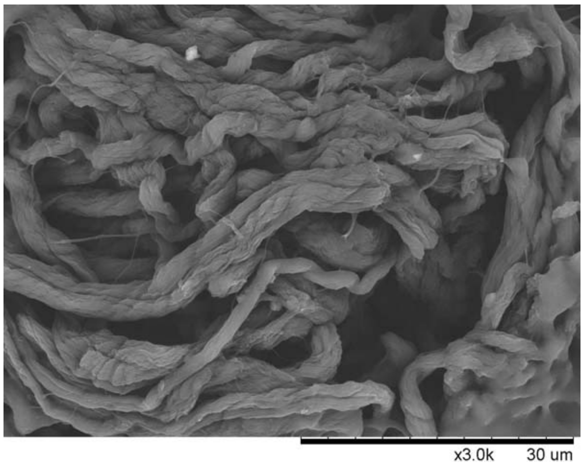

Figure 2. SEM image of CF.

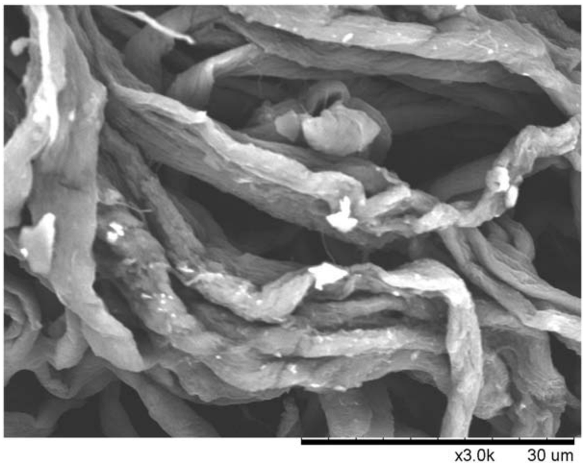

Figure 3. SEM image of CCF.

Contrast Experiments. About 0.1 g adsorbents CF and CCF were individually suspended in a 100 mL chrome solution that had 100 mg/L Cr(III). The initial pH values of the solutions were adjusted to 4.5 by using 0.1*M* NaOH. The adsorption experiments were conducted at 308 K for 4 h and were subjected to constant shaking. The Cr(III) concentration of the solutions was determined using the UV-1009 spectrophotometer. Finally, the adsorption results of CF and CCF on Cr(III) were compared by using the adsorption capacity and removal rate of Cr(III) as the reference indexs.

Adsorption Isotherms. The Cr(III) stock solution was prepared by dissolving chromium powder with distilled water, and was

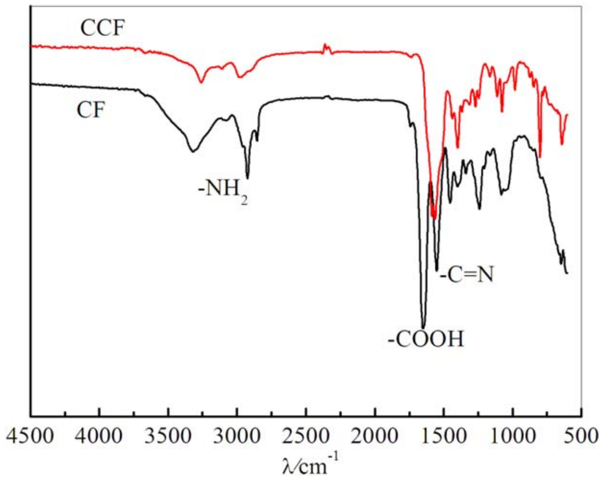

Figure 4. FT-IR spectra of CF and CCF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

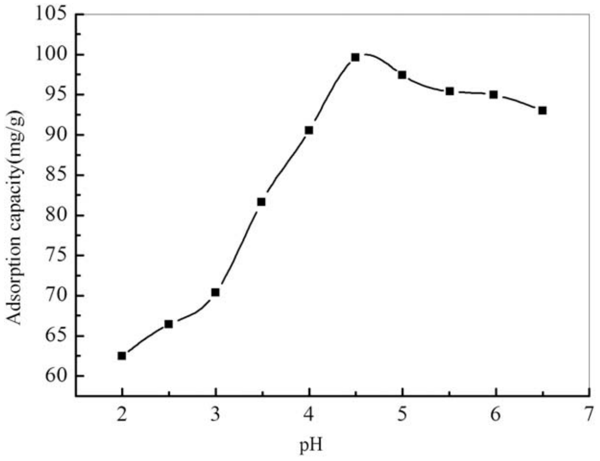

Figure 5. Effect of pH on adsorption.

further diluted to achieve the desired concentration for future use.

A 0.08 g portion of CCF was suspended in 100 mL of Cr(III) solution containing 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L Cr(III), respectively. The initial pH of each solution was adjusted to 4.5 using 0.1 M NaOH. The adsorption experiments were conducted by constant shaking for 4 h at 303 K, 308 K, and 313 K, and the adsorption isotherm curves in different temperatures were obtained accordingly.[19]

Adsorption Kinetics. The procedures used to determine the adsorption kinetics were similar to those of the adsorption isotherms. However, the Cr(III) concentration during the adsorption process was analyzed per hour. A total of 0.20 g of the adsorbent CCF was suspended in 300 mL of 100 mg/L Cr(III) solution. The initial pH of the Cr(III) solution was adjusted to 4.5 using 0.1*M* NaOH. The adsorption experiments were performed at 303 K, 308 K, and 313 K with constant shaking until reaching the adsorption equilibrium and obtaining the adsorption dynamics curves of different temperatures.[20]

Table I. The Removal Rate and Adsorption Capacity of CF and CCF on Cr(III)

	Removal rate of Cr(III) /%	Adsorption capacity/(mg g^{-1})
CF	46.47	75.82
CCF	80.92	106.88

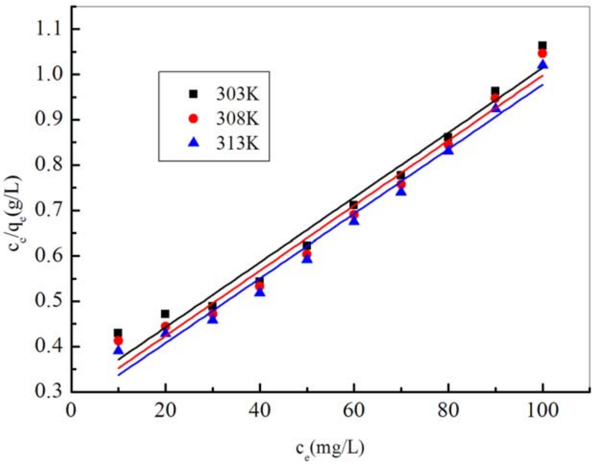

Figure 7. Langmuir isotherm of CCF at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Characterization of CCF

The amino and carboxyl contents of CF and CCF were determined according to the alicylaldehyde method[21] and Boehm titration,[22] respectively. The results indicated that the amino and carboxyl contents of CF were 5.15% and 6.42%, whereas those of CCF were 1.58% and 9.81%, respectively. The amino content decreased by 69.23%, whereas the carboxyl content increased by 52.77% after modification.

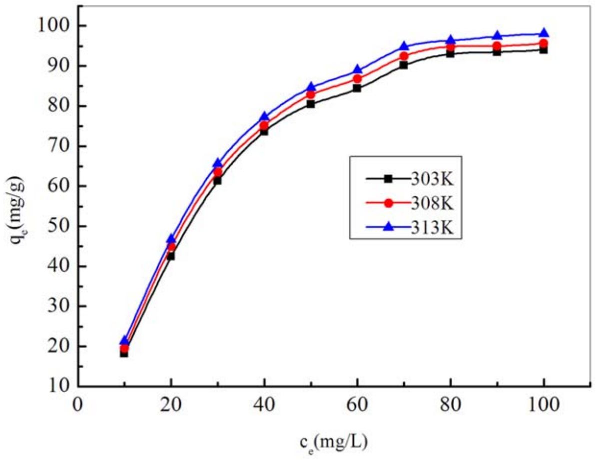

Figure 6. Adsorption isotherms of CCF at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

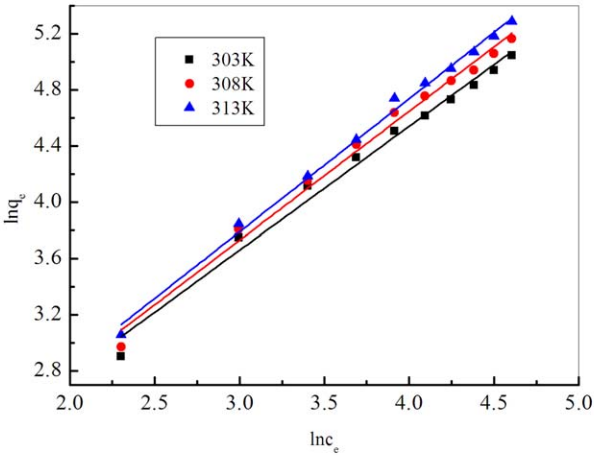

Figure 8. Freundlich isotherm of CCF in different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Freundlich and Langmuir Equation Fitting Parameters for CCF

	Langmuir equation			Freundlich equation		
Temperature	b (L/mg)	q_0 (mg/g)	R^2	$1/n$	K	R^2
303K	0.02384	139.86	0.9811	0.88169	2.6524	0.9991
308K	0.02555	139.47	0.9743	0.91807	2.5787	0.9986
313K	0.02773	138.89	0.9682	0.94746	2.4147	0.9963

The SEM images of CF and CCF are shown in Figures 2 and 3. The morphology of CCF was more diffused than CF, so the physical adsorption of Cr(III) was possibly enhanced.[23] The FT-IR spectra of CF and CCF are shown in Figure 4. The band at 3400 cm^{-1} was weakened, whereas the bands at 1600 and 1700 cm^{-1} were considerably strengthened after carboxyl modification. The band at 3400 cm^{-1} corresponded to -NH$_2$ stretching, whereas the bands at 1600 and 1700 cm^{-1} were attributed to the –C=N stretching vibration and the –COOH characteristic absorption, respectively.

Effect of pH on Adsorption

The pH of the adsorbate–adsorbent system has a significant function in the entire adsorption process. Thus, the effect of pH on adsorption has been investigated in many studies.

The effect of pH on Cr(III) adsorption is shown in Figure 5. The adsorption capacity of Cr(III) increased with increasing of pH up to 4.5, although it slightly decreased as the pH reached 4.5 or higher. CCF can be easily hydrolyzed in low pH, which destroys the three-dimensional network structure and decreases the adsorption capacity; with increasing pH, the degrees of hydrolysis, olation, and oxylation of Cr(III) in the solution strengthen, leading to an increase in molecule mass of the complexes, which is beneficial to the Cr(III) and CCF combination.[24] Moreover, the ionization degree of carboxyl increases with increasing pH, and the combination with Cr(III) is strengthened. As the Cr(III) ions in the solution precipitate at pH 4.5 and higher, the adsorption capacity decreases. The results indicate that the optimum pH for the adsorption of Cr(III) was 4.5.

Contrast Experiments

The removal rate and adsorption capacity of Cr(III) on CF and CCF were shown in Table I. The results showed that the adsorption capacity of Cr(III) from the chromium solution was increased significantly after modifying with glyoxalic acid. The efficiency of Cr(III) removal rate increased from 46.47% to 80.92%. The adsorption ability of CCF of Cr(III) was 106.88 mg g^{-1} while that of CF was only 75.82 mg g^{-1}. These results indicated that the carboxyl content increased significantly after carboxyl modification, and the adsorption of Cr(III) strengthened.

Table III. Thermodynamic Parameters of Adsorption

Temperature	ln K	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1}K^{-1})
303K	0.9755	−2.457	7.405	−16.271
308K	0. 9473	−2.426		
313K	0.8816	−2.294		

Adsorption Isotherms

The adsorption isotherms of Cr(III) at different temperatures are shown in Figure 6. The adsorption isotherms of Cr(III) on CCF indicate that the adsorption capacity increased slightly as the temperature and the equilibrium concentration of Cr(III) increased, which suggests that the adsorption of Cr(III) on CCF was mainly chemical. Figure 6 also showed that the effect of temperature on the adsorption was not so obvious and the adsorption can be proceeded at room temperature. Adsorption equilibrium data were analyzed by the Langmuir [Eq. (1)] and Freundlich equations [Eq. (2)].[25] The results of Langmuir and Freundlich equation fittings of the adsorption isotherm are shown in Figures 7 and 8, and the Langmuir and Freundlich parameters of the Cr(III) adsorbed on CCF are listed in Table II. Thus,

$$\frac{c_e}{q_e}=\frac{c_e}{q_0}+\frac{1}{bq_0} \tag{1}$$

$$\ln q_e=\frac{1}{n}\ln c_e+\ln K \tag{2}$$

where q_e (mg g^{-1}) and c_e (mg L^{-1}) are the amounts adsorbed and the bulk concentration at equilibrium, respectively; q_0 is the maximum adsorption amount (mg g^{-1}); b is the coefficient related to the adsorption strength, $b=k_a/k_d$ (k_a is the rate constant of adsorption, k_d is the rate constant of desorption); and K and $1/n$ are the Freundlich constants representing adsorption capacity and adsorption intensity, respectively.

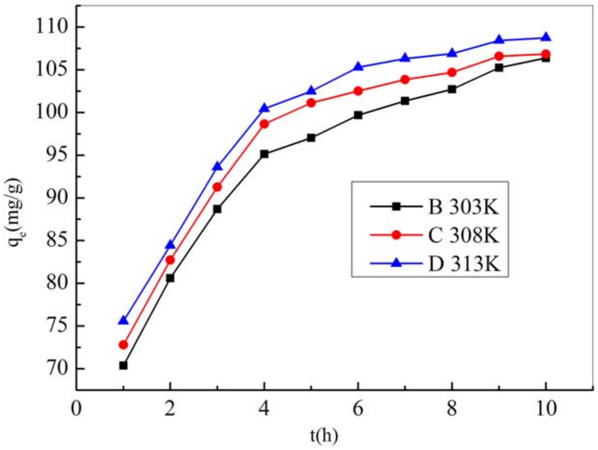

Figure 9. Adsorption kinetics of CCF at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

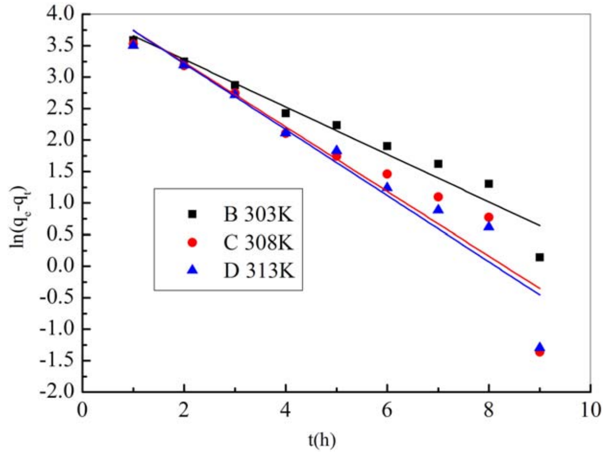

Figure 10. Pseudo-first-order rate adsorption of CCF at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

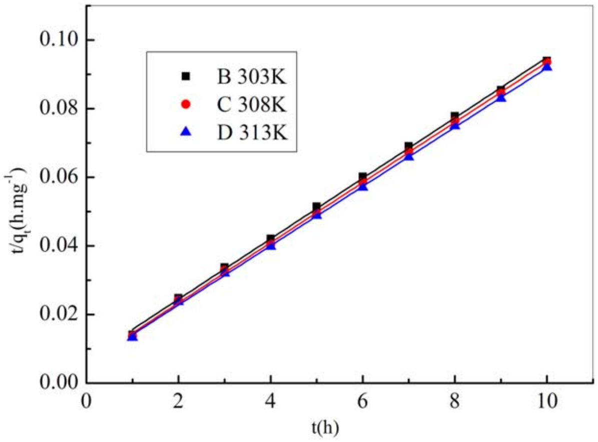

Figure 11. Pseudo-second-order rate adsorption of CCF at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The fitting parameters of the Freundlich equation were higher than 0.996, whereas those of the Langmuir equation were higher than 0.968. This result indicates that the Freundlich equation could better describe the behavior of Cr(III) on CCF. The fitting results of the Langmuir equation show a certain degree of correlation and suggest that a physical adsorption mechanism may be involved in the Cr(III) adsorption on CCF. The value of $1/n$ was lower than 1, which indicates that the surface of the adsorbent is heterogeneous and adsorption occurs easily[26]

Adsorption Thermodynamic Parameters

Thermodynamic parameters, such as Gibbs free energy, enthalpy, and entropy, can be obtained by eqs. (3) and (4), respectively, and the results are shown in Table III. The parameters show that the Cr(III) adsorption process was spontaneously endothermic and decreasing in entropy, whereas the adsorption process was endothermic[27]:

$$\Delta G=-\mathrm{RT}\ln K \tag{3}$$

$$\ln K=-\frac{\Delta H}{\mathrm{RT}}+\frac{\Delta S}{R} \tag{4}$$

where R is the gas constant, 8.314 J mol^{-1}K^{-1}; K is the constant referring to the adsorption capacity; and ΔG, ΔH, and ΔS are Gibbs free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}), and entropy (J mol$-^{1}$K^{-1}), respectively.

Adsorption Kinetics

The adsorption kinetics of Cr(III) on CCF at different temperatures are shown in Figure 9. The experimental data indicate that the Cr(III) adsorption rates on CCF were initially fast and then slowed down as equilibrium was approached. The adsorption equilibrium was attained in 4 h. The pseudo-first-order [Eq. (5)] and pseudo-second-order equations [Eq. (6)] were used to test the adsorption kinetic data and investigate the adsorption mechanism.[28] The results of the pseudo-first-order and pseudo-second-order equation fittings of the adsorption kinetics are shown in Figures 10 and 11. The pseudo-first-order and pseudo-second-order parameters of Cr(III) adsorbed on CCF are listed in Table IV:

$$\ln(\mathrm{q_e}\text{-}q_t)=\ln q_e-\frac{k_1}{2.303}t \tag{5}$$

$$\frac{t}{q_t}=\frac{1}{k_2 {q_e}^2}+\frac{t}{q_e} \tag{6}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of adsorbed Cr(III) at equilibrium and at time t, respectively; k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}); and k_2 is the constant of the pseudo-second-order rate (mg g^{-1}h^{-1}).

The pseudo-second-order adsorption constants (R^2) were all above 0.999, whereas the pseudo-first-order adsorption constants (R^2) were all below 0.95. These results suggest that the pseudo-second-order model could perfectly fit the experimental data on the Cr(III) adsorption processes of CCF, whereas the equilibrium adsorption capacities calculated by the pseudo-second-order model were highly close to the actual measurements. Thus, the pseudo-second-order equation can better describe the adsorption behavior of Cr(III) on CCF.

On the other hand, temperature adsorption kinetics for 288 K and 298 K has also been studied, and the results showed that

Table IV. Pseudo-First-Order and Pseudo-Second-Order Parameters of CCF at Different Temperatures

	Pseudo-first-order equation			Pseudo-second-order equation		
Temperature	k_1 (h^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} h^{-1})	q_e (mg g^{-1})	R^2
303K	0.86823	56.4827	0.9460	0.01139	113.636	0.99913
308K	1.17983	70.6683	0.8875	0.01305	114.943	0.99953
313K	1.20769	71.1797	0.9223	0.01345	116.279	0.99955

CCF also has strong adsorption capacity toward Cr(III) at temperature of 288 K and 298 K. All these results indicated that the CCF involved in this paper can be used for the treatment of wastewater containing Cr(III).

CONCLUSIONS

1. CCF was prepared by modifying CF using glyoxylic acid. After modification, the amino content decreased by 69.23% and the carboxyl content increased by 52.77%.
2. CCF is an effective adsorbent for the removal of Cr(III) from aqueous solutions and the adsorption capacity of Cr(III) increased by 74.13% after modification.
3. The results of adsorption isotherm and adsorption kinetics indicate that the Freundlich equation and the pseudo-second-order model provided a better description of the adsorption behavior of Cr(III) on CCF.
4. The adsorption kinetics study at different temperatures showed that CCF has strong adsorption capacity of Cr(III), which indicated that the CCF involved in this paper can be used for the treatment of wastewater containing Cr(III).

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REFERENCES

1. Yan, X.; Li, Y. F. *Liaoning Chem. Ind.* **2010**, *39*, 143.
2. Zhang, B.; Wu, T.; Qin, T.; Liu, J. H. *West leather* **2009**, *31*, 36.
3. Vinod, G.; Dinesh, M. *The environmentalist* **1998**, *19*, 129.
4. Xin, X.; Xin, H.; Ke, C. *J Environ. Eng.* **2010**, *4*, 2273.
5. Kratochvil, D.; Pimentel, P.; Volesky, B. *Environ. Sci. Technol.* **1998**, *32*, 2693.
6. Al-Asheh, S.; Duvnjak, Z. *Adv. Environ. Res.* **1997**, *1*, 194.
7. Yavuz, M.; Godea, F.; Pehlivanb, E.; Ozmerta, S.; Sharma, Y. *Chem. Eng. J.* **2008**, *137*, 453.
8. Huang, G. L.; Jeffrey, X. S.; Tim, A. G. *Chem. Eng. J.* **2009**, *152*, 434.
9. Quintelas, C.; Fernandes, B.; Castro, J. *J. Hazard. Mater.* **2008**, *153*, 799.
10. Li, K. B.; Wang, Q. Q.; Dang, Y.; Wei, H.; Luo, Q.; Zhao, F. *Acta Chim. Sin.* **2012**, *70*, 929.
11. Chen, S. H. Study on the modification of corn stalks and its adsorption properties of hexavalent chromium ion, Shan-Dong, Shandong University, **2012**.
12. Zhang, B.; Liu, B.; Yue, M.; Xu, X. *Shandong Chemical Industry* **2013**, 42, 20.
13. Vladescu, L.; Costache, M.; Badea, I. *Acta Chromatogr.* **2004**, *14*, 187.
14. Qiang, T. T.; M. Luo, Bu, Q. Q.; Wang, X. C. *Chem. Eng. J.* **2012**, *197*, 343.
15. Wang, R.; Liao, X. P.; Shi, B. *Ind. Eng. Chem. Res.* **2005**, *44*, 4221.
16. Guo, J. L.; Wu, H.; Liao, X. P.; Shi, B. *J. Phys. Chem.* **2011**, *115*, 23688.
17. Cheng, H. M.; Wang, R.; Wang, Y. M. *J. Sichuan Univ. (Eng. Sci. Ed.)* **2007**, *39*, 78.
18. Rodrigues, L. A.; Leandro, J. M. *J Hazard. Mater.* **2010**, *173*, 630.
19. Hao, H.; Feng, J. G.; Ma, C. *CIESC J.* **2011**, *62*, 3179.
20. Mohammad, A. A.; Sohrab, Z.; Ali, S.; James, L. *Ind. Eng. Chem. Res.* **2012**, *51*, 9894.
21. Zhang, Z. X.; Zhang, R. G. Quantitative Analysis of Organic Functional Groups; Chemical industry press: Beijing, **1990**.
22. You, Y. J.; Qu, M. Z.; Zhou, G. M. *Chin. J. Synth. Chem.* **2006**, *5*, 446.
23. Liao, X. L.; Wang, X. Q.; Zhou, A. N.; Yao, T. G. *Coal Conversion* **2007**, *30*, 18.
24. Chen, W. Y.; Li, G. Y. Tanning Chemistry; Chinese light industry press: Beijing, **2005**.
25. Yi, C. H.; Tang, Q. Q.; Huang, X.; Qiu, X. Q. *CIESC J.* **2012**, *63*, 2460.
26. Friess, W. G. *Eur. J. Pharm. Biopharm.* **1998**, *45*, 113.
27. Liu, F. Q.; Chen, J. L.; Li, A. M.; Zhang, Q. X. *Acta Polym. Sin.* **2004**, *5*, 661.
28. Xiong, Z. H.; Wang, L.; Zhou, J. G.; Liu, J. M. *Acta Phys. Chim. Sin.* **2010**, *26*, 2890.