RESEARCH ON Cr⁶⁺ ADSORPTION OF MODIFIED CARBONIZED STRAW AND ITS MECHANISM DURING WASTEWATER TREATMENT BY RESPONSE SURFACE METHODOLOGY

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(Received 22nd May 2019; accepted 28th Aug 2019)

Abstract. Heavy metal contaminated wastewater is difficult to treat, and trace amounts of heavy metals can produce toxic effects. In order to provide a more reliable basis for controlling heavy metal pollution, modified carbonized straw was used to adsorb Cr⁶⁺ in this study, and the optimal adsorption conditions and adsorption effects of Cr⁶⁺ were studied. Finally, the adsorption kinetics and adsorption activation thermodynamics were analyzed and studied. The results showed that the iodine adsorption value of carbonized wheat straw modified using FeCl₂ activation method was the highest at 1161.15 mg/g. The response surface method can be used to optimize the adsorption conditions of Cr⁶⁺ adsorbed by modified carbonized straw and predict the optimal conditions for Cr⁶⁺ adsorption. Experiments showed that the actual value was in agreement with the predicted value, indicating that the response surface methodology was feasible to optimize the adsorption of Cr⁶⁺ by modified carbonized straw. In the kinetic analysis, the Elovich equation could better describe the adsorption of Cr⁶⁺ by modified carbonized wheat straw, and its fitting degree exceeded 0.91. In the analysis of thermodynamic parameters, $\Delta H > 0$, $\Delta G < 0$, indicating that the adsorption of Cr⁶⁺ by modified wheat straw was a spontaneous endothermic process. During the adsorption process, $\Delta S > 0$, indicating that the adsorption of Cr⁶⁺ by modified carbonized wheat straw increased the disorder of the system.

Keywords: *modified carbonization straw, Cr⁶⁺, response surface methodology, adsorption kinetics, heavy metal wastewater, heavy metal wastewater treatment, iodine adsorption value, agricultural waste*

Introduction

With the development of industry in China, heavy metal pollution has seriously endangered human health. In fact, heavy metal pollution is difficult to be degraded and removed by simple methods, and it tends to accumulate in organisms and produce toxic effects (Zhao, 2016). At present, the aggravation of heavy metal pollution poses a great threat to the healthy development of human beings and other organisms, and the treatment of heavy metal wastewater has become an urgent problem to be solved. Therefore, it is of great significance to analyze and study the treatment and disposal of heavy metal wastewater (Zeng, 2014a; Zeng and Li, 2014b).

China is a country of traditional agricultural production (Cao et al., 2012). At present, China's agricultural straw production is high. However, with the improvement of people's living standards, straw is no longer needed in daily life. Nowadays, most of

the straw is treated by incineration and disposal, and has not been reused (Sud et al., 2008), which not only wastes resources, but also brings more and more serious air pollution problems. Therefore, a large number of agricultural straws have not been properly utilized, and the conventional disposal methods have been unable to meet the current straw disposal requirements. In response to the call for building a resource-conserving and environment-friendly society, reusing these residues to dispose of waste is a good way to deal with agricultural waste (Ngah and Hanafiah, 2008). Straw is a biomass waste with high crude fiber content and low protein content (Zhu et al., 2010), which is difficult to be corroded, and it is not good to be directly returned to the field. However, the carbonized product of straw has good physicochemical properties, such as good combustibility, adsorption and low electrical resistance (Sun and Jiang, 2009), which can be used as fuels, soil conditioners and filling materials for electromagnetic shielding screen. Therefore, it is a feasible path to improve the comprehensive utilization rate of straw and carry out biochar utilization of straw and other biomass.

On the basis of the previous studies (Zeng et al., 2018), wheat, corn and paddy straw from farmland around Chengdu, Sichuan Province were carbonized to produce carbonized straw, which is used as activated carbon to study the best adsorption conditions and effects for Cr^{6+} , and the adsorption kinetics and thermodynamics of adsorption activation state were studied finally. In addition, this study evaluated the treatment of Cr^{6+} by modified carbonized straw, which is expected to provide some technical and theoretical support for the practical application of this method.

Materials and methods

Materials, reagents and instruments

The materials used in this experiment were waste wheat, corn, and rice straw produced by agriculture. Corn stalks were taken from Xihe Town, Longquanyi, Chengdu. Wheat straw and rice straw were taken from Huayang Town, Shuangliu, Chengdu.

The object of this experiment was a solution containing Cr^{6+} . The reagents used in the experiment were ZnCl_2 , KOH , HCl , HNO_3 , H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, FeCl_2 , I_2 , KI , $\text{Na}_2\text{S}_2\text{O}_3$, soluble starch. All reagents were analytical pure. The equipments of the experiment include electrothermal constant temperature blast drying oven (DHG-9140A), visible light spectrophotometer (V-1200), water bath oscillator (HH-4), electronic analytical balance (ESJ120-4), pH meter (PHS-3C), constant temperature oscillator (THZ-032), electric stirrer (JJ-1), ultrasound instrument (KQ-50), high speed centrifuge (H1650R), universal electric furnace (BDW1-6), mesh screen (40 to 200 mesh).

Preparation of modified carbonized straw

In this paper, wheat, corn and rice straw were used as raw materials to prepare activated carbon by using chemical activation method, and the activator were zinc chloride, potassium hydroxide, concentrated sulfuric acid and ferrous chloride, the experimental scheme is shown in *Table 1* (Nu et al., 2017). First, distilled water was applied to clean three kinds of straws. Then straws were dried under the condition of $100\text{ }^\circ\text{C}$ in the electrothermal constant temperature blast drying oven and cut into long strips of 3-4 cm. Next, the dried material was sealed with a foil paper and placed on a

universal electric furnace for 30 min (the temperature of wheat straw was 800 °C (Xiao et al., 2010), the temperature of corn straw was 600 °C (Chen et al., 2010), and the temperature of rice straw was 300 °C (Pinto et al., 2005), then the outer wrapped tin foil paper was removed, and the crude carbonized straw obtained after activation was ground and sieved (40 to 60 mesh). Next, the three sieved carbonized straws were mixed with ZnCl_2 (3 mol/L), KOH (3 mol/L), H_2SO_4 (37%) and FeCl_2 (2 mol/L) in a mass ratio of 1:3 in a 100 mL stoppered conical flask and closed it immediately, and then it was oscillated in the constant temperature oscillator (temperature: 25 °C, oscillation speed: 150 r/min, oscillation time: 120 min). At the end of the oscillation, solid modified carbonized straw was obtained by filtering the mixed liquor. Firstly, it was washed by 1:9 dilute hydrochloric acid solution (1 mol/L). Secondly, it was washed repeatedly with distilled water to neutral. Thirdly, it was dried to constant weight. After grinding, the activated carbon in 200-mesh was selected for use.

Table 1. Experimental design of carbonized straw modification

Number	Straw	Activator	Mass ratio (g:mL)	Temperature (°C)	Oscillation speed (r/min)	Oscillation time (min)
1	Wheat	ZnCl_2	1:3	25	150	120
2	Wheat	KOH	1:3	25	150	120
3	Wheat	H_2SO_4	1:3	25	150	120
4	Wheat	FeCl_2	1:3	25	150	120
5	Corn	ZnCl_2	1:3	25	150	120
6	Corn	KOH	1:3	25	150	120
7	Corn	H_2SO_4	1:3	25	150	120
8	Corn	FeCl_2	1:3	25	150	120
9	Rice	ZnCl_2	1:3	25	150	120
10	Rice	KOH	1:3	25	150	120
11	Rice	H_2SO_4	1:3	25	150	120
12	Rice	FeCl_2	1:3	25	150	120

Method for determining iodine value of modified carbonized straw

The iodine level is related to the adsorption capacity of activated carbon. It is generally believed that the higher the iodine value, the higher the porosity of activated carbon, which means the high adsorption capacity. In this experiment, the iodine value of modified carbonized straw was determined by national standard GB/T12496.8-2015 “Determination of iodine adsorption value by wood activated carbon experimental method” (Chen et al., 2007).

Drawing method of standard curve of Cr^{6+}

A certain concentration of Cr^{6+} -containing solution was configured with distilled water as a reference, and absorbance was measured at its maximum absorption wavelength (each sample was measured three times, averaged and recorded, $n = 3$). Taking 540 nm as the maximum absorption wavelength of Cr^{6+} , the concentration of the Cr^{6+} -containing solution respectively was 0 mg/L, 0.02 mg/L, 0.1 mg/L, 0.4 mg/L, and 0.8 mg/L. Then, the experiment was performed, the measured absorbance was taken as the ordinate, the concentration was taken as the abscissa, and the standard curve was drawn.

Configuration of Cr⁶⁺-containing solution

First, the best grade pure potassium dichromate was weighed 1.4135 g and dissolved in water, and then the volume of solution reached at 500 mL by adding water. Therefore, the standard reserve solution containing Cr⁶⁺ 1.0 mg/mL was obtained. When the solution needs to be used, the standard reserve solution is absorbed with 1.0 mL nitric acid, and then a standard solution containing 100 mg/mL Cr⁶⁺ was obtained (Chen et al., 2010).

Response surface experiment of Cr⁶⁺

The experiment used the Box-Behnken design to predict the optimal adsorption conditions and explore the interaction between the factors through Design Expert software (Hadjmohammadi et al., 2016). In this experiment, temperature (A), adsorption time (B), and adsorbent dosage (C) were used as independent variables, the removal rate of Cr⁶⁺ by activated carbon modified under different conditions as a response value, and then the adsorption performance of modified carbonized straw for adsorption of Cr⁶⁺ was optimized. The experimental design was shown in *Table 4*.

Adsorption kinetics

In this study, the first-order kinetic equation, the double-constant equation, and the Elovich equation were used to analyze the adsorption kinetics of the Cr⁶⁺-containing solution by modified carbonized straw.

The linear expression of the first-order kinetic equation is as follows *Equation 1* (Takeshi et al., 2004). In the formula, C_t is the mass concentration at time t (mg/L), a and k are the kinetic constants, t is the adsorption time.

$$\ln C_t = a - kt \quad (\text{Eq.1})$$

The double-constant equation is suitable for complex non-homogeneous diffusion processes, and the linear expression of which is as follows (*Eq. 2*) (Wu, 2015). In the formula, X is adsorption capacity (mg/g), a and k are the kinetic constants, t is the adsorption time.

$$\ln X = a + k \ln t \quad (\text{Eq.2})$$

The linear expression of the Elovich equation (Shi and Li, 2014) is as follows (*Eq. 3*). In the formula, X is adsorption capacity (mg/g), a and k are the kinetic constants, t is the adsorption time.

$$X = a + k \ln t \quad (\text{Eq.3})$$

Adsorption thermodynamics

Calculating the change of standard thermodynamic function based on experimental data of adsorption thermodynamics is an important part of adsorption thermodynamics research, which has theoretical and practical significance (McKay, 1984). In the adsorption process, the relationships between the thermodynamic functions ΔG , ΔH , ΔS and the adsorption partition coefficient K are as follows (*Eqs. 4–7*).

$$K = \frac{q_e}{C_e} \quad (\text{Eq.4})$$

$$\Delta G = -RT \ln K \quad (\text{Eq.5})$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{Eq.6})$$

From the above formulas:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (\text{Eq.7})$$

In the formulas, q_e is the equilibrium adsorption amount (mg/g), C_e is the mass concentration of adsorbate in solution during adsorption equilibrium (mg/L), T is the thermodynamic temperature (K), R is the gas constant (8.314 J/(mol·K)), K is the adsorption partition coefficient, ΔH is the change of adsorption enthalpy (kJ/mol), ΔS is the change of adsorption entropy (J/(mol K)), ΔG is adsorption free energy (kJ/mol).

Experimental results and analysis

Results of modified carbonized straw

The straw obtained after carbonization was dark black, and it had a brittle texture and was lighter in weight than raw materials. The activated carbonized straw was black powder after drying and grinding, and the straw components were shown in *Table 2*.

Table 2. Component of straw

Straw	Lignin	Crude fiber	Crude ash	Crude protein
Rice	6.3%	35.1%	19.4%	3.2%
Corn	4.6%	29.3%	7.0%	9.3%
Wheat	9.5%	43.6%	2.6%	2.6%

It could be seen from *Table 2* that the lignin content and crude fiber content of wheat straw were higher than those of rice straw and corn straw, and the pore structure of cellulose directly affected subsequent adsorption properties.

In the process of carbonization and modification, the average pore size of straw decreased, which made the total pore volume increase. At the same time, the non-microcrystalline carbon of the carbon structure was oxidized, which made the specific surface area larger, and the microcrystalline carbon was rearranged to make pores more stable. Therefore, the specific surface area of the modified carbonized straw was much higher than the specific surface area of the original straw. In fact, the increase in specific surface area increased the adsorption area of the adsorbent for heavy metals, and then the adsorption rate was increased (Zhong, 2011).

During the adsorption process, with the increase of temperature, raw materials were rapidly decomposed by heat, so C—OH, C—O—C, C—H and other groups in cellulose molecular structure were decomposed at 280~380 °C, and small amount of molecule fragments or groups were decomposed continuously when the temperature more than

380 °C. At the same time, carbon element was rearranged to form graphite microcrystalline (Zhu and Zhou, 2014).

Determination and analysis of iodine value of modified carbonized straw

Through the measurement experiment of iodine value, the iodine values of the experimental samples were shown in *Table 3*.

Table 3. Iodine value of different modified carbonized straw

Number	Carbonized straw	Modifier	Iodine value (mg/g)
1	Wheat	ZnCl_2	1005.32
2	Wheat	KOH	993.84
3	Wheat	H_2SO_4	994.86
4	Wheat	FeCl_2	1161.15
5	Corn	ZnCl_2	1072.23
6	Corn	KOH	1135.19
7	Corn	H_2SO_4	1101.27
8	Corn	FeCl_2	962.80
9	Rice	ZnCl_2	1021.13
10	Rice	KOH	993.87
11	Rice	H_2SO_4	937.04
12	Rice	FeCl_2	1007.25

In this study, different carbonized straws were modified by different modifiers, and the iodine adsorption value was used as an indicator to compare the adsorption capacity of different modified carbonized straws. After the four modifiers were applied separately, the adsorption capacity of the modified wheat straw was greater than that of corn and rice straw, which might be closely related to the content of crude fiber and lignin in wheat straw. In the experiment, the modified carbonized wheat straw with 2 mol/L FeCl_2 as modifier had the highest iodine adsorption value 1161.15 mg/g. Therefore, the subsequent adsorption experiments selected modified carbonized wheat straw as the main research object, which used 2 mol/L FeCl_2 as modifier.

Response surface analysis of Cr^{6+}

Based on single factor experiments and orthogonal experiments, this study used Design Expert software to design a response surface experimental scheme in Box-Behnken mode, and then used model analysis to predict the optimal adsorption conditions and the interaction between the factors. In the experiments, temperature (A), adsorption time (B), and dosage of adsorbent (C) were used as independent variables, and the removal rate of Cr^{6+} by activated carbon was used as the response value, and then the adsorption conditions for the adsorption of Cr^{6+} by modified carbonized straw were optimized. The experimental results were shown in *Table 4*.

The results of the *Table 4* were analyzed and modeled, and then the quadratic polynomial regression equations of temperature (A), adsorption time (B), adsorbent dosage (C), and Cr^{6+} adsorption rate R were obtained as follows (*Eq. 8*):

$$R = 98.20 + 1.66A + 0.57B + 0.51C - 0.010AB + 0.23AC + 0.22BC - 1.81A^2 - 0.69B^2 - 0.42C^2 \quad (\text{Eq. 8})$$

Table 4. Results of response surface experiments

Number	Condition			Response value-removal rate R (%)
	Temperature A (°C)	Time B (h)	Dosage C (g)	
1	25	2.5	2.4	98.17
2	25	2.5	2.4	98.45
3	35	3.5	2.4	98.28
4	25	3.5	3.6	98.23
5	15	3.5	2.4	94.18
6	15	2.5	3.6	95.16
7	25	2.5	2.4	98.12
8	25	2.5	2.4	98.68
9	35	2.5	3.6	98.14
10	15	1.5	2.4	93.09
11	25	3.5	1.2	97.14
12	35	1.5	2.4	97.23
13	25	1.5	1.2	96.38
14	25	2.5	2.4	97.88
15	35	2.5	1.2	96.31
16	15	2.5	1.2	94.24
17	25	1.5	3.6	96.53

The quadratic polynomial model and the results of various variance analyses were shown in *Table 5*, which could be used to judge the adaptability of the model to the study and lay the foundation for subsequent research.

Table 5. Variance analysis of the model

Resource	Quadratic sum	Degree of freedom	Mean square	F value	Prob > F	Significance
Model	44.91	9	4.99	18.48	0.0004	**
A-temperature	22.08	1	22.08	81.76	< 0.0001	**
B-time	2.59	1	2.59	9.58	0.0174	*
C-dosage	2.04	1	2.04	7.56	0.0286	*
AB	1.31	1	1.31	0.86	0.9704	Not significant
AC	0.21	1	0.21	0.77	0.4103	Not significant
BC	0.20	1	0.20	0.73	0.4201	Not significant
A^2	13.83	1	113.83	51.23	0.0002	**
B^2	2.02	1	2.02	7.48	0.0291	*
C^2	0.76	1	0.76	2.82	0.1372	Not significant
Residual	1.89	7	0.27			
Unfitting term	1.55	3	0.52	6.02	0.0577	Not significant
Pure error	0.34	4	0.086			
Total deviation	46.80	16				
R^2	0.9596	Adj R^2	0.9077	CV	0.54%	
Precision	12.354					

*Significant (P < 0.05), **highly significant (P < 0.01)

According to the *Table 5*, the P value of the model was 0.0004, and the unfitting term was 0.0577, which indicated that the model was not significant, but the regression was significant. The correlation coefficient (R^2) was 0.9596, indicated that the fitting effect was better; the variation coefficient was 0.54%, indicated that the model had good reliability and accuracy. The precision indicated the ratio of signal to noise, which should normally be greater than 4. The precision of this experiment was 12.354, indicated that the model could appropriately reflect the experimental results (Han et al., 2018). In addition, correlation coefficient (R^2) and correction correlation coefficient (Adj R^2) showed that the fitting degree and correlation of the model were high, which indicated that the model could be used to predict the optimal adsorption conditions of Cr^{6+} on modified carbonized straw.

Effect of temperature and time on the adsorption rate of Cr^{6+}

In *Figure 1*, the left graph was a three-dimensional model of temperature, time, and chromium ion adsorption rate, and the right graph was the equal adsorption rate line for adsorption time and temperature. The shape of the equal adsorption rate line could reflect the strength of the interaction of the investigation factors. If it was circular, it meant that the interaction effect was not significant. However, if it was elliptical, it meant that the interaction effect was significant (Pang et al., 2017).

Figure 1. Effect of temperature and time on the adsorption rate of Cr^{6+}

As shown in *Figure 1*, the adsorption rate increased with the increase of temperature, indicated that heating was beneficial to the adsorption reaction. In addition, when the treatment time increased from 1.5 to 3.5 h, the adsorption rate increased first and then tended to be slow, indicated that the modified carbonized straw adsorbed Cr^{6+} rapidly first and then gradually reached adsorption equilibrium. According to *Table 5*, the P value of temperature (A) was < 0.0001 , the P value of time (B) was 0.0174, and the P value of AB was $0.9704 > 0.05$, indicated that the influence of factors A and B on the adsorption rate of Cr^{6+} had no interaction. According to the multiple quadratic regression equation obtained from the response surface, the coefficient of AB was -0.010, indicated that the interaction of the two factors had a negative effect on the result.

Effect of temperature and dosage on the adsorption rate of Cr^{6+}

As shown in *Figure 2*, the adsorption rate increased with increasing temperature, and a high adsorption rate could be achieved at 25 °C. And then the temperature continued to increase, but the adsorption rate increased slowly. Under the condition of constant temperature, the adsorption rate increased with the increase of dosage. However, when

the dosage reached 2.4 g, the adsorption rate increased very slowly. According to Table 5, the P value of temperature (A) was < 0.0001 , the P value of dosage (C) was 0.0286, and the P value of AB was $0.4103 > 0.05$, indicated that the influence of factors A and C on the adsorption rate of Cr^{6+} had no interaction. According to the multiple quadratic regression equation obtained from the response surface, the coefficient of AC was + 0.23, indicated that the interaction of the two factors had a positive effect on the result.

Figure 2. Effect of temperature and dosage on the adsorption rate of Cr^{6+}

The effect of time and dosage on the adsorption rate of Cr^{6+}

It could be seen from Figure 3 that when the time was constant, the adsorption rate increased with the increase of the dosage, but when the dosage exceeded 2.4 g/L, the increase rate of the adsorption rate gradually decreased. At the same time, when the dosage was constant, the adsorption rate also increased with the time, and the growth rate was low. Theoretically, that was because the adsorbent rapidly adsorbed Cr^{6+} in the initial stage and had reached saturation in the later stage, so the adsorption rate did not increase significantly in the later stage. According to Table 5, the P value of time (B) was 0.0174, the P value of dosage (C) was 0.0286, and the P value of BC was $0.4201 > 0.05$, indicated that the influence of factors B and C on the adsorption rate of Cr^{6+} had no interaction. According to the multiple quadratic regression equation obtained from the response surface, the coefficient of BC was + 0.22, indicated that the interaction of the two factors had a positive effect on the result.

Figure 3. Effect of time and dosage on the adsorption rate of Cr^{6+}

The optimal solution was selected by response surface analysis

Further analysis was performed using the fitted multiple quadratic regression equation and Design-Expert 8.0.6 software. And the predicted values of the optimal values and optimal processing conditions were obtained within the experimental design

conditions. The optimal conditions for prediction were as follows: when the temperature was 30.12 °C, time was 3.05 h, the dosage was 3.45 g, the modified carbonized straw had the best adsorption effect on Cr^{6+} . And then it was proved that the actual and predicted values were well fitted, which indicated that it was feasible to optimize the modified carbonized straw to absorb Cr^{6+} by response surface method.

Adsorption kinetics of Cr^{6+} adsorbed by modified carbonized straw

The adsorption kinetics curves of different dosages (1.2 g/L, 2.4 g/L, 3.6 g/L) of carbonized wheat straw to 200 ml for 100 mg/L Cr^{6+} were shown in *Figure 4*, and the reaction conditions were as follows: temperature was 25 °C, pH was 9, oscillation speed was 250 r/min. The results showed that the larger the dosage of adsorbent, the smaller the adsorption capacity at equilibrium, and the time needed to reach adsorption equilibrium was close, which might be related to the concentration of Cr^{6+} . In addition, under different adsorbent dosages, the adsorbent exhibits similar adsorption kinetic behavior, and each curve could be divided into the following three stages: the dosage of 1.2 g/L was taken as an example. The slope of the first stage was very large, and the adsorption amount increased from 3.13 mg/g to 15.21 mg/g within 1.5 h, which might be caused by the Van der Waals' force between the adsorbent and the adsorbate, indicated that the adsorption process was a fast physical process (Gong, 2011). In the second stage, the adsorption amount increased from 15.21 mg/g to 16.34 mg/g within 0.5 h, which was slow. In the third stage, when the adsorption time was longer than 2 h, the adsorption amount reached equilibrium.

The data of *Figure 4* were fitted using the first-order kinetic equation, the double-constant equation, and the Elovich equation. The fitting results are presented in *Figures 5–7* and *Table 6*.

Table 6. Fitting results of reaction rate equations under different dosages

m (g/L)	First-order kinetic equation			Double-constant equation			Elovich equation		
	k_1	a	R^2	k_2	a	R^2	k_3	a	R^2
1.2	1.0457	4.5353	0.868	0.4701	2.2424	0.8732	5.4529	9.7438	0.9192
2.4	1.0877	4.390	0.8642	0.915	1.2643	0.9399	3.1211	4.4071	0.9123
3.6	1.0367	4.0728	0.8608	0.7668	0.8036	0.8946	2.2832	2.7421	0.9277

Figure 4. Adsorption kinetic curves of different adsorbent dosages

Figure 5. First-order kinetic equation

Figure 6. Double-constant equation

Figure 7. Elovich equation

It could be seen from Table 6 that R^2 values of the first-order kinetic equation, the two-constant equation and the Elovich equation increase in turn, and R^2 values exceed 0.86. Therefore, the three kinetic equations could better fit the process of adsorbing Cr^{6+} by modified carbonized straw before the adsorption reaches equilibrium. However, Elovich equation had the highest fitting degree, and its R^2 was > 0.91 , which indicated that the fitting effect of Elovich equation was the best, indicated that the fitting range of the first-order kinetic equation could not meet the process of adsorbing Cr^{6+} by modified carbonized straw. This might be due to the multiple effects of the modified carbonized straw on the adsorption of Cr^{6+} , rather than being limited to the first-order

kinetic range. In addition, the adsorption process was not a single adsorption mechanism, but a combination of interlayer cation exchange and surface complex adsorption, and it was also related to changes in structure and functional groups after straw modification (Li, 2015).

Thermodynamic analysis of Cr^{6+}

According to the thermodynamic experimental results of adsorption of Cr^{6+} by modified carbonized straw at different temperatures, the equilibrium partition coefficient K was obtained. $\ln K$ was used as the ordinate and $1/T$ was used as the abscissa to get a straight line, as shown in *Figure 8*. ΔS and ΔH could be calculated from the intercept and slope of the line respectively, and then ΔG was calculated. The calculation results were shown in *Table 7*.

Figure 8. $\ln K$ - $1/T$ curve

Table 7. Thermodynamic parameters

ΔS (J/mol·K)	ΔH (kJ/mol)	T (K)	ΔG (kJ/mol)
128.35	36.45	288	-0.51 kJ/mol
		298	-1.80 kJ/mol
		308	-3.08 kJ/mol

It could be seen from *Table 7* that $\Delta H > 0$ in the adsorption process, indicated that the reaction process was an endothermic reaction, so the temperature rise was favorable for the adsorption process. ΔG could reflect the driving force of a reaction. It could be known from the above data that $\Delta G < 0$ under the temperature conditions of 288 K, 298 K and 308 K, indicated that the adsorption of Cr^{6+} by modified carbonized straw was a spontaneous process. Therefore, chromium ions tended to spontaneously adsorb from the liquid body to the surface of the modified carbonized straw, and the spontaneity increased with the increase of temperature. In addition, $\Delta S > 0$ indicated that the adsorption of Cr^{6+} by the modified carbonized straw increased the disorder of the system. According to the adsorption exchange theory, the adsorption of ions in the solution by the adsorbent was a process of entropy reduction. At the same time, the adsorbent would shrink and release part of the water molecules, which would increase the entropy of the system, and the combination of the two would increase the entropy of the system (Li, 2013).

Conclusions

In the experiment, different carbonized straws were modified by different modifiers, and the iodine adsorption value was used as an indicator to compare the adsorption capacity of different modified carbonized straws. It was found that the modified carbonized wheat straw with 2 mol/L FeCl_2 as modifier had the highest iodine adsorption value 1161.15 mg/g.

Response surface analysis showed that adsorption rate was taken as the response value, temperature, pH and dosage were taken as the factors, and the quadratic response surface regression model of chromium ion adsorption on modified carbonized straw was obtained. The model was significant, the unfitting term was not significant, and the fitting degree of the equation was high. Therefore, it was feasible to optimize the adsorption conditions of Cr^{6+} on modified carbonized straw by response surface methodology.

Using wheat straw as raw material, the modified carbonized straw prepared by FeCl_2 activation method could effectively absorb chromium ions. The Elovich equation, the double constant equation and the first-order kinetic equation could be well fitted to the process of adsorbing chromium ions by modified carbonized straw. However, Elovich equation had the highest fitting degree, and its R^2 was > 0.91 , indicated that the fitting range of the first-order kinetic equation could not meet the process of adsorbing Cr^{6+} by modified carbonized straw. This might be due to the fact that the main form of adsorption of chromium ions by modified carbonized wheat straw was interlayer cation exchange and surface complex adsorption, rather than a single adsorption mechanism, and it was also related to changes in structure and functional groups after straw modification.

The adsorption of chromium ions by modified wheat straw was a spontaneous endothermic process, and the temperature rise was beneficial to the reaction. Moreover, in the adsorption process, $\Delta S > 0$ indicated that the adsorption of Cr^{6+} by the modified carbonized straw increased the disorder of the system. This might be due to the change in the surface structure of the modified carbonized straw after the adsorption of chromium ions by the modified carbonized straw, resulting in the increase of the disorder of adsorption system.

The results of this research could raise concerns over possible the comprehensive utilization of agricultural wastes and the treatment of heavy metal wastewater. The authors plan to further study the treatment of different types of heavy metal wastewater by other types of activated carbon under different conditions in the future.

Acknowledgements. This research was financed by the National Natural Science Foundation of China (No. 31600253), the Science and Technology Department Foundation of Sichuan Province (No. 2017JY0087), the Education Department Foundation of Sichuan Province (No. 18ZA0119), the Science and Technology Bureau Foundation of Chengdu (No. 2016-HM01-00004-SF), the Teaching Reform Project Foundation of Chengdu University (CDJGB2017050), the Meat Processing Key Laboratory Foundation of Sichuan Province (No.18-R-17) and the Excellence Project Foundation of Chengdu University (No. 82502&33111).

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