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Adsorption, reduction and regeneration behavior of high surface area activated carbon in removal of Cr(VI)

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ABSTRACT

Hexavalent chromium Cr(VI) pollution problem has become increasingly serious. In this study, activated carbon CGP-K3-800 was prepared from commercial Norit CGP by using KOH as activator for the removal of Cr(VI). The surface area of CGP-K3-800 was increased up to 3,098 m^2/g. The adsorbent CGP-K3-800 exhibited an adsorption capacity of 4.99 mmol/g (259.5 mg/g) in the solution pH of 2 at 25°C, which was 1.64 times larger than that of the original CGP. Adsorption equilibrium data were described and analyzed by the Langmuir models, indicating that Cr(VI) adsorption on CGP-K3-800 tended to be monolayer adsorption. The calculated thermodynamic parameters showed that the adsorption process of Cr(VI) onto CGP-K3-800 was an endothermic process. By investigating the effect of pH, the acid condition is conducive to the adsorption and reduction process of Cr(VI). CGP-K3-800 had good regeneration performance, and the reduction ability of Cr(VI) on the CGP-K3-800 would be gradually lost. CGP-K3-800 shows a higher adsorption capacity and better regeneration performance in removal of Cr(VI), can be applied as a promising adsorbent for the removal of Cr(VI) from wastewater.

Keywords: Hexavalent chromium; Activated carbon; Adsorption; Reduction; Isotherm; Regeneration

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1. Introduction

With the development of global industrialization, environmental pollution has become increasingly serious. In view of the harm of heavy metals to human beings, heavy metal pollution in water has become one of the hot research issues in environmental research [1]. Chromium is a recognized carcinogen which is widely found in environmental media [2]. The chromium pollution mainly comes from waste water in industries such as leather tannins, electroplating, metallurgy, printing and dyeing. In addition, some natural activities (volcanic activity and rock weathering) also produce chromium pollution [3]. These chromium elements can accumulate in body through the food chain, and excessive chromium content in human body will lead to upper respiratory tract stimulation, causing liver and kidney failure and even cancer [4,5].

Chromium mainly presents as Cr(III) and Cr(VI) in the environment. Cr(III) is approximately 500 times less toxic than Cr(VI) [6], while Cr(VI) has good water solubility and stronger toxicity. Cr(VI) can be easily absorbed and accumulated by human body, especially by kidneys, stomach and liver [7]. The permissible limit for Cr(VI) in drinking water in Japan is 0.05 mg/L, which is identical to the drinking water guideline value recommended by World Health Organization [8].

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At present, common treatment methods of chromium containing wastewater include separation [9], reduction [10], ion exchange [11] and adsorption [12]. Among these methods, adsorption is a preferred method due to its high efficiency, flexibility, simplicity of design and operation [13]. The adsorption method mainly adopts the intermolecular physical and chemical effects to remove the heavy metal ions in the wastewater [14]. Commonly-used adsorbents generally have large specific surface area, such as activated carbon, zeolite, molecular sieve, etc., in which activated carbon is the most widely used.

Activated carbon is a black porous adsorbent with large surface area, high internal porosity and good adsorption capacity [15]. Activated carbon is a widely used adsorbent because of its stable nature, good acid and alkali resistance, heat resistance and sound regenerability. Activated carbon, as a common adsorbent, is very effective in the treatment of organic matter in water. Activated carbon also plays an important role in soil amendment, climate change and soil pollution remediation [16–18]. Compared with other water treatment methods, activated carbon adsorption as a more conventional way is also more convenient, economical and practical [19].

In the past, the adsorbed amount of anion was mainly increased by making nitrogen-doped activated carbon. For example, the activated carbon was heated by NH_3 gas at high temperature to enhance the adsorption capacity of nitrate [20]. Heat treatment of urea and melamine were applied to enhance the adsorption capacity of Cr(VI) [21]. However, nitrogen-doped activated carbon may have complex reaction and produce carbon, and nitrogen functional groups tend to degrade during the nitrogen removal process, which leads to non-recyclability of activated carbon [22]. Therefore, it is still a challenge to prepare activated carbon with high adsorption capacity and recyclable carbon.

Surface structural modification for activated carbon refers to the process of increasing the specific surface area by physical or chemical activation methods. The carbonization and activation of the materials were realized by selectively heating raw materials under inert atmosphere using different activators. The main activators used include $ZnCl_2$ [23,24], H_3PO_4 [25], alkali such as KOH [26] and NaOH [27]. It is worth noting that KOH activation method can significantly increase the specific surface area of activated carbon.

Previous studies showed that the adsorbed amount of Cr(VI) on activated carbon was relatively higher under acidic conditions [28]. However, under acidic conditions, Cr(VI) has strong oxidation and redox reaction may occur on the surface of activated carbon [29]. To our best knowledge, there are relatively few investigations on separating the reduction process from the adsorption process of Cr(VI) onto activated carbon. Therefore, the reduced amount and adsorbed amount were separated for the study of adsorption of Cr(VI) onto activated carbon.

Based on these considerations, the commercial activated carbon NORIT CGP SUPER (CGP) was further activated by KOH in this study to increase the specific surface area of CGP, and expected to get into the highest group of adsorbents in the removal efficiency of Cr(VI). Therefore, the adsorption and reduction cycles were studied in the experiment, and the regeneration performance of activated carbon was evaluated.

2. Materials and methods

2.1. Preparation of activated carbon

The activated carbon NORIT CGP SUPER (CGP) was purchased from CABOT Company (Japan). The CGP was dried in an oven at 110°C for 1 h. In activation step, the samples were mixed with solid KOH by different impregnation ratios (KOH/CGP mass ratio of 1:1, 2:1 and 3:1). Then, the mixtures were transferred to a stainless steel tube reactor and heated up to the temperature ranging from 500°C to 800°C in N_2 gas atmosphere and held for 1 h. The N_2 gas flow rate was 400 mL/min. After cooling to room temperature, the carbons were placed in 1 M HCl solution, stirred for 1 h, then washed with hot distilled water until the pH in a Soxhlet extracted water was unchanged. Finally, the activated carbon was dried in an oven at 100°C overnight to remove the moisture, then cooled down in desiccators to room temperature. The obtained samples were referred to as CGP-K*x*-*y*, where *x* is the impregnation ratio (g KOH/g CGP) and *y* is the activation temperature in degree centigrade.

2.2. Characterization of activated carbon

The specific surface area (S_{BET}), mesopore volume (V_{meso}) and micropore volume (V_{micro}) of the prepared activated carbon were calculated based on N_2 adsorption/desorption isotherms at –196°C using Bellsorp-mini II (MicrotracBEL, Co., Ltd., Japan) surface area analyzer. The surface morphology of the activated carbon was observed by Hitachi S-4800 SEM instrument (Hitachi, Japan). The elemental composition of C, H and N for the adsorbents was determined with PerkinElmer 2400 II (PerkinElmer Japan, Co., Ltd., Japan), and O content was obtained by difference. X-ray photoelectron spectroscopy (XPS) analysis was performed using an ULVAC-PHI Model-1800 spectrometer. The zeta potential of samples was measured by zeta potential analyzer (ZC-3000 MICROTEC, Japan) at 30 mV.

2.3. Batch adsorption

Batch experiments for Cr(VI) adsorption were conducted to examine the adsorption and reduction performance of the prepared activated carbons as adsorbents. All batch experiments were carried out in Erlenmeyer flask. CGP, CGP-K3-800 and ion exchange resin HP555 were mainly compared in the experiment. The effects of the adsorbent dosage, contact time, initial pH, initial concentration of Cr(VI) and temperature were investigated in the batch experiments. The solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH. The flasks were agitated in a thermostatic shaker at 100 rpm for 24 h. The concentration of Cr(VI) in the aqueous solution was determined by 1,5-diphenylcarbohydrazide using UV-spectrophotometer (UV-2550, Shimadzu, Japan) at 540 nm. The concentration of total chromium was measured by atomic absorption spectrometer novAA300 (Analytik Jena AG, Germany), based on which the adsorbed amount of Cr(VI) on activated carbons at the equilibrium was calculated by the following equation:

$$Q_e = \left(C_0 - C_{e1}\right) V / m \tag{1}$$

The removal percentage (R%) of Cr(VI) was calculated by the following equation:

$$R(\%) = \left(C_0 - C_{e2}\right) \times 100\% \tag{2}$$

where C_0 (mmol/L) represents the initial concentration of Cr(VI), C_{e1} (mmol/L) is the final adsorption equilibrium concentration of total chromium, C_{e2} (mmol/L) is the final adsorption equilibrium concentration of Cr(VI) as shown in Fig. 1. The m is the mass of sample (mg), V is the volume of solvent (mL).

The Langmuir isothermal adsorption model is a theoretical model assuming that the adsorbates are adsorbed in monolayer on the surface of the adsorbent. The linear form of Langmuir equation can be given as:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K_L} + \frac{1}{X_m} C_e \tag{3}$$

where Q_e (mmol/g) is the adsorptive amount of Cr(VI) at equilibrium, C_e (mmol/L) is the equilibrium concentration of Cr(VI) in the solution, X_m (mmol/g) is the monolayer adsorption capacity and K_L (L/mmol) is the Langmuir constant related to adsorption energy. The Langmuir isothermal adsorption model defines R_L as the separation factor, which is represented as Eq. (4):

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where C_0 is the initial Cr(VI) concentration in the solution. R_L is the adsorption equilibrium parameter. There are three possibilities for the R_L value: $0 < R_L < 1$; favorable adsorption, $R_L = 1$; unfavorable linear adsorption and $R_L = 0$; irreversible adsorption [30].

The linear form of Freundlich equation is:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

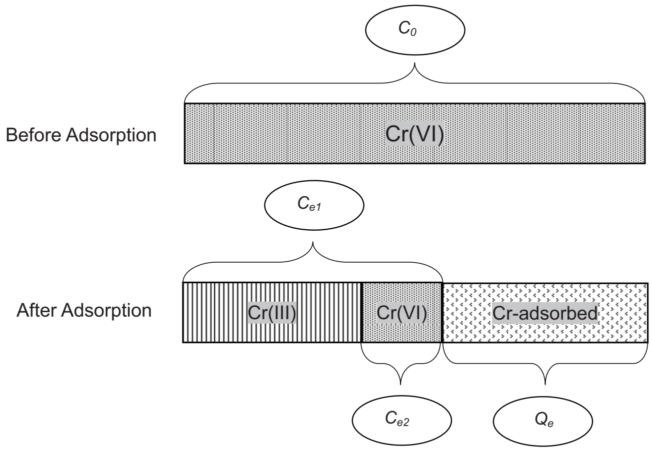

Fig. 1. State diagram of Cr(VI) before and after adsorption.

where K_F is the Freundlich constant and $1/n$ is the heterogeneity factor. The greater the value of n is, the better the adsorption performance will be.

The thermodynamic parameters were calculated in the experiment of the effect of temperature. The thermodynamic parameters of Gibbs free energy change $\Delta G°$ (KJ/mol), enthalpy change $\Delta H°$ (KJ/mol) and $\Delta S°$ (entropy change, KJ/mol K) are calculated by Eqs. (6)–(8) [31] as follows:

$$\Delta G° = -RT \ln K_d \tag{6}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

$$\ln K_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{8}$$

where R (8.314 J/mol K) is a general gas constant, T (K) is the thermodynamic temperature, and K_d (L/mg) is the standard thermodynamic equilibrium constant defined by q_e/C_e, which is from the Langmuir equation (K_L) or Freundlich equation K_F.

The kinetics study was performed in a 100 mL of 100 mg/L Cr(VI) solution at pH 2. The linear form of the pseudo-first-order equation can be expressed as Eq. (9):

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{9}$$

where Q_e is the adsorbed amount of Cr(VI) at equilibrium (mmol/g), Q_t is the adsorbed amount of Cr(VI) (mmol/g) at time t (min), and k_1 is the rate constant of the pseudo-first-order model (1/min).

The linear form of the pseudo-second-order model equation is given in Eq. (10) as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{10}$$

where k_2 is the rate constant of the pseudo-second-order model (g/mmol min).

The effect of coexisting anions on phosphate adsorption was examined by adding same dosage of CGP-K3-800 (1 g/L) into 20 mL of 4 mmol/L Cr(VI) solution with and without coexistent anions (Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}). The concentration of each coexisting anion was 8 mmol/L, and the concentration of all coexistent anions was two times higher than that of Cr(VI) ion. In order to examine the influence of coexisting ions HCO_3^- species, the initial pH must be adjusted to 6. After 24 h of shaking, the supernatant was taken to measure the Cr(VI) concentration.

2.4. Regeneration experiment

In regeneration experiment, 100 mg of adsorbents were added in a Erlenmeyer flask (500 mg/L) containing 100 mL of Cr(VI) solution with initial pH of 2. Then, the Erlenmeyer flask was placed in a reciprocal shaker and agitated at

100 rpm at 25°C. Meanwhile, 1 mol/L NaOH solution was used as the desorption agent. In the desorption agent, the solution was heated to 90°C and kept for 1 h before filtering out the adsorbents. This process was repeatedly performed until the filtered solution was clear. The regeneration experiment was repeated in the successive adsorption–desorption cycles that were conducted for five times.

3. Results and discussion

3.1. Physicochemical characterization

The specific surface area (BET) and micro-/mesoporous structure parameters of the adsorbent were calculated, and shown in Table 1. It can be seen that when the activation ratio is 3:1 and the activation temperature was 800°C, the adsorbent had maximum specific surface area and microporous volume. Moreover, the BET of CGP-K3-800 (3,098 m^2/g) nearly doubles that of CGP (1,634 m^2/g). Fig. 2 shows SEM images of the CGP and CGP-K3-800, where the surface of the samples can be clearly observed. The surface of the CGP-K3-800 is rougher than that of the original CGP. It has been reported that the high surface area and high pore volume can facilitate the transfer of heavy metal ions [32]. Therefore, CGP-K3-800 is expected to have higher removal efficiency of Cr(VI). The elemental composition of CGP and CGP-K3-800 is shown in Table 2. It can be seen from Table 2 that the nitrogen contents in CGP and CGP-K3-800 were very low, indicating that there are a very limited number of nitrogen functional groups in the two adsorbents. The zeta-potential values of CGP-K3-800 at different pH_e in pure water are shown in Fig. 3. The CGP-K3-800 was positively charged for $pH_e < 4.4$ and negatively charged for $pH_e > 5.4$, which meant that the IEP of CGP-K3-800 is between 4.4 to 5.4. The isoelectric point for the CGP-K3-800 is near 5.0. The electrophoretic mobility curve indicates that the CGP-K3-800 has negative zeta potential when pH is higher than 5.0.

3.2. Removal efficiency of Cr(VI) for each prepared adsorbent

The experiment was carried out with the Cr(VI) concentration of 500 mg/L at pH 2.0 for 24 h. The Cr(VI) removal efficiency by different prepared adsorbents are shown in Fig. 4. It showed that the removal efficiency of the CGP modified by KOH activation (51.6%–87.8%) was higher than that of the original CGP (42.3%). When the impregnation ratio (KOH/CGP mass ratio) was 3:1 and the activation temperature was 800°C, the removal efficiency can reach 87.8%. Compared with the results of Table 1, it can be seen that the relatively larger specific surface area of CGP-K3-800 would be effective to the removal of Cr(VI) in the activated carbons of modified CGPs.

Table 1
Textural and surface properties of each prepared activated carbon

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_{ave} (nm)
CGP	1,634	1.36	1.2	0.13	0.95
CGP-K1-500	1,532	1.25	1.1	0.11	0.92
CGP-K1-600	1,610	1.10	1.0	0.10	0.84
CGP-K1-700	1,897	1.27	1.2	0.10	0.86
CGP-K1-800	1,858	1.07	1.0	0.10	0.90
CGP-K2-800	1,918	1.36	1.3	0.10	1.02
CGP-K3-800	3,098	2.23	2.1	0.14	1.30

3.3. Effect of initial solution pH

Initial solution pH has a significant impact on the removal efficiency of Cr(VI) in aqueous solution. Different solution pH values will cause different surface charges of the activated carbon and different anionic forms of the Cr(VI).

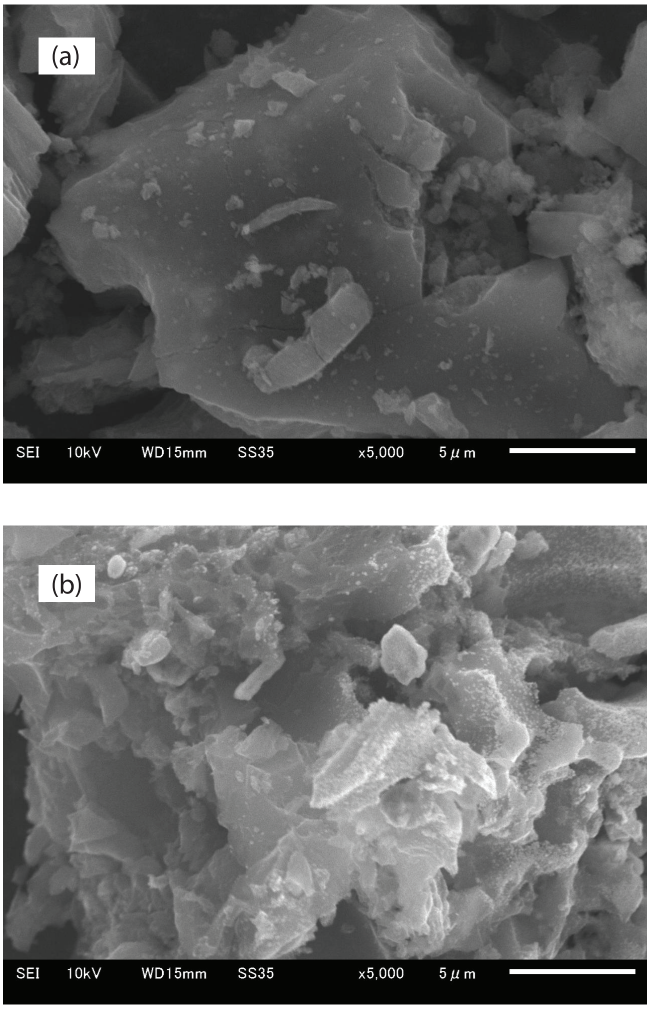

Fig. 2. SEM images of CGP (a) and CGP-K3-800 (b).

Table 2
Elemental composition of CGP and CGP-K3-800

Sample	C (%)	H (%)	N (%)	O[a] (%)
CGP	79.6	2.0	0.4	18.1
CGP-K3-800	91.4	0.1	0.3	8.2

[a] Calculated by difference.

The Cr(VI) presents as different ionic forms in aqueous solution, when solution pH > 6, it presents as CrO_4^{2-}; when pH is ranging from 1.0 to 6.0, the species is $Cr_2O_7^{2-}$ and $HCrO_4^-$, H_2CrO_4 will be dominant in case of pH < 1.0 [33]. In this experiment, the solution pH was adjusted from 2.0 to 12.0 with 0.1 M HCl and 0.1 M NaOH. The adsorbed amount and the reduced amount were investigated within pH range from 2.0 to 12.0. The results are given in Fig. 5. It can be seen that lower the solution pH value, larger the adsorption capacity for Cr(VI). This is because the solution pH value significantly affected the structure of the adsorbents and the surface charges of the adsorbent and the surface-reactive functional groups in the solution. As shown in Fig. 3, when pH value is low, the zero point potential is higher, which is favorable for the adsorption of Cr(VI). When the solution pH was less than 6, Cr(VI) was reduced to Cr(III) to some extent on CGP-K3-800, so it can be known that the acid condition was conducive to the reduction process of Cr(VI).

3.4. Effect of adsorbents dosage

Adsorbents dosage can change the adsorbent–adsorbate equilibrium of the system. The effect of adsorbents dosage on Cr(VI) removal rate was investigated with the Cr(VI) concentration of 500 mg/L at pH 2.0 for 24 h in this work. As shown in Fig. 6, the removal rate of Cr(VI) increased with

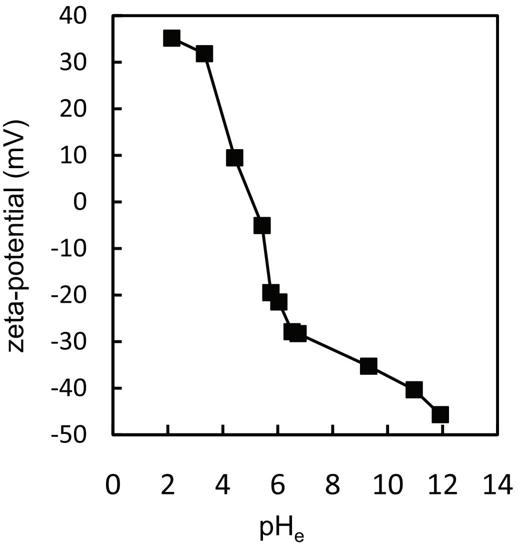

Fig. 3. Zeta-potential of CGP-K3-800 as a function of pH_e.

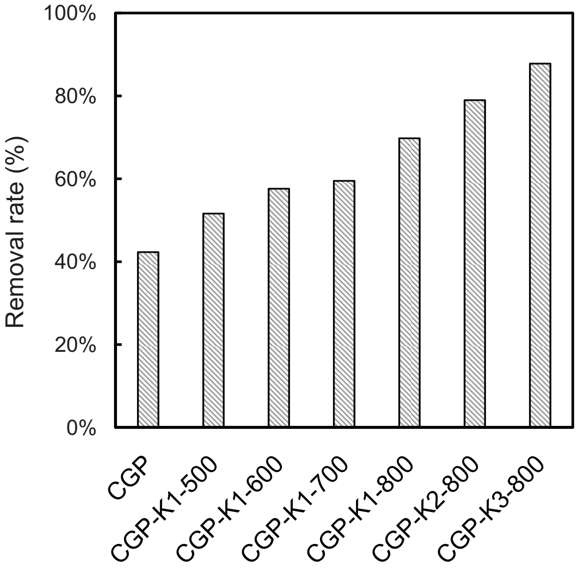

Fig. 4. Removal rate of Cr(VI) for each adsorbent (conditions: pH 2; initial concentrations of Cr(VI): 500 mg/L; contact time: 24 h; concentration of adsorbent: 1 g/L; temperature: 298 K).

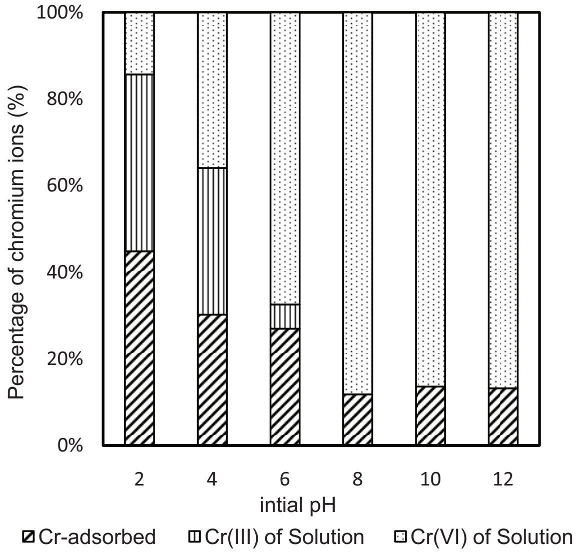

Fig. 5. Effect of pH of Cr(VI) adsorption onto CGP-K3-800 (conditions: pH 2–12; initial concentrations of Cr(VI): 500 mg/L; contact time: 24 h; concentration of adsorbent: 1 g/L; temperature: 298 K).

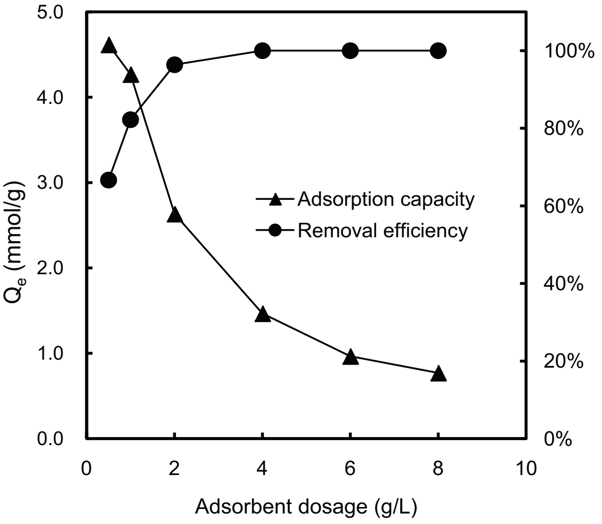

Fig. 6. Effect of adsorbent dosage on the CGP-K3-800 of Cr(VI) (conditions: pH 2; initial concentrations of Cr(VI): 500 mg/L; contact time: 24 h; concentration of adsorbent: 0.5–8 g/L; temperature: 298 K).

the adsorbent dosage, which reached nearly 100% at the adsorbent dosage of 4 g/L. However, the adsorption capacity decreases with the increase of the adsorbents dosage, this may be due to the adsorption competition for adsorbents. Therefore, it is necessary to determine the dosage of adsorbents in actual water treatment. In this work, the adsorbent dosage was set to 1 g/L for experiments.

3.5. Adsorption isotherms

The adsorption isotherms of Cr(VI) on CGP, CGP-K3-800 and ion exchange resin HP555 under different initial concentrations (from 100 to 1,000 mg/L) of Cr(VI) solution are shown in Fig. 7. Langmuir and Freundlich models were applied to investigate the adsorption process of Cr(VI) at 25°C. The different isotherm constants determined are shown in Table 3. Through the Langmuir and Freundlich data fitting of adsorption isotherms of Cr(VI), the R^2 values were greater than 0.99, indicating that the two models could well describe Cr(VI) adsorption behavior. In the Langmuir isothermal adsorption models, $0 < R_L < 1$, indicating favorable adsorption of Cr(VI) on the adsorbents. Langmuir model-based fitting data were slightly better than Freundlich adsorption model-based fitting data, indicating that Cr(VI) adsorption on CGP-K3-800 tended to be monolayer adsorption. Similar trends could be drawn from the adsorption isotherm data of CGP-K3-800. In comparison with the maximum adsorption capacity (X_m) of three adsorbents in adsorption isotherm experiment, the X_m value for CGP-K3-800 was larger than that for CGP and ion exchange resin HP555, implying that the adsorption capacity of CGP-K3-800 was better than that of CGP and ion exchange resin HP555. This may be because CGP-K3-800 has a greater specific surface area as shown in Table 1. Moreover, the adsorption capacity of CGP-K3-800 for Cr(VI) was higher than that reported in the literature, as shown in Table 4 [2,21,34,35].

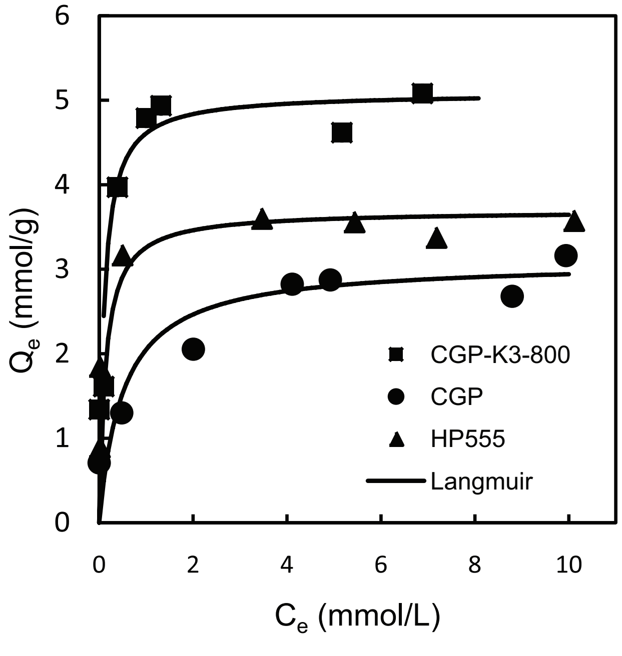

Fig. 7. Adsorption isotherms of Cr(VI) onto HP555, CGP and CGP-K3-800 (conditions: initial concentrations of Cr(VI): 100 to 1,000 mg/L; contact time: 24 h; adsorbent: 1 g/L, respectively; temperature: 298 K).

3.6. Adsorption thermodynamics parameters

The correlation coefficients (R^2) are given in Table 5. Since Cr(VI) adsorption data on the CGP-K3-800 fitted better to the Langmuir adsorption isothermal equation in the study, thereby the Langmuir adsorption isothermal constant K_L was adopted. The slopes and intercepts of the plots of ln K_L against $1/T$ are shown in Fig. 8. The values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ for Cr(VI) adsorption on CGP-K3-800 are given in Table 6. The positive values of $\Delta H°$ indicate that the adsorption process was an endothermic process. The negative value of $\Delta G°$ indicates that all adsorption processes were viable and spontaneous [36].

3.7. Adsorption kinetics

The experimental data in Fig. 9 were fitted with pseudo-first-order model and pseudo-second-order models when CGP-K3-800, CGP and HP555 were used. The results of the kinetic analysis are shown in Table 7.

The pseudo-first-order model had lower correlation coefficient (R^2) compared with that of the pseudo-second-order models, and all R^2 values are greater than 0.99 for

Table 4
Comparison with other similar adsorbents for Cr(VI) removal

Adsorbent	Q_{max} (mmol/g)	Reference
Bamboo	1.83	[21]
*Auricularia auricul*a	0.23	[35]
Hyacinth	0.84	[34]
Longan seed	3.26	[2]
HP555[a]	3.69	This work
CGP[a]	3.09	This work
CGP-K3-800	4.99	This work

[a]Commercially available.

Table 3
Langmuir and Freundlich adsorption isotherm parameters of Cr(VI) at 298 K in aqueous solutions

Sample	Langmuir model				Freundlich model		
	X_m (mmol/g)	K_L (L/mmol)	R_L	R^2	n	K_F ([mmol/g][mmol/L])^n	R^2
CGP	3.09	1.97	0.031	0.981	3.55	1.68	0.916
CGP-K3-800	4.99	11.0	0.006	0.996	4.41	3.82	0.673
HP555	3.69	7.48	0.008	0.997	24.0	3.29	0.693

Table 5
Langmuir and Freundlich adsorption isotherm parameters of Cr(VI) at different temperature onto CGP-K3-800

Temperature (K)	Langmuir model			Freundlich model		
	X_m (mmol/g)	K_L (L/mmol)	R^2	n	K_F [(mmol/g)(mmol/L)^n]	R^2
298	4.99	11.0	0.996	4.41	3.82	0.673
308	5.78	15.6	0.998	5.38	4.78	0.855
318	6.79	18.9	0.999	8.89	5.93	0.824

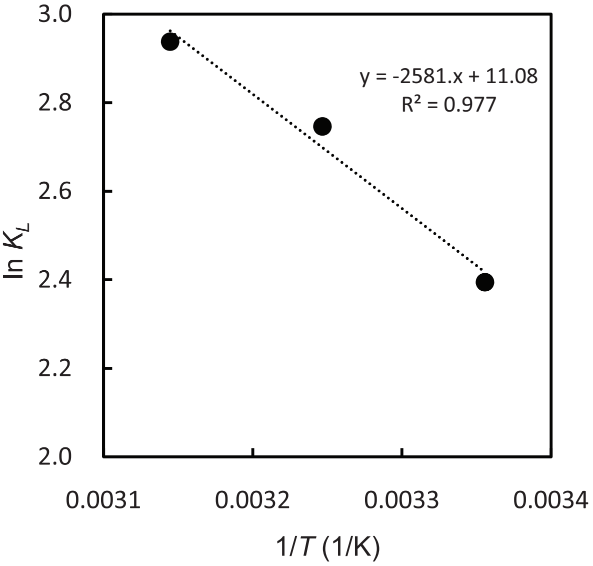

Fig. 8. Plot of ln K_L vs. $1/T$ for Cr(VI) adsorption on CGP-K3-800.

Table 6
Thermodynamic parameters of CGP-K3-800 for the adsorption of Cr(VI)

$\Delta S°$ (KJ/mol K)	0.0921
$\Delta H°$ (KJ/mol)	21.5
$\Delta G_1°$ (298 K) (KJ/mol)	–5.99
$\Delta G_2°$ (308 K) (KJ/mol)	–6.91
$\Delta G_2°$ (318 K) (KJ/mol)	–7.83

pseudo-second-order models. It can be seen from Fig. 9 that both CGP and CGP-K3-800 had very high adsorption rates. The adsorption equilibrium can be reached within 30 min for CGP and CGP-K3-800, and their adsorption rates are appreciably higher than that of HP555.

3.8. Effect of coexisting anions

Generally, Cr(VI) ions do not exist alone in industrial wastewater but coexist with other anions such as Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}. To investigate the influence of coexistent anions on Cr(VI) adsorption, the adsorption experiments with and without the presence of other anions (Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}) were carried out, and the results are shown in Fig. 10. All the anions showed indistinctive effect on the Cr(VI) adsorption, except HCO_3^-. This suggested that HCO_3^- ions compete for the active sites.

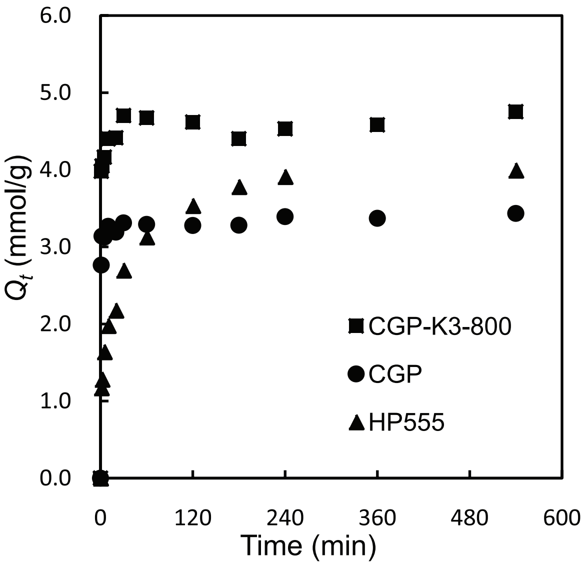

Fig. 9. Effect of contact time on the adsorption capacity of HP555, CGP and CGP-K3-800 (conditions: pH 2; initial concentrations of Cr(VI): 500 mg/L; adsorbent: 1 g/L, respectively; temperature: 298 K).

3.9. XPS analysis

Detailed XPS survey of the regions for Cr $2p_{3/2}$ of Cr(VI)-loaded CGP-K3-800 is shown in Fig. 11. Chromium element was detected which indicated the successful adsorption of chromium on the carbon surface. This result also demonstrates that reduction of Cr(VI) happens in the process of Cr adsorption. The peak at 576.5 eV in the $Cr2p_{3/2}$ of CGP-K3-800 after adsorption in Fig. 9 can be assigned to Cr(III), and the binding energy of Cr(VI) in the $Cr2p_{3/2}$ was generally higher than that of Cr(III), so the peaks at 578.1 eV in the $Cr2p_{3/2}$ can be assigned to Cr(VI) [37]. According to the $Cr2p_{3/2}$ peak areas, the ratio of adsorbed Cr(III) to Cr(VI) onto the CGP and CGP-K3-800 surface were all about 1.5:1, it was indicated that about 3/5 of the Cr(VI) was reduced to Cr(III) on the CGP-K3-800.

3.10. Regeneration experiment

In order to ascertain the reusability of the Cr(VI) on the adsorbents, this study evaluated the reproducible properties of CGP and analyzed the adsorption and reduction of Cr(VI) in the regeneration process. Fig. 12 shows that the adsorption capacity and reduction efficiency decrease with the increase of cycle times. The Cr(VI) adsorption efficiencies of the CGP and CGP-K3-800 are 23.8% and 40.7% in the first

Table 7
Kinetic parameters for Cr(VI) adsorption onto prepared adsorbents

Sample	Pseudo-first-order			Pseudo-second-order		
	Q_e (mmol/g)	k_1 (min^{-1})	R^2	Q_e (mmol/g)	k_2 (g/mmol min)	R^2
HP555	1.48	0.016	0.916	4.06	0.022	0.999
CGP	7.87	0.013	0.242	3.42	0.155	0.998
CGP-K3-800	7.45	0.021	0.366	4.69	0.099	0.999

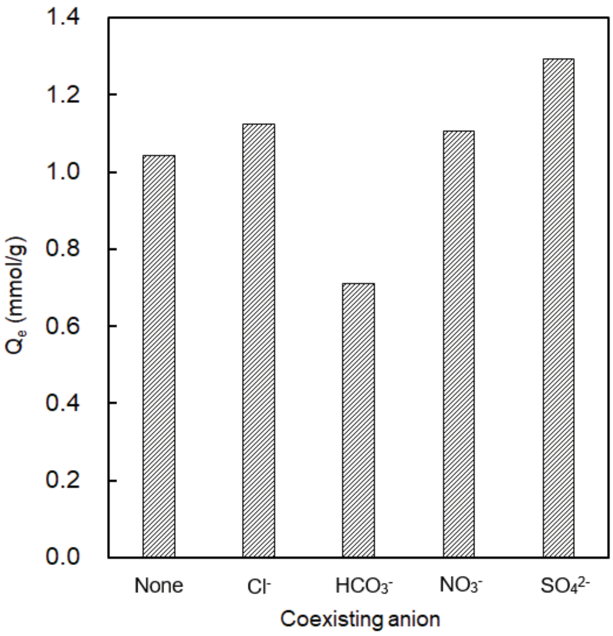

Fig. 10. Effect of coexisting anions on Cr(VI) adsorption by CGP-K3-800 (conditions: initial Cr(VI) concentration: 4 mmol/L; adsorbent dosage: 1 g/L; initial pH: 6 ± 0.02).

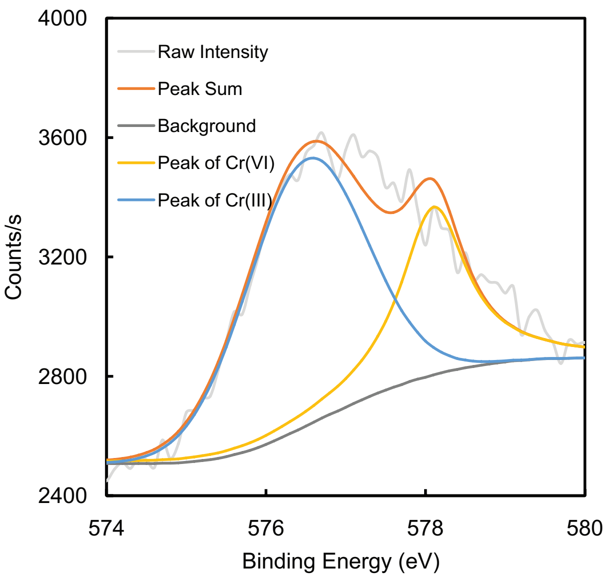

Fig. 11. Detailed XPS survey of the region Cr $2p_{3/2}$.

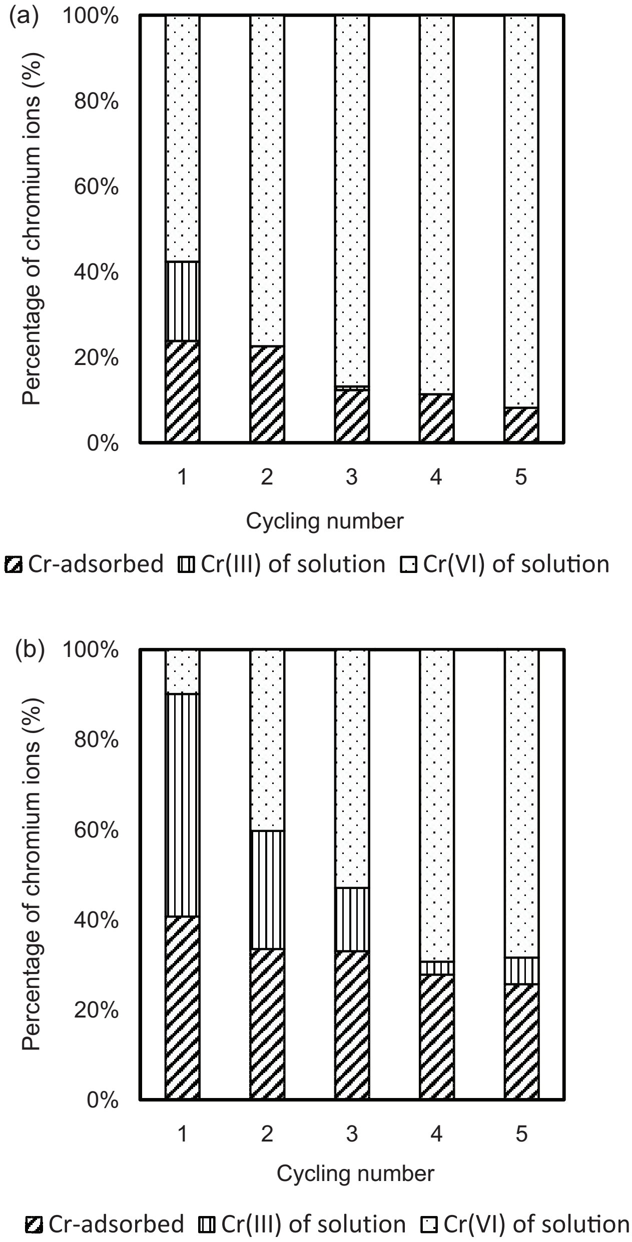

Fig. 12. Adsorption and reduction capacity of CGP and CGP-K3-800 for Cr(VI) at different adsorption–desorption cycles (conditions: pH 2; initial concentrations of Cr(VI): 500 mg/L; adsorbent: 1 g/L, respectively; temperature: 298 K). (a) CGP and (b) CGP-K3-800.

batch experiment, and decreased in the following cycle runs. In the fifth run, the adsorption ratios remained at 8.2% and 25.6%, indicating that CGP-K3-800 had a higher regeneration rate than CGP, and kept high adsorption capacity until the fifth cycle. Moreover, it can be seen that the reduction performance gradually decreased, which was contributed to the decline of the percentage of removal. And with the increase of cycle times, the Cr(VI) reduction efficiency of the CGP is decreased from 18.5% to 0%, and the reduction efficiency of the CGP-K3-800 is decreased from 49.4% to 5.9%. The decrease in reducing properties may be due to the continuous oxidation of the surface of the activated carbon.

4. Conclusions

In conclusion, the adsorbent CGP-K3-800 activated by KOH activation has a larger specific surface area and better effect on the removal of Cr(VI). The adsorbent CGP-K3-800 exhibits an adsorption capacity of 4.99 mmol/g (259.5 mg/g) at 25°C, which is 1.64 times larger than that of the CGP. The Cr(VI) adsorption capacity and capacity amount of CGP-K3-800 decrease with increase of solution pH value. The adsorption reaction conforms to the Langmuir model, and the increase of temperature can enhance the adsorption capacity of CGP. The CGP-K3-800 also shows a higher adsorption rate, and its adsorption equilibrium can be reached within 30 min. With respect to regenerative performance, CGP-K3-800 has better regeneration performance than CGP. With the increase of reutilization times, the surface of activated carbon is step wisely oxidized, which leads to gradual decrease of the reducing capacity. Therefore, CGP-K3-800 is expected to be a promising adsorbent for the efficient removal of Cr(VI) from wastewater.

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