An exploratory study on low-concentration hexavalent chromium adsorption by Fe(III)-cross-linked chitosan beads

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In this study, Fe(III)-cross-linked chitosan beads (Fe(III)-CBs) were synthesized and employed to explore the characteristics and primary mechanism of their hexavalent chromium (Cr(VI)) adsorption under low concentration Cr(VI) (less than 20.0 mg l\(^{-1}\)) and a pH range from 2.0 to 8.0. Batch tests were conducted to determine the Cr(VI) adsorption capacity and kinetics, and the effects of pH and temperature on the adsorption under low concentration Cr(VI) and a pH range from 2.0 to 8.0. Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy were employed to explore the characteristics of Fe(III)-CBs and their Cr(VI) adsorption mechanisms. The results show that, unlike the adsorption of other absorbents, the Cr(VI) adsorption was efficient in a wide pH range from 2.0 to 6.0, and well described by the pseudo-first-order model and the Langmuir–Freundlich isotherm model. The capacity of Cr(VI) adsorption by Fe(III)-CBs was as high as 166.3 mg g\(^{-1}\) under temperature 25°C and pH 6.0. The desorption test was also carried out by 0.1 mol l\(^{-1}\) NaOH solution for Fe(III)-CBs regeneration. It was found that Fe(III)-CBs could be re-used for five adsorption–desorption cycles without significant decrease in Cr(VI) adsorption capacity. Ion exchange was confirmed between functional groups (i.e. amino group) and Cr(VI) anions (i.e. CrO\(_2\)\(^{-}\)). The amino-like functional groups played a key role in Cr(VI) distribution on the Fe(III)-CBs surface; Cr(VI) adsorbed on Fe(III)-CBs was partially reduced to Cr(III) with alcoholic group served as electron donor, and then formed...
another rate-limiting factor. So, Fe(III)-CBs has a good prospect in purifying low concentration Cr(VI) water with a pH range from 2.0 to 6.0.

1. Introduction

Chromium is a common contaminant not only in industrial wastewater, derived from electroplating, metal finishing, leather tanning, steel fabrication and textile activities [1,2], but also in natural water including surface water and groundwater [3], originating from native geological environment. In nature, chromium exists in two stable oxidation states, i.e. the hexavalent (Cr(VI)) and trivalent (Cr(III)) states. The former is known to be much more toxic than the latter [4,5]. Cr(VI) is detrimental to the health when its concentration in drinking water exceeds 0.05 mg l$^{-1}$ [6]. Therefore, it is mandatory to remove Cr(VI) anions before water supply [7]. Numerous treatment processes, including chemical precipitation, biological reduction, ion exchange and adsorption, have been studied extensively for Cr(VI) removal [8–10]. Among them, adsorption has been recognized as an economical and effective technique, and much attention has been paid to the development of cost-effective and efficient adsorbents [11–13]. Various adsorbents, such as active carbon [14], silica-gel [15], raw clays [16] and hydrotalcite [17], have been used for Cr(VI) adsorption. However, these adsorbents focused on treating industrial wastewater; although they had high adsorption capacities under acid pH, the treated water still had Cr(VI) anion, whose concentration was not low as expected, limiting their broad application. To overcome this, further treatment is needed. Meanwhile, in natural surface water and groundwater, where Cr(VI) is in low concentration and pH closes to neutrality, the Cr(VI) also needs to be treated [3]. Up to now, few studies on these have been conducted.

Chitosan is a linear cationic semisynthetic polysaccharide, which could be easily separated from seafood-processing wastes and employed as an adsorbent for pollution control [18,19]. In addition, its characteristic in adsorption was found to be superior to other adsorbents in terms of non-toxicity, hydrophilicity, biocompatibility, antibacterial activity and biodegradability [20,21]. Chitosan has also been used for Cr(VI) adsorption in water environments. Nevertheless, the capacity was found to be only 76.9 mg g$^{-1}$ [22,23]. So enhancing the adsorption capacity of chitosan is currently one of the major tasks for Cr(VI) removal. Previous studies have indicated that binding with special metal could significantly improve the adsorption capacity of the adsorbent. The composites via linking zirconium and Fe have been employed to remove Cr(VI) in aqueous solution. And the adsorption capacities could reach 175.0 and 173.1 mg g$^{-1}$, respectively [24,25]. The higher adsorption capacities of these metal-chitosan adsorbents imply their potential popularity in practical Cr(VI) removal. Although Cr(VI) removal at high concentrations (greater than 100 mg l$^{-1}$) and low pH (less than 5.0) by Fe-cross-linked chitosan has been reported, no detailed study on the Cr(VI) removal by Fe-cross-linked chitosan under low concentration Cr(VI) and natural pH was carried out. Meanwhile, the mechanism of this composite to adsorb Cr(VI) deserves exploration.

In this study, Fe(III)-cross-linked chitosan beads (Fe(III)-CBs) were synthesized. The beads were employed to conduct the adsorption tests to determine the capacity, equilibrium isotherm and kinetics of the low concentration Cr(VI) (less than 20.0 mg l$^{-1}$) adsorption under pH range from 2.0 to 8.0 pH. The surface morphology and functional groups of the beads were characterized through scanning electron microscopy (SEM) and Fourier-transform infrared (FT-IR). The oxidation states of chromium during its adsorption by Fe(III)-CBs were confirmed by X-ray photoelectron spectroscopy (XPS). Based on these data in this study, the possible mechanism of low concentration Cr(VI) adsorption by Fe(III)-CBs was proposed. These results strongly proved that Fe(III)-CBs have a good prospect in purifying low concentration Cr(VI) water with pH range 2.0–6.0.

2. Material and methods

2.1. Materials

All the reagents used in this study were of analytical grade. Chitosan (MW = 200 000, DA = 90%) was purchased from Shanghai DEMO Medical Tech. Co., Ltd (Shanghai, China). Epichlorohydrin was obtained from FUCHEN chemical reagents factory (Tianjin, China). K$_2$CrO$_7$, FeCl$_3$·H$_2$O, HCl, NaOH,
Na₂SO₄, Na₃PO₄, Na₂CO₃, NaCl and NaNO₃ were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). De-ionized water was used in the preparation of all solutions. The stock solution with 100.0 mg l⁻¹ Cr(VI) was prepared by dissolving 0.2848 g K₂Cr₂O₇ in 1 l de-ionized water. The studied water with different Cr(VI) levels was obtained by diluting the stock K₂Cr₂O₇ standard solution.

2.2. Methods

2.2.1. Preparation of Fe(III)-CBs

The Fe(III)-CBs were prepared following the method described by Dos Santos et al. [26] and Qi et al. [27]. The main steps were as follows: Chitosan powder (2.0 g) was dissolved in 0.1 mol l⁻¹ FeCl₃ aqueous solution (100 ml), followed by stirring the solution at room temperature for 4 h. Subsequently, the Chitosan-FeCl₃ solution was added into NaOH solution (200 ml, 10%, w/v) dropwise using a syringe to make the beads. Then the beads were separated from NaOH solution and washed with de-ionized water. Afterwards, the beads were added into de-ionized water (100 ml) before pure epichlorohydrin solution (4 ml) was added. The pH of the reaction system was adjusted to 6.0 using 0.1 M HCl or 0.1 M NaOH and kept at 70°C for a further 3 h. The cross-linked beads were dried in an oven at 60°C after the filtration. Finally, the products were treated with HCl solution (0.01 mol l⁻¹) for another 3 h to remove the iron compounds on the surface and protonate the cross-linked beads.

2.2.2. Characterization of Fe(III)-CBs

Surface morphology of synthesized Fe(III)-CBs was observed by SEM with an FEI Quanta 200 FEG field emission scanning electron microscope at an accelerating voltage of 20 kV. The surfaces of samples were gold coated before analysis. FT-IR spectra of Fe(III)-CBs before and after sorption were recorded at room temperature using a Bruker TENSOR 27 FT-IR spectrometer in the range of 4000–400 cm⁻¹. The samples were pre-treated according to the KBr pellet method. XPS analysis was conducted before and after Cr(VI) adsorption by a Kratos Axis Ultra DLD spectrometer. All the binding energies were referenced to the C 1s peak at 284.8 eV from surface adventitious carbon.

2.2.3. Batch adsorption test

The batch test was designed and carried out to evaluate the adsorption capacity of Cr(VI) on Fe(III)-CBs (2.0 g l⁻¹ dosage). The temperature of all batch reactors was kept at 25 ± 1°C in an air-conditioned room and the reactors were well mixed by the shaker (Ningbo Jiangnan Instrument Factory, China) at 100 r.p.m. During the adsorption tests, the mixed liquor sample was withdrawn regularly to determine the concentration of Cr(VI).

To study the effect of pH on the Cr(VI) (5.0 mg l⁻¹ initial Cr(VI) concentration) adsorption on Fe(III)-CBs, the initial pH values of the solution were adjusted to 2.0–8.0 by 0.1 mol l⁻¹ HCl or 0.1 M NaOH solution. Only the optimum pH would be used in the further study.

A measure of 0.2 g Fe(III)-CBs was dosed to five batch reactors containing 100 ml of Cr(VI) solution but with different concentrations (2.5, 5.0, 10.0, 15.0, 20.0 mg l⁻¹) to research the effect of Cr(VI) initial concentration for kinetic studies and variable for isotherm studies.

The influence of competing anions (SO₄²⁻, CO₃²⁻, Cl⁻, NO₃⁻ and PO₄³⁻) with varying the concentration at 0.01, 0.025, 0.05, 0.1 and 0.5 mol l⁻¹ on the adsorption process was studied with 5.0 mg l⁻¹ initial Cr(VI) concentration.

For desorption and regeneration, the Fe(III)-CBs were subjected to successive adsorption–desorption cycle tests. After the test equilibration with the initial Cr(VI) concentration of 5.0 mg l⁻¹ as mentioned above, the adsorbent was separated from the solution and washed well. Thereafter, desorption tests were performed by keeping 50 ml 0.1 M NaOH solution in contact with the spent adsorbent. At the end of each cycle, the Fe(III)-CBs were washed several times with de-ionized water to remove excess base from the adsorbent surface. The reusability of Fe(III)-CBs for Cr(VI) adsorption was evaluated by conducting five cycles.

The Cr(VI) analysis was carried out spectrophotometrically at 540 nm in a spectrophotometer (Spectrovision WFJ7200, Shanghai, China), using diphenylcarbazide as the complexing agent. The amount of Cr(VI) adsorption qₑ (mg g⁻¹) was calculated from the equation as follows:

\[ qₑ = \frac{(C₀ - Cₑ)V}{W}, \]  

(2.1)
Table 1. Langmuir, Freundlich and Langmuir–Freundlich isotherm models and their parameters for Cr(VI) adsorption on Fe(III)-CBs (the adsorbent dosage 2.0 g l⁻¹, the temperature 25 ± 1°C, the contact time 200 min). \( q_m \) is the maximum adsorption capacity (mg g⁻¹); \( K_L \) is the Langmuir constant (l mg⁻¹) related to the energy of adsorption. \( K_F \) is the Freundlich constant (mg l⁻¹); \( 1/n \) is the heterogeneity parameter. \( K_L-f \) is the Langmuir–Freundlich constant (l mg⁻¹) related to the energy of adsorption; \( c \) is the heterogeneity parameter, which indicates relatively heterogeneous distribution of binding sites, while \( c \) is close to zero.

| isotherm                  | equation                              | parameters          | \( R^2 \) | \( \chi^2 \) |
|--------------------------|---------------------------------------|---------------------|-----------|-------------|
| Langmuir                 | \( q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \) | \( q_m \) (mg g⁻¹) | 59.05     | 2.50        | 0.986 | 1.175 |
|                          |                                       | \( K_L \) (l mg⁻¹)  |           |             |       |       |
|                          |                                       | \( R^2 \)           |           |             |       |       |
|                          |                                       | \( \chi^2 \)        |           |             |       |       |
| Freundlich               | \( q_e = K_F C_e^1/n \)               | \( K_F \) (mg l⁻¹)  | 48.58     | 0.62        | 0.996 | 1.164 |
|                          |                                       | \( 1/n \)           |           |             |       |       |
|                          |                                       | \( R^2 \)           |           |             |       |       |
|                          |                                       | \( \chi^2 \)        |           |             |       |       |
| Langmuir–Freundlich      | \( q_e = \frac{q_m K_{L-f} C_e^c}{1 + K_{L-f} C_e^c} \) | \( q_m \) (mg g⁻¹) | 166.28    | 0.388       | 0.71  | 0.996 | 0.771 |
|                          |                                       | \( K_{L-f} \) (l mg⁻¹) |           |             |       |       |
|                          |                                       | \( c \)             |           |             |       |       |
|                          |                                       | \( R^2 \)           |           |             |       |       |
|                          |                                       | \( \chi^2 \)        |           |             |       |       |

Table 2. Kinetic models for Cr(VI) adsorption on Fe(III)-CBs.

| model                              | equation                              | parameters          |
|------------------------------------|---------------------------------------|---------------------|
| pseudo-first-order kinetic model   | \( \ln(q_t - q_e) = \ln(q_e - k_1 t) \) | \( q_e \) and \( q_t \) denote the amount of Cr(VI) adsorbed at equilibrium and at time \( t \) (mg g⁻¹), respectively; \( k_1 \) is the rate constant of the model (min⁻¹) |
| pseudo-second-order kinetic model  | \( t = \frac{1}{k_2 q_t^2} + \frac{t}{q_0} \) | \( k_2 \) is the rate constant of pseudo-second-order model (mg g⁻¹ min⁻¹) |
| intraparticle diffusion model      | \( q_t = k_p t^{1/2} + c \)           | \( k_p \) is the intraparticle diffusion constant (mg g⁻¹ min⁻¹/2) and \( c \) (mg g⁻¹) is the constant that give an idea about the effect of boundary layer thickness |

where \( C_0 \) is the initial Cr(VI) concentration (mg l⁻¹), \( C_e \) is the instantaneous Cr(VI) concentration (mg l⁻¹) during the test, \( V \) is the volume of the aqueous phase (l) in the batch reactor and \( W \) is the weight of the adsorbent used (g).

The adsorption removal rate (R) of Cr(VI) was calculated as follows:

\[
R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\%.
\] (2.2)

Langmuir, Freundlich and Langmuir–Freundlich isotherms [28,29] were used for the mathematical description of the adsorption equilibrium of Cr(VI) ions on Fe(III)-CBs (table 1). The operating parameters were \( T = 25 \pm 1°C \), pH = 6.0, time = 200 min. The kinetic data were analysed using the pseudo-first-order, pseudo-second-order and intraparticle diffusion models (table 2) [30].

3. Result and discussion

3.1. Characterization of synthesized Fe(III)-CBs

The SEM images of the Fe(III)-CBs surface are shown in figure 1. The beads appeared in the well-shaped spherical form with relatively rough and non-porous surface. The diameter of the spheres was approximately 1 mm. These findings were in agreement with the fact that beads were prepared with the suspension in aqueous solution and subsequent cross-linking [26]. Figure 1 also illustrates the existence of folds on the surface. These folds provide a large specific area and numerous active sites distributed on the surface, offering favourable conditions for Cr(VI) adsorption.

The FT-IR spectra of chitosan and Fe(III)-CBs are presented in figure 2. For chitosan, the overlapped peak at 3415 cm⁻¹ corresponded to −OH and −NH₂ stretching vibrations. Two adsorption bands at 2924 and 2873 cm⁻¹ were assigned to asymmetric and symmetric vibration of −CH₂ groups, respectively, and the adsorption peak at 1600 cm⁻¹ was attributed to the characteristic peak of −NH₂. The spectra of Fe(III)-CBs confirm the presence of both −NH₂ and −OH groups. It can be seen that the spectra had
two significant shifts. The first shift of peak was at 1665–1600 cm$^{-1}$. This shift in $\text{–NH}_2$-bending mode reflects the interaction between Fe$^{3+}$ ion and $\text{–NH}_2$ group. The second band at 1080 cm$^{-1}$ corresponding to primary $\text{–OH}$ stretching was shifted to 1068 cm$^{-1}$, indicating the interaction between Fe$^{3+}$ ion and $\text{–OH}$ group due to hydrogen bonding [6]. These depress hydrogen bonding to other ions, but promote the chitosan to be more positive. Thus, Fe(III)-CBs should have larger potential for Cr(VI) adsorption.

3.2. Characteristics of Cr(VI) adsorption by Fe(III)-CBs

3.2.1. Effect of initial pH of the solution on Cr(VI) adsorption

The pH could significantly impact the adsorption process, because it affects not only the surface charge of the adsorbent and the degree of ionization, but also the species of adsorbate [6,31,32]. In this study, the effect of initial pH (from 2.0 to 8.0) on the adsorption process was investigated and the results are shown in figure 3. The Cr(VI) adsorption removal rate strongly depended on the initial pH (figure 3). After 200 min reaction, Cr(VI) adsorption rate increased from 74.9 to 99.8% with pH increasing from 2.0 to 3.0, but kept similar between pH 3.0 and 6.0, finally decreased from 99.36 to 31.61% with pH constantly increasing from 6.0 to 8.0. Therefore, the optimal pH for Cr(VI) adsorption by Fe(III)-CBs ranged from 3.0 to 6.0. Similar pH-dependent trend was also found in Cr(VI) adsorption by magnetic chitosan nanoparticles [33] and protonated cross-linked chitosan [34]. In this work, the initial pH may exert effect on Cr(VI) adsorption via two facets: the surface characteristics of Fe(III)-CBs and the species of Cr(VI). The protonation by hydrogen ions (H$^+$) presented in the amino groups ($\text{–NH}_2$) of Fe(III)-CBs in acid solutions is depressed under basic conditions [6]. Cr(VI) exists predominantly in the form of HCrO$_4^-$ as the pH ranges from 3.0 to 6.0. The form of HCrO$_4^-$ shifts to H$_2$CrO$_4$ with pH lower 3.0 and shifts to
Figure 3. Effect of initial pH on the Cr(VI) adsorption.

Table 3. Comparison of adsorption capacities of Fe(III)-CBs with other adsorbents.

| adsorbent                                      | \( q_{\text{max}} \) (mg g\(^{-1}\)) | pH  | initial concentration (mg l\(^{-1}\)) | ref.  |
|-----------------------------------------------|-------------------------------------|-----|--------------------------------------|-------|
| Fe(III)-CBs                                    | 166.3                               | 6.0 | 20.0                                 | this study |
| \( \gamma \)-Fe\(_2\)O\(_3\)-chitosan beads     | 106.5                               | 5.0 | 1000                                 | [32]  |
| magnetic chitosan nanoparticles               | 55.8                                | 3.0 | 180                                  | [33]  |
| composite chitosan biosorbent                 | 153.8                               | 2.0 | 400                                  | [18]  |
| ethylenediamine-modified cross-linked magnetic chitosan resin | 51.8                               | 2.0 | 100                                  | [35]  |
| cross-linked chitosan-Fe(III) complex          | 148.4                               | 4.8 | 380                                  | [36]  |
| metal ion imprinted chitosan resin            | 76.9                                | 5.5 | 100                                  | [37]  |
| Fe\(_6\) nanorods modified with chitosan      | 118.8                               | 5.0 | 200                                  | [15]  |
| zirconium cross-linked chitosan composite     | 175.0                               | 5.0 | 300                                  | [25]  |

CrO\(_4\)\(^{-2}\) with pH higher than 6.0 [3]. Both of them worked and resulted in the characteristics of the initial pH effects, and concluded that Fe(III)-CBs adsorbed Cr(VI) as HCrO\(_4\)\(^{-}\) form. The optimal pH value for Fe(III)-CBs is approximately 6.0, which is higher than others (table 3). Especially, pH is a restrictive factor for Cr(VI) absorbent and it could be overcome.

3.2.2. Adsorption capacity and isotherms by Fe(III)-CBs

To examine the capacity of Cr(VI) adsorption by Fe(III)-CBs, the batch tests were performed at initial Cr(VI) concentrations, i.e. 2.5, 5.0, 10.0, 15.0 and 20.0 mg l\(^{-1}\) (figure 4).

All the parameters as well as the regression coefficients of Langmuir, Freundlich and Langmuir–Freundlich models are obtained and presented in table 1. As the coefficients of correlation (\( R^2 \)) were close to each other (table 1), \( \chi^2 \) analysis was carried out to identify the suitable isotherm for the adsorption of Cr(VI). The \( \chi^2 \) was analysed according to the following equation:

\[
\chi^2 = \sum \frac{(q_e - q_m)^2}{q_m},
\]

where \( q_e \) is the quantity of Cr(VI) adsorbed at the equilibrium (mg g\(^{-1}\)), \( q_m \) is the maximum adsorption capacity based on the model prediction (mg g\(^{-1}\)). It can be found that the Langmuir–Freundlich isotherm fitted best with the experimental data, i.e. the \( R^2 \) values were higher, and \( \chi^2 \) values were lower. And these results (table 1) suggested that the active sites on the surface of Fe(III)-CBs are not homogeneous [38], and the Langmuir–Freundlich isotherm model is the best in the present study.
Based on the Langmuir–Freundlich isotherm model, Cr(VI) adsorption capacity of Fe(III)-CBs was determined to be 166.3 mg g$^{-1}$ under the present conditions. As mentioned above, chitosan and its modified derivatives were characterized as great potential for Cr(VI) adsorption. The adsorption capacities of Fe(III)-CBs and other adsorbents are listed in table 3. The highest Cr(VI) removal capacity could be achieved by Fe(III)-CBs, probably attributed to its own surface characteristics (see §3.1). In view of its high adsorption capacity, Fe(III)-CBs can be recommended as an efficient alternative for the low concentration Cr(VI) adsorption.

3.2.3. Adsorption kinetics

The effect of initial Cr(VI) concentration on adsorption capacity on Fe(III)-CBs is presented in figure 5. Figure 5 shows that the adsorbed amount of Cr(VI) increased rapidly in the first 100 min, contributing to approximately 80% of the ultimate adsorption capacity. And the adsorption equilibrium reached within 200 min. Comparatively, the required times to achieve equilibrium for the zirconium–chitosan composite and $\gamma$-Fe$_2$O$_3$–chitosan beads were approximately 300 and 360 min [39] respectively; as a result, the Fe(III)-CBs shows better performance in Cr(VI) adsorption.

To determine the adsorption kinetics, the models in table 2 were applied here to show whether they could match the experimental data (table 4). Table 4 shows that the coefficient of correlation ($R^2$) was much higher, and the theoretical $q_{e,cal}$ value was closer to the experimental $q_{e,exp}$ value in the case of the pseudo-first-order kinetic model. Therefore, the pseudo-first-order model fitted the experimental
data better than the pseudo-second-order model. This is in accordance with the Cr(VI) adsorption on Fe(III) hydroxide-loaded sugar beet pulp [11]. Because the pseudo-first-order model is based on the adsorption rate being proportional to the difference between the equilibrium adsorption capacity and the adsorbed amount [20,40], while the adsorbed amount is controlled by Cr(VI) diffusion to the adsorbent, Fe(III)-CBs have the higher kinetic constant \( k_1 \), indicating that this adsorbent is easy to close for Cr(VI).

3.2.4. Effect of coexisting anions

During the adsorption process, the coexisting anions may compete with Cr(VI) for active sites on the adsorbent, and thus negatively affect Cr(VI) adsorption performance. This competition is the result of electrostatic interaction and ligand exchange reaction [24,31]. So the effects of several common anions in natural water [17], such as \( \text{HCO}_3^- \), \( \text{H}_2\text{PO}_4^- \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and \( \text{NO}_3^- \) on Cr(VI) adsorption, were evaluated.

The results show that all the anions selected here could depress the Cr(VI) adsorption capacity (figure 6). Nevertheless, the extent of depression by each anion is different and ranked as \( \text{HCO}_3^- \approx \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-} > \text{Cl}^- \approx \text{NO}_3^- \). When \( \text{HCO}_3^- \), \( \text{H}_2\text{PO}_4^- \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) or \( \text{NO}_3^- \) presented with 10-fold of Cr(VI) concentration, the equilibrium Cr(VI) adsorption capacities were lowered by 16.1%, 18.1%, 45.8%, 79.5% and 83.5% compared with that without any coexisting anion. And increasing the above coexisting anion concentration to 50-fold of Cr(VI) concentration, the adsorption capacities were further decreased by 6.4%, 4.5%, 29.7%, 46.2% and 50.0%, respectively. Compared with the influence of \( \text{Cl}^- \) and \( \text{NO}_3^- \), \( \text{HCO}_3^- \) and \( \text{H}_2\text{PO}_4^- \) may lead to stronger competition with Cr(VI) in the activated sites of Fe(III)-CBs and depress the Cr(VI) removal to a larger extent.

3.2.5. Regeneration and reuse of Fe(III)-CBs

Reusability is one of the most important parameters to assess the applicability of an adsorbent in practice. Based on the results above, 0.1 mol l

**Figure 6.** Effect of coexisting anions on Cr(VI) adsorption.

**Table 4.** Kinetic parameters for Cr(VI) adsorption on Fe(III)-CBs.

| initial Cr(VI) concentration (mg l\(^{-1}\)) | \( q_{e,exp} \) (mg g\(^{-1}\)) | \( q_{e,cal} \) (mg g\(^{-1}\)) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_{e,cal} \) (mg g\(^{-1}\)) | \( k_2 \) (mg g\(^{-1}\) min\(^{-1}\)) | \( R^2 \) |
|--------------------------------------------|-----------------|-----------------|-----------------|------|-----------------|-----------------|------|
| 2.5                                       | 1.24            | 1.35            | 0.023           | 0.989| 2.67            | 0.0024          | 0.809|
| 5.0                                       | 2.49            | 2.78            | 0.019           | 0.987| 8.76            | 0.0028          | 0.356|
| 10.0                                      | 4.99            | 5.15            | 0.018           | 0.989| 17.73           | 0.0027          | 0.458|
| 15.0                                      | 7.44            | 8.00            | 0.017           | 0.996| 25.02           | 0.0026          | 0.731|
| 20.0                                      | 9.97            | 11.68           | 0.016           | 0.997| 24.22           | 0.0043          | 0.883|
used as desorption solution. The desorption removal rates were 2.54%, 18.40%, 48.00%, 65.80% and 0.58% for the five desorption solutions, respectively. Among them, NaOH solution desorbing Cr(VI) was most effective [25]. This result was consistent with the results of the pH effect above, indicating that electrostatic interaction between the adsorbent and Cr(VI) plays a significant role in the adsorption. So, in this view, adjusting pH is a practical way to regenerate Fe(III)-CBs. So NaOH solution was used as desorption solution for the regeneration and reuse of Fe(III)-CBs. The tests were conducted with 0.01, 0.05, 0.1, 0.5 or 1.0 mol l$^{-1}$ NaOH concentration to determine its optimal concentration. Their results, lower than 0.1 mol l$^{-1}$ of NaOH solution, more or less the desorption rate; and higher than 0.1 mol l$^{-1}$, the desorption rate, hardly varied and kept close to 70%. So, the optimal concentration is 0.1 mol l$^{-1}$ for NaOH solution as desorption solution.

The tests were still conducted to evaluate the possibility of Fe(III)-CBs reuse for Cr(VI) adsorption undergoing five cycles (figure 7). Their data proved that the adsorption capacity for Cr(VI) was not significantly changed with the cycle number and more than 93% of initial adsorption capacity was maintained after five adsorption/desorption/regeneration cycles.

### 3.3. Proposed process and mechanism

Generally, the adsorption process can be divided into three steps: (i) external surface adsorption, (ii) intraparticle diffusion and (iii) the final equilibrium [20,41]. Among them, the intraparticle diffusion is generally regarded as the rate-limiting step [42]. Based on the intraparticle diffusion model, when the plot of $q_t$ versus $t^{1/2}$ gives a straight line and passes through the origin, the adsorption process is considered to be controlled only by intraparticle diffusion. When the plot of $q_t$ versus $t^{1/2}$ exhibits the multilinear plot, the adsorption process should be controlled by both intraparticle diffusion step and other steps [20,42–45]. In this work, the value of $k_p$ became higher as initial Cr(VI) concentration increased (table 5), suggesting the concentration of Cr(VI) has significant influence on the intraparticle diffusion. Meanwhile, the value of $R^2$ higher than 0.99 revealed that the intraparticle diffusion plays a vital role in the adsorption process. However, the plot of $q_t$ versus $t^{1/2}$ shown in figure 8 illustrates that the intraparticle diffusion was not the only rate-limiting step.

### Table 5. Parameters for Cr(VI) adsorption on Fe(III)-CBs.

| initial Cr(VI) concentration (mg l$^{-1}$) | parameters for intraparticle diffusion |
|------------------------------------------|----------------------------------------|
|                                          | $C$ (mg g$^{-1}$)                      |
| 2.5                                      | −0.228                                 |
| 5.0                                      | −0.579                                 |
| 10.0                                     | −1.199                                 |
| 15.0                                     | −1.774                                 |
| 20.0                                     | −2.386                                 |
|                                          | $k_p$ (mg g$^{-1}$ min$^{0.5}$)        |
| 2.5                                      | 0.122                                  |
| 5.0                                      | 0.249                                  |
| 10.0                                     | 0.499                                  |
| 15.0                                     | 0.701                                  |
| 20.0                                     | 0.964                                  |
|                                          | $R^2$                                   |
| 2.5                                      | 0.996                                  |
| 5.0                                      | 0.993                                  |
| 10.0                                     | 0.991                                  |
| 15.0                                     | 0.997                                  |
| 20.0                                     | 0.994                                  |
Figure 8. Plots of $q_t$ versus $t^{1/2}$ for the adsorption of Cr(VI) ranging from 2.5 to 20.0 mg l$^{-1}$ (the Fe(III)-CBs dosage 2.0 g l$^{-1}$, the temperature 25±1°C).

It has been the Cr(VI) adsorption by Chitosan mainly through the interaction between several function groups (such as amino group) and Cr(VI) [6]. So, the quantities of groups and their exposure to Cr(VI) are essential for the adsorption. As shown in figure 2, the FT-IR spectrum of Cr(VI) adsorbed on Fe(III)-CBs displayed an obvious formation of new bands at 945 and 807 cm$^{-1}$. According to the literature [24,44], these two peaks were attributed to Cr(VI)$-$O and Cr(III)$-$OH vibration. This confirms the presence of Cr(VI) on the surface of Fe(III)-CBs and demonstrates a part of adsorbed Cr(VI) was reduced to Cr(III) on the sorbent.

XPS spectra of Fe(III)-CBs before and after Cr(VI) adsorption are presented as figure 9. The photoelectron peaks for the Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ are located at 576.9 and 586.8 eV (figure 9a), respectively. The broad peak of Cr 2p$_{3/2}$ could be fitted into two peaks at binding energies of 579.3 and 576.8 eV, which were the characteristics of Cr(VI) and Cr(III), respectively. On the other hand, the peaks at 588.0 and 586.5 eV could be attributed to Cr(VI) and Cr(III) binding energies for 2p$_{1/2}$ orbits [24,45], manifesting both Cr(VI) and Cr(III) coexisted on the surface of the Fe(III)-CBs after adsorption. The photoelectron peaks for O 1s could be fitted by three peaks at binding energies of 530.8, 531.9 and 532.6 eV (figure 9b), respectively. The dominant peak located at 532.6 eV assigned to C−O, O=H or bound H$_2$O, and the peak at around 530.8 suggested the existence of Fe(III)=O. As the adsorption proceeded, the peak that appeared at 531.9 eV showed an obvious increasing intensity, indicating that the bond of C=O enhanced significantly after adsorption of Cr(VI). The C=O bond was attributed to the oxidation of alcoholic group (−CH$_2$OH) on the molecular chain of chitosan [24]. It is therefore suggested that the alcoholic group was the electron donor in the process of the redox reaction, in which Cr(VI) was reduced to Cr(III), while the CH$_2$OH was oxidized to C=O. When the pH ranges from 3.0 to 6.0, Cr(III) exists predominantly as Cr(OH)$_2^{2+}$ [46], the bond between Cr(VI) and Fe(III)-CBs was broken due to the change of the electrostatic interaction. Furthermore, the free Cr(OH)$_2^{2+}$ may be chelated with amine groups or precipitated onto the surface of Fe(III)-CBs in the hydroxide nature. The reduction of Cr(VI) to Cr(III) is the reason for not only the desorption rate, but also the adsorption rate-limiting step.

Therefore, the possible mechanism of Cr(VI) adsorbed on Fe(III)-CBs can be proposed: HCrO$_4^-$ was first adsorbed onto Fe(III)-CBs through electrostatic interaction and ligand–exchange interaction. Then, the Cr(VI) adsorbed via electrostatic interaction was partially reduced to Cr(III) with the −CH$_2$OH on the adsorbent served as the electron donor. The resulted Cr(III) was either chelated with NH$_2$ on the Fe(III)-CBs or precipitated onto the surface of the adsorbent.

4. Conclusion

In this study, Fe(III)-CBs were synthesized and characterized by SEM, FT-IR and XPS, and applied for low concentration Cr(VI) adsorption. The efficient Cr(VI) adsorption was achieved by the composites within low concentration Cr(VI) and pH range from 2.0 to 6.0. And the adsorption process was well agreed with the Langmuir–Freundlich adsorption model and pseudo-first-order kinetic model. The
maximum adsorption efficiency and capacity were 99.36% and 166.3 mg g$^{-1}$ at pH 6.0, respectively. Both electrostatic interaction and ligand exchange reaction play important roles in the adsorption processes, and the anions including OH$^-$, SO$_4^{2-}$, CO$_3^{2-}$ and PO$_4^{3-}$ could compete with Cr(VI) on the active adsorption sites. The beads were about 1 mm in average diameter and easy to be separated by filtration, and then regenerated and re-used effectively for the adsorption of Cr(VI). A part of Cr(VI) adsorbed on the beads was reduced to Cr(III) with the $\text{CH}_2\text{OH}$ serving as the electron donor, which reduced the toxicity of chromium. Over all, Fe(III)-CBs have the potential of practical application for the adsorption of Cr(VI) from water.

Data accessibility. All of the data in this investigation have been reported in the paper and are freely available.

Authors’ contributions. Y.W. designed the experiments, coordinated the study and wrote the manuscript. Y.Z., S.H. and S.Z. performed the preparation experiments. J.W. and Y.Z. performed the adsorption experiments. Y.W., S.H., X.X. and J.Q. analysed the results. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.

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References

1. Ma J, Zuo-Jiang SZ, He Y, Sun Q, Wang Y, Liu W, Sun S, Chen K. 2016 A facile, versatile approach to hydroxyl-anchored metal oxides with high Cr(VI) adsorption performance in water treatment. R. Soc. open sci. 3, 160524. (doi:10.1098/rsos.160524)
2. Mohseni-Bandpi A, Kakavandi B, Kalantary RR, Azari A, Keramati A. 2015 Development of a novel magnetite–chitosan composite for the removal of fluoride from drinking water: adsorption modeling and optimization. RSC Adv. 5, 73279–73289. (doi:10.1039/C5RA11294I)
3. Rakhunde R, Deshpande L, Juneja HD. 2015 Chemical speciation of chromium in water: a review. Crit. Rev. Environ. Sc. Technol. 42, 776–810. (doi:10.1080/10643389.2015.104029)
4. Shi LN, Zhang X, Chen ZL. 2011 Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. Water Res. 45, 886–892. (doi:10.1016/j.watres.2010.09.025)
5. Metters JP, Kadara RO, Banks CE. 2012 Electroanalytical sensing of chromium (III) and (VI) utilizing gold screen printed macro electrodes. Analyst 137, 896–902. (doi:10.1039/c2an16054d)
6. Zimmermann AC, Mecabô A, Fagundes T, Rodrigues CA. 2010 Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe). J. Hazard. Mater. 179, 192–196. (doi:10.1016/j.jhazmat.2010.02.078)
7. Chen DK, Wang H. 2015 Cr(VI) removal by combined redox reactions and adsorption using pectin-stabilized nanoscale zero-valent iron for simulated chromium contaminated water. RSC Adv. 5, 65 066–65 073. (doi:10.1039/C5RA10573K)
8. Fang J, Gu ZM, Gang DC, Liu CX, Ilton ES, Deng BL. 2007 Cr(VI) removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine). Environ. Sci. Technol. 41, 4748–4753. (doi:10.1021/es060966b)
9. Keshmirizadeh E, Yousef S, Rafouei MK. 2011 An investigation on the new operational parameter effective in Cr(VI) removal efficiency: a study on electrocoagulation by alternating pulse current. J. Hazard. Mater. 190, 119–124. (doi:10.1016/j.jhazmat.2011.03.010)
10. Wang P, Lo IMC. 2009 Synthesis of mesoporous magnetic gamma-Fe$_2$O$_3$ and its application to...

**Figure 9.** XPS spectra of Cr 2p (a) and O 1s (b) on Cr-adsorbed Fe(III)-CBs.
20. Dragan ES, Apopei Loghin DF, Cocarta AI. 2014 Highly efficient detoxification of Cr(VI) by chitosan–Fe(III) complex: process and mechanistic studies. J. Hazard. Mater. 244, 689–697. (doi:10.1016/j.jhazmat.2012.06.011) 21. Zhang LF, Xia W, Tang B, Liu X, Zhang WQ. 2013 Zirconium cross-linked chitosan composite: preparation, characterization and application in adsorption of Cr(VI). Chem. Eng. J. 229, 1–8. (doi:10.1016/j.cej.2013.10.022) 22. dos Santos HH, Demarchi CA, Rodrigues CA, Greneche JM, Nedelko N, Slawska-Waniewska A. 2011 Adsorption of Au(III) on chitosan–Fe3+-crosslinked complex (Ch-Fe). Chemosphere 82, 278–283. (doi:10.1016/j.chemosphere.2010.09.033) 23. Owlad M, Aroua MK, Wan AWD, Baroutian S. 2008 Adsorption of hexavalent chromium–contaminated water and wastewater: a review. Water Air Soil Poll. 200, 59–77. (doi:10.1007/s11270-008-9893-7) 24. Shen CS, Chen H, Wu SS, Wen YZ, Li LN, Jiang Z, Li MC, Liu WP. 2013 Efficient photodegradation of Cr(VI) by titaniasilica coated with acid-activated reşadiye and hançılıclays. Desalin. Water Treat. 57, 7763–7772. (doi:10.1081/SS-120005467) 25. Li XT, Han CY, Zhu WJ, Ma WH, Luo YM, Zhou Y, Yu J, Wei KX. 2014 Cr(VI) Removal from aqueous by adsorption on amine-functionalized mesoporous silica prepared from silica fume. J. Chem. 11, 1–10. (doi:10.1155/2014/685865) 26. Gölş F, Öztürk N, Sert Y, Bahçeli S. 2010 Adsorption of Cr(VI) from aqueous solutions onto raw and acid-activated red clay and hancılı clay. Spectr. Lett. 43, 68–78. (doi:10.1080/00387010903261164) 27. Xu YF, Zhang Q, Qiao SZ. 2010 Effective Cr(VI) removal from water using a granular adsorbent: Fe3+–Mn binary oxide impregnated chitosan bead. Bioresour. Technol. 193, 243–249. (doi:10.1016/j.biotech.2011.06.012) 28. Aydin YA, Aksoy ND. 2009 Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics. Chem. Eng. J. 151, 188–194. (doi:10.1016/j.cej.2009.02.010) 29. Hena S. 2010 Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer. J. Hazard Mater. 181, 474–479. (doi:10.1016/j.jhazmat.2010.05.037) 30. Sağ Y, Aktay Y. 2002 A comparative study for the removal of Cr(VI) from aqueous by activated carbon prepared from luffa sponge. Desalin. Water Treat. 87, 921–925. (doi:10.1080/19443994.2015.1015453) 31. Meenakshi S, Viswanathan N. 2007 Identification of selective ion exchange resin for fluoride sorption. J. Colloid Interface Sci. 308, 458–450. (doi:10.1016/j.jcis.2006.12.052) 32. Zhu HY, Jiang R, Xiao L, Li W. 2010 A novel biosorbent: preparation, characterization and application of equilibrium and masstransfer mechanism studies. J. Chem. Eng. Data 55, 3142–3149. (doi:10.1021/je060063p) 33. Liu Y, Liu ZC, Gao J, Dai JD, Han JA, Wang Y, Xie JM, Yan YS. 2011 Selective adsorption behavior of Pb(II) by mesoporous silica SBA-15-supported Phl(III)-imprinted polymer based on surface molecularly imprinting technique. J. Hazard Mater. 186, 197–205. (doi:10.1016/j.jhazmat.2010.10.105) 34. Ma J et al. 2012 Enhanced adsorptive removal of methyl orange and methylene blue from aqueous solution by alkali-activated multilayered carbon nanotubes. ACS Appl. Mater. Inter. 4, 5749–5760. (doi:10.1021/am300153m) 35. Yang LG, Qin LL, Yu HQ, Li S, Shan RR, Du B. 2015 Adsorption of acid dyes from aqueous solution by CNTMAb modified bentonite: kinetic and isotherm modeling. J. Mol. Liq. 217, 1074–1081. (doi:10.1016/j.molliq.2015.08.032) 36. Shaaban AF, Fadel DA, Mahmoud AA, Elcomy MA, Elbathy SM. 2014 Synthesis of a new chelating resin bearing amidoxime group for adsorption of Cu(II), Ni(II) and Pb(II) by batch and fixed-bed column methods. J. Environ. Chem. Eng. 2, 632–641. (doi:10.1016/j.jece.2013.11.001) 37. Das SK, Manabendra M, Guha AK. 2008 Interaction of chromium with resistant strain Aspergillus versicolor: investigation with atomic force microscopy and other physical studies. Langmuir 24, 8643–8650. (doi:10.1021/la080958u) 38. Park D, Yun YS, Park JM. 2008 XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption. J. Colloid. Interface Sci. 317, 54–61. (doi:10.1016/j.jcis.2007.09.049) 39. Yun YS, Park D, Park JM, Volerys B. 2001 Biosorption of trivalent chromium on the brown seaweed biomass. Environ. Sci. Technol. 35, 4535–4538. (doi:10.1021/es010866k)