

Enhanced removal of Cr(VI) using a modified environment-friendly adsorbent

Shan Liu, Lei Cao, Xincheng Tian, Xuanni Li, Lei Liao and Chunpeng Zhao

ABSTRACT

Chitosan (CS) was modified with ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium laurylsulfonate (SLS) to prepare the compound adsorbent CS-Fe-SLS. Taking Cr(VI) as the target pollutant, the influence of different factors (solution pH, adsorption time, initial adsorption concentration and coexisting ions) were investigated. The results showed that the optimal pH value was 3.0; the adsorption equilibrium was reached at 120 min, with both physical and chemical process being involved in the adsorption process; the maximum adsorption value was 131.91 mg/g, with the adsorption being both single-layer and multi-layer adsorption; Cl^- , NO_3^- and SO_4^{2-} had little effect on adsorption, CO_3^{2-} reduced it and Cu(II) increased it. The characterization results of scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction showed that CS-Fe-SLS and chitosan had different morphological characteristics: in contrast with chitosan, CS-Fe-SLS had a larger volume and more flakes on the surface. CS-Fe-SLS was significantly lower in crystallinity than chitosan, and was more irregular and amorphous in shape, and the experimental results showed that CS-Fe-SLS had better adsorption capacity for Cr(VI). The adsorption Cr(VI) was related to -NH and -OH on the material. Some Cr(VI) was reduced to Cr(III) during the adsorption process.

Key words | adsorption, chitosan, ferric iron, heavy metal, sodium laurylsulfonate

Shan Liu
Lei Cao
Xincheng Tian (corresponding author)
Xuanni Li
Lei Liao
Chunpeng Zhao
School of Water and Environment,
Chang'an University,
Xi'an 710054,
China
E-mail: 1137834147@qq.com

Shan Liu
Lei Cao
Xuanni Li
Lei Liao
Chunpeng Zhao
Key Laboratory of Subsurface Hydrology and
Ecological Effect in Arid Region of Ministry of
Education, School of Water and Environment,
Chang'an University,
Xi'an, Shaanxi 710054,
China

Xincheng Tian
China United Northwest Engineering Design &
Research Institute Co., Ltd,
16 Zhangbasi Road, Xi'an 710054,
China

HIGHLIGHTS

- Chitosan was modified by ferric chloride hexahydrate and SLS to prepare the compound adsorbent CS-Fe-SLS.
- Fe(III) and SLS enhanced the adsorption of Cr(VI) by chitosan.
- Most co-anions had little effect on the adsorption except for CO_3^{2-} .
- When Cu(II) and Cr(VI) coexisted in solution, Cr(VI) removal increased.
- Some Cr(VI) was reduced to the non-toxic form Cr(III) during adsorption.

INTRODUCTION

Chromium pollution in industrial wastewater is mainly Cr(VI), which usually exists in the form of the chromate ion $[(\text{CrO}_4)^{2-}]$ (Jha 2008). Cr(VI) is carcinogenic (Abou El-Reash *et al.* 2011; Zendejdel *et al.* 2015) and is one of eight

chemicals that are universally recognized as being most harmful to human beings (Koilkos 2017). Human intake of Cr(VI) is mainly through the respiratory tract, digestive tract, skin and mucous membranes.

At present, the chemical precipitation, biological, and ion exchange methods are all used to treat Cr(VI) in sewage. The chemical precipitation method has the advantages of mature technology, simple operation, and effectiveness, but it does produce chromium-containing sludge, and the experimental

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reagents are expensive. The ion exchange method has the advantages of strong selectivity, large amounts of removal, and the processed chromic acid can be recovered, but due to the particular the material, the operation and management are complicated, and the initial investment is too large. The biological method has the advantages of low processing costs and no secondary pollution, and it is worth mentioning that it can also purify the environment while removing chromium. However, as the toxicity tolerance of organisms to chromium is limited, the method is only suitable for conditions below a certain degree of pollution, and nutrients need to be added (Tran *et al.* 2010; Barakat 2011; Ge *et al.* 2012).

Compared with the three methods above, adsorption is a superior physicochemical method: it has high removal efficiency, low cost, ease of operation and absence of harmful by-products. It has great advantages in the treatment of heavy-metal-containing wastewater (Zhang *et al.* 2017; Liu *et al.* 2018). Kobya *et al.* (2005) prepared activated carbon with sulfuric acid at 400 °C to adsorb heavy metals in water. Alinnor (2007) used fly ash as an adsorbent to treat Pb(II) and Cu(II) in solution at pH 4–12 and temperatures of 30–60 °C. Zhang *et al.* (2017) used the freeze-drying method to prepare millimeter-scale chitosan gel spheres for the adsorption of Cu(II) and Cr(VI) in solution, and showed that this method enhanced the adsorption capacity of chitosan to heavy metal ions.

The direct removal of Cr(VI) is the primary purpose of the treatment of wastewater, but reducing Cr(VI) to Cr(III) during treatment is a major focus to avoid secondary pollution. Some researchers have found that toxic Cr(VI) can be reduced to non-toxic Cr(III) during the adsorption process by modifying natural adsorbents.

In this study, chitosan (CS) was selected as the carrier for modification as an adsorbent to treat chromium-containing wastewater. Chitosan is a high-molecular-weight polymer obtained by deacetylating chitin. A large number of amines (-NH₂) and hydroxyls (-OH) on the molecular surface effectively adsorb heavy metal ions. Chitosan is easy to obtain, cheap, environmentally friendly and biodegradable, but it also has certain disadvantages, such as low stability under acidic conditions and poor adsorption capacity. Therefore, in this study, chitosan was modified with ferric chloride hexahydrate (FeCl₃·6H₂O) and sodium laurylsulfonate (SLS). The addition of Fe(III) to chitosan increases the network structure of the complex and enhances the overall stability of the material. SLS is an anionic surfactant that improves the surface hydrophobicity of chitosan molecules, and solves the problem of the high viscosity of chitosan in acidic solutions.

The adsorption characteristics of Cr(VI) onto CS-Fe-SLS were systematically studied under static conditions. In order

to explore the practical engineering applications, the influence of common coexisting anions (Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻) and cations (Cu(II)) on the adsorption of Cr(VI) by CS-Fe-SLS were also studied. The surface shape, morphology, material structure, and crystallinity of CS-Fe-SLS were analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) to further explore the adsorption mechanism.

MATERIALS AND METHODS

Materials

Chitosan ((C₆H₁₁NO₄)_n, molecular weight 700,000 ~ 800,000, deacetylation degree ≥90.0%, Sinopharm Chemical Reagent Co., Ltd), ferric chloride hexahydrate (FeCl₃·6H₂O, AR, Sinopharm Chemical Reagent Co., Ltd), sodium laurylsulfonate (C₁₂H₂₅SO₃Na, AR, Fuchen (Tianjin) Chemical Reagent Co. Ltd), hydrochloric acid (HCl, AR, Sinopharm Chemical Reagent Co., Ltd), sodium hydroxide (NaOH, AR, GHTECH), sulfuric acid (H₂SO₄, AR, HeNan Dongke Chemical Products Sales Co. Ltd), and methanol (CH₃OH, AR, GHTECH).

Instruments

Constant-temperature magnetic stirrer (MPLR-702, Jintan Dadi Automation Instrument Factory), pH meter (PHB-4, Shanghai Yidian Scientific Instrument Co. Ltd), desktop electric thermostatic drier (202, Shanghai Keheng Industrial Co. Ltd), vacuum filter (AP-019, Tianjin Aotesaiens Instrument Co. Ltd), electronic analytical balance (BSA224S, Shanghai Shunyu Hengping Scientific Instrument Co. Ltd), Fourier transform infrared spectrometer (Avatar 360, Nicolet, Inc.), X-ray diffractometer (Smartlab 9 kW, Rigaku, Japan), scanning electron microscope (S-3400NII, Hitachi, Japan).

Preparation of CS-Fe-SLS

About 4.0 g of FeCl₃·6H₂O was dissolved in 100 mL of distilled water and stirred magnetically until it was completely dissolved. After that, 2.0 g of chitosan was added to the iron salt solution prepared and stirred using a magnetic stirrer for 5 hours to obtain a CS-Fe complex. Then 2.0 g of SLS was dissolved in 100 mL distilled water at 45 °C and the CS-Fe solution was added drop-wise using a burette and magnetically stirred for 5 hours to obtain a CS-Fe-SLS mixed solution. After agitation, the pH of the CS-Fe-SLS mixture was neutralized with NaOH (4%). Finally

the mixture was filtered and washed with distilled water several times. The washed solid was baked at 55 °C for 24 hours in an oven, dried and then ground through a 100-mesh sieve to obtain CS-Fe-SLS (Figure 1). As shown in Figure 2, the amino groups and adjacent hydroxyl groups in the Fe(III) and CS underwent a chelation reaction to form a more stable compound (CS-Fe). When SLS was added, it formed bonds with the partially protonated amino groups on the chitosan surface (Han et al. 2007; Shen et al. 2013).

Experimental and analytical methods

Determination of Cr(VI): diphenylcarbazide spectrophotometry (GB:7467-87) was used to measure the Cr(VI) concentration according to different absorbances to calculate the corresponding adsorption amount of the material. After the reaction, the concentration of Cr(VI) in the supernatant was determined by spectrophotometer after a certain dilution of the supernatant. The Cr(VI) removal rate (E) and adsorption capacity (Q_e) were calculated using Equations (1) and (2):

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

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$



Figure 1 | Physical image of CS-Fe-SLS.

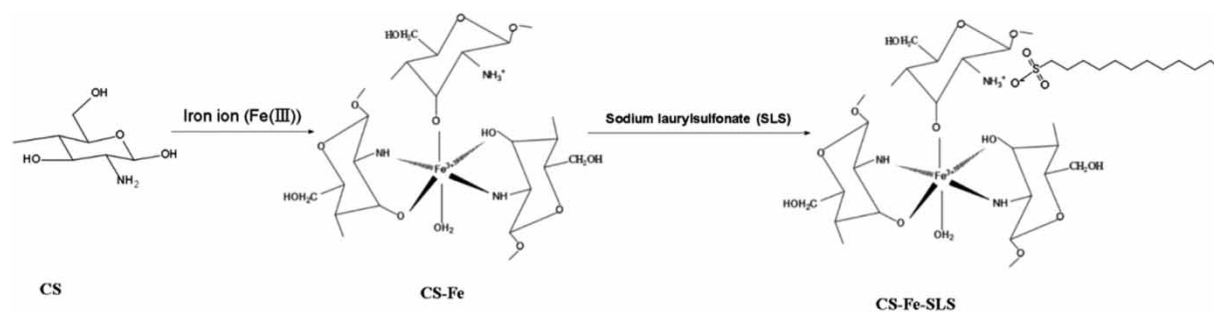


Figure 2 | Synthesis process of CS-Fe-SLS.

where C_0 is the initial concentration of heavy metal ions (mg/L); C_e is the concentration of heavy metal ions at adsorption equilibrium (mg/L); Q_e is the adsorption capacity of the material (mg/g); m is the amount of adsorbent (mg); V is adsorbed solution volume (mL).

Scanning electron microscope (SEM) characterization

The prepared material was dispersed in water, and the dispersion was placed on a 200-mesh copper mesh coated with amorphous carbon after ultrasonic treatment. The sample was dried at room temperature to form a layer of amorphous carbon film that is protective in the air, and then the morphology of the material was observed on the sample stage.

Infrared spectroscopy (FTIR) characterization

KBr was dried at 70 °C for 4 hours, then mixed with the materials to be characterized in the ratio material:KBr = 1:100, and after milling and tableting they were placed on the sample holder. The Fourier transform infrared spectrometer was used at a resolution of 1 cm⁻¹ and a measurement range of 4,000 cm⁻¹–400 cm⁻¹.

X-ray diffraction (XRD) characterization

After the material to be characterized had been dried in a vacuum, the crystal form of the particles was determined by an X-ray diffractometer, using a Cu-ray as the light source; tube pressure: 40 KV; tube current: 30 mA; 2θ with a scan range of 10–90°; angle reproducibility: $\pm 0.0001^\circ$; minimum controllable step size: 0.0001°; and scan rate 5.0°/min.

RESULT AND DISCUSSION

Results analysis

SEM analysis

It can be seen from Figure 3(a) and (b) that the surface of chitosan was smooth, and flaky, and there was no obvious agglomeration. Figure 3(c) and (d) show the polymerized CS-Fe-SLS, which took on the appearance of petals, with increased surface area and volume. The reason for the above might be that chitosan chelated Fe(III) to form a chelate complex, increasing the network structure, thereby increasing the surface area of the material, which indicated that the chelation of chitosan and Fe(III) enhanced the overall material stability (Sun *et al.* 2007). There were more flakes on the surface of CS-Fe-SLS, which was considered to be caused by the binding of SLS to the material. This increased the contact area between the adsorbent and pollutants, and made it easily trap heavy metal ions, enhancing the material's ability to adsorb them.

FTIR analysis

The infrared spectra of CS-Fe-SLS and its adsorption of Cr(VI) are shown in Figure 4.

Comparing three different infrared spectra shows that in the infrared spectrum of chitosan, the absorption band at $3,440\text{ cm}^{-1}$ was the superimposed stretching vibration of NH and -OH on chitosan; the absorption band at $2,874\text{ cm}^{-1}$ and $2,150\text{ cm}^{-1}$ were the stretching vibrations of CH and C-NH₂ respectively; the absorption band at 897 cm^{-1} was the bending vibration of NH; the peaks of $1,656\text{ cm}^{-1}$ and $1,596\text{ cm}^{-1}$ were the stretching vibration of C = O in the NHCOCH₃ group and the bending vibration of NH in -NH respectively; the peaks of $1,323$, $1,080$, $1,030\text{ cm}^{-1}$ correspond to -CN, the stretching vibration of C₃-OH and C₆-OH respectively (Zhang *et al.* 2012; Borsagli *et al.* 2015).

In the infrared spectrum of chitosan-Fe-SLS, there were a symmetrical stretching vibration peaks of -CH₂- at $2,919\text{ cm}^{-1}$ and $2,849\text{ cm}^{-1}$. The peak at $1,427\text{ cm}^{-1}$ was the bending vibration peak of -CH₂-, and the peaks at $1,068\text{ cm}^{-1}$ and $1,181\text{ cm}^{-1}$ corresponded to the symmetrical stretching and asymmetric stretching vibration peaks of SO₃-, respectively. These were characteristic peaks of the alkyl chain of SLS, indicating that SLS had been successfully loaded onto chitosan. In addition, the N-H stretching

vibration peak on chitosan shifted from 897 cm^{-1} to 894 cm^{-1} , because the amino functional group on chitosan had coordinated with Fe(III) (Sun *et al.* 2007). At the same time, the band of CS-Fe-SLS at $400\text{--}800\text{ cm}^{-1}$ was significantly different from that of chitosan in this interval. It was considered that Fe-O appears in the band. The above results indicated that SLS and Fe(III) had been successfully loaded on chitosan.

Two new peaks at 940 cm^{-1} and 807 cm^{-1} on the spectrum of Cr(VI) adsorbed by CS-Fe-SLS were attributed to the absorption peaks of Cr(VI)-O and Cr(III)-O, indicating that Cr(VI) was reduced to Cr(III) during the adsorption process.

XRD analysis

XRD analysis results for chitosan and CS-Fe-SLS are shown in Figure 5.

Comparing the diffraction patterns of CS-Fe-SLS and chitosan, it could be shown that: chitosan had an obvious characteristic peak at $2\theta = 20^\circ$, but the diffraction peak of CS-Fe-SLS was obviously weakened around $2\theta = 20^\circ$, indicating that chitosan had a higher crystallinity than CS-Fe-SLS. The diffraction peak of the modified material clearly decreased, the main reason being the coordination reaction between Fe(III) with -OH and -NH₂ on chitosan, so the intramolecular and intermolecular hydrogen bonds of chitosan were destroyed to reduce the overall crystallinity of the material (Ge *et al.* 2009; Shen *et al.* 2013). The crystallinity of chitosan is an important factor that affects the entry of ions in water into chitosan molecules. The crystallinity of CS-Fe-SLS was significantly lower than that of chitosan, which enhanced the adsorption of heavy metal ions in water. At the same time, the results showed that CS-Fe-SLS was more amorphous and irregular than chitosan.

Analysis of adsorption mechanism

According to the above three characterization methods of SEM, FTIR and XRD, the modified materials were characterized, and their structural changes and adsorption mechanism were explored. The main conclusions reached are as follows:

The main conclusions reached are as follows: the SEM results showed that CS-Fe-SLS had different morphological characteristics from chitosan. CS-Fe-SLS had a larger volume than chitosan, and more flakes on the surface. The FTIR results showed that SLS and Fe(III) were successfully supported on chitosan, the adsorption of Cr(VI) was related to -NH and -OH on the material, and some Cr(VI) was reduced to Cr(III). The XRD results showed that the

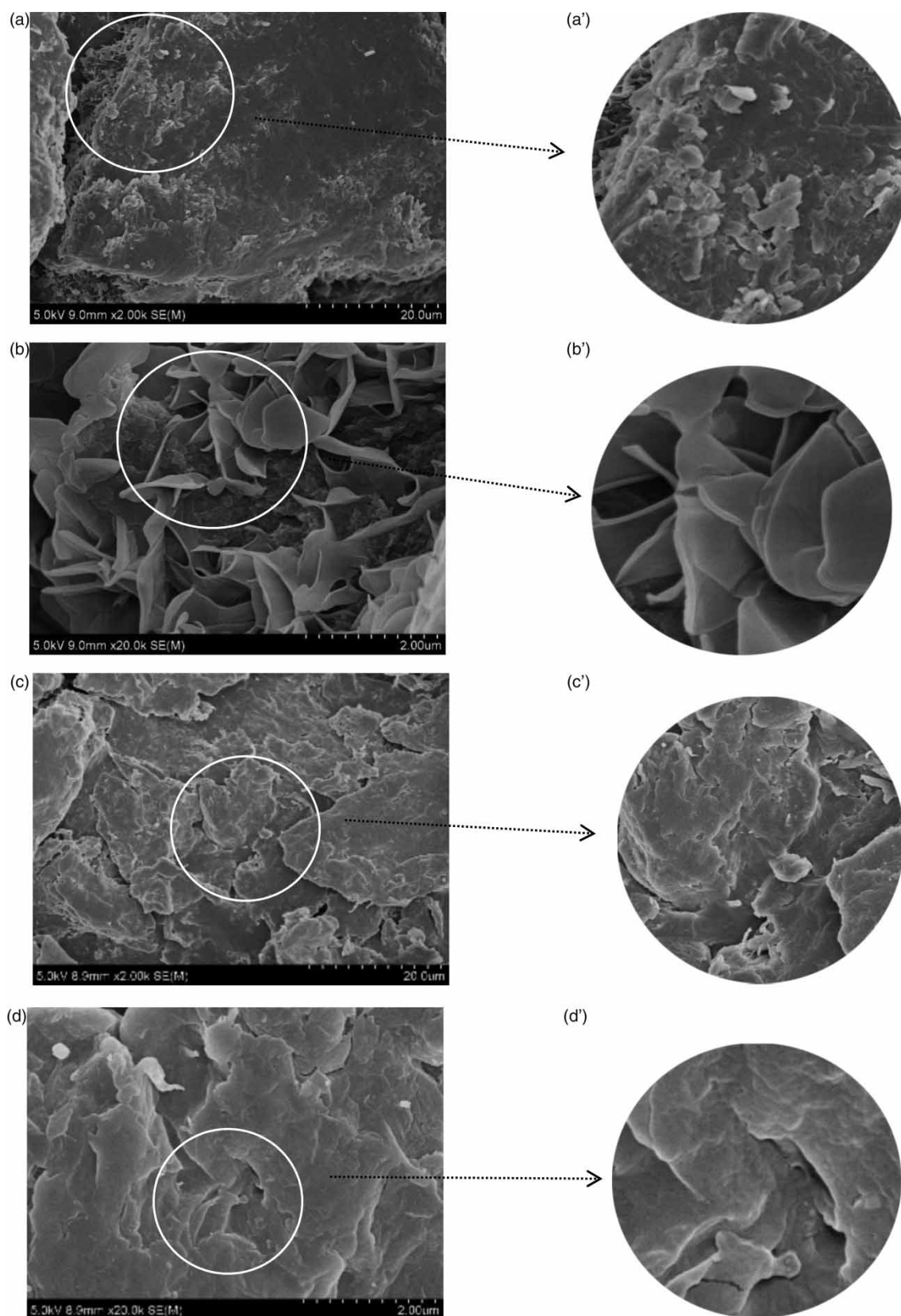


Figure 3 | SEMs of CS-Fe-SLS (a and b); a' and b' are local magnifications of a and b, respectively, magnified 2.5 times; c and d are SEMs of chitosan; c' and d' are local magnifications of c and d magnified 2.5 times.

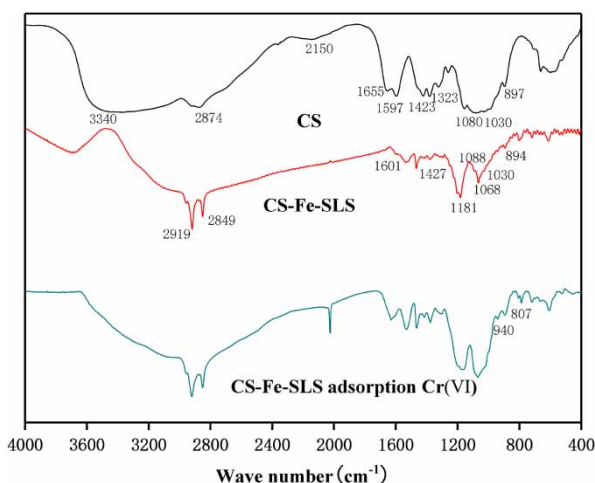


Figure 4 | Infrared spectra of CS-Fe-SLS before and after adsorption.

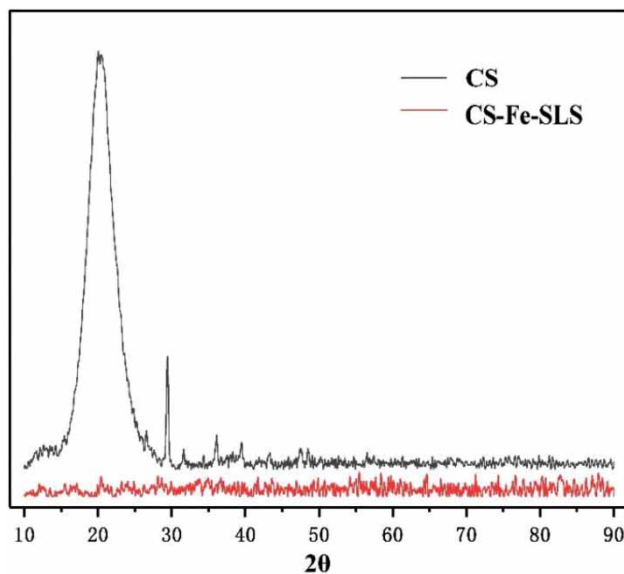


Figure 5 | XRD patterns of chitosan and CS-Fe-SLS.

crystallinity of the modified material was significantly lower than that of chitosan, and the morphology was more irregular and amorphous.

The introduction of Fe(III) could increase the positive charge of the adsorption material, enhancing the adsorption capacity of the adsorption material for Cr(VI). SLS changed the crystallinity of chitosan and improved the surface hydrophobicity of chitosan, which solved the problem of the high viscosity of chitosan in acidic solutions.

As shown in Figure 6, the anionic Cr(VI), $\text{Cr}_2\text{O}_7^{2-}$ was first adsorbed onto the composite material by the chelation of the Fe(III) center in the material or by the electrostatic attraction of a protonated amine group. Then, the adsorbed

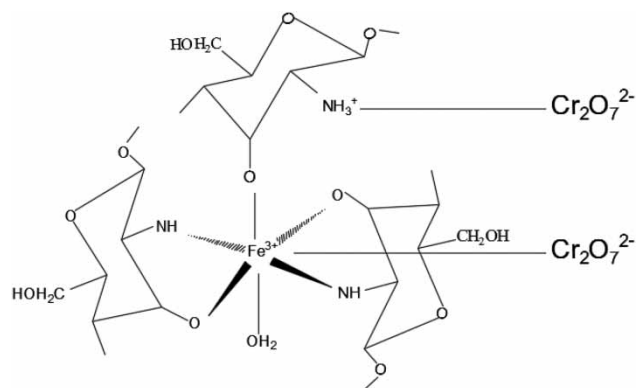


Figure 6 | The principle of CS-Fe-SLS adsorption of Cr(VI).

Cr(VI) atoms were partially reduced by the adjacent primary alcoholic function on C-6 and alcohol hydroxyl was oxidized to carbonyl group. Next, the free Cr(III) was reabsorbed by CS-Fe-SLS. Meanwhile, the unreduced Cr(VI) was still bound to the CS-Fe-SLS. Finally, it was removed in the form of Cr(VI) and Cr(III) (Shen et al. 2013). The transformation of Cr(VI) in solution is shown in Figure 7.

Effect of pH on adsorption performance

Cr(VI) solutions (concentration 100 mg/L) were prepared and the pH was adjusted to between 3.0 and 9.0. To the as prepared solutions of Cr(VI), 0.1 g of CS-Fe-SLS was added and the supernatant liquid was taken to measure the concentration of Cr(VI). The experimental results are shown in Figure 8.

The pH of the Cr(VI) solution is an important controlling factor for adsorption performance. It is a characteristic of chitosan that the glycosidic bond is unstable in acid, therefore the pH range was maintained between 3.0 and 10 in this experiment (Fu et al. 1999; Liu Lin 2011). When the pH is between 3 and 10, the amount of Cr(VI) adsorbed by CS-Fe-SLS decreases with the decrease in pH, from 28.43 mg/g to 17.55 mg/g. At pH 3–6, the effect of pH on the adsorption of Cr(VI) on the material is greater; when pH is between 5 and 9, the effect of pH on the adsorption of Cr(VI) on the material is relatively small. In the experimental range, the adsorption was best at 3.0, so the initial pH value of subsequent experiments was set at 3.0.

The main reason for this phenomenon is: the pH of the adsorption environment can change the charged state of

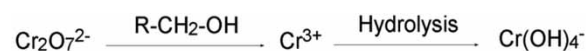


Figure 7 | The transformation of Cr(VI) in solution.

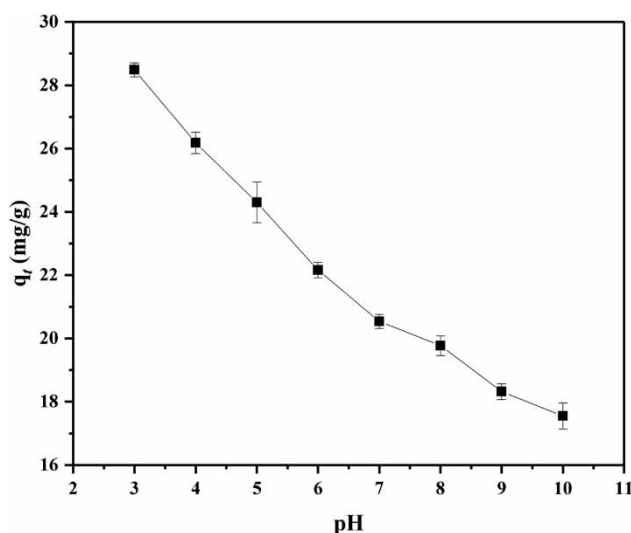


Figure 8 | Effect of pH on Cr(VI) adsorption capacity.

chitosan surface, so it will affect the adsorption ability of chitosan to some specific heavy metal ions in water. Protonation of the amino group on chitosan under acidic conditions can enhance its electrostatic attraction to Cr(VI) in water, thereby enhancing the adsorption capacity. Under alkaline conditions, a large amount of OH⁻ and Cr(VI) in water will have a competitive effect, thus reducing the amount of Cr(VI) adsorbed by the adsorbent (Geng *et al.* 2009). In addition, the introduction of Fe(III) into chitosan increases its active adsorption sites for Cr(VI), thereby increasing the amount of Cr(VI) adsorbed (Shen *et al.* 2013).

Effect of adsorption time on Cr(VI) adsorption

100 mL solutions of 100 and 200 mg/L concentrations were prepared and the pH was set to 3.0; adsorption time was set to 1 min, 3 min, 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 40 min, 45 min, 60 min, 70 min, 75 min, 90 min, 105 min, 120 min, 135 min, 150 min, and 180 min. About 0.1 g of CS-Fe-SLS was added to the Cr(VI) solutions and the supernatant liquid was taken at different points to determine the concentration of Cr(VI) until the adsorption had reached equilibrium. The results are shown in Figure 9.

The adsorption process of CS-Fe-SLS on Cr(VI) reached equilibrium in 120 min. The experimental data were fitted and analyzed using pseudo-first-order and pseudo-second-order kinetics models:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

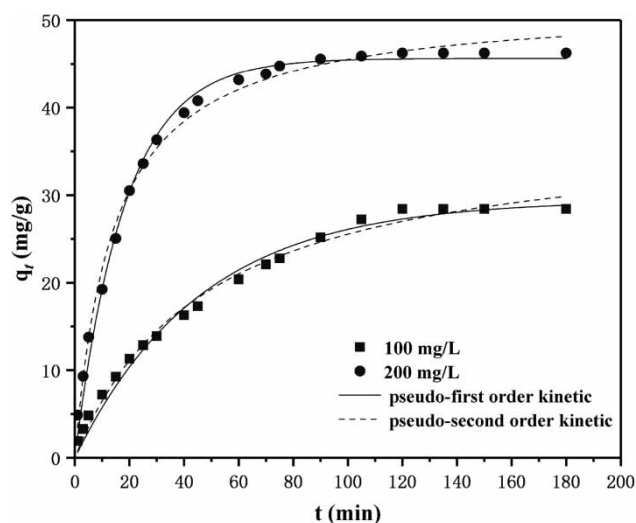


Figure 9 | Adsorption kinetics of Cr(VI) onto CS-Fe-SLS.

where q_t is the adsorption capacity of the unit mass adsorbent at time t (mg/g), q_e is the equilibrium adsorption quantity (mg/g), k_1 and k_2 are the pseudo-first-order kinetics adsorption rate constant (min^{-1}) and pseudo-second-order kinetics adsorption rate constant [$\text{g}/(\text{mg}\cdot\text{min})$], respectively. The obtained adsorption kinetic parameters are detailed in Table 1.

According to the data, the R^2 of the pseudo-second-order kinetics was slightly larger than the pseudo-first-order kinetics, but the difference was not large, which indicated that the adsorption process of Cr(VI) by CS-Fe-SLS was both physical and chemical. After Fe(III) was introduced into the material, firstly the Cr(VI) had a chelation reaction with CS-Fe-SLS or electrically adsorbed with $-\text{NH}_3^+$ on the material, and then some Cr(VI) was replaced by $-\text{OH}$ on the material. It was reduced to Cr(III), and finally absorbed and removed by the material in the form of Cr(III).

The adsorption of Cr(VI) by CS-Fe-SLS might be mainly formed by two aspects: (1) the amino functional group on chitosan was partially protonated under acidic conditions, so that it could electrically adsorb Cr(VI) in the form of CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , etc. so as to achieve the removal effect; (2) the introduction of Fe(III) could increase the positive charge of the adsorption material, and also enhance the ability of the adsorption material to reduce Cr(VI) to Cr(III), thereby further enhancing the adsorption of Cr(VI) (Shen *et al.* 2013).

Effect of initial Cr(VI) concentration

Cr(VI) solutions with initial concentrations of 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L and

Table 1 | The kinetic parameters of Cr(VI) absorption by CS-Fe-SLS

Initial concentration (mg/L)	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
	q_e (mg/g)	$k_1 \times 10^{-2}$ (min ⁻¹)	R ²	q_e (mg/g)	$k_2 \times 10^3$ [g/(mg·min)]	R ²
100	29.44	2.17	0.9872	37.85	0.55	0.9905
200	45.64	5.58	0.9919	51.91	1.37	0.9928

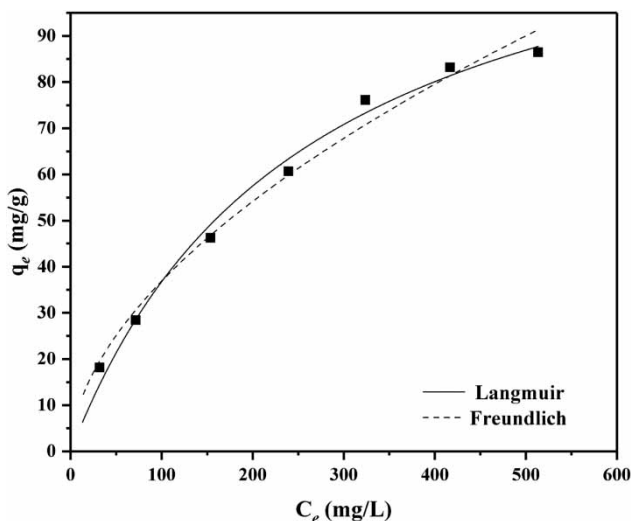
600 mg/L were prepared and the pH was set at 3.0. The solutions were shaken for 120 min at a temperature of 25 °C and a rotation speed of 120 r/min. After the adsorption was complete, the supernatant was taken to measure the Cr(VI) concentration. The experimental results are shown in Figure 10.

When the Cr(VI) concentration was 50–300 mg/L, the equilibrium adsorption capacity of the adsorbent increased rapidly with the increase in the initial Cr(VI) concentration in the solution. When the initial Cr(VI) concentration was 500 mg/L, the increase in the equilibrium adsorption capacity of the adsorbent gradually became slower. Because the Cr(VI) concentration in the solution was too high, most of the active sites on the material were soon occupied, therefore, the effect of increasing the initial Cr(VI) concentration of the solution became smaller and smaller.

The Langmuir model (5) and the Freundlich model (6) were used for fitting analysis of the experimental data:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

**Figure 10** | Adsorption isotherm of CS-Fe-SLS to Cr(VI).

where q_m is the saturated adsorption capacity (mg/g); K_L is the equilibrium constant of Langmuir adsorption (L/mg). C_e is the equilibrium concentration of metal ions in solution (mg/L). K_F is the Freundlich adsorption equilibrium constant (L/mg), which is related to adsorption capacity; n is the constant related to adsorption strength in the Freundlich model, which can reflect the non-uniformity of the adsorbent surface.

The obtained fitting parameters are detailed in Table 2, from which it can be seen that the saturated adsorption capacity of CS-Fe-SLS is 131.91 mg/g by fitting the Langmuir and Freundlich models. The correlation coefficients are 0.9889 and 0.9899, which are relatively close, so the adsorption of Cr(VI) onto CS-Fe-SLS involves both single-layer and multi-layer adsorption, and the adsorption process is more complicated, which is consistent with the conclusion that it is both chemical and physical. As shown in Table 3, compared with other materials in the literature, CS-Fe-SLS is better effect for the adsorption of Cr(VI).

Effect of coexisting ions

In an actual wastewater treatment plant, other ions, such as anions and metal cations in common metal salts and non-metal salts, may compete for adsorption with Cr(VI), thereby affecting the adsorption effect of the adsorbent.

Effect of common anions

This section mainly discusses the effect of common anions (Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-}) on the adsorption performance of Cr(VI) onto CS-Fe-SLS.

Table 2 | Langmuir and Freundlich model parameters for absorption of Cr(VI)

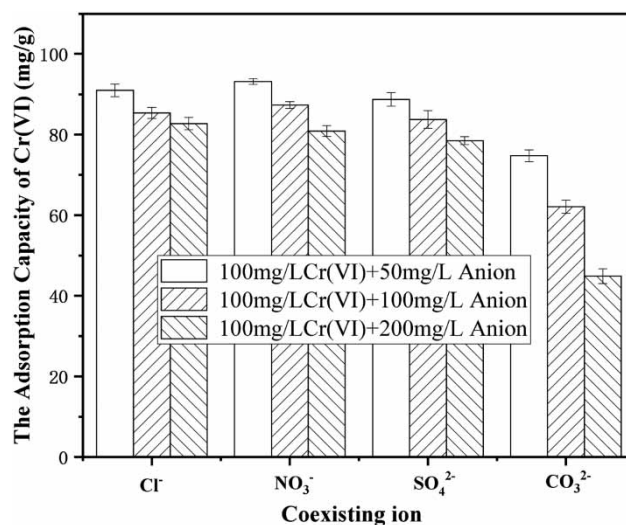
adsorbent	Langmuir model			Freundlich model		
	q_m (mg/g)	$K_L \times 10^3$ (L/mg)	R ²	K_F (L/mg)	n	R ²
CS-Fe-SLS	131.91	3.86	0.9889	2.87	1.8	0.9899

Table 3 | Saturated adsorption capacity of Cr(VI) by different adsorbents

Adsorbent	q_m (mg/g)	Reference
Cross-linked magnetic chitosan anthranilic acid glutaraldehyde Schiff's base (CAGS)	58.48	Abou El-Reash et al. (2011)
Chitosan/polycaprolactam (PA6) nanofibrous filter paper (NFP)	81.7	Li et al. (2016)
Chitosan cinnamaldehyde CTS-Cin	61.35	Khalil et al. (2019)
Magnetite-modified chitosan cinnamaldehyde Fe ₃ O ₄ @CTS-Cin	58.14	Khalil et al. (2019)
Modified graphene oxide/chitosan composite with disodium ethylenediaminetetraacetate	86.17	Zhang et al. (2016)
Fly ash	23.86	Bhattacharya et al. (2008)
Active aluminum	25.57	Bhattacharya et al. (2008)
Compound modified chitosan	131.91	Present work

- (1) The anions were selected: Cl⁻, NO₃⁻, SO₄²⁻, and CO₃²⁻ with each being formulated into a 1,000 mg/L solution, and the Cr(VI) solution concentration being 1,000 mg/L.
- (2) The reactions were carried out in 200 mL Erlenmeyer flasks, to test the effect of three concentration ratios of coexisting ion on Cr(VI): 1:2, 1:1, and 2:1. The three groups of experiments used 10 mL of Cr(VI) solution. All experiments were diluted to 100 mL with deionized water, then 0.1 g of CS-Fe-SLS was added and shaken in a constant temperature water bath shaker at 25 °C and 120 r/min; after the adsorption equilibrium, the concentration of Cr(VI) in the supernatant was measured.
- (3) The adsorption capacity of Cr(VI) was calculated. The Cr(VI) solution without coexisting ions was set as the control, and a control experiment was conducted under the same conditions to explore the effect of coexisting ions.

As can be seen from Figure 11, the adsorption capacity decreased with the increase in the concentration of coexisting ions. With the increase in the concentration of Cl⁻, the adsorption capacity of Cr(VI) on CS-Fe-SLS slowly decreased from 90.96 to 82.73 mg/g. With the increase in NO₃⁻ concentration, the adsorption capacity of Cr(VI) gradually decreased from 93.15 to 80.88 mg/g. With the increase in SO₄²⁻ concentration, the adsorption capacity of Cr(VI) gradually decreased from 88.73 to 78.5 mg/g. With the increase in CO₃²⁻ concentration, the adsorption capacity

**Figure 11** | Effect of common anions on Cr(VI) adsorption by CS-Fe-SLS.

of Cr(VI) decreased significantly, from 74.74 to 44.88 mg/g. The main reason for this was the presence of CO₃²⁻, which increased the pH of the solution due by hydrolysis. This agreed with the earlier observation that with the increase in pH, the adsorption capacity of Cr(VI) onto CS-Fe-SLS was significantly reduced.

Based on the above analysis, it was concluded that apart from CO₃²⁻, common anions (Cl⁻, NO₃⁻, SO₄²⁻) in natural water bodies have little effect on the amount of Cr(VI) adsorbed by CS-Fe-SLS, and the effect was in the order: CO₃²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻.

Effect of Cu(II)

In order to understand the interaction between a common heavy metal ion and Cr(VI), this section examined the effect of different interference ion intensity conditions. Cu(II) solutions of different concentrations (50, 100, 200, 300, 400, 500 mg/L) were prepared. The additive amount of CS-Fe-SLS was 0.1 g. In order to ensure that the reaction was complete, the adsorption was extended for 24 hours at 25 °C. After the adsorption reached equilibrium, the ion concentration of Cr(VI) was measured and the adsorption amount was calculated.

Figure 12 shows that with an increase in the concentration of Cu(II), the adsorption of Cr(VI) increased, and then leveled off. When the concentration of Cr(VI) was 50 mg/L, the adsorption of Cr(VI) with increasing Cu(II) concentration increased from 14.41 mg/g to 20.53 mg/g, an increase of 42%. When the concentration of Cr(VI) was 100 mg/L, the adsorption of Cr(VI) increased with increasing

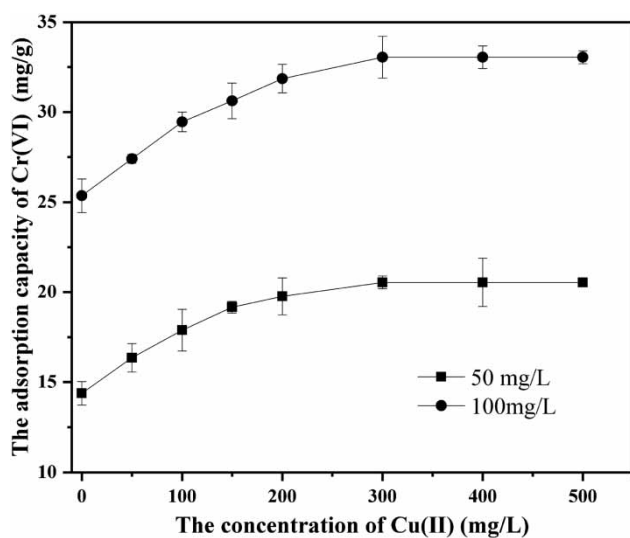


Figure 12 | Effect of Cu(II) on Cr(VI) adsorption by CS-Fe-SLS.

Cu(II) concentration from 25.35 mg/g to 33.04 mg/g, an increase of 30%.

The reasons for this may be as follows: (1) after coordination with CS-Fe-SLS, Cu(II) can be used as cationic bridge, preconcentrating Cr(VI) by electrostatic force, then the hydroxyl group causes strong oxygen reduction, to strengthen the effect of adsorption (Zhu et al. 2016); (2) the active points used for adsorption on the material are limited, so when the adsorption amount reaches a certain limit, it does not increase.

CONCLUSION

In the study, adsorption experiments of Cr(VI) in water onto CS-Fe-SLS were carried out, from which the following conclusions can be drawn:

- (1) pH had a significant effect on Cr(VI) adsorption, which decreased with increasing pH. The optimal adsorption pH was 3.0.
- (2) The adsorption of Cr(VI) by CS-Fe-SLS reached equilibrium at 120 min. The kinetics model fitting showed that the adsorption of Cr(VI) was both chemical and physical.
- (3) With the increase of the initial concentration the equilibrium adsorption amount of Cr(VI) to the material gradually increased. Fitting Langmuir and Freundlich models showed that the adsorption of Cr(VI) was both single-layer adsorption and multi-layer, which was

consistent with the results of the kinetics experiments. The maximum adsorption capacity of Cr(VI) onto CS-Fe-SLS was 131.91 mg/g.

- (4) CO_3^{2-} significantly decreased Cr(VI) adsorption Cl^- , NO_3^- and SO_4^{2-} had no significant effect and Cu(II) increased Cr(VI) removal by CS-Fe-SLS.
- (5) The modification mechanism and the adsorption mechanism of heavy metals could be further understood through the characterization of the material. SEM results showed that CS-Fe-SLS had a higher specific surface area than chitosan; FTIR results showed that SLS and Fe(III) were successfully loaded onto the chitosan; XRD results showed that the crystallinity of CS-Fe-SLS was significantly lower than that of chitosan, and the morphology was more irregular and amorphous.
- (6) Some Cr(VI) was reduced to the less toxic form Cr(III) during the adsorption. It was removed in the form of Cr(VI) and Cr(III).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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