Chitosan-silanol groups functional magnetic nanoparticles for heavy metals and bacteria removal

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Abstract

Studies have shown that there are multiple co-existence pollutants in environmental water over recent years. In this study, we report the design and synthesis of magnetic adsorbents incorporating chitosan-silanol groups ($\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$) with improved physicochemical properties for the removal of various heavy metals and bacteria from polluted water. $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ was synthesised using the coprecipitation method. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), Brunauer-Emmett-Teller (BET), Vibrating sample magnetometer (VSM), and Zeta techniques were used to characterise. The effects of factors such as pH, adsorption time, and adsorbent dosage were optimised. The results indicated that $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ had high adsorption efficiency and adsorption capacity for Cr (VI), As, Hg and Se. Moreover, Cr (VI) and As have a preferential adsorption effect when multiple metal ions coexist. The adsorption performance of $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ to bacteria was verified using $\text{E. coli}$ (gram-negative) and $\text{S. aureus}$ (gram-positive). The developed adsorbent also showed good adsorption efficiency for both gram-negative and gram-positive bacteria. Overall, the synthesised $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ adsorbent showed high removal efficiency and adsorption capacity with a stable structure and easy separation. It has promising applications for the removal of heavy metals and bacteria from water.

1. Introduction

Water pollution caused by illegal discharge of wastewater, accidental leakage of raw materials, and poor water management or monitoring has severely affected water quality safety (Gothandam et al., 2020). The pollutants can include organic pollutants, heavy metals, pharmaceuticals, and drug-resistant bacteria (Chen et al., 2020). Among these contaminants, heavy metals are toxic, accumulative, non-degradable, and carcinogenic; therefore, their potential risk to people and the ecosystem is immense (Ma et al., 2011). Antibiotics and other chemicals induce the development of resistance-harbouring resistance genes. Because of horizontal gene transfer, numerous drug-resistant bacteria have emerged, posing a risk to human health (Na et al., 2021).

Presently, there are many methods for removing heavy metals or bacteria from water. The commonly used methods include membrane filtration, wet heat sterilisation, chemical precipitation, and electrochemical treatment (Ince et al., 2019; Bairagi et al., 2020). The adsorption method has been widely used for the removal of pollutants from water because of its advantages such as low cost, high adsorption efficiency, simple operation, and short adsorption cycle (Liu et al., 2019; Panda et al., 2020). The quality of the adsorption method depends on the adsorbent; therefore, it is important to select a suitable adsorbent to eliminate pollutants from water (Hussain et al., 2021). In recent years, a variety of materials for removing heavy metals and bacteria have been reported, including carbon-based materials such as activated carbon (Yuan et al., 2021), carbon nanotubes (Zhu et al., 2020), and graphene (Perumal et al., 2020), as well as natural polymers such as cellulose (Pei et al., 2020) and chitosan (Li et al., 2020).
Chitosan, derived from chitin, is one of the most abundant biopolymers in nature (Gabriel et al., 2020). Because chitosan contains amino, acetylamino, and hydroxyl groups, it is relatively active and can be modified, activated, and coupled (Tanhaei et al., 2015; Bala et al., 2017). Moreover, its biodegradability, cell affinity, biological effects, and many other unique properties, have contributed to chitosan’s extensive applications in the pharmaceutical and light industries and for environmental protection (Nayak et al., 2015; Altun et al., 2020; Anwar et al., 2020; Zhao et al., 2020). For instance, Li et al. (2020) prepared a novel amidoxime-based magnetic adsorbent (AO-PAN-g-Chitosan/ Fe₃O₄) for the adsorption of heavy metals in water. Mu et al. (2020) prepared a porous lignosulfonate/chitosan adsorbent by an acrylic radical polymerisation method for removing Cu²⁺ and Co²⁺ from water. A previous study has shown that chitosan not only increases the specific surface area of the material but also improves the adsorption efficiency and adsorption capacity (Saheed et al., 2020).

Silicon-based biomaterials have been widely studied for application in bone regeneration because of their antibacterial properties. The antibacterial potential of biomaterials containing Si-OH groups has been previously investigated. Reis et al. observed the antibacterial properties of silicon-related biomaterials when high concentrations of silicon were used as biomaterials (Mortazavi et al., 2010). Allan et al. and Zehnder et al. (2007) suggested that the antibacterial activity of 45S5 was strongly correlated with high Si ion levels in the supernatant.

In this study, chitosan-silanol functional magnetic nanoparticles (Fe₃O₄@Si-OH@CS) were synthesised by a co-precipitation method with improved physicochemical properties for the removal of various heavy metals and bacteria (Fig. 1). The magnetic composite exhibits high adsorption capacity for both heavy metals such as, Hg, Se, and Cr(VI), and bacteria including \textit{Escherichia coli} (gram-negative) and \textit{Staphylococcus aureus} (gram-positive).

### 2. Materials And Methods

#### 2.1. Materials

Ferrous sulfate (FeSO₄·7H₂O), ammonium hydroxide (NH₃·H₂O, 25–28%), glutaraldehyde (C₅H₈O₂, 50%), and glacial acetic acid (CH₃COOH) were obtained from Tianjin Fengchuan Chemical Reagent Co., Ltd. Anhydrous ethanol (C₂H₅OH) was obtained from Tianjin Damao Chemical Reagent Factory. Ethyl orthosilicate (C₈H₂₀O₄Si, 28.0%) was obtained from Tianjin Jinke Fine Chemical Research Institute. Chitosan (C₆H₁₂NO₄, low viscosity < 200 mPa·s), hydrochloric acid (HCl), and ferric chloride hexahydrate (FeCl₃·6H₂O) were purchased from Tianjin Fuchen Chemical Reagent Factory. All reagents were of analytical grade and were used directly as received without further treatment. Ultrapure water with a resistivity of 18 MΩ/cm was used for all the experiments.

#### 2.2. Synthesis of Fe₃O₄@Si-OH@CS
Fe₃O₄@Si-OH were prepared using a previously reported method (Tang et al., 2020). First, FeCl₃·6H₂O (5.21 g) and FeSO₄·7H₂O (4.22 g) were added to 250 mL of deionised water. HCl (850 µL) was added to the mixture and subjected to ultrasonic deoxidisation for 30 min. Then, 22 mL of NH₃·H₂O was added to the solution after ultrasound, and the mixture was stirred at 80°C for 40 min. A black precipitate was obtained after standing for 60 min. The precipitate was separated by an external magnetic field, and magnetic fluid Fe₃O₄ was obtained (Luo et al., 2010). In the second step, the magnetic fluid was dispersed with 500 mL of C₂H₅OH and 250 mL of deionised water with ultrasound for 10 min. Then, 38 mL NH₃·H₂O and 50 mL ethyl orthosilicate were added with agitated at 60°C for 4.5 h. Fe₃O₄@Si-OH was obtained by magnetic separation. In the third step, the Fe₃O₄@Si-OH magnetic nanoparticles (0.20 g) were dispersed in a chitosan solution (60 mL, 1%). Then, 3 mL of glutaraldehyde solution (5%) was added, and the mixture was stirred at 60°C for 30 min. The products were separated by an external magnetic field, washed with acetic acid (3%), and dried at 80°C. Fe₃O₄@Si-OH@CS was obtained and stored at 25 ℃.

2.3. Characterisation

The adsorbent was dispersed in 3% acetic acid and ultrasonicated. The particle size and particle size distribution of the obtained uniform suspension were determined using a laser scattering particle size analyser (LS13-320, Beckman Coulter, USA). The conductive adhesive was coated on the surface of the sample in a vacuum environment, and the adsorbent was observed by scanning electron microscopy (SEM) with SU-1510 (Japan) at a voltage of 5 kV. The X-ray diffraction (XRD) patterns were measured at 100 mA in the 2θ range of 5~80° with a Smartlab (Neo-Confucianism, Japan) using Cu Kα radiation. A Nicolet Nexus 6700 FTIR (USA) spectrometer was used to determine the Fourier transform infrared (FTIR) spectra of the Fe₃O₄, Fe₃O₄@Si-OH, Fe₃O₄@Si-OH@CS, and chitosan solution (1%) samples in the region between 400 and 4000 cm⁻¹. At 243.15 K, a Belsorp Max nitrogen gas adsorption analyser (BLE, USA) was used to determine the pore size, specific surface area, and pore volume of the adsorbent surface by nitrogen adsorption-desorption analysis using the Brunauer–Emmett–Teller (BET) method. The surface potentials (zeta) of Fe₃O₄@Si-OH and Fe₃O₄@Si-OH@CS were measured using a nanoparticle potentiometer (Zetasizer Nano ZS90, Malvern, UK). A Versalab vibrating sample magnetometer (VSM, Quantum Design, USA) was used for the magnetisation measurements of the adsorbents.

2.4. Batch adsorption experiments

First, 1 mL of Cr(VI) (20 µg/mL) solution and 50 mg of adsorbent were mixed in a 5 mL centrifuge tube for batch adsorption experiments. In addition to exploring the factors influencing pH, other adsorption experiments were carried out under the experimental conditions of pH 2.5. 0.1 M HCl and NaOH (0.1 M) were used to adjust the pH value of Cr(VI) (from 1.0 to 7.0) to explore the effect of pH on the adsorption efficiency. The effect of adsorbent dosage on the adsorption efficiency was investigated by changing the amount of adsorbent from 25 to 150 mg. The effect of adsorption time was studied by changing the adsorption time from 5 to 90 min. To study the adsorption efficiency of the adsorbent on heavy metal ions, 20 µg/L As, 1 µg/L Hg, 50 µg/L Se, 40 µg/L Pb, and 7 µg/L Cd were used for adsorption. To study
the adsorption capacity of the adsorbent on heavy metal ions, 50 mg Fe$_3$O$_4$@Si-OH@CS was added, and the concentrations of As, Hg, Se, Pb, and Cd were changed from 0 to 800 mg/L, respectively. Furthermore, 200 µg/L Cr(VI), 20 µg/L As, 10 µg/L Hg, and 50 µg/L Se were used for the cation adsorption competition experiments. The concentration of Cr(VI) was determined using a UV/visible spectrophotometer (UV-2550, Tianjin, China). The concentrations of As, Hg, and Se were determined using an atomic fluorescence photometer (AFS-930, Beijing Jitian Instrument Co., Ltd., China). The adsorption capacity of the adsorbents toward heavy metal ions $q_e$ (mg/g) and the removal percentage $\eta$ (%) were determined based on the following equations:

$$ q_e = \frac{\left( C_0 - C_e \right) V}{m} $$  

$$ \eta = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% $$  

where $q_e$ (mg/g) is the adsorption capacity of heavy metals, $C_0$ (µg/L) is the initial concentration of heavy metal ions, $C_e$ (µg/L) is the equilibrium concentration of heavy metal ions, $V$ (mL) is the volume of the adsorbate solution, $m$ (mg) is the amount of adsorbent, and $\eta$ (%) is the percentage of heavy metal ions adsorbed from the solution.

### 2.5. Fe$_3$O$_4$@Si-OH@CS application for bacteria

*Escherichia coli* was cultured in accordance with the standard test method (GB/T 5750.12-2006). Nutritional AGAR medium was used instead of beef extract peptone medium to reduce the pH adjustment steps. First, 2.5 mg Fe$_3$O$_4$@Si-OH@CS was added to a certain volume of bacterial liquid for vibration adsorption. After magnetic separation, 200 µL of the supernatant was collected and coated on the plate. This step was carried out in a biosafety cabinet. The coated plate was then placed in an electric thermostatic incubator and cultured at 37°C for 24–48 h. The number of colonies that grew on the plates was counted. Finally, 200 µL of bacterial solution from the bacterial solution diluted 1000 times was coated onto the plate to calculate the blank colony. This step was carried out in a biosafety cabinet. The adsorption rate (AR) was calculated using the following equation:

$$ AR = \frac{N_a}{N_0} $$

where AR indicates the removal efficiency (%), $N_a$ is the number of bacteria after adsorption, and $N_0$ is the number of bacteria in the control group.

### 3. Results And Discussions

#### 3.1. Characterisation of adsorbents
The synthesis of Fe$_3$O$_4$@Si-OH@CS involves three steps (Fig. S1). SEM and SEM mapping were used to characterise the size, shape, and surface element distribution of Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, and Fe$_3$O$_4$@Si-OH@CS. As shown in Fig. 2 (a), Fe$_3$O$_4$ has an irregular blocky structure. In Fig. 2 (b), Fe$_3$O$_4$@Si-OH is a regular spherical structure with a smooth surface and a particle size of approximately 125 nm, possibly because Si–OH is coated on the surface of Fe$_3$O$_4$. As shown in Fig. 2 (c), the particle size of Fe$_3$O$_4$@Si-OH@CS increased slightly compared with that of Fe$_3$O$_4$@Si-OH, approximately 170 nm, likely because the coating of chitosan increased the particle size of the material. Fe$_3$O$_4$@Si-OH@CS exhibited an agglomeration phenomenon, which may be the result of the uneven dispersion of chitosan. The local elemental information of Fe$_3$O$_4$@Si-OH@CS is shown in Fig. 2 (d). The results show that Fe, O, Si, and N are uniformly distributed on the surface of Fe$_3$O$_4$@Si-OH@CS, indicating that Si–OH and CS-coated Fe$_3$O$_4$ successfully.

The crystal structure and integrity of the adsorbents were determined using XRD patterns. Fig. 2(e) shows the XRD patterns of Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, and Fe$_3$O$_4$@Si-OH@CS. The diffraction peaks of 30.3°, 35.5°, 43.1°, 53.7°, 57.2°, 62.8°, and 72.9° are (3451), (6480), (3170), (2780), (3602), (4168), and (2394) respectively. This indicates that Fe$_3$O$_4$ has a cubic phase and a face-centred cubic structure (JCPDS card no. 19-0629) and stably exists throughout the synthesis process. The peak value of 2θ widened between 20° and 70°, which was likely the result of the amorphous Si–OH coating on Fe$_3$O$_4$. The peaks broadened for Fe$_3$O$_4$@Si-OH@CS at 20° and 30°, which may be attributed to the addition of chitosan. Therefore, the Si–OH and CS-coated Fe$_3$O$_4$ were successfully prepared.

The chemical functional groups on the surface of Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, Fe$_3$O$_4$@Si-OH@CS, and chitosan in 400-4000 cm$^{-1}$ region were determined by Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 2(f), Fe-O stretching vibration peaks can be observed at 583 cm$^{-1}$ in Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, and Fe$_3$O$_4$@Si-OH@CS (Lei, Chao et al., 2020). The peak value of 2880 cm$^{-1}$ was caused by the vibration of the C-H bond contraction. The vibration absorption peak of the O-H bond in water is 3440 cm$^{-1}$ (Bing-Qiang Lu et al., 2013). The peak at 1100 cm$^{-1}$ was caused by the stretching vibration of the Si-O bond (Zhang et al., 2015). This indicates that Si-OH successfully coated the surface of Fe$_3$O$_4$. At 1620 cm$^{-1}$, the vibration absorption peak of N-H in chitosan was observed, indicating that chitosan was successfully coated on Fe$_3$O$_4$@Si-OH (Gedam & Dongre, 2015).

BET and Barrett-Joyner-Halenda (BJH) methods were used to analyse the specific surface area, pore volume, and pore size of the adsorbents with N$_2$ desorption and adsorption isotherms. As shown in Fig. 2(g), a typical characteristic of the type-III isotherm accompanying by H3 type hysteresis loop, indicating that Fe$_3$O$_4$@Si-OH@CS is a mesoporous material (Kruk and Jaroniec, 2001). The pore parameters of the three materials are listed in Table S1. The specific surface area of Fe$_3$O$_4$ is 141.86 m$^2$/g, which is favourable for Si-OH coating. The specific surface area of Fe$_3$O$_4$@Si-OH is 21.82 m$^2$/g and may be due to the addition of the Fe$_3$O$_4$ surface Si-OH. The specific surface area of Fe$_3$O$_4$@Si-
OH@CS is 27.34 m²/g, which may be because the -NH₂ coating increases the specific surface area and provides more adsorption sites for adsorbents.

The zeta potential was used to determine the charge type on the surface of the adsorbent. As shown in Fig. S2, the surface of Fe₃O₄@Si-OH is negatively charged (-41.3 mV), which may be caused by the addition of Si-OH on the surface of Fe₃O₄@Si-OH. However, the surface of Fe₃O₄@Si-OH@CS is positively charged (+28.89 mV), indicating that -NH₂ successfully modified Fe₃O₄@Si-OH, which is more conducive to electrostatic adsorption.

The magnetic properties of the three materials were studied by examining their magnetic hysteresis loops. As seen in Fig. S3, the remanent magnetism and coercivity of these three particles are close to zero, indicating that they have superparamagnetic properties (Meng et al., 2018). The saturation magnetisations of Fe₃O₄, Fe₃O₄@Si-OH, and Fe₃O₄@Si-OH@CS were 84.2, 76.4, and 57.8 emu/g. The decrease in saturation magnetisation may be due to the addition of non-magnetic Si-OH and CS. Although the magnetic field intensity of Fe₃O₄@Si-OH@CS was reduced, it could still be rapidly separated by an applied magnetic field (Inset). Therefore, the adsorbent can be rapidly separated from the solution using an external magnetic field (Huang and Chen, 2009).

### 3.2. Adsorption of heavy metals

#### 3.2.1. Effect of pH

The pH is a significant factor that can affect adsorption efficiency. Cr(VI) was selected as the model heavy metal for further condition optimisation. As shown in Fig. 3(a), the removal efficiency increased when the pH changed from 1 to 2.5. This is mainly because Cr(VI) primarily exists in the form of H₂CrO₄⁻ and HCrO₄⁻ in an acidic environment. The concentration of HCrO₄⁻ increased with increasing pH. More anionic Cr(VI) could be absorbed on the surface of Fe₃O₄@Si-OH@CS based on electrostatic adsorption (Jiang et al., 2018). However, the number of protonated amino groups decreases with increasing pH, resulting in a lower adsorption capacity at higher pH values (Lei et al., 2020). Therefore, a pH of 2.5 was selected for further experiments.

#### 3.2.2. Effect of adsorption time

The adsorption time influenced the adsorption equilibrium between the adsorbents and the targets. Fig. 3(b) shows the relationship between the adsorption time and the adsorption efficiency. The adsorption efficiency increased rapidly when the adsorption time was below 15 min. This may be due to the fact that the surface of adsorbents can initially provide a large number of adsorption sites for targets. When the adsorption time was changed from 15 to 90 min, the adsorption efficiency increased slowly. This may be due to a large number of occupied active sites on the surface of the adsorbent as well as complexation playing a dominant role. This process is slow, and the maximum adsorption capacity is 82.5 mg/g after adsorption for 180 min (Zhou et al., 2019). Combined with the factors of time cost and adsorption efficiency, an adsorption time of 15 min was selected.
3.2.3. Effect of absorbent dosage

The weight of the adsorbent is suitable for adsorption and elution. Fig. 3(c) shows the relationship between the absorbent dosage and the adsorption efficiency. The adsorption efficiency increased from 62.5–90.5% when the absorbent dosage was increased from 25 to 100 mg. This is because the adsorption sites increase with increasing absorbent dosage. The adsorption efficiency increased from 90.5–94.5% when the absorbent dosage was increased from 100 to 150 mg. The reason may be that the mass ratio of adsorbent to Cr(Ⅲ) decreases with the increased dosage of adsorbent, which leads to the under-utilisation of Fe₃O₄@Si-OH@CS surface adsorption sites (Zeng et al., 2020). Based on our results, we inferred that a good adsorption efficiency can be achieved with 100 mg adsorbents.

3.2.4. Adsorption of other heavy metals

Various heavy metal ions present in water pose severe risks to environmental and public health. Therefore, the performance of materials for removing multiple heavy metal ions is very important for practical applications. The adsorption efficiencies of Fe₃O₄@Si-OH@CS for several typical heavy metals, including As, Hg, and Se, were further studied. As shown in Fig. 3(d), the proposed material also exhibited excellent adsorption performance under the optimum adsorption conditions for Cr(Ⅲ). The adsorption efficiencies for As, Hg, and Se were 73.5%, 91.6%, and 100.0%, respectively. Under the optimum adsorption conditions for Cr(Ⅲ), the adsorption capacities of Fe₃O₄@Si-OH@CS for Cr(Ⅲ), As, Hg, and Se were also studied. As shown in Fig. 3(e), the adsorption capacity is not directly proportional to the adsorption efficiency. As shown in Table S2, the adsorption capacity of Fe₃O₄@Si-OH@CS for heavy metals was also higher than that of other materials reported in the literature. Therefore, Fe₃O₄@Si-OH@CS can potentially be applied for the simultaneous removal and enrichment of heavy metal ions.

3.2.5. Effect of competing metal ions

When multiple metal ions coexist in the environment, the adsorption capacity of the adsorbent may be reduced, because they compete with each other for the adsorption site. Therefore, a series of metal cations were selected as the research objects to explore the Fe₃O₄@Si-OH@CS priority adsorption order of heavy metals. The adsorption efficiency of Fe₃O₄@Si-OH@CS for various metal cations was also studied. As shown in Fig. 3(f), when Cr(VI), As, Hg, and Se coexist, the adsorption efficiency of Cr(Ⅲ) ≈ As > Hg > Se, which differs from that for single metal ions. According to the literature (Dan et al., 2019), both Cr(VI) and As exist in the form of typical oxygen anions (HCrO₄⁻, H₂AsO₄⁻, and HAsO₄²⁻) under acidic conditions. The oxygen anion possesses preferential electrostatic adsorption with protonated amino groups on the surface of the Fe₃O₄@Si-OH@CS surface. Therefore, the adsorption efficiencies of Cr(Ⅲ) and As were higher than those of Hg and Se when they coexist.

3.3. Adsorption of bacteria

3.3.1. Effect of pH
Antibiotic resistance, especially that of gram-negative bacteria, is one of the greatest public health threats worldwide. Moreover, as the most significant microbial habitat, aquatic environments are known to be favourable for antibiotic gene transfer. It has been reported that they play a crucial role in the spread of drug resistance in the environment (Cherak, Z et al., 2021). As a typical representative of gram-negative bacteria, the adsorption ability of Fe₃O₄@Si-OH@CS for E. coli was evaluated. First, the pH of the system was optimised. As shown in Fig. 4(a), Fe₃O₄@Si-OH@CS demonstrated sufficient adsorption of E. coli from pH 3.0 to 9.0. This occurred because the isoelectric point of most bacteria was estimated to be 2-5. Therefore, when the pH of the system was higher than the isoelectric point, the bacteria were negatively charged. The free amino group with a cationic charge on the surface of Fe₃O₄@Si-OH@CS could attract E. coli with anions (J Lin et al., 2018) and improve the adsorption efficiency. The adsorption efficiency of Fe₃O₄@Si-OH@CS to E. coli fluctuated slightly when the pH was higher than 5.0. The results indicate that the proposed material is suitable for use in most water bodies.

### 3.3.2. Effect of adsorption time

The adsorption time plays an important role in practical applications. As shown in Fig. 4(b), when the amount of magnetic material was 1.0 mg and the adsorption time was 5 min, the AR reached 74.95%. When the adsorption time was changed from 10 to 180 min, the adsorption efficiencies changed from 79.94–97.41%. Combined with the need for practical application, 5 min was selected for further experiments.

### 3.3.3. Effect of adsorbent dosage

The adsorption sites of Fe₃O₄@Si-OH@CS increased with increasing adsorbent dosage. Various amounts including 0.001, 0.0025, 0.005, 0.0075, and 0.01 g of Fe₃O₄@Si-OH@CS were studied (Fig. 4(c)). The initial concentration of E. coli was 656500 CFU/ml, and the adsorption time was 5 min. The adsorption efficiency of 0.001 g of Fe₃O₄@Si-OH@CS reached 88.4%. When the dosage of adsorbent was changed from 0.0025 to 0.01 g the adsorption efficiency was further increased from 96.82% to approximately 100%.

### 3.3.4 Effect of adsorption time

As reported in the literature, all active sites on the material would be occupied when a large number of bacteria are present in the samples, and excessive bacterial fluid would not be adsorbed (Rihayat, et al., 2020). Therefore, multiple adsorption experiments were conducted using 0.0025 g of adsorbent. As shown in Fig. 4(d), the adsorption efficiency was 94.6% at an adsorption time of 5 min when the concentration of E. coli was 451500 CFU/ml. The adsorption efficiency was 100% after four adsorption cycles. Therefore, the proposed materials can be used to efficiently remove bacteria through repeated adsorption.

### 3.3.5 Adsorption of gram-positive bacterium
The performance of the proposed materials was further verified for gram-positive bacteria. *Staphylococcus aureus* is a typical gram-positive bacterium. It can cause various illnesses, from minor skin infections to life-threatening diseases (Tong S et al., 2010.). Moreover, *S. aureus* is widespread in the environment, including air and sewage. Therefore, *S. aureus* was used as a model bacterium to demonstrate this adsorption method. As shown in Fig. 5(b), under the optimal conditions for *E. coli*, the proposed material also showed excellent adsorption and removal performance for *S. aureus*. With a 5 min adsorption time and 25 mg adsorbent, *S. aureus* could be removed completely after two adsorption cycles, because the isoelectric point of most gram-positive bacteria was estimated to be 2-3, which was lower than that of gram-positive bacteria. Therefore, the proposed adsorption method exhibited good adsorption performance.

4. Conclusions

In summary, we developed a magnetic adsorbent (Fe$_3$O$_4$@Si-OH@CS) incorporating chitosan-silanol groups. The proposed strategies showed good performance for both heavy metals (Cr(VI), As, Hg, and Se) and bacteria (gram-negative and gram-positive). The adsorbent is low cost, has a high adsorption capacity, is readily synthesised, and can be widely applied. It is expected to be an effective adsorbent for the removal of heavy metals and bacteria from environmental water.

Declarations

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**Author Contributions:** Huanying Zhou and Zhangrun Xu conceived the project. Tie Han and Zhixian Gao prepared all the materials for experiments and characterizations. Shuyue Ren, Shuang Li performed data analysis. Xueli Liu, Yonghui Wang and Qibo Liu, summarized all data and drafted the manuscript. All authors discussed the results and commented on the manuscript.

**Ethical Approval:** Not applicable.

**Consent to Participate:** Yes.

**Consent to Publish:** Yes.

References
1. Altun E, Elik E, Ersan HY (2020) Tailoring the microbial community for improving the biodegradation of chitosan films in composting environment. J Polym Environ 28(2). https://doi.org/10.1007/s10924-020-01711-0

2. Anwar M, Muhammad F, Akhtar B, Rehman SU, Saleemi MK (2020) Nephroprotective effects of curcumin loaded chitosan nanoparticles in cypermethrin induced renal toxicity in rabbits. Environ Sci Pollut Res 27(13):14771–14779. https://doi.org/10.1007/s11356-020-08051-5

3. Yin-Jie Bing-QiangLYing-JieZXin-YuZGuo-FengC Ruan (2013) Sodium polyacrylate modified Fe₃O₄ magnetic microspheres formed by self-assembly of nanocrystals and their applications. Mater Res Bull 48(2). https://doi.org/10.1016/j.materresbull.2012.11.078

4. Bala M, Shweta, Kumar A, Sharma et al (2017) Fabrication and characterization of chitosan-crosslinked-poly (alginic acid) nanohydrogel for adsorptive removal of Cr(â…¥) metal ion from aqueous medium. International Journal of Biological Macromolecules Structure Function & Interactions. doi:org/10.1016/j.ijbiomac.2016.11.072

5. Begum S, Yuhana NY, Saleh NM, Kamarudin NN, Sulong AB (2021) Review of chitosan composite as a heavy metal adsorbent: material preparation and properties. Carbohydr Polym 259(5):117613. https://doi.org/10.1016/j.carbpol.2021.117613

6. Cherak Z, Loucif L, Moussi A, Rolain JM (2021) Carbapenemase producing Gram-negative bacteria in aquatic environments: a review. Journal of Global Antimicrobial Resistance. https://doi.org/10.1016/j.jgar.2021.03.024

7. Dan H, Jizi Wu, Lu et al (2019) Novel insight into adsorption and co-adsorption of heavy metal ions and an organic pollutant by magnetic graphene nanomaterials in water. Chem Eng J. https://doi.org/10.1016/jcej.2018.10.138

8. Dobrzyńska J (2021) Amine-and thiol-functionalized SBA-15: Potential materials for As (V), Cr (VI) and Se (VI) removal from water. Comparative study. Journal of Water Process Engineering 40:101942. https://doi.org/10.1016/j.jwpe.2021.101942

9. Gedam AH, Dongre RS (2015) Adsorption characterization of pb(ii) ions onto iodate doped chitosan composite: equilibrium and kinetic studies. RSC Adv 5(67):54188–54201. https://doi.org/10.1039/c5ra09899h

10. Gothandam KM, Ranjan S, Dasgupta N, Lichtfouse E (2020) Environmental Chemistry for a Sustainable World. Environmental Biotechnology Vol 2., Volume 45. https://doi.org/10.1007/978-3-030-38196-7

11. Gabriel SK, Peters L, Mucalo M (2020) Chitosan: a review of sources and preparation methods. Int J Biol Macromol. https://doi.org/10.1016/j.ijbiomac.2020.12.005

12. Hussain S, Abid M, Munawar K, Saddiya A, Amjad M (2021) Choice of suitable economic adsorbents for the reduction of heavy metal pollution load. Polish Journal of Environmental Studies. https://doi.org/10.15244/pjoes/125016

13. Guo X, Du B, Wei Q, Yang J, Hu L, Yan L, Xu W (2014) Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from...
contaminated water. J. Hazard. Mater. 278, 211e220. https://doi.org/10.1016/j.jhazmat.2014.05.075

14. Huang S, Chen D (2009) Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent. J Hazard Mater 163:174–179. https://doi.org/10.1016/j.jhazmat.2008.06.075

15. Tang H, Wang Y, Li S, Wu J, Li J (2019) Huan ying Zhou, Zhixian Gao. Graphene oxide composites for magnetic solid-phase extraction of twelve quinolones in water samples followed by MALDI-TOF MS. Anal Bioanal Chem 411:7039–7049. https://doi.org/10.1007/s00216-019-02081-w

16. Lin J, Song T, Liu Y, Yang J, Shu W, Wenru Li, Chen J, Qiu X, Shi Q (2018) Preparation of modified silica/silver nanoparticles and its antibacterial properties. Industrial microorganism 48(05),19–22. https://doi.org/10.3969/j.issn.1001-6678

17. Jiang Y, Cai W, Tu W, Zhu M (2018) Facile cross-link method to synthesize magnetic Fe₃O₄@SiO₂–chitosan with high adsorption capacity toward hexavalent chromium. Journal of Chemical & Engineering Data. https://doi.org/10.1021/acs.jced.8b00738

18. Leus K, Folens K, Nicomel NR, Perez JPH, Filippousi M, Meledina M, Dîrtu MM, Turner S, Van Tendeloo G, Garcia. Y (2018) Removal of arsenic and mercury species from water by covalent triazine framework encapsulated γ-Fe2O3 nanoparticles, J. Hazard. Mater. 353 (2018) 312–319. https://doi.org/10.1016/j.jhazmat.2018.04.027

19. Kruk M, Jaroniec M (2001) Gas adsorption characterization of ordered organic-inorganic nanocomposite materials. Chem Mater 13:3169–3183. https://doi.org/10.1021/cm0101069

20. Bin L, Xiao-Jie S, Feng Z, Ao X, Jian-Hua YWu-LiHu, Wang Chang-Chun (2010) Multi-Functional Thermosensitive Composite Microspheres with High Magnetic Susceptibility Based on Magnetite Colloidal Nanoparticle Clusters. Am Chem Soc 26(3):1674–1679. https://doi.org/10.1021/la902635k

21. Lei C, Wang C, Chen W, He M, Huang B (2020) Polyaniline@ magnetic chitosan nanomaterials for highly efficient simultaneous adsorption and in-situ chemical reduction of hexavalent chromium: Removal efficacy and mechanisms. Sci Total Environ 733:139316. https://doi.org/10.1016/j.scitotenv.2020.139316

22. Li H, Fei-Xiang Zhou, Bin-Hong He Guo-Xiang, Wang X, Liang E (2020) Efficient adsorption of heavy metal ions by a novel ao-pan-g-chitosan/Fe₃O₄ composite. ChemistrySelect, 5. https://doi.org/10.1002/slct.202001965

23. Hashim MA, Soumyadeep M, Jaya, Narayan S, Bhaskar S (2011) Remediation technologies for heavy metal contaminated groundwater. J Environ Manage 92(10):2355–2388. https://doi.org/10.1016/j.jenvman.2011.06.009

24. Meng C, Zhikun W, Qiang L, Chunling L, Shuangqing S, Songqing H (2018) Preparation of amino-functionalized Fe₃O₄@mSiO₂ core-shell magnetic nanoparticles and their application for aqueous Fe³⁺ removal. J Hazard Mater 341:198–206. https://doi.org/10.1016/j.jhazmat.2017.07.062

25. Ince MInceOK (2019) Book: Toxicity of Nanomaterials, Chapter: Heavy Metal Removal Techniques Using Response Surface Methodology: Water/Wastewater Treatment. https://doi.org/10.5772/intechopen.88915, 2019
26. Mu R, Liu B, Chen X, Wang N, Yang J (2020) Adsorption of Cu (â…¡) and Co (â…¡) from aqueous solution using lignosulfonate/chitosan adsorbent. Int J Biol Macromol 163. https://doi.org/10.1016/j.ijbiomac.2020.06.260

27. Mortazavi V, Nahrkhalaji MM, Fathi MH, Mousavi SB, Esfahani BN (2010) Antibacterial effects of sol-gel-derived bioactive glass nanoparticle on aerobic bacteria. Journal of Biomedical Materials Research Part A The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials. 94(1):160–168. https://doi.org/10.1002/jbm.a.32678. An Official Journal of The Society for Biomaterials

28. Na G, Zhang W, Gao H, Wang C, Li R, Zhao F, Hou C (2021) Occurrence and antibacterial resistance of culturable antibiotic-resistant bacteria in the Fildes Peninsula, Antarctica. https://doi.org/10.1016/j.marpolbul.2020.111829. Marine Pollution Bulletin

29. Nayak V, Jyothi MShivanna, Balakrishna R, Geetha., Padaki M, Ismail AF (2015) Preparation and Characterization of Chitosan Thin Films on Mixed-Matrix Membranes for Complete Removal of Chromium. ChemistryOpen 4(3):278–287. https://doi.org/10.1002/open.201402133

30. Popovic AL, Rusmirovic JD, Velickovic Z, Radovanovic Z, Ristic M, Pavlovic VP, Marinkovic AD (2020) Novel amino-functionalized lignin microspheres: high performance biosorbent with enhanced capacity for heavy metal ion removal. Int J Biol Macromol 156:1160–1173. https://doi.org/10.1016/j.ijbiomac.2019.11.152

31. Panda L, Jena SK, Rath SS, Misra PK (2020) Heavy metal removal from water by adsorption using a low-cost geopolymer. Environ Sci Pollut Res 9 https://doi.org/10.1007/s11356-020-08482-0

32. Perumal S, Atchudan R, Yoon DH, Joo J, Cheong IW (2020) Graphene oxide-embedded chitosan/gelatin hydrogel particles for the adsorptions of multiple heavy metal ions. J Mater Sci. https://doi.org/10.1007/s10853-020-04651-1

33. Pei X, Gan L, Tong Z, Gao H, Chen Y (2020) Robust cellulose-based composite adsorption membrane for heavy metal removal. J Hazard Mater 406:124746. https://doi.org/10.1016/j.jhazmat.2020.124746

34. Rihayat T, Suryani S, Riskina S, Nurhanifa N (2020) Synthesis and characterization of chitosan-bentonite modified polyurethane with biomedical potential. IOP Conference Series: Materials Science and Engineering, 830, 042016. https://doi.org/10.1088/1757-899x/830/4/042016

35. Bairagi. S, SW. Ali (2020) Conventional and Advanced Technologies for Wastewater Treatment. Environmental Nanotechnology for Water Purification 33–56. https://doi.org/10.1002/9781119641353.ch2

36. Saheed IO, Da OW, Suah FBM (2020) Chitosan modifications for adsorption of pollutants-a review. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2020.124889

37. Shah KH, Yameen MA, Yousef T, Waseem M, Ahmad H (2020) Adsorption of bacteria by highly efficient, economic and biodegradable magnetic coated chitosan adsorbent. J Solution Chem. https://doi.org/10.1007/s10953-020-01010-1
38. Tanhaei B, Ayati A, Lahtinen M, Sillanp M (2015) Preparation and characterization of a novel chitosan/Al$_2$O$_3$/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of methyl orange adsorption. Chem Eng J 259:1–10. https://doi.org/10.1016/j.cej.2014.07.109

39. Tong S, Shi R, Zhang H, Ma C (2010) Catalytic performance of Fe$_3$O$_4$-CoO/Al$_2$O$_3$ catalyst in ozonation of 2-(2, 4-dichlorophenoxy) propionic acid, nitrobenzene and oxalic acid in water. J Environ Sci 22(10):1623–1628. https://doi.org/10.1016/S1001-0742(09)60298-9

40. Wu S-P, Dai X-Z, Kan J-R, Shilong F-D, Zhu M-Y (2017) Fabrication of carboxymethyl chitosan–hemicellulose resin for adsorptive removal of heavy metals from wastewater. Chin Chem Lett 28(3):625–632. https://doi.org/10.1016/j.cclet.2016.11.015

41. Liu X, Chuang MA, Fan WU, Zhao B (2019) Adsorption of Cr(VI) on Chitosan/Magnetic Bagasse Biochar Composite Material. Hydrometallurgy, 38(03), 208–214 https://doi.org/10.13355/j.cnki.sfyj.2019.03.008

42. Yuan Y, An Z, Zhang R, Wei X, Lai B (2021) Efficiencies and mechanisms of heavy metals adsorption on waste leather-derived high-nitrogen activated carbon. J Clean Prod 1126215. https://doi.org/10.1016/j.jclepro.2021.126215

43. Zhou G, Wang Y, Zhou R, Wang C, Jin Y, Qiu J et al (2019) Synthesis of amino-functionalized bentonite/CoFe$_2$O$_4$@MnO$_2$ magnetic recoverable nanoparticles for aqueous Cd$^{2+}$ removal. Sci Total Environ 682(SUP10):505–513. https://doi.org/10.1016/j.scitotenv.2019.05.218

44. Zeng H, Zhai L, Zhang J, Li D (2020) As(V) adsorption by a novel core-shell magnetic nanoparticles prepared with iron-containing water treatment residuals. Sci Total Environ 753:142002. https://doi.org/10.1016/j.scitotenv.2020.142002

45. Zhao L, Zhang M, Wang H, Devahastin S (2020) Effect of carbon dots in combination with aqueous chitosan solution on shelf life and stability of soy milk. Int J Food Microbiol 326:108650. https://doi.org/10.1016/j.ijfoodmicro.2020.108650

46. Zhang MM, Liu YG, Li TT, Xu WH, Zheng BH, Tan XF et al (2015) Chitosan modification of magnetic biochar produced from eichhornia crassipes for enhanced sorption of Cr(VI) from aqueous solution. RSC Adv 5. https://doi.org/10.1039/C5RA02388B

47. Zhang Y, Ye Y, Liu Z, Li B, Liu, Qinzhuang, Liu, Qiangchun, Li X (2016a) Monodispersed hierarchical aluminum/iron oxides composites micro/nanoflflowers for efficient removal of As(V) and Cr(VI) ions from water. J Alloys Compd. https://doi.org/10.1016/j.jallcom.2015.12.062

48. Zhu Z, An L, Chen T, Jia X (2020) The adsorption of divalent heavy metal ions on (8,0) carbon nanotubes: the first-principles study. Mod Phys Lett B. https://doi.org/10.1142/S0217984920503686

**Figures**
Figure 1

Synthesis and representation of pollutant-removal abilities of adsorbents.

Figure 2

SEM images of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@Si-OH, and (c) Fe$_3$O$_4$@Si-OH@CS. (d) SEM-mapping image of Fe$_3$O$_4$@Si-OH@CS. (e) XRD patterns of Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, and Fe$_3$O$_4$@Si-OH@CS. (f) FTIR spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@Si-OH, Fe$_3$O$_4$@Si-OH@CS and chitosan. (g) N$_2$ adsorption-desorption isotherms of Fe$_3$O$_4$@Si-OH@CS (Inset:BJH pore size distribution).
Figure 3

Adsorption efficiency effect of (a) pH, (b) contact time, and (c) amount of adsorbent. (d) Adsorption efficiency of adsorbents for other heavy metals. (e) Adsorption capacity of adsorbents for Cr (Ⅵ), As, Hg, and Se. (f) Adsorption efficiency of adsorbents with cationic competitive of multiple heavy metals.
Figure 4

(a) Removal efficiency with different pH for *Escherichia coli*. (b) Removal efficiency with different absorption time for *E. coli*. (c) Effect of different amount of adsorbent on the adsorption efficiency of *E. coli*. (d) The effects of different adsorption times on the adsorption efficiency of *E. coli*. 
Figure 5

(a) Adsorption of *Escherichia coli* by adsorbent. (b) Adsorption of *Staphylococcus aureus* by adsorbent.

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