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 ($\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$) with improved physicochemical properties for the removal of various heavy metals and bacteria from polluted water. $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ was synthesised using the co-precipitation 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ to bacteria was verified using *E. coli* (gram-negative) and *S. aureus* (gram-positive). The developed adsorbent also showed good adsorption efficiency for both gram-negative and gram-positive bacteria. Overall, the synthesised $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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-harboured 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/ Fe_3O_4) 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 Cu^{2+} and Co^{2+} 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 ($\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$) 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 *Escherichia coli* (gram-negative) and *Staphylococcus aureus* (gram-positive).

2. Materials And Methods

2.1. Materials

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25–28%), glutaraldehyde ($\text{C}_5\text{H}_8\text{O}_2$, 50%), and glacial acetic acid (CH_3COOH) were obtained from Tianjin Fengchuan Chemical Reagent Co., Ltd. Anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$) was obtained from Tianjin Damao Chemical Reagent Factory. Ethyl orthosilicate ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, 28.0%) was obtained from Tianjin Jinke Fine Chemical Research Institute. Chitosan ($\text{C}_6\text{H}_{12}\text{NO}_4$, low viscosity < 200 mPa·s), hydrochloric acid (HCl), and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$

$\text{Fe}_3\text{O}_4@\text{Si-OH}$ were prepared using a previously reported method (Tang et al., 2020). First, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.21 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (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 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 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 Fe_3O_4 was obtained (Luo et al., 2010). In the second step, the magnetic fluid was dispersed with 500 mL of $\text{C}_2\text{H}_5\text{OH}$ and 250 mL of deionised water with ultrasound for 10 min. Then, 38 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 50 mL ethyl orthosilicate were added with agitated at 60°C for 4.5 h. $\text{Fe}_3\text{O}_4@\text{Si-OH}$ was obtained by magnetic separation. In the third step, the $\text{Fe}_3\text{O}_4@\text{Si-OH}$ 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 . $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ was obtained and stored at 25°C .

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 $5-80^\circ$ with a Smartlab (Neo-Confucianism, Japan) using Cu K α radiation. A Nicolet Nexus 6700 FTIR (USA) spectrometer was used to determine the Fourier transform infrared (FTIR) spectra of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$, 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 $\text{Fe}_3\text{O}_4@ \text{Si-OH}$ and $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 $\mu\text{g/mL}$) 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 $\mu\text{g/L}$ As, 1 $\mu\text{g/L}$ Hg, 50 $\mu\text{g/L}$ Se, 40 $\mu\text{g/L}$ Pb, and 7 $\mu\text{g/L}$ Cd were used for adsorption. To study

the adsorption capacity of the adsorbent on heavy metal ions, 50 mg Fe₃O₄@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 η (%) were determined based on the following equations:

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (1)$$

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

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 η (%) is the percentage of heavy metal ions adsorbed from the solution.

2.5. Fe₃O₄@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 Fe₃O₄@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:

$$AR = \frac{N_a}{N_0} \quad (3)$$

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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ involves three steps (Fig. S1). SEM and SEM mapping were used to characterise the size, shape, and surface element distribution of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, and $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$. As shown in Fig. 2 (a), Fe_3O_4 has an irregular blocky structure. In Fig. 2 (b), $\text{Fe}_3\text{O}_4@\text{Si-OH}$ 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_3O_4 . As shown in Fig. 2 (c), the particle size of $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ increased slightly compared with that of $\text{Fe}_3\text{O}_4@\text{Si-OH}$, approximately 170 nm, likely because the coating of chitosan increased the particle size of the material. $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ exhibited an agglomeration phenomenon, which may be the result of the uneven dispersion of chitosan. The local elemental information of $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ is shown in Fig. 2 (d). The results show that Fe, O, Si, and N are uniformly distributed on the surface of $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$, indicating that Si-OH and CS-coated Fe_3O_4 successfully.

The crystal structure and integrity of the adsorbents were determined using XRD patterns. Fig. 2(e) shows the XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, and $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$. 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_3O_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_3O_4 . The peaks broadened for $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ at 20° and 30° , which may be attributed to the addition of chitosan. Therefore, the Si-OH and CS-coated Fe_3O_4 were successfully prepared.

The chemical functional groups on the surface of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$, and chitosan in $400\text{--}4000\text{ cm}^{-1}$ 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_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, and $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ (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_3O_4 . At 1620 cm^{-1} , the vibration absorption peak of N-H in chitosan was observed, indicating that chitosan was successfully coated on $\text{Fe}_3\text{O}_4@\text{Si-OH}$ (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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ 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_3O_4 is $141.86\text{ m}^2/\text{g}$, which is favourable for Si-OH coating. The specific surface area of $\text{Fe}_3\text{O}_4@\text{Si-OH}$ is $21.82\text{ m}^2/\text{g}$ and may be due to the addition of the Fe_3O_4 surface Si-OH. The specific surface area of $\text{Fe}_3\text{O}_4@\text{Si-OH}@\text{CS}$ is $141.86\text{ m}^2/\text{g}$.

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 adsorbent dosage

The weight of the adsorbent is suitable for adsorption and elution. Fig. 3(c) shows the relationship between the adsorbent dosage and the adsorption efficiency. The adsorption efficiency increased from 62.5–90.5% when the adsorbent dosage was increased from 25 to 100 mg. This is because the adsorption sites increase with increasing adsorbent dosage. The adsorption efficiency increased from 90.5–94.5% when the adsorbent dosage was increased from 100 to 150 mg. The reason may be that the mass ratio of adsorbent to Cr(VI) 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(VI). The adsorption efficiencies for As, Hg, and Se were 73.5%, 91.6%, and 100.0%, respectively. Under the optimum adsorption conditions for Cr(VI), the adsorption capacities of Fe₃O₄@Si-OH@CS for Cr(VI), 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(VI) $\approx$ 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(VI) 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ for *E. coli* was evaluated. First, the pH of the system was optimised. As shown in Fig. 4(a), $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ could attract *E. coli* with anions (J Lin et al., 2018) and improve the adsorption efficiency. The adsorption efficiency of $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ increased with increasing adsorbent dosage. Various amounts including 0.001, 0.0025, 0.005, 0.0075, and 0.01 g of $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 $\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$ 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 ($\text{Fe}_3\text{O}_4@\text{Si-OH}@CS$) 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.

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Figures

Figure 1

Synthesis and representation of pollutant-removal abilities of adsorbents.

Figure 2

SEM images of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{Si-OH}$, and (c) $\text{Fe}_3\text{O}_4@\text{Si-OH@CS}$. (d) SEM-mapping image of $\text{Fe}_3\text{O}_4@\text{Si-OH@CS}$. (e) XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, and $\text{Fe}_3\text{O}_4@\text{Si-OH@CS}$. (f) FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{Si-OH}$, $\text{Fe}_3\text{O}_4@\text{Si-OH@CS}$ and chitosan. (g) N_2 adsorption-desorption isotherms of $\text{Fe}_3\text{O}_4@\text{Si-OH@CS}$ (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 (Cr^{6+}), 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 adsorption 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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