A comparative study on Fe(III)-chitosan and Fe(III)-chitosan-CTAB composites for As(V) removal from water: preparation, characterization and reaction mechanism

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**A comparative study on Fe(III)-chitosan and Fe(III)-chitosan-CTAB composites for As(V)
removal from water: preparation, characterization and reaction mechanism**

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The concise and informative title: **Novel adsorbents for As(V) removal from water**

Abstract

Fe(III)-chitosan and Fe(III)-chitosan-CTAB composites were prepared using an ionotropic gelation method. Various techniques were used to analyze the morphology, structure, and property of the adsorbents, including SEM, EDS, FT-IR, XPS, and zeta potential. Compared with Fe(III)-chitosan, Fe(III)-chitosan-CTAB was more effective for As(V) adsorption at a wide range of pH (3–8). The adsorption of As(V) onto Fe(III)-chitosan and Fe(III)-chitosan-CTAB could reach equilibrium in 20 min, and their maximum adsorption capacities were 33.85 and 31.69 mg g⁻¹, respectively. The adsorption kinetics was best described by the pseudo-second-order model ($R^2=0.998$ and 0.992), whereas the adsorption isotherms was fitted well by the Freundlich model ($R^2=0.963$ and 0.987). The presence of H₂PO₄⁻ significantly inhibited the adsorption of As(V) onto Fe(III)-chitosan and Fe(III)-chitosan-CTAB, and humic acid also led to a slight decrease in As(V) adsorption by Fe(III)-chitosan-CTAB. Over 94% of As(V) at the initial concentration of no more than 5 mg L⁻¹ was removed from real water by the two adsorbents. 1% (w/v) NaOH solution was determined to be the most suitable desorption agent. Fe(III)-chitosan and Fe(III)-chitosan-CTAB still maintained their initial adsorption capacities after five adsorption-desorption cycles. Based on different characterization results, both electrostatic attraction and surface complexation mechanisms played important roles in As(V) adsorption on Fe(III)-chitosan and Fe(III)-chitosan-CTAB.

Keywords Adsorbent · Adsorption · Arsenic · Cationic surfactant · Toxic metal

Introduction

Arsenic (As) is a common occurring environmental pollutant that enters aquatic ecosystems through both

geological processes and anthropogenic activities (Smedley and Kinniburgh, 2002). It has attracted widespread attention because of its toxicity and carcinogenicity (Clancy et al., 2013). The toxicity of As is related to its chemical form. Inorganic As (iAs) tends to be more toxic than organic As (oAs). iAs generally exists in two predominant oxidation states, arsenate [As(V)] and arsenite [As(III)]. As(III) is the major species in reductive environment, while As(V) is the predominant species under oxidative environment. Unfortunately, an estimated more than 296 million people worldwide, which include 200 million from Asia (India, Bangladesh, China, Vietnam, Cambodia, Pakistan, and Nepal), are potentially exposed to iAs contamination above World Health Organization (WHO) guideline value of iAs in drinking water (0.01 mg L^{-1}) (Shaji et al., 2021). Given the risk of chronic iAs exposure via drinking water, it is necessary to develop proper remediation technologies.

Many technologies have been applied to the remediation of iAs-contaminated water, including electrocoagulation, chemical precipitation, membrane filtration, adsorption, ion exchange, and bioremediation (Dadwal and Mishra, 2017). Among these technologies, adsorption is an easy but effective and economical method (Gadd, 2009). Over the last decades, a variety of natural and synthetic adsorbents has been used for the removal of iAs from water. Owing to their easy availability and low cost, natural materials such as zeolite, clay, chitosan, and agricultural waste were used as adsorbents to remove metal ions (Gupta et al., 2021). Chitosan, a unique cationic polysaccharide, has received attention as a renewable, nontoxic, and biodegradable chelating agent for some metal ions (Bakshi et al., 2020). It could provide distinctive adsorption functions because of the existence of active hydroxyl ($-\text{OH}$) and amino ($-\text{NH}_2$) groups in its molecular structure (Liu et al., 2013). However, chitosan is only soluble in few organic acids and dilute inorganic acids, such as acetic acid and dilute hydrochloric acid (HCl), which limits its utilization for a specific application. The adsorption capacity and selectivity of chitosan

are also still unsatisfactory (Alves and Mano, 2008). Surface modification of chitosan is thus required to overcome these limitations.

There has recently been growing concern about the chemical modification of chitosan to improve its favorable properties. Both cross-linking and grafting are considered as the most useful methods to improve native properties of chitosan, such as enhancing complexation property and increasing the adsorption capacity (Saheed et al., 2021). Iron (Fe) is a commonly used metal ion for ionic cross-linking of chitosan. The crosslinked Fe(III)-chitosan has exhibited superior performance towards removing Cr^{6+} from aqueous solution with pH 2.0 (Demarchi et al., 2015). Fe(III)-chitosan synthesized by Shinde et al. (2013) showed better adsorption efficiency for As(V) than La(III)-chitosan. Furthermore, chitosan modification utilizing ionic surfactants (e.g., cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS)) also could make adsorbents with large adsorption capacity, high selectivity, and good stability. It has been reported that the chitosan beads impregnated with 0.05% CTAB had higher adsorption capacity for Congo red than the normal chitosan beads (Chatterjee et al., 2009). This was partly due to the electrostatic interaction between CTAB and Congo red, and partly because of the hydrophobic interaction between the cationic surfactant and dye. Nevertheless, little literature is available on the utilization of cationic surfactant CTAB to improve the removal efficiency of anionic As(V) by Fe(III)-chitosan.

In this study, Fe(III)-chitosan and Fe(III)-chitosan-CTAB composites were synthesized, characterized, and applied for anionic As(V) removal. As(V) adsorption property of the two adsorbents was investigated based on different factors like pH, contact time, initial As(V) concentration, and co-existing ions. The experimental data were fitted with typical kinetic and isotherm models to evaluate the adsorption mechanism. In addition, the regeneration of the adsorbents was used repeatedly up to five

cycles for examining their reusability.

Materials and methods

Materials

Chitosan (80–95% degree of deacetylation), CTAB ($\geq 99.0\%$), sodium hydroxide (NaOH, 99.9%), ferric trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$), HCl (36.0–38.0%), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$), sodium nitrate (NaNO_3 , $\geq 99.0\%$), and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium sulfate (Na_2SO_4 , $\geq 97.0\%$), hydrogen peroxide (H_2O_2 , 30wt.% in H_2O), and nitric acid (HNO_3 , 70%) were acquired from Aladdin Biochemical Technology Co., Ltd. Humic acid (HA, FA $\geq 90\%$) and sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$) were purchased from Shanghai Macklin Biochemical Co., Ltd. Arsenic trioxide (As_2O_3 , 99.95–100%) was provided from Shanghai Chemical Reagent Factory. All solutions were prepared using ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Direct-Q3, Millipore SAS, Molsheim, France). A stock solution of $1,000 \text{ mg L}^{-1}$ As(V) was prepared via dissolving 0.66 g of As_2O_3 in NaOH solution, oxidating it with excess H_2O_2 and then diluting to 500 mL using ultrapure water. Simulated wastewaters containing varying concentrations of As(V) were prepared via diluting the stock solution in ultrapure water.

Preparation of adsorbents

Fe(III)-chitosan and Fe(III)-chitosan-CTAB composites were prepared using an ionotropic gelation method (Lobo et al., 2020). First, 1.0 g of chitosan powder was dissolved in 50 mL of FeCl_3 solution (4% w/v) and magnetically stirred at room temperature for 5 h. The resulting gel was named as Fe(III)-chitosan. Subsequently, 1.0 g of CTAB was added into the Fe(III)-chitosan gel and stirred for 3 h to

obtain a Fe(III)-chitosan-CTAB gel. Then, each gel was slowly dropped into the NaOH solution (2 M) and stirred for 1 h. After stirring, each suspension was centrifuged for 5 min at 5,000 rpm for no less than three times. The precipitate was washed with ultrapure water several times and then dried at 60 °C. Finally, Fe(III)-chitosan and Fe(III)-chitosan-CTAB were ground, sieved through a 100-mesh sieve, and then stored in a desiccator for further experiments.

Characterization of adsorbents

The surface morphologies of the adsorbents were investigated via scanning electron microscopy (SEM) (Zeiss Gemini 300, Carl Zeiss AG, Oberkochen, Germany) operated at 3.0 kV. Surface elemental composition of the adsorbents was confirmed using energy dispersive X-ray spectroscopy (EDS) (X-Max, Oxford Instruments, Abingdon, UK). Fourier transform infrared spectra were obtained with FT-IR spectrometer (Nicolet iS50, Thermo Fisher Scientific Inc., Madison, WI, USA) using KBr pellets in the range 4000–500 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB Xi+ instrument (Thermo Fischer Scientific Inc., Waltham, MA, USA) with a monochromatic Al-K α X-ray source ($h\nu = 1486.60$ eV) at 12.5 kV. The zeta potential was observed at pH 3–10 using Zetasizer Nano ZS90 analyzer (Malvern Panalytical, Malvern, Worcestershire, UK).

Adsorption experiments

Batch adsorption experiments were performed in a 50 mL centrifuge tube via mixing 0.8 g L^{-1} adsorbent with 25 mL As(V) solution at 25°C and 250 rpm in triplicate. The effect of pH on As(V) adsorption was evaluated by adjusting the initial pH of As(V) solution (10 mg L^{-1}) to 2–10. The pH was adjusted to an appropriate value via adding negligible amount of 0.1 M NaOH or HCl. After 5 h adsorption reaction, aliquots of the adsorption solution were taken outside the centrifuge tube and centrifuged to isolate the adsorbents. The supernatant was passed through a 0.22- μm pore size membrane filter. The residual As(V)

concentration in the supernatant was determined using Agilent 7700× ICP-MS (Agilent, Tokyo, Japan).

The operating parameters of ICP-MS were presented in Table S1. The removal efficiency ($R\%$) and adsorption capacity (q_t (mg g⁻¹)) of As(V) were calculated as follows:

$$R\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 (mg L⁻¹) and C_t (mg L⁻¹) are the initial and residual concentrations of As(V), respectively, V (L) is the solution volume, and m (g) is the mass of adsorbent. q_e (mg g⁻¹) can be acquired by replacing C_t in Eq. (2) with the residual As(V) concentration at equilibrium (C_e).

Adsorption kinetic experiments were conducted by using 10 mg L⁻¹ As(V) solutions at optimal pH via taking samples at intervals during the 5-h period. The pseudo-first- and pseudo-second-order kinetic models were employed to predict adsorption kinetics. The best-fit model was selected based on the correlation coefficient (R^2) value for regression. These two kinetic models are given as follows:

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

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

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts of As(V) adsorbed at equilibrium and at time t (min), respectively, k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first- and pseudo-second-order rate constants.

Adsorption isotherms experiments were determined with As(V) in the concentration range of 1–100 mg L⁻¹ for 2 h at optimal pH. Both Freundlich and Langmuir isotherm models were adopted to fit the experimental data. These models are given by the following equations:

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

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

where q_e (mg g⁻¹) is the adsorption capacity at equilibrium, q_m (mg g⁻¹) is the maximum adsorption

capacity, C_e (mg L^{-1}) is the residual As(V) concentration at equilibrium, $K_F [(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}]$ is the Freundlich constant related to adsorption capacity, K_L (L mg^{-1}) is the Langmuir constant related to the affinity of adsorption sites, and n is the dimensionless Freundlich intensity parameter.

The effects of co-existing ions (Mg^{2+} , Ca^{2+} , NO_3^- , SO_4^{2-} , and H_2PO_4^- , 1 mmol L^{-1}) and dissolved organic matter (HA, 10 mg L^{-1}) were studied at optimal pH for 2 h using As(V) concentration of 10 mg L^{-1} . Three water samples from different sources (Xiang River water, Hou Lake water, and tap water) were used to evaluate the As(V) removal performance of adsorbents in different water matrices. Because of their extremely low concentrations of As(V) (see Table S2), these samples were spiked to final concentrations of $0.1\text{--}10 \text{ mg L}^{-1}$ with As(V) solution.

Desorption and regeneration experiments

The desorption and regeneration behaviors of adsorbents were investigated to evaluate their reusability. The influence of the concentration of desorbing agent (NaOH solution) on the adsorption capacity of regenerated adsorbents was studied. After obtaining the optimal NaOH concentration, an adsorption-desorption experiment was performed over five cycles. The adsorption experiment was conducted with 0.2 mg of adsorbents to treat 10 mg L^{-1} of As(V) solution at 25°C and optimal pH for 2 h. The As(V)-loaded adsorbents were then eluted down with a 1% (w/v) NaOH solution for 3 h. The adsorbents were collected via centrifugation, washed with ultrapure water, dried at 60°C , and reused for the next cycle.

Results and discussion

Characterization of adsorbents

Surface morphology and elemental composition

The morphology of Fe(III)-chitosan and Fe(III)-chitosan-CTAB powders exhibited irregular particles

with a particle size of 10 to 150 μm (Figs. 1a–d). The surface of Fe(III)-chitosan was rough with some fibrous particles attached. After modification with CTAB, more small particles were observed on the surface of Fe(III)-chitosan-CTAB, creating a much rougher surface compared with Fe(III)-chitosan. This may be due to the hydrophobic interaction between some hydrophobic moieties of chitosan and CTAB tails when the concentration of CTAB reached the critical micelle concentration (Zhao et al., 2008). The elemental composition of Fe(III)-chitosan-CTAB was analyzed by EDS. As shown in Fig. 1e, five elements of C, N, O, Fe and Br were present onto the surface of Fe(III)-chitosan-CTAB, where Br came from CTAB. It was suggested that CTAB was successfully loaded onto Fe(III)-chitosan.

Fig. 1 SEM images of Fe(III)-chitosan (a, b) and Fe(III)-chitosan-CTAB (c, d) and EDS spectrum of Fe(III)-chitosan-CTAB (e).

FT-IR spectra

The FT-IR spectra verified the existence of surface functional groups of adsorbents. Figure 2 reports the FT-IR spectra of chitosan, Fe(III)-chitosan and Fe(III)-chitosan-CTAB before and after As(V) adsorption. For chitosan, the FT-IR spectrum exhibits the typical absorption bands at 3450, 3280, 2851, 1653, 1580, 1418, 1376, 1258, 1150, 1058, 1027, and 896 cm^{-1} . The characteristic broad absorption band at 3450 cm^{-1} is assigned to the stretching vibration of the –OH group in absorbed water molecules. The absorption band at 3280 cm^{-1} can be ascribed to the stretching vibration of N–H, and the other band at 1580 cm^{-1} is

in good agreement with the bending vibration of N–H in amide II (Jiang et al., 2021; Matet et al., 2013).

The three bands at 2851, 1418, and 1258 cm^{-1} can be corresponded to the symmetric and asymmetric stretching vibrations of $-\text{CH}_2$ (Matet et al., 2013). The characteristic band appeared at 1653 cm^{-1} is related to the $-\text{C}=\text{O}$ stretching vibration in amide I. The band at 1376 cm^{-1} corresponds to the C–N stretching vibration in amide III (Kloster et al., 2020; Matet et al., 2013). The two bands at 1150 and 896 cm^{-1} can be associated with the stretching vibration of C–O–C. The bands occurring at 1058 and 1027 cm^{-1} are referred to the C–OH stretching vibration (Medeiros Borsagli et al., 2015). For Fe(III)-chitosan, the presence of additional new bands at 792 and 890 cm^{-1} (overlapping with C–O–C stretching vibration at 896 cm^{-1}) can be observed, attributing to Fe–OH bending vibration (Adio et al., 2017). It was indicated that the –OH groups of chitosan were involved in the complexation with ferric ions. According to the literatures, the ferric ions in chitosan could be penta- or hexacoordinated, depending on the preparation conditions (Shen et al., 2013). For Fe(III)-chitosan-CTAB, the additional bands at 2920 cm^{-1} (from antisymmetric stretching vibration of methylene in CTAB) and 1465 cm^{-1} (due to the N–H bending of the primary aliphatic amine) are observed (Chatterjee et al., 2009). Furthermore, the appearance of vibrational peak at 600 cm^{-1} in Fe(III)-chitosan and Fe(III)-chitosan-CTAB after As(V) adsorption, ascribed the metal-oxygen interactions (Chatterjee et al., 2009; Harutyunyan et al., 2019).

Fig. 2 FT-IR spectra of chitosan, Fe(III)-chitosan and Fe(III)-chitosan-CTAB before and after the adsorption of As(V).

XPS spectra

The chemical composition and surface oxidation state of Fe(III)-chitosan and Fe(III)-chitosan-CTAB before and after As(V) adsorption were investigated by XPS. As shown in Fig. 3, the XPS spectra revealed the presence of Fe, O, N, C, and As elements, which was consistent with the EDS results. The high-resolution XPS spectra of Fe 2p show four peaks at binding energies of 710.6, 712.6, 719.0, and 724.6 eV. The doublet at 710.6 and 712.6 eV is assigned to Fe(III) 2p_{3/2}, while the 724.6 eV is assigned to Fe(III) 2p_{1/2} (Du et al., 2019; Yamashita and Hayes, 2008). The presence of a Fe(III) satellite peak at 719.0 eV and absence of Fe(II) satellite peaks at 715.0 or 730.0 eV confirm that only ferric ions are present near the surface of Fe(III)-chitosan and Fe(III)-chitosan-CTAB. These results indicated that chitosan was successfully complexed with Fe(III). N 1s spectra were split into two peaks at 398.6 eV for C–N–Fe and 401.7 eV for –N⁺(CH₃)₃ (Rufato et al., 2021; Shen et al., 2013). The prominent N 1s peak at 398.6 eV indicates the complexation of the amino group of chitosan with ferric ions. The other peak at 401.7 eV was observed only after Fe(III)-chitosan was impregnated with CTAB, indicating that the surface of synthesized Fe(III)-chitosan was successfully modified by cationic surfactant CTAB to increase surface functionality. C 1s spectra were divided into three major components at 284.8 eV, 286.5±0.1 eV, and 288.5±0.2 eV, corresponding to C–C, C–N/C–O from overlapping of C–O–C and C–OH, and C=O, respectively (Rufato et al., 2021; Yu et al., 2021). An increase in atomic percent of C–C from 49.1% for Fe(III)-chitosan to 75.5% for Fe(III)-chitosan-CTAB was noted, which further confirms the formation of Fe(III)-chitosan-CTAB.

Fig. 3 XPS fully-scanned spectra (a, b) and corresponding high-resolution XPS spectra of Fe 2p, N 1s, C1s and As 3d of Fe(III)-chitosan (c) and Fe(III)-chitosan-CTAB (d) before and after As(V) adsorption.

Adsorption characteristics

Effect of pH

The solution pH is a critical factor that may affect the surface charge of the adsorbents through protonation of the functional groups, as well as the chemical speciation of As ([Escudero et al., 2009](#)).

The effect of pH on As(V) adsorption by Fe(III)-chitosan and Fe(III)-chitosan-CTAB is presented in [Fig. 4a](#).

For Fe(III)-chitosan, the removal efficiency of As(V) increased sharply as the solution pH increased from 2 to 3, and then gradually decreased with further increase in pH up to 10. For Fe(III)-chitosan-CTAB, the removal efficiency reached its maximal value ($99.1 \pm 0.1\%$) at pH 4, and then slightly decreased to $93.6 \pm 0.2\%$ with increase of pH from 4 to 7. The removal efficiency could remain $76.6 \pm 2.0\%$ at pH 10. It was attributed to the increased electrostatic attraction, because CTAB could enhance

the electrostatic attraction by quaternary ammonium cations towards arsenate anions (Wang et al., 2016a). At pH 2, the removal efficiencies of As(V) by the two adsorbents were around 20.0%, and Fe(III) was detected in As(V) solutions treated with Fe(III)-chitosan and Fe(III)-chitosan-CTAB with means of 137.21 ± 1.54 and 119.96 ± 1.54 mg L⁻¹, respectively (see Table S3). The leaching of Fe(III) into water at pH 2 may be one of the reason for the low removal efficiencies of As(V) by the two adsorbents.

Fig. 4 Effect of pH on As(V) adsorption (a) and the corresponding zeta potential of Fe(III)-chitosan and Fe(III)-chitosan-CTAB at different pH (b).

Figure 4b shows the zeta potentials of Fe(III)-chitosan and Fe(III)-chitosan-CTAB in As(V) solutions measured at different pH values. The zeta potential of Fe(III)-chitosan changed from positive (+10.3 mV) at pH 3 to negative (−8.7 mV) at pH 4, with the point of zero charge at around pH 3.4. By contrast, the zeta potential of Fe(III)-chitosan-CTAB was positive over the entire studied pH range (3–10). The absolute value of the zeta potential increased from pH 3 to 4, then decreased from 4 to 10. At pH 3–10, As(V) exists as a monovalent (H_2AsO_4^-) or divalent (HAsO_4^{2-}) anion. Higher removal of As(V) from an aqueous solution can be attributed to the adsorption of H_2AsO_4^- and HAsO_4^{2-} onto the positively charged surface of Fe(III)-chitosan at pH 3. As pH increased, the positively charged amino groups deprotonated, which may lead to a rapid decline in the removal efficiency of As(V) (Seyed Dorraji et al.,

2014; Wang et al., 2016b). Fe(III)-chitosan-CTAB was maintained at a positive electric potential at pH 3–10, indicating that the adsorbent could effectively adsorb negative As(V). The reason why the As(V) removal decreased with an increase in pH might be attributed to the decrease of the positive surface potential of Fe(III)-chitosan-CTAB (Sun et al., 2019). Compared with Fe(III)-chitosan, Fe(III)-chitosan-CTAB was more conducive to As(V) the removal from water. Therefore, pH 3 ± 0.1 and 4 ± 0.1 were selected as optimum solution pH in the subsequent experiments for Fe(III)-chitosan and Fe(III)-chitosan-CTAB, respectively.

Adsorption kinetics

The contact time is one of the significant parameters for the successful application of adsorbents. Figures 5 a and b show the effect of the contact time on the adsorption capacities of Fe(III)-chitosan and Fe(III)-chitosan-CTAB for As(V). It was found that the adsorption equilibrium of the adsorbents for As(V) adsorption was attained within 20 min. The maximum adsorption capacities of Fe(III)-chitosan and Fe(III)-chitosan-CTAB were 12.94 and 12.88 mg g⁻¹, respectively. The rate of As(V) adsorption was fast, with more than 95% (for Fe(III)-chitosan) and 87% (for Fe(III)-chitosan-CTAB) of adsorption occurred during the first 20 min (see Table S4). The equilibrium time may depend on the characteristics of the synthetic chitosan derived materials. The adsorption equilibrium of the cross-linked Fe(III)-chitosan for As(V) adsorption could be reached within 2 h (Neto et al., 2013), while 30 minutes were reported for the uncross-linked one (Lobo et al., 2020). Besides, a higher value of removal efficiency may correspond to a higher degree of protonation of amino groups at pH 3.

Fig. 5 Pseudo-first- and pseudo-second-order kinetic models of Fe(III)-chitosan (a) and Fe(III)-chitosan-CTAB (b); adsorption isotherm curves for As(V) on Fe(III)-chitosan (c) and Fe(III)-chitosan-CTAB (d).

To identify the adsorption mechanism, the pseudo-first- and pseudo-second-order kinetic models were applied to test the experimental data. The results showed that the As(V) adsorption process followed the pseudo-second-order kinetic model. The correlation coefficients for pseudo-second-order kinetic model were higher ($R^2=0.998$ for Fe(III)-chitosan and $R^2=0.992$ for Fe(III)-chitosan-CTAB) than pseudo-first-order kinetic model ($R^2=0.980$ for Fe(III)-chitosan and $R^2=0.942$ for Fe(III)-chitosan-CTAB) (Table 1). It was indicated that chemisorption was the rate-controlling factor for As(V) adsorption onto the two adsorbents (Pillewan et al., 2011). The pseudo-second-order kinetic model has also been found more suitable for modeling the adsorption of As(V) and As(III) onto the other modified chitosan-based adsorbents, such as chitosan/clay/magnetite composite and chitosan/nano-iron oxide films (Cho et al. 2012; Kloster et al. 2020).

Table 1 Kinetic parameters for As(V) adsorption on Fe(III)-chitosan and Fe(III)-chitosan-CTAB.

Adsorbents	Pseudo-first-order model			Pseudo-second-order model		
	k_1	q_e	R^2	k_2	q_e	R^2
	(min ⁻¹)	(mg g ⁻¹)		(g mg ⁻¹ min ⁻¹)	(mg g ⁻¹)	
Fe(III)-chitosan	0.487	12.593	0.980	0.065	13.114	0.998
Fe(III)-chitosan-CTAB	0.357	12.026	0.942	0.044	12.705	0.992

Adsorption isotherms

To examine the effect of initial concentration of As(V) on the adsorption capacity, adsorption isotherm experiments were conducted. The adsorption isotherm is very important to understand how the adsorbate interact with the adsorption sites of the adsorbent surface. The Freundlich and Langmuir isotherm models were applied to analyze the adsorption equilibrium data. The adsorption isotherms were shown in Fig. 5c and d, and the calculated adsorption parameters are summarized in Table 2. The experimental data were well fitted with the Freundlich isotherm model (correlation coefficient 0.963 for Fe(III)-chitosan and 0.987 for Fe(III)-chitosan-CTAB). The Freundlich isotherm model is valid for multilayer adsorption onto a heterogeneous surface (Jeyaseelan et al., 2018). Hence, the results demonstrated that the adsorption of As(V) onto Fe(III)-chitosan and Fe(III)-chitosan-CTAB occurred in multilayer possessing heterogeneous adsorption sites. The adsorption capacity for As(V) at equilibrium increased infinitely with increasing initial As(V) concentration, suggesting that the adsorption sites of adsorbents were not equivalent or independent (Nisticò et al., 2018). In addition, the values of n (Freundlich isotherms) were 5.891 for Fe(III)-chitosan and 4.956 for Fe(III)-chitosan-CTAB, respectively, indicating that the adsorption between As(V) and adsorbents was favorable ($1 < n < 10$). That's because the value of n above 1 is indicative of favorable chemisorption mechanism on heterogeneous surface (Foo and Hameed 2010). The larger n value also denoted the stronger interaction between As(V) and Fe(III)-chitosan. Accordingly,

the adsorption capacity of Fe(III)-chitosan for As(V) was a little more than that of Fe(III)-chitosan-CTAB.

Table 2 Isothermal parameters for As(V) adsorption on Fe(III)-chitosan and Fe(III)-chitosan-CTAB.

Adsorbents	Langmuir model			Freundlich model		
	q_L (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	n	R^2
Fe(III)-chitosan	25.076	5.896	0.761	14.606	5.891	0.963
Fe(III)-chitosan-CTAB	25.288	3.129	0.834	13.049	4.956	0.987

Effect of co-existing ions

Some anions and cations generally present in water could interfere in the removal efficiency of As(V) by competitive binding or complexation (Bhakat et al., 2006). So, the effects of co-existing anions (NO₃⁻, SO₄²⁻, and H₂PO₄⁻), cations (Mg²⁺ and Ca²⁺), and organic matter (HA) on the As(V) adsorption were investigated. As seen in Fig. 6, the presence of Mg²⁺, Ca²⁺, SO₄²⁻, and NO₃⁻ had no significant impact on the adsorption of As(V), whereas H₂PO₄⁻ significantly reduced As(V) removal. Decrease in As(V) adsorption onto Fe(III)-chitosan and Fe(III)-chitosan-CTAB in the presence of H₂PO₄⁻ may be explained as a result of competition for the adsorption sites between H₂PO₄⁻ and As(V). Another reason for this phenomenon could be that H₂PO₄⁻ has chemical characteristics (such as ion size, structure, and pK_a) very similar to those of As(V) (Sun et al., 2019). Phosphate also had a strong tendency to form complexes with Fe(III) at low pH (Gupta et al., 2009). However, the phosphate concentration in most natural water are low enough (20–50 µg L⁻¹) (Katsoyiannis and Zouboulis, 2002). The competitive adsorption of phosphate on Fe(III)-chitosan and Fe(III)-chitosan-CTAB would be limited. Natural organic matter (NOM) is ubiquitous in underground and surface water. HA is a major constituent of NOM found in water systems (Chaukura et al., 2018). In this study, HA had no observed inhibitory effect on the removal of As(V) by Fe(III)-chitosan, while the removal of As(V) by Fe(III)-chitosan-CTAB was declined from

98.2% to 85.6%. This decrease may be related to the amphiphilic nature of both CTAB and HA, which causes their mutual attraction especially when HA and surfactant are oppositely charged (Ishiguro et al., 2007).

Fig. 6 Effects of co-existing ions and HA on As(V) removal by Fe(III)-chitosan and Fe(III)-chitosan-CTAB.

Application to real water samples

To assess the effect of real water matrices, Fe(III)-chitosan-CTAB was used to real water naturally contaminated with As(V) and collected from the water pipe, lake, and river. The pH values of these samples ranged from 7.91 to 8.01, and the removal efficiencies of As(V) by Fe(III)-chitosan-CTAB were 80.0%, 95.5%, and 88.5%, respectively (see Table S2). Considering low concentration of As(V) in real water (2.85, 17.69, and 12.08 $\mu\text{g L}^{-1}$, respectively), three different water matrices were spiked with various concentrations of As(V) (0.1, 0.2, 0.5, 1.0, 5.0, and 10.0 mg L^{-1}). It was showed that the residual concentration of As(V) reduced to less than 0.01 mg L^{-1} (WHO permissible limit for drinking water) with more than 99.0% removal efficiency, when the initial As(V) concentration raised from 0.1 to 1.0 mg L^{-1} (Fig. 7). However, 97.8%, 93.5%, and 93.9% removal of As(V) were achieved at initial As(V) concentration of 5 mg L^{-1} for tap water, lake water, and river water, respectively. Just as the initial As(V) concentration rose from 5 to 10 mg L^{-1} , the As(V) removal efficiency declined to 90.7%, 76.8%, and

78.2%. It showed a more decrease tendency in lake water and river water, which may be caused by more complex matrix components (such as suspended solids and macromolecules). Generally, the concentrations of As in natural waters are often below 5 mg L⁻¹ (Mandal and Suzuki, 2002). Accordingly, Fe(III)-chitosan-CTAB could effectively be used to remove As(V) from natural waters.

Fig. 7 Removal efficiency (a) and residual concentration (b) of As(V) in spiked water samples by Fe(III)-chitosan-CTAB.

Reusability of the adsorbents

Reusability is a critical property of adsorbents due to the economic applicability. From the desorption studies it was found that the structure of both adsorbents got destroyed within few minutes in strong acid (HCl) aqueous solution. However, use of NaOH solution was found to be effective. Figure 8a shows the desorption efficiency of Fe(III)-chitosan and Fe(III)-chitosan-CTAB by various concentrations of NaOH solution (1, 2, 5, and 10% w/v). As shown in Fig. 8a, the desorption of As(V) from the two adsorbents reached 96.3% and 96.1%, respectively, when using 1% w/v NaOH solution. The adsorption-desorption cycle was repeated five times by using the same adsorbents. It can be seen from Fig. 8b that the adsorption capacity of Fe(III)-chitosan remained almost unchanged after five cycles. Fe(III)-chitosan-CTAB only decreased slightly from 7.16 mg g⁻¹ to 6.29 mg g⁻¹ with an increase in the reuse cycles. The slight

decrease in adsorption of As(V) on Fe(III)-chitosan-CTAB is possibly explained by the loss of active sites during the desorption process. Moreover, the surface structure of Fe(III)-chitosan-CTAB may be partially destroyed after stirring and washing. According to the obtained results, the two adsorbents had good reusability and chemical stability. It was indicated that both Fe(III)-chitosan and Fe(III)-chitosan-CTAB were of excellent potential for application in adsorptive removal of As(V) from water.

Fig. 8 Reusability of Fe(III)-chitosan and Fe(III)-chitosan-CTAB for As(V) adsorption. (a) Desorption efficiency of As(V) from adsorbents in NaOH solution with different concentrations. (b) Adsorption capacities of the regenerated adsorbents in five consecutive cycles.

Possible mechanism of As(V) adsorption on adsorbents

The adsorption mechanism of As(V) onto Fe(III)-chitosan and Fe(III)-chitosan-CTAB can be supposed to both electrostatic attraction, as well as complexation (Fig. 9). From the FT-IR spectra data, it was observed that three new peaks appeared at 890, 792, and 600 cm⁻¹ after the adsorption of As(V) (Fig. 2). The peak at 792 cm⁻¹ is attributed to Fe–O–As bending vibration (Adio et al., 2017). The peaks at 890 and 600 cm⁻¹ are assigned to the asymmetrical stretching of the As–O bond in the H₂AsO₄⁻ group (Kloster et al., 2020; Kumar and Jiang, 2016). These results revealed the possible mechanism of the complexation of As(V) with Fe–OH of Fe(III)-chitosan and Fe(III)-chitosan-CTAB via the formation of monodentate

and bidentate inner-sphere complexes (Li et al., 2010). In addition, the decreases of the relative intensities of the peaks at 3450, 3280, 1058, and 1027 cm^{-1} after As(V) adsorption are mainly associated with the interaction of As(V) with $-\text{NH}_2$ and $-\text{OH}$ of the adsorbents. The nitrogen and oxygen atoms of $-\text{NH}_2$ and $-\text{OH}$ could provide lone pair of electrons for bonding with As(V), which suggests that the adsorption mechanism of Fe(III)-chitosan and Fe(III)-chitosan-CTAB for As(V) in water includes electrostatic attraction.

XPS analyses were applied to further explore the adsorption mechanism of Fe(III)-chitosan and Fe(III)-chitosan-CTAB for As(V). As seen from Fig. 3c and d, the typical new peaks of As 3p_{5/2} appeared at 44.79 and 44.64 eV. These results indicated the presence of As(V) on the surface of Fe(III)-chitosan and Fe(III)-chitosan-CTAB after adsorption, which are similar to previous studies like Du et al., 2019. For the C 1s spectra, the peak area ratio at 286.5 eV (C–OH) decreased from 26.5% to 23.6% for Fe(III)-chitosan and from 17.11% to 13.93% for Fe(III)-chitosan-CTAB. These decreases may be due to the substitution of H_2AsO_4^- for part of hydroxyl groups during adsorption (Sun et al., 2019). For the N 1s spectra, the intensity of the peak at 398.6 eV decreased, which may be related to $-\text{NH}_2 \dots \text{Fe}$ located in the inner sphere of the complex. A new peak appeared at a higher binding energy of 401.0 eV showing the formation of protonated amino group ($-\text{NH}_3^+$) on Fe(III)-chitosan after As(V) adsorption. (Rufato et al., 2021). Theoretically, the $-\text{NH}_2$ group on Fe(III)-chitosan is easily protonated to form positively charged $-\text{NH}_3^+$ group. H_2AsO_4^- , a negatively charged ion, could be attracted to the $-\text{NH}_3^+$ group, leading to the enrichment of H_2AsO_4^- on the surface of Fe(III)-chitosan. With regard to Fe(III)-chitosan-CTAB, the peak intensity at 401.8 eV decreased, suggesting that the positively charged $-\text{NH}_3^+$ and $-\text{N}^+(\text{CH}_3)_3$ groups attracted the H_2AsO_4^- ions after As(V) adsorption (Rufato et al., 2021; Shen et al., 2013). The binding energy of Fe 2p was slightly shifted by 0.1–0.4 eV after As(V) adsorption. As previously noted,

it can be inferred that the functional groups of Fe–OH, C–OH, $-\text{NH}_3^+$, and $-\text{N}^+(\text{CH}_3)_3$ were the main active sites engaged in the As(V) adsorption.

Fig. 9 Proposed adsorption mechanism of As(V) by Fe(III)-chitosan and Fe(III)-chitosan-CTAB.

Conclusions

Fe(III)-chitosan and Fe(III)-chitosan-CTAB were successfully synthesized via a ionotropic gelation method for efficient As(V) removal from water. The two adsorbents exhibited irregular shapes and rough surfaces with a diameter of 10–150 μm . The best removal efficiency of As(V) was observed at pH=3 for Fe(III)-chitosan, while high removal efficiency was achieved in a wide pH range (3–8) for Fe(III)-chitosan-CTAB. The kinetics data described well with pseudo-second-order kinetic model, and their adsorption behavior can be considered as chemisorption. Equilibrium adsorption values were satisfied with the Freundlich isotherm model, and supported the occurrence of multilayer adsorption process. The presence of co-existing ions, with the exception H_2PO_4^- , had no negative effect on As (V) removal efficiency by the two adsorbents. They had stable adsorption capability after five cycles and when utilized in real water matrixes. Complexation and electrostatic attraction were the dominant mechanisms

involved in the adsorption of As(V) on Fe(III)-chitosan and Fe(III)-chitosan-CTAB. In summary, both Fe(III)-chitosan and Fe(III)-chitosan-CTAB provide an efficient method for removing As(V) from water and they have the potential for practical application.

Supplementary Information The online version contains supplementary material available at .

Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Changjin Jiang. The first draft of the manuscript was written by Changjin Jiang. The first draft of the manuscript was revised by Ting Zhang. All authors read and approved the final manuscript.

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Declarations

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References

Adio SO, Omar MH, Asif M, Saleh TA (2017) Arsenic and selenium removal from water using

- 438 biosynthesized nanoscale zero-valent iron: A factorial design analysis. *Process Safety and*
439 *Environmental Protection* 107: 518–527
- 440 Alves NM, Mano JF (2008) Chitosan derivatives obtained by chemical modifications for biomedical and
441 environmental applications. *International Journal of Biological Macromolecules* 43(5): 401–414
- 442 Bakshi PS, Selvakumar D, Kadirvelu K, Kumar NS (2020) Chitosan as an environment friendly
443 biomaterial—A review on recent modifications and applications. *International Journal of Biological*
444 *Macromolecules* 150: 1072–1083
- 445 Bhakat PB, Gupta AK, Ayoob S, Kundu S (2006) Investigations on arsenic(V) removal by modified
446 calcined bauxite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 281(1–3):
447 237–245
- 448 Chatterjee S, Lee MW, Woo SH (2009) Influence of impregnation of chitosan beads with cetyl trimethyl
449 ammonium bromide on their structure and adsorption of congo red from aqueous solutions.
450 *Chemical Engineering Journal* 155(1–2): 254–259
- 451 Chaukura N, Moyo W, Mamba BB, Nkambule TI (2018.) Abatement of humic acid from aqueous
452 solution using a carbonaceous conjugated microporous polymer derived from waste polystyrene.
453 *Environmental Science and Pollution Research* 25(4): 3291–3300
- 454 Cho DW, Jeon BH, Chon CM, Kim Y, Schwartz FW, Lee ES, Song H (2012) A novel
455 chitosan/clay/magnetite composite for adsorption of Cu(II) and As(V). *Chemical Engineering*
456 *Journal* 200: 654–662
- 457 Clancy TM, Hayes KF, Raskin L (2013) Arsenic waste management: A critical review of testing and
458 disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water.
459 *Environmental Science and Technology* 47(19): 10799–10812

- 460 Dadwal A, Mishra V (2017) Review on biosorption of arsenic from contaminated water. *CLEAN-Soil*
461 *Air Water* 45(7): 1600364
- 462 Demarchi CA, Debrassi A, Dal Magro J, Nedelko N, Ślawska-Waniewska A, Dłużewski P, Greneche J,
463 Rodrigues CA (2015) Adsorption of Cr(VI) on crosslinked chitosan-Fe(III) complex in fixed-bed
464 systems. *Journal of Water Process Engineering* 7: 141–152
- 465 Du M, Zhang Y, Hussain I, Du X, Huang S, Wen W (2019) Effect of pyrite on enhancement of zero-
466 valent iron corrosion for arsenic removal in water: A mechanistic study. *Chemosphere* 233: 744–
467 753
- 468 Escudero C, Fiol N, Villaescusa I, Bollinger JC (2009) Arsenic removal by a waste metal (hydr)oxide
469 entrapped into calcium alginate beads. *Journal of Hazardous Materials* 164(2–3): 533–541
- 470 Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chemical*
471 *Engineering Journal* 156(1): 2–10
- 472 Gadd GM (2009) Biosorption: critical review of scientific rationale, environmental importance and
473 significance for pollution treatment. *Journal of Chemical Technology and Biotechnology* 84(1): 13–
474 28
- 475 Gupta A, Chauhan VS, Sankararamakrishnan N (2009) Preparation and evaluation of iron-chitosan
476 composites for removal of As(III) and As(V) from arsenic contaminated real life groundwater. *Water*
477 *Research* 43(15): 3862–3870
- 478 Gupta G, Khan J, Singh NK (2021) Application and efficacy of low-cost adsorbents for metal removal
479 from contaminated water: A review. *Materials Today: Proceedings* 43(5): 2958–2964
- 480 Harutyunyan LR, Harutyunyan RS, Gabrielyan GA, Lasareva EV (2019) Modification of chitosan and
481 chitosan succinate by surfactants and investigation of their properties. *Colloids and Surfaces A:*

- 482 Physicochemical and Engineering Aspects 578: 123622
- 483 Ishiguro M, Tan W, Koopal LK (2007) Binding of cationic surfactants to humic substances. *Colloids and*
- 484 *Surfaces A: Physicochemical and Engineering Aspects* 306(1–3): 29–39
- 485 Jeyaseelan C, Chaudhary N, Jugade R (2018) Sulphate-crosslinked chitosan as an adsorbent for the
- 486 removal of congo red dye from aqueous solution. *Air, Soil and Water Research* 11: 1–8
- 487 Jiang Z, Li N, Li P, Liu B, Lai H, Jin T (2021) One-step preparation of chitosan-based magnetic adsorbent
- 488 and its application to the adsorption of inorganic arsenic in water. *Molecules* 26(6): 1785
- 489 Katsoyiannis IA, Zouboulis AI (2002) Removal of arsenic from contaminated water sources by sorption
- 490 onto iron-oxide-coated polymeric materials. *Water Research* 36(20): 5141–5155
- 491 Kloster GA, Valiente M, Marcovich NE, Mosiewicki MA (2020) Adsorption of arsenic onto films based
- 492 on chitosan and chitosan/nano-iron oxide. *International Journal of Biological Macromolecules*
- 493 165(Pt A): 1286–1295
- 494 Kumar ASK, Jiang SJ (2016) Chitosan-functionalized graphene oxide: A novel adsorbent an efficient
- 495 adsorption of arsenic from aqueous solution. *Journal of Environment Chemical Engineering* 4(2):
- 496 1698–1713
- 497 Li Z, Deng S, Yu G, Huang J, Lim VC (2010) As(V) and As(III) removal from water by a Ce-Ti oxide
- 498 adsorbent: Behavior and mechanism. *Chemical Engineering Journal* 161(1–2): 106–113
- 499 Liu B, Wang D, Yu G, Meng X (2013) Adsorption of heavy metal ions, dyes and proteins by chitosan
- 500 composites and derivatives—A review. *Journal of Ocean University of China* 12(3): 500–508
- 501 Lobo C, Castellari J, Colman Lerner J, Bertola N, Zaritzky N (2020) Functional iron chitosan
- 502 microspheres synthesized by ionotropic gelation for the removal of arsenic (V) from water.
- 503 *International Journal of Biological Macromolecules* 164: 1575–1583

- 504 Mandal BK, Suzuki KT (2002) Arsenic round the world: A review. *Talanta* 58(1): 201–235
- 505 Matet M, Heuzey MC, Pollet E, Ajji A, Averous L (2013) Innovative thermoplastic chitosan obtained by
506 thermo-mechanical mixing with polyol plasticizers. *Carbohydrate Polymers* 95(1): 241–251
- 507 Medeiros Borsagli FGL, Mansur AAP, Chagas P, Oliveira LCA, Mansur HS (2015) O-carboxymethyl
508 functionalization of chitosan: Complexation and adsorption of Cd (II) and Cr (VI) as heavy metal
509 pollutant ions. *Reactive and Functional Polymers* 97: 37–47
- 510 Nisticò R, Celi LR, Bianco Prevot A, Carlos L, Magnacca G, Zanzo E, Martin M (2018) Sustainable
511 magnet-responsive nanomaterials for the removal of arsenic from contaminated water. *Journal of*
512 *Hazardous Materials* 342: 260–269
- 513 Pillewan P, Mukherjee S, Roychowdhury T, Das S, Bansiwala A, Rayalu S (2011) Removal of As(III) and
514 As(V) from water by copper oxide incorporated mesoporous alumina. *Journal of Hazardous*
515 *Materials* 186(1): 367–375
- 516 Rufato KB, Souza PR, de Oliveira AC, Berton SBR, Sabino RM, Muniz EC, Popat KC, Radovanovic E.,
517 Kipper MJ, Martins AF (2021) Antimicrobial and cytocompatible chitosan, N,N,N-trimethyl
518 chitosan, and tanfloc-based polyelectrolyte multilayers on gellan gum films. *International Journal*
519 *of Biological Macromolecules* 183: 727–742
- 520 Saheed IO, Oh WD, Suah FBM (2021) Chitosan modifications for adsorption of pollutions—A review.
521 *Journal of Hazardous Materials* 408: 124889
- 522 Seyed Dorraji MS, Mirmohseni A, Tasselli F, Criscuoli A, Carraro M, Gross S, Figoli A (2014)
523 Preparation, characterization and application of iron(III)-loaded chitosan hollow fiber membranes
524 as a new bio-based As (V) sorbent. *Journal of Polymer Research* 21(4): 399
- 525 Shaji E, Santosh M, Sarath KV, Prakash P, Deepchand V, Divya BV (2021) Arsenic contamination of

- 526 groundwater: A global synopsis with focus on the Indian Peninsula. *Geoscience Frontiers* 12(3):
527 101079
- 528 Shen C, Chen H, Wu S, Wen Y, Li L, Jiang Z, Li M, Liu W (2013) Highly efficient detoxification of
529 Cr(VI) by chitosan-Fe(III) complex: process and mechanism studies. *Journal of Hazardous*
530 *Materials* 244–245: 689–697
- 531 Shinde RN, Pandey AK, Acharya R, Guin R, Das SK, Rajurkar NS, Pujari PK (2013) Chitosan-transition
532 metal ions complexes for selective arsenic(V) preconcentration. *Water Research* 47(10): 3497–3506
- 533 Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in
534 natural waters. *Applied Geochemistry* 17(5): 517–568
- 535 Sun J, Zhang X, Zhang A, Liao C (2019) Preparation of Fe-Co based MOF-74 and its effective adsorption
536 of arsenic from aqueous solution. *Journal of Environmental Science-China* 80: 197–207
- 537 Wang F, Liu D, Zheng P, Ma X (2016a) Synthesis of rectorite/Fe₃O₄-CTAB composite for the removal
538 of nitrate and phosphate from water. *Journal of Industrial and Engineering Chemistry* 41: 165–174
- 539 Wang X, Liu Y, Zheng J (2016b) Removal of As(III) and As(V) from water by chitosan and chitosan
540 derivatives: a review. *Environmental Science and Pollution Research* 23(14): 13789–13801
- 541 Yamashita T, Hayes P (2008) Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials. *Applied*
542 *Surface Science* 254(8): 2441–2449
- 543 Yu X, Zhang J, Zheng Y (2021) Perchlorate adsorption onto epichlorohydrin crosslinked chitosan
544 hydrogel beads. *Science of the Total Environment* 761: 143236
- 545 Zhao X, Shi Y, Cai Y, Mou S (2008) Cetyltrimethylammonium Bromide-coated magnetic nanoparticles
546 for the preconcentration of phenolic compounds from environmental water samples. *Environmental*
547 *Science and Technology* 42(4): 1201–1206

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