Enhanced removal of As(III) and As(V) from water by a novel zirconium-chitosan modified spherical sodium alginate composite

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Abstract

Most nano-scaled adsorbents have trouble in separating from aqueous solution, thus, a need for new materials of facile separation and predominant adsorption performance has arisen. This present study focused on a novel segregative zirconium-chitosan modified sodium alginate (Zr-CTS/SA) composite preparation and its performance for As(III/V) removal from aqueous solution. The obtained composite presented a spherical structure with a diameter of 2.0-3.0 mm and favorable thermal stability. Experimental data showed that Zr-CTS/SA had considerable adsorbability for As(III) and As(V), the adsorption capacities were enhanced about at least 20 and 6 times separately compared with pristine SA beads. The adsorption processes of As(III) and As(V) could both be described with Langmuir isotherm model and the maximum adsorption capacities reached 43.19 and 76.78 mg g-1, respectively. The kinetic data of As(III) followed the intra-particle diffusion model while As(V) fitted the pseudo-first-order model. Moreover, the adsorption mechanisms of As(III/V) involved ligand exchange with Cl on the surface of Zr-CTS/SA, another reaction pathway for As(V) was the electrostatic attraction with protonated -OH and -NH2 groups. Note that the employment of Zr-CTS/SA in low-concentration arsenic solution exhibited a residue concentration as low as the 10 μg L-1 WHO guideline for drinking water.

Keywords

sodium alginate; zirconium-chitosan composite; arsenic adsorption

1. Introduction

Arsenic contamination is of acute concern to human health ubiquitously due to its toxicity and carcinogenicity. Long-term intake of arsenic contaminated water causes cancers in the skin, lungs and bladder as well as hyperpigmentation and hyperkeratosis[1,2]. Arsenic in natural water primarily exists as oxyanion compounds of inorganic species i.e. arsenite (As(III) as H3AsO3, H2AsO3-, HAsO32-, and AsO33-) and arsenate (As(V) as H3AsO4, H2AsO4-, HAsO42-, and AsO43-)[3]. As is reported, compounds of As(III) are about 60 times more toxic than oxidized As(V) state[4,5]. In view of the fatal impact of arsenic, the World Health Organization (WHO) classified arsenic as a primary carcinogen and specified 10 μg L-1 as the maximum arsenic contamination limit in drinking water[6,7]. With a view to mitigating the effects of arsenic pollution in water, diverse techniques have been explored to eliminate arsenic such as precipitation, chemical oxidation, adsorption, membrane filtration, ion exchange, and biological remediation, etc.[8-13]. Among these, the adsorption method has become widely used and is deemed to be one of the most promising techniques for arsenic removal because of its relatively high removing efficiency, convenient operation, low cost, and no sludge[11]. Researchers have studied various categories of adsorbents in several areas, including inorganic minerals[14-16], carbon-based materials[17], metal oxides[18,19] and biosorbents[20], etc. However, these adsorbents generally have the disadvantage of either tiny adsorption capacity or low efficiency, hence the demand for further improvements.

To fulfil the objective of high efficiency and large capacity of arsenic sequestration, nano-scaled adsorbents have recently become high on the list of research topics. Due to their high specific surface area, reactivity and specificity[21], some nanomaterials have shown outstanding performance in arsenic adsorption applications. Gupta and Ghosh[22] synthesized a hydrous nanostructured iron(III)-titanium(IV) binary oxide as a novel adsorbent for arsenic removal from aqueous solution, the Langmuir capacity values of the material for As(III) and As(V) were 85.0 and 14.0 mg g-1, respectively. A core-shell structured zero-valent manganese (ZVM) was synthesized for sequestration of total arsenic from drinking water[23]. Both As(III) and As(V) could be removed within a wide pH range where the maximum adsorption capacities were found to be 30.9 and 72.5 mg g-1. Despite their impressive performance in adsorption, nano-scaled materials have a common shortcoming that is difficult to separate from the aqueous phase. Additionally, nanoparticles are prone to agglomeration in some cases, which greatly lowers the adsorption performance and reusability of the material.

In order to overcome this weakness, designing the materials to be magnetic and separated by an external magnetic field is usually adopted. Tang et al.[24] synthesized ultrafine superparamagnetic magnesium ferrite nanocrystallites by doping Mg2+ into α-Fe2O3 via a solvothermal method, the adsorption capacities of As(III) and As(V) reached respectively 9.3 and 10 mg g-1. Nonetheless, the route for preparing magnetic nanomaterials are relatively complicated, and additional energy is required in large-scale applications, resulting in higher costs. Another approach to handle the separation trouble is loading the materials on certain segregative substrates. For example, chitosan films[25], molecular sieves[26], resins[27], and alginate[28] have all been employed to support immobilization of nanoadsorbents.

The aforementioned alginate, a naturally occurring anionic polymer, is widely studied and applied as a noteworthy substrate in the field of adsorption materials due to its mild gelation under the action of divalent cations such as Ca2+ [29]. From another perspective, zirconium-based adsorbents present a higher affinity towards arsenic species, which are widely employed in arsenic removal from aqueous solutions. Aside from amorphous zirconium oxide (am-ZrO2) nanoparticles synthesized by Cui et al.[30], a Zr2(OH)6SO4·3H2O nano-adsorbent was synthesized and exhibited remarkable adsorption capacity for As(V) at the optimal pH[31], yet they still had the problem of separation after utilization. There have also been researches that combined zirconium with alginate, such as hydrous zirconium oxide-immobilized alginate beads (ZOAB) synthesized by Kwon et al.[32], but the performance was hardly prominent. Besides, chitosan has superior performance and prospects in adsorption applications, as well as a tendency to complex with metal ions thus forms new adsorbents. Quite a few literatures have focused on Zr cross-linked chitosan to unite their strengths for employment in methyl orange[33], fluoride[34], nitrate and phosphate[35] removal, gaining satisfying results. Inspired by the above reports, alginate as the substrate to combine with the superiorities of zirconium and chitosan, forming a novel adsorbent for pollutant removal is worthy of further research.

Therefore, this paper focuses on the development of zirconium-chitosan modified spherical sodium alginate (Zr-CTS/SA) composite to prepare a novel adsorbent for arsenic removal with the goal of overcoming the weaknesses of low adsorption capacity and inconvenient separation. The preparation contained the synthesis of Zr-CTS powders and the gelation of Zr-CTS/SA sol. Appearance and structural components of the obtained composite were characterized by SEM, EDS, FT-IR, TGA and XPS methods. The isothermal model, kinetic model, thermodynamic parameters and the possible mechanisms were further discussed by studying the adsorption performance under different conditions such as pH, initial arsenic concentration, adsorption time, temperature and co-existing ions.

1. Materials and methods
   1. Materials

Chitosan (CTS, 110 KDa molecular weight, ≥ 96% degree of deacetylation) and zirconium oxychloride octahydrate (ZrOCl2·8H2O, analytical reagent) were purchased from Shanghai D&B Biotechnology Co., Ltd; Sodium alginate (SA, chemical pure, 200±20 mPa·s of viscosity) and glutaraldehyde (25%) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. Other chemical reagents were of at least analytical grade and the water used in this work was purified to a resistivity of 18.2 MΩ cm-1.

* 1. Preparation of Zr-CTS powders

3.0 g of water-soluble chitosan (CTS) powders were added to 150 mL of 1.0% acetic acid, continuously stirred for 1 h to form a homogenous sol. Then 4.83 g (0.015 mol) of ZrOCl2·8H2O was slowly added into the obtained chitosan sol, continued stirring for 30 min to fully dissolved. 2.0 mol L-1 sodium hydroxide solution was slowly dripped into the sol to adjust pH, when the pH value reached around 6 and no obvious precipitation generated, 10 mL of 5.0% glutaraldehyde aqueous solution was added to cross-link zirconium metal ions to chitosan under this condition. Stirred intensely until the solution became sticky and once again adjusted pH to more than 11 to get complete precipitation using 2.0 mol L-1 sodium hydroxide. The obtained Zr-CTS suspension was sealed and placed in a refrigerator at 4 °C for further cross-linking for 24 h. The precipitation was washed for several times using ultrapure water until the pH reached neutral and was dried in an infrared drying oven afterwards. 10 g of brown Zr-CTS powders were prepared to use.

* 1. Preparation of Zr-CTS/SA composite

2.0 g of sodium alginate (SA) powders were slowly added to 100 mL of water under the heating and stirring condition, covered with a perforated film to prevent excessive water loss. After 1 h of continuous stirring, they were fully dissolved to form a viscous solution. 6.0 g of the Zr-CTS powders obtained in Sec. **2.2** were added to sodium alginate solution slowly and were stirred to disperse equably and generate a Zr-CTS/SA sol.

The above Zr-CTS/SA sol was added into 300 mL of 2% ZrOCl2 solution dropwise through a constant-current pump to transform the droplets into water-insoluble composite gel beads, which were washed with ultrapure water several times to remove the residual salt subsequently. Finally, the spherical Zr-CTS/SA composite material was obtained by freeze-drying.

In addition, a batch of SA beads was also prepared as a comparison by dropping 2% SA sol into 2% CaCl2 solution.

* 1. Adsorption experiments
     1. Adsorption properties at different pH values

100.0 mg per sample of Zr-CTS/SA composite was added into 50 mL of 50.0 mg L-1 As(III) or As(V) solution, where the pH values were adjusted to 2-11 respectively using 1.0 mol L-1 HNO3 or 2.0 mol L-1 NaOH. The above-mentioned solutions were shaken frequently and the residual arsenic contents were measured by inductively coupled plasma optical emission spectrometer (ICP-OES 710-ES, Varian, USA) to determine the optimum adsorbing pH conditions of As(III) and As(V).

In order to study the adsorption effect of SA beads on As(III) and As(V) at different pH and compare them with Zr-CTS/SA, the same experiment was carried out in accordance with the above steps.

* + 1. Adsorption isotherms

100.0 mg per sample of Zr-CTS/SA composite was added into 100 mL of As(III) and As(V) solutions with initial arsenic concentrations of 1.0-300.0 mg L-1. After being adsorbed at their respectively optimal pH conditions for a certain time, the residual As(III) and As(V) concentrations were measured by ICP-OES. Langmuir, Freundlich and Temkin models were used to fit the two sets (As(III) and As(V)) of experimental data[36].

* + 1. Adsorption kinetics

100 mL of two different concentrations (1.0 mg L-1 and 20.0 mg L-1) of As(III) and As(V) solutions were prepared, the pH of which were adjusted to the two arsenic species’ respectively optimal values. The residual arsenic concentration of each solution was detected within the range of 0-144 h after 100.0 mg of Zr-CTS/SA was put in. The pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle diffusion model were used to fit the obtained four sets of data[37,38].

* + 1. Effects of temperature

100.0 mg of Zr-CTS/SA was added into 100 mL of 10.0 mg L-1 As (III) and As (V) solutions at optimal pH values. The adsorption was carried out at 277, 296 and 313 K, respectively. After being adsorbed for a certain time, the residual As(III) and As(V) concentrations were measured by ICP-OES. The obtained data were fitted by Van't Hoff equation to calculate the thermodynamic parameters.

* + 1. Effects of co-existing ions

The effects of co-existing ions to arsenic adsorption on the composite was studied in 100 mL of 50.0 mg L-1 As(III) and As(V) solutions with the presence of 100.0 mg of Zr-CTS/SA and two different dosages (50.0 mg L-1 and 100.0 mg L-1) of NaNO3, Na2SO4, NaCl, KCl and CaCl2. After being adsorbed for a certain time, the final arsenic concentrations were determined by ICP-OES.

* + 1. Adsorption at low arsenic concentration

100 mL of low concentration (100.0 μg L-1) of As(III) and As(V) solutions were prepared, the pH of which were adjusted to optimal values. The residual arsenic concentration of each solution was detected by inductively coupled plasma-mass spectrometer (ICP-MS, NexION 2000-(A-10), PerkinElmer, USA) within the range of 0-72 h after 100.0 mg of Zr-CTS/SA was put in.

* 1. Characterization of Zr-CTS/SA composite

The Fourier transform infrared (FT-IR) spectra of Zr-CTS/SA before and after arsenic (As(III) and As(V)) adsorption were recorded by Nicolet 6700 (Thermo Electron, Waltham, MA, USA) from 400-4000 cm-1 wavenumbers at the resolution of 4 cm-1. The surface structure of Zr-CTS/SA was examined by scanning electron microscope (SEM, JSM-6360LV, JEOL, Tokyo, Japan). The elements existed in Zr-CTS/SA were quantified by energy dispersive spectrometer (EDS, Falcon energy dispersive X-ray analyzer, JEOL, Tokyo, Japan). The thermal properties of Zr-CTS/SA were detected by thermogravimetric analysis (TGA, TGA 8000, PerkinElmer, USA) with the range of 50-800 °C at 10 °C min-1 heating rate in N2 atmosphere and the elemental species on the surface of Zr-CTS/SA were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, Waltham, MA, USA).

* 1. Reusability studies

The reusability studies of Zr-CTS/SA after batch adsorption experiments were conducted by being eluted with 0.5 mol L-1 NaCl solution. The composite was then collected and washed by ultrapure water for using in the next adsorption-desorption cycle, which was repeated for 3 times.

1. Results and discussion
   1. Characterization
      1. SEM analysis

Fig. 1(a-i) are respectively SEM images of initial Zr-CTS/SA composite, As(III)-saturated and As(V)-saturated Zr-CTS/SA at different magnification. It can be seen from Fig. 1(a, d, g) that the diameter of single Zr-CTS/SA particle was about 2.0-3.0 mm, while the actual particle size after adsorption experiment was slightly reduced because the adsorbents were obtained by re-drying. It also presented in the image magnified 1000 times (Fig. 1(b, e, h)) that the material had a rough surface, which provided good physical conditions for adsorption process.

Fig. 1(c) showed that Zr-CTS/SA sphere presented a sunken and low-lying structure in local area, which also provided good binding sites for adsorption. After the adsorption experiments (Fig. 1(f, i)), the surface of the material became smoother. On the one hand, this phenomenon might be induced by the adsorbates from aqueous solution occupying the material surface as well as filling in the dents; on the other hand, it was also related to the secondary drying after adsorption.

* + 1. EDS analysis

EDS was used to obtain the element composition and content of the Zr-CTS/SA composite before and after adsorption. Fig. 2(a) refers to the Zr-CTS/SA composite before adsorption. The main elements contained were C, O, Zr and Cl. The approximate relative content of the corresponding elements could be obtained by integrating the area of each peak. For example, the relative weight percentage of C, which was from the framework of chitosan, sodium alginate and glutaraldehyde, was 29.03%. Cl that rooted in ZrOCl2 took up 5.15%. Since chitosan, sodium alginate, glutaraldehyde, ZrOCl2 and the crystal water carried by the material all contained O, its weight percentage accounted for 36.21%, more than one third of the total weight. Most momentously, the relative content of Zr reached 29.62%, which was a solid evidence to prove that Zr4+ was indeed cross-linked to the material.

After adsorbing As(III) and As(V), there were clear As peaks that did not exist before. The relative mass percentages were 2.79% (Fig. 2(b)) and 8.65% (Fig. 2(c)), respectively. This result pointed out that the adsorption capacity of Zr-CTS/SA composite for As(V) was preferred over As(III). Compared with Fig. 2(a), another evident difference was that there were almost no Cl peaks in Fig. 2(b) and Fig. 2(c), with the relative content of 0.89% (Fig. 2(b)) and 0.42% (Fig. 2(c)), respectively Fig. 3. This could be the outcome of As adsorbed on the material replacing the site where Cl was on, combing with Zr.

* + 1. FT-IR analysis

Fig. 3 shows the FT-IR spectrograms of (a) Zr-CTS/SA, (b) As(III) adsorbed Zr-CTS/SA and (c) As(V) adsorbed Zr-CTS/SA, the latter two both went through adsorption process to ensure the saturated adsorption of arsenic.

In spectrum (a), the peak at 3407.7 cm-1 represented O-H stretching vibration of the crystal water contained in Zr-CTS/SA materials, and N-H stretching vibration of -NH2 on the surface of the material[39,40]. The peak centered at 2925.5 cm-1 was C-H stretching vibration of chitosan and alginate structure[41,42]. As for 1614.2 cm-1, the peak here might be the result of N-H bending vibration of -NH2 or C=O stretching vibration of alginate and crosslinking agent glutaraldehyde. The two peaks (1149.4 and 1078.0 cm-1) could be assigned to the bending vibration of hydroxyl groups of metal oxides (Zr-OH)[43]. The absorption peak caused by Zr-N asymmetric stretching vibration was located at 632.5 cm-1[44]. The peak at 489.8 cm-1 was identified as the bending vibration of Zr-O[45].

In spectrum (b) and (c), O-H and N-H stretching vibration appeared at 3427.3 and 3423.4 cm-1, respectively, with a distinctive peak shift compared to the spectrogram before adsorption (spectrum (a)). This fact indicated the involvement of these functional groups in the adsorption of As(III) and As(V). Simultaneously, N-H bending vibration was shifted to 1623.4 cm-1 (spectrum (b)) and 1623.1 cm-1 (spectrum (c)) from the original location at 1614.2 cm-1, further illustrating -NH2 was the functional group participating in As(III/V) adsorption. In addition, a new peak arose at 403.1 cm-1 in spectrum (b) while a large amount of tiny peaks appeared at the fingerprint region (400-500 cm-1) in spectrum (c). This might be due to the generation of complexes of arsenic ions with Zr-O functional groups according to the study by Zheng et al.[46], providing additional evidence for As(III) and As(V) being adsorbed by Zr-CTS/SA.

* + 1. TGA analysis

The thermal stability of Zr-CTS/SA composite was evaluated by TGA. presents the TG and DTG curves of Zr-CTS/SA. As shown in the figure, the thermal weight loss process of Zr-CTS/SA could be roughly divided into three stages, including loss of bound water, degradation of the composite, and decomposition of residues. When the temperature was lower than 219.97 °C, the weight loss rate was 11.93%. The second stage, which was the main stage of thermal decomposition, occurred at 219.97-531.96 °C, and the weight loss rate was up to 46.77%, involving the decomposition of chitosan, alginate and other organic components. When the temperature was higher than 531.96 °C, it reached the third stage, and the weight showed a steady as well as slow decline trend. The DTG curve in the third stage shows an approximately horizontal tendency, and the maximum weight loss rate reached 51.73%. There were two points of rapid loss, respectively at 228.78 °C and 281.14 °C, the material presented good thermal stability overall.

* 1. Experimental data processing

After various adsorption experiments, the concentration of arsenic solution after being adsorbed by Zr-CT/SA composite was measured, and the adsorption capacity q of Zr-CTS/SA was obtained according to the following formula:

or (1)

where qe and qt (mg g-1) are respectively the adsorption capacity of Zr-CTS/SA for As(III/V) at equilibrium and at t time; c0 ,ct and ce (mg L-1) represent for arsenic concentration at initial status, at t time and when adsorption equilibrium is reached, respectively. V (L) is the volume of arsenic solution and m (mg) is the mass of adsorbent added in the solution.

* + 1. Effects of pH

Considering that the ionic properties and structures of adsorbates and adsorbents will change with different pH values, thus the pH of solution is one of the significant parameters affecting the adsorption properties of Zr-CTS/SA composite. The effects of pH on Zr-CTS/SA adsorbing As(III) and As(V) are as shown in Fig. 5(a) (the upper two polylines). For As(III), the experimental results showed that the influence of pH on the adsorption was not that prominent, its adsorption capacity fluctuated between 20-30 mg g-1 without an obvious optimal pH value within the selected pH range of 2-11. While for As(V), pH took an important part in the adsorption. It was noticeable that the adsorption capacity in acidic condition was much larger than that in alkaline or neutral condition. The optimum adsorbing pH of Zr-CTS/SA to As(V) was identified to be around 2-3 with the adsorption capacity up to 39.79 mg g-1. When the pH value exceeded 5, adsorption capacity began to decrease significantly. This may be because As(III) is electrically neutral in the form of H3AsO3 within a wide range of pH from 0 to 10, thus is less affected by pH; however, As(V) usually tends to be negatively charged as H2AsO4- or HAsO42- within pH 2-11[47]. With the decrease of pH, the protonation degree of surface function groups increased and the electrostatic attraction to As(V) enhanced, so that its adsorption capacity for As(V) was improved. Considering excessive low pH may cause dissolution of Zr ion in Zr-CTS/SA and reduction of its adsorption ability, all subsequent adsorption experiments of As(V) were carried out in the condition of pH 3; as for As(III), there was no additional need to adjust pH value.

As the lower two polylines present, under acidic conditions, SA beads had a tiny adsorption effect on As(III) and As(V), with the adsorption capacity of only about 5 mg g-1. Comparing the adsorption capacities of the two materials, it was notable that the performance of Zr-CTS/SA was specifically better (at least 20 times for As(III) and 6 times for As(V)) than that of pristine SA beads, which was attributed to the introduction of Zr and CTS.

Besides, a simulation experiment was conducted to study the leaching of zirconium ions. As shown in Fig. 5(b), the highest Zr leaching (which happened at pH 2) of Zr-CTS/SA after adsorption in As(III/V) solutions did not exceed 0.040 mg g-1, which is very low. Therefore, Zr-CTS/SA showed a satisfying stability against the leaching of zirconium ions.

* + 1. Adsorption isotherms

This experiment studied the As(III) and As(V) solutions within the initial concentration range of 1.0-300.0 mg L-1, and adopted Langmuir, Freundlich and Temkin adsorption isotherm models to interpret the qe-ce experimental data.

1. Langmuir isotherm model can be represented by the following equation[48]:

(2)

where k1 is the desorption rate constant; k2 (L mg-1) is the adsorption rate constant; qe and qm (mg g-1) are respectively equilibrium adsorption capacity and maximum adsorption capacity; ce (mg L-1) is the equilibrium concentration of arsenic in solution; kL (L mg-1) is the Langmuir constant calculated by the ratio of k2 and k1. The value of qm and kL could be calculated by nonlinear fitting on the experimental data using Eq. (2).

The most essential feature of the Langmuir adsorption isotherm model can be described by a dimensionless constant RL, namely the equilibrium coefficient, which is defined by the following equation:

(3)

where c0 (mg L-1) is the initial concentration of arsenic in solution. If the value of RL lies between 0 and 1, it indicates that the isotherm is favorable for adsorption.

1. Freundlich isotherm model can be represented by the following equation[49]:

(4)

where kF is the Freundlich adsorption coefficient; n is a constant related to temperature. The values of kF and n can be obtained by nonlinear fitting of experimental data points with Eq. (4).

1. Temkin isotherm model can be represented by the following equation[50]:

(5)

where B (J mol-1) is adsorption thermodynamic constant; AT (L g-1) is the Temkin adsorption constant. The values of B and AT can be obtained by nonlinear fitting of experimental data points with Eq. (5).

The fitting results of the above three isotherm models are as shown in Fig. 6. And parameters based on the fitting results are presented in Table 1, it is apparent to see that the adsorption behavior of Zr-CTS/SA for arsenic (both As(III) and As(V); R2=0.987 and 0.999, respectively) was most consistent with Langmuir adsorption isotherm model among the above three models. Calculations of the maximum adsorption capacity of Zr-CTS/SA composite for As(III) and As(V) were respectively 43.19 and 76.78 mg g-1, which were close to the experimental qe values being 42.60 mg g-1 for As(III) and 72.33 mg g-1 for As(V), further proving the fitness of Langmuir isotherm model.

* + 1. Adsorption kinetics

The adsorption time is of great significance in practical applications. Therefore, the adsorption kinetics of Zr-CTS/SA for As(III) and As(V) was studied. In this experiment, two different initial arsenic concentrations (1.0 mg L-1 and 20.0 mg L-1) were selected, and the pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle diffusion model were used to fit the obtained qt-t experimental data points.

(1) The pseudo-first-order kinetic model assumes that the entire adsorption process is controlled by free diffusion and can be expressed by the following equation[51]:

(6)

where k1 (min-1) is the first-order adsorption rate constant. The values of qe and k1 can be obtained by using Eq. (6) to perform non-linear fitting on experimental data points.

(2) The pseudo-second-order kinetic model assumes that the adsorption rate is controlled by chemisorption and can be expressed by the following equation[52]:

(7)

where k2 (g min-1 L-1) is the second-order adsorption rate constant. The values of qe and k2 can be obtained by using Eq. (7) to perform non-linear fitting on experimental data points.

(3) The intra-particle diffusion model describes the entire diffusion process of adsorbates inside the adsorbent particles and can be expressed by the following formula[53]:

(8)

where kid (mg g-1 min-0.5) is the constant of intra-particle diffusion rate; C (mg g-1) is a constant. The values of kid and C can be obtained using Eq. (8) to fit the experimental data points nonlinearly.

The fitting results of Zr-CTS/SA composite adsorbing two concentrations of As(III) and As(V) solutions using the three adsorption kinetic models above are shown in Fig. 7.

The parameters of the three adsorption kinetic models obtained from the nonlinear fitting results are shown in. It can be seen that for the adsorption of As(III), the intra-particle diffusion model is the best description of the three models selected, whose R2 reached 0.974 and 0.991 at 1.0 mg L-1 and 20.0 mg L-1, respectively. While for As(V), it was found that R2 values of the fitting results for the pseudo-first-order and pseudo-second-order kinetic models were all close to 1. However, the calculating results suggested that the adsorption capacity obtained by the pseudo-second-order kinetic model exceeded the initial arsenic concentration, which was inconsistent with the facts. Therefore, the adsorption of As(V) by Zr-CTS/SA composite was considered to follow the pseudo-first-order kinetic model.

* + 1. Adsorption thermodynamics

In order to understand the effect of temperature on the adsorption of As(III) and As(V) by Zr-CTS/SA composite, the adsorption thermodynamics shall be studied, thermodynamic parameters such as enthalpy change (ΔH°, kJ mol-1), entropy change (ΔS°, J mol-1 K-1) and Gibbs free energy (ΔG°, kJ mol-1) could be determined using the following formulas[54]:

(9)

(10)

where Keq, whose value is the ratio of qe to ce at a certain temperature, is the adsorption distribution coefficient at that temperature; R (8.314 J mol-1 K-1) is the molar gas constant; T (K) is the temperature. Using Van't Hoff equation, namely Eq. (9), the values of ΔH° and ΔS° can be calculated by the slope and intercept of the (lnKeq)-(1/T) linear fitting.

The thermodynamic parameters calculated according to the linear equation are shown in Table 3. At different temperatures, the ΔG° values of As(III) and As(V) are all negative and decrease with the increase of temperature, indicating that Zr-CTS/SA adsorbed As(III) and As(V) spontaneously, and increasing temperature is favorable for the adsorption process. ΔH° of both are positive values, further confirming that the adsorption is an endothermic process; ΔS° > 0 indicates that the surface disorder of the adsorbents will increase during the adsorption process.

* + 1. Influence of interfering ions

Fig. 8(a) and Fig. 8(b) are respectively diagrams of the adsorption capacity for As(III) and As(V) in the presence of five inorganic salts at concentrations of 50.0 mg L-1 and 100.0 mg L-1 comparing with the blank solution. The adsorption capacity for As(III) would decrease slightly with the increase of the concentration of interfering ions. The adsorption for As(V) was basically not affected by the added interferences, the adsorption capacity was approximately consistent with that of the blank As(V) solution (39.79 mg g-1). The experimental results demonstrated that Zr-CTS/SA has relatively stable arsenic adsorption performance even in the presence of interfering ions.

A river water sample obtained nearby was used to test the actual environmental adsorption effect. The main elements contained and their contents in the sample were tested by ICP-OES and listed as follows: Al (0.09 mg L-1), B (0.09 mg L-1), Ca (47 mg L-1), K (7.7 mg L-1), Mg (11 mg L-1), Na (57 mg L-1), P (0.13 mg L-1), S (30 mg L-1), Si (1.6 mg L-1). The sample was used to prepare a mixed As(III) + As(V) solution with a total arsenic content of 20.0 mg L-1. After adding Zr-CTS/SA composite to reach adsorption saturation, the total arsenic concentration was reduced to 4.43 mg L-1, demonstrating that the adsorption capacity of the composite was almost not affected, which was coincidence with the results of simulation experiments. Zr-CTS/SA is capable for the employment in real sample processing.

* + 1. Adsorption at low concentrations

This experiment was to study the adsorption performance of Zr-CTS/SA for As(III) and As(V) at low concentrations and to figure out whether the application of this material could satisfy the 10 μg L-1 guideline for drinking water. ICP-MS served to monitor the concentration of arsenic in 100.0 μg L-1 of As(III) and As(V) solutions after different adsorption times. The comparisons between the ct-t relationships of the two arsenic species are shown in Fig. 9.

It is noted that after adsorption treatment by Zr-CTS/SA composites, the concentrations of both As(III) and As(V) can be reduced from the initial 100.0 μg L-1 to below the 10.0 μg L-1WHO guideline for drinking water (as shown by a dashed line in the figure). Although this effect could only be achieved after 72 h of adsorption time, the results signified that Zr-CTS/SA had a bright prospect in arsenic removal from drinking water.

* + 1. Reutilization of Zr-CTS/SA composite

As for the post-treatment of arsenic-adsorbed Zr-CTS/SA composite, reusability studies were carried out, which could further reduce the cost of the application of Zr-CTS/SA. According to the reported literature[55], 0.5 mol L-1 NaCl solution was chosen as the eluent in this experiment for desorption. As is presented in Fig. 10, after 3 cycles of adsorption and desorption, Zr-CTS/SA still maintained a satisfactory adsorption capacity for As(III/V). Especially for As(V), more than 90% performance was successfully kept, which means that the reuse of Zr-CTS/SA after desorption is fairly feasible. Although the adsorption capacity for As(III) decreased with the increase of cycles, Zr-CTS/SA still maintained a performance higher than 70%.

* 1. Discussion on mechanism

In order to comprehensively understand the arsenic adsorption process of Zr-CTS/SA composite, XPS analysis of the composite before and after arsenic adsorption were examined. The survey spectra of the composite before and after adsorption are shown in Fig. 11(a). The As 3d spectra of As(III) (Fig. 11(b)) and As(V) (Fig. 11(c)) both showed a single peak at the binding energy value of 44.27 eV and 45.18 eV, respectively, indicating the presence of As(III/V) over the surface of Zr-CTS/SA and no valence shift during the adsorption. Given that the position and peak amounts of the Zr 3d spectra (Fig. 11(d-f)) before and after adsorption had almost no distinction, it can be inferred that Zr did not directly bond with As during the adsorption process. The high-resolution XPS scans over the O 1s spectral region of Zr-CTS/SA (Fig. 11(g)) shows multiple peaks centered at 532.20, 531.00 and 530.05 eV, which were assigned to adsorbed crystal water (H-O-H), the hydroxyl group bonded to metal (M-OH), and the oxygen bonded to metal (M-O), respectively[23,30]. After As(III) adsorption, the area ratio of the M-OH peak suddenly increased from 2.83% to 16.55% (Fig. 11(h)), and for As(V) it increased to 19.31% (Fig. 11(i)). On the contrary, the area ratio of the peak for M-O decreased from 14.71% to 6.29% and 4.25% after the adsorption of As(III) and As(V), respectively, implying the participation of the oxygen bonded to metal in the arsenic adsorption process, and some of them might convert into hydroxyl groups afterwards.

Focusing on the experimental data of the effect of different pH, it is speculated that when Zr-CTS/SA adsorbed As(V), -NH2 and -OH were protonated to -NH3+ and -OH2+ at low pH. Subsequently, they provided electrostatic attraction to negatively charged H2AsO4- or HAsO42- and bound it to the surface of the material in the form of ionic bonds, serving as an extra adsorption pathway for As(V). As for the adsorption of As(III), which ordinarily existed in the form of uncharged H3AsO3 at experimental pH, the adsorption was more inclined to attach As(III) to the material by forming Zr-O-As covalent bonds. Combining XPS data with pH results, FT-IR and EDS characterization, the possible mechanisms were proposed in Fig. 12.

1. Conclusions

In this work, a zirconium-chitosan modified spherical sodium alginate composite was prepared and batch arsenic adsorption experiments were conducted to study the performance of this novel segregative adsorbent, drawing the following conclusions. Zr-CTS/SA had a particle size of 2.0-3.0 mm, which provided a basis for facile separation, and the material had satisfying thermal stability. The adsorption of As(III) was less affected by pH value, while the adsorption of As(V) achieved the best effect near pH 3. The adsorption of both As(III) and As(V) were in line with Langmuir adsorption isotherm model, with the corresponding maximum adsorption capacities reaching 43.19 and 76.78 mg g-1, showing outstanding arsenic adsorption performance in either lab-prepared or natural water samples. As for adsorption kinetics, the adsorption of As(III) and As(V) separately followed the intra-particle diffusion model and the pseudo-first-order kinetic model. The thermodynamics of the adsorption was found to be spontaneous and endothermic in nature. Additionally, Zr-CTS/SA could reduce low initial arsenic concentration to below 10.0 μg L-1, which is as low as the WHO guideline for arsenic in drinking water, proving that this material could be likely to dispose arsenic-contained drinking water.

Acknowledgements

Funding

This work was supported by the National Natural Science Foundation of China [grant number 21407050].

We also thank the Research Center of Analysis and Test (ECUST) for help on data and characterization.

Credit Author Statement

Sichao Lou: Conceptualization, Methodology, Investigation, Writing - Original Draft.

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**Fig. 1.** SEM images of (a-c) Zr-CTS/SA, (d-f) As(III) adsorbed Zr-CTS/SA, (g-i) As(V) adsorbed Zr-CTS/SA.

**Fig. 2.** EDS spectra of (a) Zr-CTS/SA, (b) As(III) adsorbed Zr-CTS/SA, (c) As(V) adsorbed Zr-CTS/SA.

**Fig. 4.** TG-DTG curves of Zr-CTS/SA.

**Fig. 5.** (a) Effect of solution pH on the removal of As(III) and As(V) by Zr-CTS/SA and SA beads; (b) Zr leaching of Zr-CTS/SA after adsorption in As(III) and As(V) solutions under different pH values (Condition: Initial concentration of As(III)/As(V): 50 mg L–1; Solution volume: 50 mL; Temperature: 298 K; Adsorbent dosage: 35 mg; Agitation speed: 80 rpm; Contact time: 24 h).

**Fig. 6.** Fitting of isotherm models on the adsorption of (a) As(III) and (b) As(V) by Zr-CTS/SA (Condition: Initial concentration of As(III)/As(V): 1-300 mg L–1; Solution volume: 100 mL; pH: As(III) 7, As(V) 2; Temperature: 298 K; Adsorbent dosage: 100 mg; Agitation speed: 80 rpm; Contact time: 72 h).

**Fig. 7.** Fitting of kinetic models on the adsorption of (a, b) As(III) and (c, d) As(V) by Zr-CTS/SA (Condition: Initial concentration of As(III)/As(V): (a, c) 1 mg L–1, (b, d) 20 mg L–1; Solution volume: 100 mL; pH: As(III) 7, As(V) 2; Temperature: 298 K; Adsorbent dosage: 100 mg; Agitation speed: 80 rpm; Contact time: 0-144 h).

**Fig. 8.** Effect of co-existing ions on (a) As(III) and (b) As(V)removal by Zr-CTS/SA (Condition: Initial concentration of As(III)/As(V): 50 mg L–1; Concentration of co-existing ions: 50 and 100 mg L–1; Solution volume: 100 mL; pH: As(III) 7, As(V) 2; Temperature: 298 K; Adsorbent dosage: 100 mg; Agitation speed: 80 rpm; Contact time: 72 h).

**Fig. 9.** Comparison of As(III) and As(V) concentration changes over time (Condition: Initial concentration of As(III)/As(V): 100 μg L-1; Solution volume: 100 mL; pH: As(III) 7, As(V) 2; Temperature: 298 K; Adsorbent dosage: 100 mg; Agitation speed: 80 rpm; Contact time: 0-72 h).

**Fig. 10.** Adsorption capacity retention of Zr-CTS/SA for As(III) and As(V) after 3 absorption-desorption cycles (Condition: Initial concentration of As(III)/As(V): 50 mg L–1; Solution volume: 100 mL; pH: As(III) 7, As(V) 2; Temperature: 298 K; Adsorbent dosage: 100 mg; Agitation speed: 80 rpm; Contact time: 72 h; Eluent for desorption: 0.5 mol L-1 NaCl solution).

**Fig. 11.** XPS analysis of Zr-CTS/SA and As(III)/As(V) adsorbed Zr-CTS/SA: (a) survey spectra of Zr-CTS/SA, As(III)-Zr-CTS/SA and As(V)-Zr-CTS/SA; As 3d scan spectra of (b) As(III)-Zr-CTS/SA and (c) As(V)-Zr-CTS/SA; Zr 3d scan spectra of (d) Zr-CTS/SA, (e) As(III)-Zr-CTS/SA and (f) As(V)-Zr-CTS/SA; O 1s scan spectra of (g) Zr-CTS/SA, (h) As(III)-Zr-CTS/SA and (i) As(V)-Zr-CTS/SA.

**Fig. 12.** Schematic diagram of the suggested adsorption mechanism of As(III) and As(V) on Zr-CTS/SA composite.

**Table 1.** Isotherm parameters of As(III) and As(V) adsorption on Zr-CTS/SA composites.

|  |  |  |  |
| --- | --- | --- | --- |
| Adsorption isotherm model | Parameters | As(III) | As(V) |
| Langmuir | qm (mg g-1) | 43.19 | 76.78 |
| kL (L mg-1) | 0.114 | 0.0512 |
| R2 | 0.987 | 0.999 |
| RL | 0.0282-0.898 | 0.0606-0.951 |
| Freundlich | kF | 10.3 | 11.0 |
| n | 3.64 | 2.77 |
| R2 | 0.868 | 0.942 |
| Temkin | B (J mol-1) | 6.72 | 11.2 |
| AT (L g-1) | 2.68 | 1.66 |
| R2 | 0.938 | 0.909 |

**Table 2.** Kinetic Parameters of As(III) and As(V) Adsorption on Zr-CTS/SA Composites.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Adsorption kinetic models | Parameters | As(III) | | As(V) | |
| 1.0 mg L-1 | 20.0 mg L-1 | 1.0 mg L-1 | 20.0 mg L-1 |
| Pseudo-first-order | k1 (min-1) | 0.00145 | 0.00117 | 5.67×10-4 | 6.78×10-4 |
| qe (mg g-1) | 0.755 | 13.19 | 0.956 | 17.42 |
| R2 | 0.859 | 0.825 | 0.995 | 0.991 |
| Pseudo-second-order | k2 (g min-1 L-1) | 0.00190 | 8.95×10-5 | 4.72×10-4 | 3.40×10-5 |
| qe (mg g-1) | 0.873 | 15.41 | 1.19 | 21.22 |
| R2 | 0.909 | 0.888 | 0.994 | 0.998 |
| Intra-particle diffusion | kid (mg g-1 min-0.5) | 0.00957 | 0.169 | 0.0128 | 0.229 |
| C (mg g-1) | 0.126 | 1.84 | -0.04 | 0.137 |
| R2 | 0.974 | 0.991 | 0.947 | 0.946 |

**Table 3.** Thermodynamic parameters of As(III) and As(V) adsorption on Zr-CTS/SA composites.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameters | As(III) | | | As(V) | | |
| T (K) | 277.15 | 296.15 | 313.15 | 277.15 | 296.15 | 313.15 |
| ΔG° (kJ mol−1) | -2.21 | -2.63 | -2.99 | -2.46 | -6.94 | -12.41 |
| ΔH° (kJ mol−1) | 3.79 | | | 73.73 | | |
| ΔS° (J mol−1 K−1) | 21.67 | | | 274.12 | | |

Highlights

* Zirconium-chitosan modified sodium alginate (Zr-CTS/SA) composite was synthesize.
* Enhanced arsenic adsorption capacities (maximum 20 times) were achieved compared with SA.
* Facile separation efficiency was gained via spherical structure.
* Electrostatic attraction and ligand exchange mechanisms occurred on Zr-CTS/SA.