Zirconia (ZrO₂) Embedded in Carbon Nanowires via Electrospinning for Efficient Arsenic Removal from Water Combined with DFT Studies

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S Supporting Information

ABSTRACT: To use zirconia (ZrO₂) as an efficient environmental adsorbent, it can be impregnated on a support to improve its physical properties and lower the overall cost. In this study, ZrO₂ embedded in carbon nanowires (ZCNs) is fabricated via an electrospinning method to remove arsenic (As) from water. The maximum adsorption capacity values of As(III) and As(V) on the ZCNs are 28.61 and 106.57 mg/g, respectively, at 40 °C. These capacities are considerably higher than those of pure ZrO₂ (2.56 and 3.65 mg/g for As(III) and As(V), respectively) created using the same procedure as for the ZCNs. Meanwhile, the adsorption behaviors of As(III) and As(V) on the ZCNs are endothermic and pH dependent and follow the Freundlich isotherm model and pseudo-first-order kinetic model. Both As(III) and As(V) are chemisorbed onto the ZCNs, which is confirmed by a partial density of state (PDOS) analysis and Dubinin–Radushkevich (D-R) model calculations. Furthermore, the ZCNs also possess the capability to enhance or catalyze the oxidation process of As(III) to As(V) using dissolved oxygen. This result is confirmed by a batch experiment, XPS analysis and Mulliken net charge analysis. Density functional theory (DFT) calculations indicate the different configurations of As(III) and As(V) complexes on the tetragonal ZrO₂ (t-ZrO₂)(111) and monoclinic ZrO₂ (m-ZrO₂)(111) planes, respectively. The adsorption energy (E_{ad}) of As(V) is higher than that of As(III) on both the t-ZrO₂(111) and m-ZrO₂(111) planes (3.38 and 1.90 eV, respectively, for As(V) and 0.37 and 0.12 eV, respectively, for As(III)).

KEYWORDS: zirconia, carbon nanowires, electrospinning, arsenic, removal, DFT study

INTRODUCTION

Arsenic (As) water contamination has become a worldwide concern. The most noticeable problems associated with As contamination have occurred in Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam, many parts of the USA, Nepal, Myanmar and Cambodia.^{1–4} The presence of As in water can cause various cancerous and noncancerous health effects, including bladder and lung cancer, high blood pressure, diabetes and skin lesions.⁵ In natural water, arsenic exists as arsenite (As(III)) and arsenate (As(V)); of these forms, As(III) is more mobilized

and toxic than As(V).^{6,7} On the basis of the negative impact of As on human health, the US Environmental Protection Agency (USEPA) announced the reduction of the maximum contaminant level (MCL) of As from 50 to 10 µg/L in 2006. Under these circumstances, various approaches have been established for As removal, such as coprecipitation,⁸ membrane filtration,⁹ photocatalysis,¹⁰ and ion exchange.¹¹ Among them,

Received: May 20, 2016

Accepted: July 6, 2016

Published: July 6, 2016

adsorption is deemed to be a promising method to remove As from water due to its simplicity, cost effectiveness and lack of toxicity. To date, many adsorbents have been developed for the simultaneous removal of As(III) and As(V).^{12–17} However, the reported adsorbents either have relatively low adsorption capacities or high costs.

Zirconia (ZrO₂) is a widely used inorganic material that is chemically inert, nontoxic, and insoluble in water. Many substances adsorb strongly to ZrO₂, including As.^{16,18–20} In general, to use ZrO₂ as an efficient environmental adsorbent, it must be impregnated in or loaded onto a support to improve its functional properties and lower the overall cost. Therefore, it is essential and desirable to develop economical and effective support materials for ZrO₂, which can greatly lower the overall expense to synthesize zirconia-related adsorbents and promote the performance for As removal.

Electrospinning has drawn considerable attention in recent years because it is a simple, versatile, convenient and economical approach to incorporate or encapsulate other materials to create nanowire composites. Nanowires prepared by electrospinning exhibit many remarkable characteristics, including large surface areas, strong mechanical performance, flexibility in surface functionalities, and homogeneity.^{21–23} The adsorbents fabricated by electrospinning have shown good adsorption ability for the removal of many heavy metals, such as Cr(VI), Cr(III), Cu(II), Ag(I), Fe(II), Pb(II), Cd(II), and Hg(II).^{24–28} However, few studies have focused on adsorbents synthesized by electrospinning for the simultaneous removal of As(III) and As(V). Our previous study demonstrated the production of ZrO₂ embedded in carbon nanowires (ZCNs) by electrospinning and demonstrated their exceptional performance in removing antimony (Sb) from water. As and Sb are both Group V elements in the periodic table and share some physicochemical properties, whereas the species of As and Sb in the solution are different and their adsorption performance and adsorption mechanism could be different as well. So, the aim of this study is to achieve an overall understanding of As adsorption on ZCNs.

In this work, ZCNs were prepared and applied to simultaneous As(III) and As(V) removal. The ZCNs were found to exhibit a high adsorption capacity and rapid adsorption rates for As(III) and As(V). The adsorption equilibrium was reached within 20 min. In addition, the adsorption mechanisms of As(III) and As(V) on the ZCNs were further identified by XPS and DFT calculations. These results confirmed that ZCNs are excellent adsorbents for As removal due to their strong adsorption performance, environmental friendliness and lack of toxicity.

EXPERIMENTAL SECTION

Materials and Chemicals. All chemicals were of analytical grade and used without further purification. The stock solutions of 500 mg/L As(III) and As(V) were prepared in deionized (DI) water with sodium arsenate (Na₂HAsO₄·12H₂O) and sodium arsenite (NaAsO₂), respectively. Ethanol, *N,N*-dimethylformamide (DMF), polyvinylpyrrolidone (PVP, *M_w* = 1 300 000) and zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) were used for the synthesis of ZCNs.

Preparation of ZCNs. ZCNs were strictly prepared following the procedure of our previous study.²⁹ Two grams of ZrOCl₂·8H₂O was dissolved into a mixture containing 5.5 g of DMF and 5.5 g of ethanol. Then, 1.2 g of PVP powder was gradually added to the above solution. A homogeneous precursor solution of PVP/ZrOCl₂ composites was obtained after 12 h stirring at 25 °C. Subsequently, this precursor solution was loaded into a 10 mL glass syringe. A syringe pump was

used to squeeze out the homogeneous precursor solution through a needle with an inner diameter of 0.21 mm at a speed of 0.5 mL/h with a positive voltage of 13 kV applied to the tip. The distance between the needle tip and spinning collector was 10 cm. The PVP/ZrOCl₂ composite nanowires were collected on aluminum foil at 300 rpm to form nonwoven mats. The obtained nanowire mat was first dried at 70 °C for 12 h to ensure full vaporization of the solvents. Then, the calcination procedure was performed by calcinating under nitrogen (N₂) at 150 °C for 1.5 h, after which the temperature was increased to 600 °C and maintained for another 5 h. The ZCNs were obtained after gradually cooling down to room temperature.

Structural Characterization of ZCNs. A scanning electron microscope (LEO 1530 field-emission SEM) was used to identify the morphology of the adsorbents. Prior to imaging, the sample was sputtered with gold under vacuum for 30 s (Emitech K57S Sputter Coater, Emitech Ltd., Ashford Kent, UK). Fourier transform infrared (FTIR) spectra were recorded using KBr pellets with a VERTEX-70 spectrometer (Bruker, Germany). Raman spectra were collected using a Renishaw-S277 Raman spectrometer with a 514 nm laser at a power of 4.7 mW (Renishaw, UK). The crystalline phases of the samples were investigated via X-ray diffraction (XRD, Rigaku UltimaIV) using graphite monochromatized Cu Kα radiation (*λ* = 1.5406 Å). Energy-dispersive X-ray spectroscopy (EDS) was performed on a X-Max 80 silicon drift detector. X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1,486.7 eV).

Adsorption Experiments. The As(III) and As(V) solutions (50 mL), with initial concentrations ranging from 20 to 300 mg/L, were prepared by diluting the stock solutions with DI water. The As(III) and As(V) adsorption isotherm batch experiments were conducted at different temperatures (20, 30, and 40 °C). The dosage of adsorbents for all of the experiments was 1.0 g/L. The adsorption capacity (*q_e*) for As was calculated as follows:

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

where *q_e* (mg/g) is the equilibrium adsorption capacity; *C₀* and *C_e* (mg/L) are the initial and equilibrium concentrations with adsorbents in solution, respectively; *V* is the volume (mL) of the As aqueous solution; and *m* is the mass (mg) of adsorbent used in the experiment.

The equilibrium adsorption isotherm data and related isotherm parameters were fitted with the Langmuir (eq 2) and Freundlich (eq 3) isotherm equations:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2)$$

$$q_e = k_F C_e^{1/n} \quad (3)$$

where *q_e* is the amount (mg/g) of As adsorbed at equilibrium and *C_e* is the equilibrium As concentration (mg/L) in the water samples. In eq 2, *q_m* (mg/g) and *k_L* (L/mg) are the Langmuir parameters; *q_m* is the maximum adsorption capacity; and *k_L* is adsorption equilibrium constant. In eq 3, *k_F* (mg^{1–(1/*n*)} L^{1/*n*} g^{–1}) and *n* are the Freundlich parameters for values in the range of 1 < *n* < 10, which indicates favorable adsorption.

The adsorption kinetics of As(III) and As(V) were examined at 20 °C by adding 200 mg of ZCNs into 200 mL of solution with initial As(III) and As(V) concentrations of 270 and 200 mg/L, respectively, at pH 6.0 ± 0.2. Samples were taken out at a particular reaction time. The adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order models and are expressed as eqs 4 and 5, respectively.^{30,31}

$$q_t = q_e (1 - e^{-K_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (5)$$

Here, q_e is the amount of adsorbate at equilibrium (mg/g); q_t is the amount of adsorbate (mg/g) at time t (min); and K_1 (min^{-1}) and K_2 ($\text{g mg}^{-1}\text{min}^{-1}$) are the rate constants for the pseudo-first- and second-order adsorption, respectively.

To analyze the effect of pH on As(III) and As(V) removal, pH values varying from 1.0 to 13.0 were adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH. All of the suspensions were sealed and stirred. After the adsorption, all of the suspensions were filtered through a 0.22 μm cellulose acetate membranes to collect the clear supernatant solution for the As concentration analysis. The residual concentration of As in the clarified solution was determined using an 8220 atomic fluorescence spectrophotometer.

DFT Calculations. DFT calculations of As(III) and As(V) on the (111) planes, such as the tetragonal plane (PDF 42-1164) of ZrO_2 (t- ZrO_2) and monoclinic planes (PDF 37-1484) of ZrO_2 (m- ZrO_2), were performed. Both of the slab models were cut from the (111) surface of the bulk ZrO_2 . The 2×2 supercells were constructed, and the bottom of the model was fixed with a 15 Å vacuum layer. Only 4 layers of the models were used for the surface relaxation.^{32,33} All of the calculations were based on DFT and performed using Material Studio 7.0. Modeling was carried out with the DMol3 package.^{34,35} A double numerical quality basis set with polarization functions (DNP) and GGA-VWN-BP was used for all calculations.^{36–38} Core electrons were treated with DFT semicore-pseudo potentials (DSPPs).³⁹ Spin polarization was also applied, and the real space cutoff radius was maintained at 4.2 Å. The COSMO was applied, and water was selected as the solvent. The adsorption energy (E_{ad}) of the As(III)/t- ZrO_2 (111), As(III)/m- ZrO_2 (111), As(V)/t- ZrO_2 (111), and As(V)/m- ZrO_2 (111) complexes were calculated as follows:

$$E_{\text{ad}} = E_{\text{surface}} + E_{\text{As}} - E_{\text{As/surface}} \quad (6)$$

where E_{surface} is the energy of the surface; E_{As} is the energy of an isolated As(III) or As(V) molecule; and $E_{\text{As/surface}}$ is the total energy of the same molecule adsorbed on the surface. A positive value for E_{ad} indicates stable adsorption.⁴⁰

The net charge of atoms during As adsorption was calculated as follows:

$$\text{net charge} = \text{Mulliken charge}_{\text{after}} - \text{Mulliken charge}_{\text{before}} \quad (7)$$

where Mulliken charge_{after} is the charge of the atoms after As is adsorbed and Mulliken charge_{before} is the charge of atoms before adsorption. A positive value for the net charge indicates a loss of electrons.

RESULTS AND DISCUSSION

Structural and Chemical Characterization of ZCNs.

The morphology and nanostructure of the as-prepared ZCNs were characterized by SEM. As shown in Figure 1a and its inset, the ZCNs are highly uniform, with diameters of approximately 250 nm. The ZrO_2 particles are embedded homogeneously on the surface of the carbon nanowires. The XRD patterns identified both tetragonal ZrO_2 (t- ZrO_2) and monoclinic ZrO_2 (m- ZrO_2) on the ZCNs. The (111) plane is the major plane in t- ZrO_2 and m- ZrO_2 , which agrees with our previous study (Figure S1). The Raman spectra of the ZCNs (Figure 1b) further indicate that the ZCNs consist of the tetragonal and monoclinic phases of ZrO_2 according to the tetragonal peaks at 145, 254, and 447 cm^{-1} and monoclinic twin peaks at 300, 470, and 635 cm^{-1} . The twin low-intensity peaks at 174 and 186 cm^{-1} corresponding to m- ZrO_2 can be mainly attributed to ZrO_2 combined with carbon nanofibers.^{41–44} The FTIR spectra of ZCNs are presented in Figure 1c. The peaks at 506.1, 596.4, and 747.6 cm^{-1} are attributed to Zr–O stretching vibrations.^{45,46} The peak at 506.1 cm^{-1} also indicates the existence of both tetragonal and monoclinic zirconia.⁴⁷ As shown in Figure 1d, the SEM mapping identifies the elemental distribution of zirconium (Zr), oxygen (O), and carbon (C)

Figure 1. (a) SEM images of the ZCNs; (b) Raman spectra of the ZCNs; (c) FTIR spectra of the ZCNs; and (d) SEM mapping of the ZCNs.

in the ZCNs. EDS further confirms that the ZCNs only contain Zr, O, and C (Figure S2A). As can be detected after the adsorption process (Figure S2B,C).

The elemental composition and valence state of the ZCNs were measured by XPS. As shown in Figure S3A, the peaks of Zr 3d, O 1s, C 1s, and As 3d are present in the survey scan spectrum, indicating the existence of Zr, O, C, and As in the ZCNs. The Zr 3d region has Zr–O bond signals that are located at binding energy (BE) values of 182.4 and 184.8 eV.^{48,49} C 1s has signals at 284.9, 286.3, and 288.5 eV, which are correlated to C–C, C=O, and O–C=O bonds, respectively.⁵⁰ As shown in Figure 2A and Figure S3B, the BE of Zr 3d and C 1s do not change after the As adsorption. In Figure 2B, O 1s has signals at BE values of 529.9 and 531.6 eV, which correspond to surface lattice oxygen (O_{latt}) and surface adsorbed oxygen (O_{ads}), respectively.^{51,52} The dominant source of O_{ads} is originate from the As(III) and As(V), which exists as H_3AsO_3 and H_2AsO_4^- under the experiment condition (pH 6). And the O_{latt} is belonging to the ZCNs itself, and it will remains invariant during the adsorption process. According to the different ratios of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$, we can easily identifies whether the As(III) and As(V) adsorbed on the ZCNs surface or not. The ratio of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ after As(III) adsorption (0.56) is smaller than that after As(V) adsorption (0.60), which is attributed to the different molecular configuration between As(III) (which exists as H_3AsO_3) and As(V) (which exists as H_2AsO_4^-). The ratios of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ after As(III) and As(V) adsorption are larger than the initial $\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$ ratio of the ZCNs (0.54), which confirms that As(III) and As(V) have adsorbed on the ZCNs. Generally, the BE values of the As 3d core level for As(III) and As(V) are 44.3–44.5 and 45.2–45.6 eV, respectively.^{53,54} As shown in Figure 2C(b), after the As(III) adsorbs on the ZCN, As(III) and As(V) signals are present at BE values of 44.4 and 45.5 eV, respectively. These signals confirm that a portion of As(III) (38.98%) has been oxidized to As(V) during the adsorption process. Meanwhile, in Figure 2C(c), the BE at 45.4 eV demonstrates that only As(V) exists on ZCNs. The details of the XPS results are shown in Table S1.

Adsorption Isotherm and Kinetics. Figure 3a,b show the adsorption of As(III) and As(V) on ZCNs at different

Figure 2. XPS patterns, where A is the Zr 3d spectra, B is the O 1s spectra (O_{latt} (lattice oxygen), O_{ads} (surface adsorbed oxygen)), and C is the As 3d spectra. Note: panel a is pure ZCN, panel b is after As(III) adsorption, and panel c is after As(V) adsorption.

Figure 3. Adsorption isotherm under different temperatures for (a) As(III) and (b) As(V) on the ZCNs. The initial As(III) and As(V) concentrations were 20–300 mg/L; the adsorbent dose was 1.0 g/L; the solution volume was 50 mL; and the pH was 6.0.

temperatures (20, 30, and 40 °C) at pH = 6.0. The equilibrium adsorption capacity of the ZCNs for As(III) and As(V) increases rapidly in the low concentration range, increases gradually in the middle concentration range, and then gradually reaches its maximum adsorption capacity. The equilibrium adsorption isotherm data were analyzed using the Langmuir and Freundlich models. As shown in Table 1, the correlation parameters (R^2) indicate that the Freundlich model more suitable than the Langmuir model for describing the adsorption isotherm. The Freundlich model presents a heterogeneous surface adsorption of As(III) and As(V) on the ZCN and nonuniform active sites. The maximum theoretical adsorption capacity (MTAC) of the ZCNs is 28.61 and 106.57 mg/g for As(III) and As(V), respectively, at 40 °C.

The pure ZrO_2 was modeled following the same procedure as the ZCNs, which was applied to As adsorption as well. The MTAC values of pure zirconia are only 2.56 and 3.65 mg/g for As(III) and As(V), respectively, at 40 °C. This highlights the considerably improvement in the adsorption capacity of ZrO_2 that can be achieved via the electrospinning method. The

adsorption capacity of ZCNs is higher than those of many adsorbents reported in the literature (see Table S2).^{14,55–60}

As shown in Figure 3, the increase in adsorption capacity with increasing temperature demonstrates the temperature dependency of the adsorption process. Thermodynamic parameters, such as the change in the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), are calculated as follows:⁶¹

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

where R is the universal gas law constant (8.314×10^{-3} kJ/mol·K), T is the absolute temperature (K), and K_d is determined as q_e/C_e . q_e and C_e are the same as indicated above.

In addition, the parameters of ΔH° and ΔS° were determined as follows:⁶¹

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

On the basis of eq 9, the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_d$ versus $1/T$ yields, respectively (Figure S4 and Table S3). For As(III), the ΔH° value is 4.79 kJ/mol, and ΔG° decreases with increasing temperature (−13.15, −13.74, and −14.37 kJ/mol for 20, 30, and 40 °C, respectively), which indicates that the adsorption of As(III) on the ZCNs is a spontaneous endothermic process. The positive ΔS° value (0.061 kJ/mol·K) suggests that the increased randomness of solid–liquid interface during the adsorption process. A similar tendency is observed for the As(V) adsorption process. The ΔH° is 25.42 kJ/mol, and ΔS° is 0.14 kJ/mol·K. ΔG° is also calculated to be −14.93, −16.28, and −17.62 kJ/mol for 20, 30, and 40 °C, respectively.

Table 1. Langmuir and Freundlich Parameters for As(III) and As(V) Adsorption on ZCNs

temperature(°C)	equation parameters	Langmuir model			Freundlich model		
		q_m (mg/g)	k_L (L/mg)	R^2	n	k_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	R^2
20	As(III)	26.8039	0.3772	0.9187	6.3051	12.9197	0.9960
	As(V)	64.4702	0.1271	0.9476	4.4722	20.6534	0.9916
30	As(III)	28.3247	0.3610	0.9250	6.0096	12.9396	0.9990
	As(V)	84.8468	0.0741	0.9141	3.9093	22.2093	0.9931
40	As(III)	28.6079	0.6766	0.9002	6.3492	14.5651	0.9967
	As(V)	106.5693	0.0566	0.9033	3.5778	24.0715	0.9910

The Dubinin–Radushkevich (D-R) isotherm model can provide additional information for determining the nature of the adsorption mechanism (physical or chemical).

The linear equation of the D-R isotherm is expressed as follows:⁶²

$$\ln q'_e = \ln q'_m - \beta \varepsilon^2 \quad (10)$$

where q'_e is the amount of metal ions adsorbed per unit weight of adsorbent (mol/g); q'_m is the maximum adsorption capacity (mol/g); β is the activity coefficient related to the mean free energy of adsorption (mol²/kJ²); and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$).

As shown in Figure S5 and Table S4, the equilibrium data are well fitted by the D-R isotherm model. The q'_m values are calculated to be 4.02×10^{-4} and 2.36×10^{-3} mol/g for As(III) and As(V), respectively, by using the intercept of the plot. The mean free energy of adsorption (E ; kJ/mol) is expressed as follows:⁶²

$$E = \frac{1}{\sqrt{2\beta}} \quad (11)$$

The E parameter value is between 8 and 16 kJ/mol, illustrating that the adsorption process is chemical in nature.⁶³ According to the calculation, the values of E are 15.77 and 11.43 kJ/mol for As(III) and As(V) adsorption, respectively. This result indicates that both As(III) and As(V) are chemisorbed on the ZCNs.

In practical applications, the adsorption rate is a key factor for designing adsorption reactors, controlling the cycle time of a fixed bed adsorption process, and optimizing operation conditions. To compare better the adsorption kinetics in the system, the pseudo-first-order and pseudo-second-order models were used to fit the observed adsorption kinetic data. As shown in Figure 4, the adsorption process of As(III) and As(V) is

Figure 4. Adsorption kinetics for As(III) and As(V) adsorption on ZCNs fitted with pseudo-first-order and pseudo-second-order models. The initial As(III) and As(V) concentrations were 270 and 200 mg/L, respectively; the adsorbent dose was 1.0 g/L; the solution volume was 200 mL; the pH was 6.0 ± 0.2 and the temperature was 20 °C.

rapid within the first 20 min and then gradually reaches equilibrium. The high initial adsorption rate is attributed to the

presence of adequate adsorption sites on the ZCNs. In general, slightly higher correlation coefficients are observed for the pseudo-first-order model than for the pseudo-second-order model (Table 2), which confirms that the adsorption process was controlled by diffusion. The intraparticle diffusion was rate limiting based on the adsorption process following the pseudo-first-order model.³¹

The above XPS analysis above indicates that As(III) has partially oxidized. We assume that the oxidation process during the adsorption is mainly due to the ZCNs catalyzing the dissolved oxygen (DO) to oxidize As(III). To explore further this assumption, we conducted an experiment in which nitrogen (N_2) was injected to eliminate the DO in water. The As(III) solution with DO in the water was also studied for comparison. Figure S6 clearly shows that the adsorption capacity of the ZCNs toward As(III) is 10.37 mg/g lower after N_2 treatment in the condition without DO in the water. This confirms that the As(III) is partially oxidized to As(V) by the ZCNs with DO present in water, thus enabling the ZCNs to achieve a higher adsorption capacity. On the basis of the ZCNs have a higher adsorption capacity toward As(V) than As(III), the results of the adsorption experiment are convincing, which consistent with the XPS results.

Influence of pH. As shown in Figure 5, the adsorption of As(III) and As(V) on the ZCNs is pH dependent. For As(III),

Figure 5. Effect of pH on the adsorption capacities of As(III) and As(V) on the ZCNs. The initial As(III) and As(V) concentrations were 25 and 30 mg/L, respectively; the adsorbent dose was 1.0 g/L; the solution volume was 50 mL; the pH was 1.0–13.0; and the temperature was 20 °C.

the adsorption capacity increases with increasing pH from 1.0 to 5.0 and remains relatively high at pH values from 5.0 to 11.0. A marked decrease in the adsorption capacity of the ZCNs is observed at pH values from 11.0 to 13.0. A similar tendency is observed for the adsorption of As(V) on the ZCNs. The adsorption capacity increases rapidly at pH values from 1.0 to 3.0 and maintains a relatively high adsorption capacity in a wide pH range (from 3.0 to 9.0). As both As(III) and As(V) exist as uncharged species (such as H_3AsO_3 and H_3AsO_4 , respectively). The adsorption capacity of ZCNs to As(III) and As(V) increase with the pH increase from 1.0 to 3.0, which is mainly due to the

Table 2. Adsorption Kinetics Constants for As(III) and As(V) Adsorption on ZCNs

	pseudo-first-order model			pseudo-second-order model		
	K_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
As(III)	0.1420	30.42	0.9959	0.0058	33.33	0.9816
As(V)	0.1465	89.33	0.9907	0.0017	99.22	0.9707

following two reasons: (1) the surface charge of ZCNs becoming less positive, which may weak the electrostatic adsorption between the adsorbate and adsorbent; and (2) as chemisorption has been identified by D-R isotherm model, it is possible that chemisorption may act as a dominant adsorption type under pH 1.0–3.0, and cause the increasing adsorption capacity. A distinct decrease in the adsorption capacity is observed when the pH value is above 9.0. The above phenomenon can be explained by considering the ζ -potential of the ZCNs and the forms of As(III) and As(V) that exist in aqueous solution. The point of zero charge (pH_{pzc}) of the ZCNs is 7.3, indicating that the surfaces of the ZCNs exhibit a negative charge when the pH is higher than 7.3.²⁹ Meanwhile, the negative charge surface of ZCNs gradually increased with the increasing of pH, and finally reaches the maximum negative charge surface when pH is around 11. As(III) exists as H_3AsO_3 when the pH is below 8.0. At pH values above 8.0, As(III) is gradually negatively charged, changing from H_2AsO_3^- to HAsO_3^{2-} and finally to AsO_3^{3-} .⁶⁴ Because As(III) is gradually negatively charged when the pH is above 8.0, it is reasonable that the adsorption capacity decreases considerably for pH values above 11.0. Similarly, As(V) exists as H_3AsO_4 when the pH is below 4.0. With increasing pH, As(V) changes from H_2AsO_4^- to HAsO_4^{2-} and finally to AsO_4^{3-} for pH values above 8.0.⁶⁵ On the basis of the D-R isotherm model, both As(III) and As(V) are chemisorbed on the surface of ZCNs. The adsorption capacities are still very high for As(III) at pH values of 9.0 and 11.0 and for As(V) at pH 9.0, which is mainly attributed to the dominant adsorption being chemisorption under these pH values rather than the electrostatic adsorption. And the sharp decrease in the adsorption capacity when the pH is above 9.0 is rational based on the above analysis.

Regeneration and Reuse of ZCNs. To identify the reusability and stability of the ZCNs, the adsorption–desorption processes were repeated five times to investigate the ZCNs' potential practical applications. The desorption processes for As(III) and As(V) were performing in 0.5 mol/L sodium hydroxide (NaOH) solution, followed by shaking at 300 rpm for 2 h. The regenerated adsorption capacity of ZCNs is shown in Figure 6. The adsorption capacity of the ZCNs for As(III) and As(V) only decreased by 12.1% and 7.7% compared to the first cycle, illustrating that the ZCNs can be used repeatedly.

Mechanisms of As Adsorption with DFT Calculations. The t-ZrO₂(111) and m-ZrO₂(111) planes were chosen to identify the adsorption mechanisms of As(III) and As(V) using

Figure 6. Regeneration and reuse of ZCN cycles. The initial As(III) and As(V) concentration was 200 mg/L; the adsorbent dose was 1.0 g/L; the solution volume was 50 mL; the pH was 6.0 ± 0.2 ; and the temperature was 20 °C.

the previous method.²⁹ The optimized structures of t-ZrO₂(111) and m-ZrO₂(111) and the complexes after As(III) and As(V) on both slabs are displayed in Figure 7. The adsorption energy (E_{ad}) and Mulliken net charge of the As atom are summarized in Table S5.

Figure 7. Optimized (a) t-ZrO₂(111) plane and (b) m-ZrO₂(111) plane slab models for As(III) adsorption. The optimized (c) t-ZrO₂(111) plane and (d) m-ZrO₂(111) plane slab models for As(V) adsorption. Arsenic atoms are purple, oxygen atoms are red, zirconium atoms are light blue, and hydrogen atoms are white.

The E_{ad} values of As(III) on t-ZrO₂(111) and m-ZrO₂(111) are 0.37 and 0.12 eV, respectively, indicating that the adsorption site of As(III) is more stable on t-ZrO₂(111) than on m-ZrO₂(111). The different adsorption energies are mainly due to the different adsorption complexes formed on the different crystalline surfaces. As shown in Figure 7a, As(III) is tridentate on the surface of t-ZrO₂(111), including two O–Zr bonds and one weak As–O bond. The bond distances of O–Zr are 2.344 and 2.483 Å, respectively, and the As–O bond distance is 2.883 Å. For adsorption occurring on m-ZrO₂(111) (Figure 7b), As(III) is bidentate on the surface. Two bonds are formed (O–Zr and As–O bonds), and the bond distances of O–Zr and As–O are 2.391 and 2.436 Å, respectively. The Mulliken net charge of As(III) is only $-0.005 e$ on the m-ZrO₂(111) complex, whereas it is $+0.127 e$ on the t-ZrO₂(111) complex (Table S5). This result illustrates that the main plane accountable for the redox reaction is t-ZrO₂(111) rather than m-ZrO₂(111). The total Mulliken net charge on As(III) is $+0.122 e$, indicating that As(III) is partially oxidized.

Similar results are achieved for As(V) adsorption. As shown in Figure 7c, As(V) is tridentate on the surface of t-ZrO₂(111) with three O–Zr bonds (the bond distances are 2.475, 2.117, and 2.448 Å). The E_{ad} of As(V) on t-ZrO₂(111) is 3.38 eV. While on m-ZrO₂(111), As(V) forms one weak H–O bond and two O–Zr bonds with bond distances of 1.471, 2.215, and 2.430 Å, respectively (Figure 7d). As(V) is also tridentate on the surface of m-ZrO₂(111) to form one weak H–O bond and two O–Zr bonds with bond distances of 1.471, 2.215, and

Figure 8. Partial density of states (PDOS) of As(III) and Zr orbitals for the As(III)/t-ZrO₂(111) surface complex. The orbitals analysis of As(III) atom (a) before and (b) after adsorption on t-ZrO₂(111) surface, and the orbital analysis of Zr atom (c) before and (d) after As(III) adsorption. The Fermi level (E_F) is set at an energy of zero. Note: the s and p orbitals belong to the As atom, and the d orbital to the Zr atom.

Figure 9. Partial density of states (PDOS) of As and Zr orbitals for the As(V)/t-ZrO₂(111) surface complex. The orbitals analysis of As(V) atom (a) before and (b) after adsorption on t-ZrO₂(111) surface, and the orbital analysis of Zr atom (c) before and (d) after As(V) adsorption. The Fermi level (E_F) is set at an energy of zero. Note: the s and p orbitals belong to the As atom, and the d orbital to the Zr atom.

2.430 Å, respectively (Figure 7d). The E_{ad} of As(V) on t-ZrO₂(111) is 1.90 eV, considerably smaller than that on t-ZrO₂(111) (3.38 eV). The Mulliken net charges of As(V) on t-ZrO₂(111) and m-ZrO₂(111) are identical during the adsorption process (Table S5).

The E_{ad} of As(V) is considerably higher than that of As(III) according to the above results. This discrepancy is mainly due to the different complexes formed on the surfaces of t-ZrO₂(111) and m-ZrO₂(111). Other reasons may cause the difference in E_{ad} values, such as (1) As(V) being negatively charged As(III) being neutrally charged and (2) the molecular volume of As(V) being slightly larger than that of As(III). Accordingly, the adsorption mechanism of As(III) and As(V) on t-ZrO₂(111) and m-ZrO₂(111) have been revealed by the DFT calculations. The As adsorption results obtained via DFT calculations are similar to those of Sb adsorption in our previous study. The E_{ad} values of As and Sb are higher on the t-

ZrO₂(111) plane than on the m-ZrO₂(111) plane. Meanwhile, both As(V) and Sb(V) have higher E_{ad} values on the t-ZrO₂(111) plane than As(III) and Sb(III), respectively. The configurations of As surface complexes are similar to the Sb complex as well, mainly due to As and Sb being in the same group on the periodic table with similar physicochemical characters. The surface complexes and bond distances of As(III) and As(V) on the t-ZrO₂(111) plane and m-ZrO₂(111) plane are shown in detail in Figure S7 of the Supporting Information.

On the basis of the above results from the DFT calculations, the main functional plane of As(III) and As(V) adsorption is the t-ZrO₂(111) plane, not the m-ZrO₂(111) plane. Hence, the PDOS analysis was used to further study the orbital interfacial influence of As(III) and As(V) on the t-ZrO₂(111) plane. In the conduction band, several bonding peaks between 5 and 15 eV of pure As(III) (Figure 8a) have disappeared and shifted to

the lower-energy region (2.5 eV) in As(III)-t-ZrO₂(111) (Figure 8b). The shift in the PDOS in the conduction band of As(III) indicates that the chemical activity of As(III) decreases after adsorbing on the t-ZrO₂(111) slab. On the basis of the above analysis, the adsorption process of As(III) on t-ZrO₂(111) is likely chemisorption, which is consistent with the experimental results. The PDOS of the Zr atoms on the t-ZrO₂(111) slab is shown in Figure 8c,d. Few changes were observed in the PDOS of Zr, except that the intensity of the bonding peaks at 2.5 eV increases after As(III) adsorption, mainly due to the low E_{ad} value for the As(III)/t-ZrO₂(111) complex (0.37 eV).

Comparing the electronic structure of As(V) adsorbing on the t-ZrO₂(111) slab in Figure 9a,b, the bonding peaks in the conduction band between 5 and 15 eV have vanished and shifted to a lower energy level (2.5 eV). Thus, the adsorption process of As(V) on t-ZrO₂(111) is also chemisorption. The trend observed for As(V) is similar to that for the As(III) PDOS analysis. Few changes were observed in bonding region when comparing the PDOS of Zr atoms in pure t-ZrO₂(111) and the As(V)/t-ZrO₂(111) complex (Figure 9c,d). However, the antibonding peak in the conduction band at 2.7 eV for pure t-ZrO₂(111) shifts to the lower-energy region (2.2 eV) after As(V) adsorbs on t-ZrO₂(111), possibly because the E_{ad} value of the As(V)/t-ZrO₂(111) complex is larger than that of As(III)/t-ZrO₂(111).

CONCLUSIONS

In summary, the adsorption experiments present data for the adsorption isotherm and adsorption kinetics of As(III) and As(V) on ZCNs that are well fit by the Freundlich isotherm model and pseudo-first-order kinetic model, respectively. The theoretical maximum adsorption capacities for As(III) and As(V) are 28.61 and 106.57 mg/g, respectively, at 40 °C. The ZCNs have presented the ability to use DO in water to oxidize As(III) to As(V). A high adsorption capacity of the ZCNs was also achieved with a wide pH range for As(III) (approximately 5.0 to 11.0) and As(V) (approximately 5.0 to 9.0). The D-R model and PDOS analysis further confirm that As(III) and As(V) are chemisorbed on the ZCNs. The adsorption capacity of the ZCNs nearly remains unchanged after five regeneration cycles. According to the DFT calculations, the E_{ad} of As(V) is higher than that of As(III) on both the t-ZrO₂(111) plane and m-ZrO₂(111) plane, confirming that the As(V)/t-ZrO₂(111) and As(V)/m-ZrO₂(111) complexes were more stable than the As(III)/t-ZrO₂(111) and As(III)/m-ZrO₂(111) complexes. These findings suggest that the novel ZCNs can be used as a potential efficient adsorbent for the removal of As(III) and As(V) from polluted water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06046.

XRD patterns, EDS images and XPS survey spectra patterns of ZCNs; plots of $\ln K_d$ versus $1/T$, D-R isotherm; nitrogen experiment; the complexes of As(III) and As(V) on t-ZrO₂(111) and m-ZrO₂(111); and the details of XPS results, arsenic adsorption capacity on various adsorbents, thermodynamic parameters, D-R model parameters, and E_{ad} and Mulliken net charges during the As(III) and As(V) adsorption (PDF).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors appreciate the support from the Brook Byers Institute for Sustainable Systems, Hightower Chair and the Georgia Research Alliance at Georgia Institute of Technology. This work is also financially supported by the Major Program of the National Natural Science Foundation of China (No. 51290282) and the National Natural Science Foundation of China (Grant Nos. 51422813, 51378490).

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