Removal of Antimonite (Sb(III)) and Antimonate (Sb(V)) from Aqueous Solution Using Carbon Nanofibers That Are Decorated with Zirconium Oxide (ZrO₂)

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S Supporting Information

ABSTRACT: Zirconium oxide (ZrO₂)-carbon nanofibers (ZCN) were fabricated and batch experiments were used to determine antimonite (Sb(III)) and antimonate (Sb(V)) adsorption isotherms and kinetics. ZCN have a maximum Sb(III) and Sb(V) adsorption capacity of 70.83 and 57.17 mg/g, respectively. The adsorption process between ZCN and Sb was identified to be an exothermic and follows an ion-exchange reaction. The application of ZCN was demonstrated using tap water spiked with Sb (200 µg/L). We found that the concentration of Sb was well below the maximum contaminant level for drinking water with ZCN dosages of 2 g/L. X-ray photoelectron spectroscopy (XPS) revealed that an ionic bond of Zr–O was formed with Sb(III) and Sb(V). Based on the density functional theory (DFT) calculations, Sb(III) formed Sb–O and O–Zr bonds on the surface of the tetragonal ZrO₂ (t-ZrO₂) (111) plane and monoclinic ZrO₂ planes (m-ZrO₂) (111) plane when it adsorbs. Only an O–Zr bond was formed on the surface of t-ZrO₂ (111) plane and m-ZrO₂ (111) plane for Sb(V) adsorption. The adsorption energy (*E*_{ad}) of Sb(III) and Sb(V) onto t-ZrO₂ (111) plane were 1.13 and 6.07 eV, which were higher than that of m-ZrO₂ (0.76 and 3.35 eV, respectively).

INTRODUCTION

In recent decades, increased antimony (Sb) contamination in water has created a global concern. Anthropogenic activities, such as mining and industrial activities are partly responsible for the increased concentration of Sb. Generally, the inorganic forms, Sb(III) and Sb(V), are the most common oxidation states of Sb in the natural aquatic environment. The dominant Sb(V) species for environmentally relevant pH values (pH above 2.7) in oxygenated water exists is Sb(OH)₆[−], which is the deprotonated form of antimonate acid. Sb(III) is an uncharged antimonous acid Sb(OH)₃ for as the pH from 2.0 to 10.4.¹ Both species are toxic, but Sb(III) is 10 times more toxic than Sb(V).² To a large extent, the severe contamination issue is caused by Sb mining and smelting industries.³ Sb has been widely used in a variety of industrial products, including semiconductors for making infrared detectors, diodes and hall-effect devices, the hardness of alloys in lead–acid batteries, small arms bullets, ceramics and glass products.^{3,4} Chinese mining areas has been severely contaminated by Sb, and the

concentration of dissolved Sb in water ranged from 4.58 mg/L to 29.4 mg/L, as reported by He et al.⁵

It is known that prolonged exposure to Sb compounds can have negative impacts on human health, such as myalgia, abdominal colic, diarrhea, skin rashes (including cough, dyspnoea, chronic lung changes) and cardiotoxicity.⁶ This exposure may inhibit the repair of DNA damage in hamster cells and human hematopoietic cells, as well.^{7,8} Considering Sb's potential health risk and threats, the United States Environmental Protection Agency (USEPA) has classified Sb and Sb compounds as a priority pollutant. The maximum contaminate level for Sb in drinking water is 6 µg/L.⁹

Conventional techniques, such as reverse osmosis, electro-deposition, precipitation/coagulation and membrane filtration,

Received: June 15, 2015

Revised: August 19, 2015

Accepted: August 21, 2015

Published: August 24, 2015

have been to remove Sb from water.^{10–12} Most of these techniques are expensive and/or ineffective at removing Sb from very dilute solutions. Adsorption is one of the best available treatment technologies for Sb removal from water, because it is simple, safe, compact, easy to operate and highly efficient. Several studies have investigated the sorption behavior of Sb on different adsorbents. There are some reports on the removal of Sb(III), including Fe–Mn binary oxide,¹³ graphene¹⁴ and multiwalled carbon nanotubes.¹⁵ Although several studies have determined that adsorbents could remove Sb(III) and Sb(V) simultaneously, the adsorption capacity is still relatively low. Zhao et al.¹⁶ synthesized an adsorbent, called PVA-Fe⁰ that could remove both Sb(III) and Sb(V), but the adsorption capacity of Sb(III) and Sb(V) were only 6.99 mg/g and 1.65 mg/g, respectively. PVA-Fe⁰ could remove poly-aluminum chloride and ferric chloride, as well.¹⁷ Only a small number of other materials that have a with high adsorption capacity for both Sb(III) and Sb(V) have been reported. These include such as metal-loaded (Zr(IV) and Fe(III)) saponified orange waste¹⁸ and iron oxyhydroxides.¹⁹ Accordingly, adsorbents that can remove both Sb(III) and Sb(V) at the same time is limited. Therefore, there is a urgent need to develop novel high capacity adsorbents that can simultaneously remove Sb(III) and Sb(V).

Electrospinning is a simple, versatile, convenient and economical approach to incorporate or encapsulate other materials in nanofibers. All one needs to do is add these materials or their precursors into the spinning solutions to create nanofiber adsorbents. Nanofiber adsorbents have drawn wide attention for removing heavy metals, including Cu²⁺, Hg²⁺, Cd²⁺, and Pb²⁺.^{20–24} Nanofiber adsorbents show several remarkable and amazing characteristics, such as a very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance.^{25,26} Zirconium oxide (ZrO₂) is an inorganic material that has been widely used as an adsorbent, because it is nontoxic, chemically inert and insoluble in water. Meanwhile, Hristovski et al.²⁷ used ZrO₂ as an adsorbent to remove arsenate (As(V)) from water. Cui et al.²⁸ used nanostructured ZrO₂ spheres for a fix bed reactor to simultaneously remove arsenite (As(III)) and arsenate (As(V)). Because Sb and arsenic (As) are both in Group 15 elements in the periodic chart they have similar physiochemical characters and ZrO₂ may also remove Sb.

In the present work, ZrO₂-carbon nanofibers (ZCN) prepared by sol-gel process and electrospinning were developed for simultaneous removal of Sb(III) and Sb(V). We found that ZCN had high adsorption capacities for Sb(III) and Sb(V), and the Sb adsorption rate was mass transfer limited. Guo et al.²⁹ have reported the Sb(III) and Sb(V) adsorption mechanism onto the goethite and hydrous ferric oxide (HFO). They used EXAFS, and this revealed that the formation of bidentate mononuclear edge-sharing (2E) between Sb and HFO. Mitsunobu et al.³⁰ examined the adsorption mechanism for Sb(V) adsorption onto iron(III) oxide using EXAFS. They found that Sb(V) caused a larger coordination number of the Fe atom to the Sb atom during coprecipitation processes and form an inner-sphere surface complexes. We propose a possible removal mechanism for both Sb(III) and Sb(V) using XPS and DFT calculations. We demonstrate that our ZCN adsorbent is a promising candidate for the removal of Sb from water.

MATERIALS AND METHODS

Chemicals. All chemicals in this study were analytical grade. Ethanol, *N,N*-dimethylformamide (DMF), polyvinylpyrrolidone (PVP) and zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) were used for the synthesis of the ZCN. Sb(III) and Sb(V) stock solutions (500 mg/L) were prepared by dissolving C₈H₄K₂O₁₂Sb₂·xH₂O and KSb(OH)₆ in deionized (DI) water, respectively.

ZrO₂-Carbon Nanofibers Synthesis. Composite ZCN were prepared using the following procedures. First, 2.0 g of zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) was dissolved in 5.5 g of *N,N*-dimethylformamide (DMF) and 5.5 g of ethanol. Then, 1.2 g of polyvinylpyrrolidone (PVP, *M_w* = 1 300 000) powder was slowly added to this solution. After stirring the solution at room temperature for 12 h, a homogeneous precursor solution of PVP/ZrOCl₂ composites was obtained. Subsequently, this precursor solution was inserted into a 5 mL glass syringe. A syringe pump was used to squeeze out the polymer solution through a needle with an inner diameter of 0.21 mm at a speed of 0.4 mL/h and a positive voltage of 15 kV applied to the tip. The distance between the needle tip and the spinning collector was 10 cm. The PVP/ZrOCl₂ composite nanofibers were collected on aluminum foil at 300 rpm to form nonwoven mats. Then, the nanofiber mat was dried at 70 °C for 12 h to ensure full vaporization of the solvents and calcined under nitrogen (N₂) at 150 °C for 1.5 h and subsequently at 600 °C for another 5 h. After it cooled down to room temperature naturally, the ZCN were obtained.

Characterization. The crystal structure of the ZCN was analyzed using X-ray diffraction (XRD) analysis (PANalytical X'Pert Alpha 1, using Cu K-α1, λ = 1.5406 Å). Specific surface areas (BET) of the samples were investigated using a F-Sorb 3400 automatic surface area Gold APP Instrument. The morphology of the adsorbents was examined using a scanning electron microscope (LEO 1530 field emission SEM). Prior to imaging, the sample was sputtered with gold in a vacuum condition for 30 s (Emitech K575 Sputter Coater, Emitech Ltd., Ashford Kent, UK). X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al-Kα = 1486.7 eV).

Adsorption Isotherms. The adsorption isotherms of Sb(III) and Sb(V) with different temperatures (25 °C, 35 and 45 °C) were conducted at pH 7.0 ± 0.2 using 50 mL bottles by adding 20 mg of ZCN and 20 mL with the different initial concentration of the Sb(III) and Sb(V) solution (range from 10 to 500 mg/L). All of the suspensions were sealed and stirred at 240 rpm. After shaking for 12 h, the residual concentrations in solution were analyzed. The dosage of adsorbents for all the experiments was 1 g/L. Then, the adsorbents were separated using centrifugation (14 000 rpm which resulted in 23 447 g). The supernatant was then filtered using 0.45 μm filter. The initial and residual concentrations of Sb were determined using an 8220 atomic fluorescence spectrophotometer. The adsorption capacity (*q_e*) for both Sb(III) and Sb(V) were calculated according to eq 1:

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (1)$$

where *q_e* (mg/g) is the equilibrium adsorption capacity; *C₀* and *C_e* (mg/L) are the initial and equilibrium concentrations of

Figure 1. SEM images of ZCN: (a), (b) obtained nanofiber before calcination; (c), (d) obtained nanofiber calcination at 600 °C.

adsorbents in the solution, respectively; V is the volume (mL) of the Sb aqueous solution; and m is the mass (mg) of the adsorbent used in the experiment.

Adsorption Kinetics. Adsorption kinetics was conducted at 25 ± 0.2 °C by adding 200 mg of ZCN into a 200 mL solution. The initial Sb(III) and Sb(V) concentrations were 20 mg/L at pH 7.0 ± 0.2 with constantly stirred at 240 rpm. Samples were taken at various times. After shaking the sample for 80 min, the sample was centrifuged at 14 000 rpm (23,447 g) for 10 min to separate the adsorbent. The residual concentrations for both the Sb(III) and Sb(V) ions in the clarified solution were also determined using an 8220 atomic fluorescence spectrophotometer.

Effect of pH. To evaluate the effect of the solution pH on both the Sb(III) and Sb(V) adsorption, the pH value of the aqueous solution was adjusted and maintained between 1.0 to 13.0 using 0.1 mol/L HCl and 0.1 mol/L NaOH. 50 mg of ZCN was added into 50 mL of Sb(III) or Sb(V) which had an initial concentration of 200 mg/L and a specific pH value. The mixture was shaken at 25.0 ± 0.2 °C for 12 h and analyzed in the same way, as described in the adsorption isotherm experiments.

Theoretical Interatomic Sorption Analysis by DFT. DFT calculations were performed on Sb(III) and Sb(V) species on both the (111) planes: the tetragonal (PDF PDF 42-1164) ZrO_2 (t- ZrO_2) and monoclinic planes (PDF 37-1484) ZrO_2 (m- ZrO_2). Both the slab models were cut from the (111) surface of the bulk ZrO_2 , (2×2) supercells were constructed, and the bottom of the model was fixed with a 15 Å vacuum layer. In consideration of the wider diffraction peaks of the prepared materials from XRD (low crystallinity), only four layers of the models were used for the surface relaxation.^{31–33} All the calculations were based on DFT and performed using Material Studio 5.5 modeling DMol3.^{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 (DSPP).³⁹ Spin polarization was also applied and the real space cutoff radius was maintained at 4.2 Å. The COSMO was also used, and the solvent was water. The adsorption energy (E_{ad}) of the Sb molecule was calculated as eq 2:

$$E_{\text{ad}} = E_{\text{surface}} + E_{\text{Sb}} - E_{\text{Sb/surface}} \quad (2)$$

where E_{surface} is the energy of surface; E_{Sb} is the energy of an isolated Sb(III) or Sb(V) molecules; and $E_{\text{Sb/surface}}$ is the total energy of the same molecule adsorbed on the surface. Note that a positive value for E_{ad} suggests a stable adsorption.⁴⁰

The net charge of atoms during Sb adsorption was calculated as eq 3:

$$\text{net charge} = \text{Mulliken charge}_{\text{after}} - \text{Mulliken charge}_{\text{before}} \quad (3)$$

where Mulliken charge_{after} is the charge of atoms after Sb adsorbed and Mulliken charge_{before} is the charge of atoms before adsorption. Note that a positive value for the net charge suggests a loss of electrons.⁴¹

RESULTS AND DISCUSSION

Characterization of ZrO_2 –Carbon Nanofibers. The Brunauer–Emmett–Teller (BET) surface specific area of ZCN was determined to be approximately 106.3 m²/g. Figure 1, it shows the SEM images of ZCN with different treatments and magnifications. Figure 1a,b shows that the ZCN before calcining are delicate and smooth. These figures also demonstrate clearly that these ZCN were highly homogeneous separated. Figure 1c,d shows that the ZCN after calcining are cracked and coarse on the surface. It is evident that the ZrO_2 were homogeneous aggregated and embedded on the surface of the carbon nanofibers. An energy dispersive spectrometer (EDS) was used to investigate the specific elemental contents

of the ZCN. The EDS spectrum (Figure S1) shows that the ZCN are mainly composed of carbon, oxygen and zirconium. Further structural characterization can be obtained from examination of the SEM-mapping. The SEM-mapping analysis was also performed to determine the morphological characteristics of the ZCN, as shown in Figure S2. Figure S2a clearly shows that the carbon nanofibers are covered by the ZrO_2 nanoparticles. Figure S2b–d are the distributions of C, O, and Zr elements in the ZCN, is also shown by SEM-mapping from the SEM image from Figure S2a. This finding indicates that the presence of Zr is associated with O and can be found clearly on the surface of C. The mapping shapes of the Zr, C, and O elements corresponding to the ZCN indicate that the adsorbent has a uniform element composition and dispersion. This result agrees with the EDS observation. The XRD patterns of ZCN and the pure ZrO_2 particles are shown in Figure 2a,b,

Figure 2. XRD patterns of the (a) ZCN and (b) particles- ZrO_2 .

respectively. It is evident that the m-ZrO_2 is the dominant phase in the pure ZrO_2 particles (according to PDF 37-1484). After ZrO_2 was doped into the carbon nanofibers, the t-ZrO_2 was the predominant phase (according to PDF 42-1164). The relative contents of t-ZrO_2 and m-ZrO_2 can be measured by XRD pattern, which the value is 4.11. The reduction of most m-ZrO_2 peaks of ZCN demonstrates that the ZrO_2 nanoparticles

are dispersed on the carbon nanofibers' surface and do not aggregate into well-formed crystal sizes that are large enough to produce strong sharp XRD peaks; the distinctive peak at the 2θ angle of $\sim 28.1^\circ$ is broadened as well. The dramatic attenuation of ZrO_2 's m-ZrO_2 characteristic peak at 28.1° in the ZCN may due either to stacking of carbon nanofibers or incorporation of ZCN into the composites. Although the intensity in different materials of the ZrO_2 between m-ZrO_2 and t-ZrO_2 is changing, the distinctive peak at the 2θ angle of $\sim 30.4^\circ$ is typical of t-ZrO_2 structure zirconia, is still present.

Adsorption Isotherms. Figure 3 a and b shows the adsorption isotherms of Sb(III) and Sb(V) on ZCN at 25, 35, and 45°C at $\text{pH } 7.0 \pm 0.2$. Because the ZCN was formed at 600°C , the isotherms temperature would not affect geometries of the surface complexes. The adsorption amounts of Sb(III) and Sb(V) of the material increase rapidly in the low concentration range, and then increase gradually as the initial concentrations increase. Also the adsorption capacity of Sb(III) and Sb(V) on the ZCN decreased with increasing temperature.

The equilibrium adsorption isotherm data and related isotherm parameters were analyzed using both Langmuir (eq 4) and Freundlich (eq 5) isotherm:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (4)$$

$$q_e = k_F C_e^{1/n} \quad (5)$$

where q_e is the amount (mg/g) of Sb adsorbed at equilibrium; and, C_e is the equilibrium Sb concentration (mg/L) in the water samples. In eq 4, q_m (mg/g) and k_L (L/mg) are the Langmuir parameters; q_m represents the maximum adsorption capacity; and k_L is adsorption equilibrium constant. Meanwhile, in eq 5, k_F ($\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$) and n are the Freundlich parameters for values in the range of $1 < n < 10$, which indicates favorable adsorption.

Figure 3 displays the Sb(III) and Sb(V) isotherms and the parameters are listed in Table 1. The correlation coefficient (R^2) values demonstrate that the Langmuir model is more suitable than the Freundlich model for describing the adsorption process. This indicates that the adsorption site energy is a constant and that there is a maximum monolayer surface coverage. The theoretical adsorption capacity of ZCN was 70.83 and 57.17 mg/g for Sb(III) and Sb(V), respectively. The adsorption capacity of ZCN is considerably higher than the pure ZrO_2 particles, which are produced by the same

Figure 3. Adsorption isotherm with different temperatures for (a) Sb(III) and (b) Sb(V) on ZCN. Initial Sb(III) and Sb(V) concentration was 10–500 mg/L; adsorbent dose was 1 g/L; the solution volume was 20 mL; and pH was 7.0 ± 0.2 .

Table 1. Langmuir and Freundlich Parameters for Sb(III) and Sb(V) Adsorption on the ZCN

temperature (°C)	equations	Langmuir model			Freundlich model		
	parameters	q_m (mg/g)	k_L (L/mg)	R^2	n	k_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	R^2
25	Sb(III)	70.83	0.0089	0.9866	2.351	4.468	0.9576
	Sb(V)	57.17	0.0085	0.9705	2.397	3.690	0.9692
35	Sb(III)	64.40	0.0069	0.9776	2.213	3.180	0.9877
	Sb(V)	43.61	0.0125	0.9791	2.651	3.988	0.9754
45	Sb(III)	38.22	0.0243	0.9723	3.835	7.476	0.9669
	Sb(V)	36.13	0.0152	0.9610	2.964	4.293	0.9155

Figure 4. Adsorption kinetics for Sb(III) and Sb(V) adsorption on ZCN, (a) fitted with pseudo-first and pseudo-second order models, and (b) fitted with the mass transfer model. The initial Sb(III) and Sb(V) concentration was 20 mg/L; adsorbent dose was 1 g/L; the solution volume was 200 mL; the pH was 7.0 ± 0.2 and the temperature was 25 °C.

calcination procedure as the ZCN (Figure S3, details mentioned in Table S1). It is partially due the larger BET of ZCN ($106.3 \text{ m}^2/\text{g}$), compared to the BET of the ZrO_2 particles ($22.7 \text{ m}^2/\text{g}$). Another reason is the higher loading ratio of t-/m- ZrO_2 presence in the ZCN (4.11), compared to ZrO_2 particles (1.50), which will be discussed according to mathematical and DFT Calculation sections below. The adsorption capacity of ZCN is higher than many literature reports (Table S2).

The Dubinin–Radushkevich (D-R) isotherm model can be used to determine whether the nature of the adsorption process is physical or chemical. The linear equation of the D-R isotherm⁴² is expressed by eq 6:

$$\ln q'_e = \ln q'_m - \beta \varepsilon^2 \quad (6)$$

where q'_e is the amount of metal ions sorbed per unit weight of adsorbent (mol/L); q'_m is the maximum adsorption capacity (mol/g); β is the activity coefficient related to the mean free energy of adsorption (mol^2/J^2); and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$).

The D-R isotherm model fit the equilibrium data well (R^2 values were 0.9989 and 0.9954 for Sb(III) and Sb(V), respectively (Figure S4 and Table S3)). The q'_m values, determined using the intercept of the plot, were $1.8 \times 10^{-3} \text{ mol/g}$ and $9.1 \times 10^{-4} \text{ mol/g}$ for Sb(III) and Sb(V), respectively. The mean free energy of adsorption (E ; kJ/mol) is expressed by eq 7:

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

The information regarding the sorption mechanism, whether physical or chemical in nature, can be determined from the E (kJ/mol) value. The mean free energy of adsorption for both Sb(III) and Sb(V) were 8.3 and 10.0 kJ/mol, respectively, which are in the energy range of an ion-exchange reaction, that

is, 8–16 kJ/mol.⁴³ The fact that the isotherm is described best by the Langmuir equation supports the fact that both the adsorption of Sb(III) and Sb(V) onto ZCN are ion-exchange reactions.

Furthermore, a decrease in the adsorption capacity as the temperature increases demonstrates that the adsorption process is exothermic. These thermodynamic parameters can be calculated from the isotherm data: the Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0):⁴⁴

$$\Delta G = -RT \ln K \quad (8)$$

where R is the universal gas law constant ($8.314 \text{ J/mol}\cdot\text{K}$); T is the absolute temperature (K); and K is the distribution coefficient.

The parameters of ΔH^0 and ΔS^0 are estimated using eq 9:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

Based on eq 9, the ΔH^0 and ΔS^0 parameters can be calculated from the slope and intercept, respectively, of the plot of $\ln K$ versus $1/T$ (Figure S5 and Table S4). For Sb(III) adsorption on the ZCN, the negative ΔH^0 (-14.98 kJ/mol) is determined the adsorption process of Sb(III) onto ZCN is the exothermic reaction at 25, 35, and 45 °C. The ΔS^0 value ($-8.19 \text{ J/mol}\cdot\text{K}$) is caused by a decrease in degrees of freedom of the adsorbed species. ΔG^0 are also calculated to be -12.56 , -12.40 , and -12.28 kJ/mol for 25, 35, and 45 °C, respectively. The same tendency was observed in the Sb(V) adsorption: the negative ΔH^0 is -14.56 kJ/mol , ΔS^0 is $-8.11 \text{ J/mol}\cdot\text{K}$ and ΔG^0 are -12.12 , -12.05 , and -11.90 kJ/mol at 25, 35, and 45 °C, respectively.

Furthermore, because the (111) plane is the dominant plane for both t- ZrO_2 and m- ZrO_2 , the adsorption process is assumed to occur on the (111) plane. The adsorption capacity is normalized by the BET data to determine the adsorption

Table 2. Kinetics Constants for Sb(III) and Sb(V) Adsorption on the ZCN

	pseudo-first-order model			pseudo-second-order model		
	K_1 (min ⁻¹)	q_e (mg/g)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_e (mg/g)	R^2
Sb(III)	0.119	12.72	0.9526	0.0096	14.67	0.9865
Sb(V)	0.103	11.10	0.9781	0.0091	13.08	0.9953

capacity per unit area. The intensity of (111) t-ZrO₂ and m-ZrO₂ plane peaks in the XRD pattern are used to determine the adsorption capacity of the ZCN and ZrO₂ particles. The specific calculation process is shown in S1 in the [Supporting Information](#). We now discuss the difference between Sb(III) and Sb(V) adsorption on the same plane. On the t-ZrO₂ (111) plane, the maximum Sb(III) (0.31 mg/m²) adsorption capacity is considerably higher than Sb(V) (0.08 mg/m²), which demonstrates that the Sb(III) is more likely to adsorb on the t-ZrO₂ (111) plane than Sb(V). On the m-ZrO₂ (111) plane, the maximum Sb(III) (2.18 mg/m²) adsorption capacity is relatively lower than Sb(V) (2.38 mg/m²), which indicates that the Sb(V) is more likely to be adsorbed on the m-ZrO₂ (111) plane. As the intensity of t-ZrO₂ (111) is much stronger than m-ZrO₂ (111) in ZCN, the adsorption capacity of Sb(III) was much higher than Sb(V) in our study. And basically, we can regulate and create more t-ZrO₂ (111) to increase the adsorption capacity of Sb(III) in the future study. Another mechanism of Sb adsorption energy and formation onto the surface of (111) plane of t-ZrO₂ and m-ZrO₂ will be discussed later using the [DFT calculation](#).

Adsorption Kinetics. In practical applications, the adsorption rate is a key factor for designing adsorption contactors. Adsorption kinetic parameters are critical for designing adsorption units and optimizing operation conditions. Preliminary investigations indicated that the nanofibers adsorbent rapidly absorbs Sb. Both the adsorption kinetics of Sb(III) and Sb(V) by ZCN were rapid for the first 30 min. Then, Sb(III) and Sb(V) uptake gradually reached equilibrium in about 50 min ([Figure 4a](#)). The time to equilibrium is considerably faster than other new nanocomposites, such as graphene oxide/schwertmannite nanocomposites (GO-SCH),⁴⁵ which reach equilibrium in 24 h.

The adsorption kinetic data were analyzed using the pseudo-first-order⁴⁶ and the pseudo-second-order⁴⁷ models, and the external mass transfer model. The pseudo-first-order and the pseudo-second-order are expressed as [eq 8a](#) and [9a](#), respectively.

$$q_t = q_e(1 - e^{-K_1 t}) \quad (8a)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (9a)$$

where 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 (g mg⁻¹ min⁻¹) are the rate constants for the pseudo first- and second-order sorption, respectively. All the parameters are listed in [Table 2](#).

The results indicate that the pseudo-second-order mechanism is primary and the chemical absorption was the potential rate-controlling step in the Sb absorption. The reason the pseudo-second-order kinetic model primary is this model is based on the assumption that the rate-limiting step might be chemisorption involving sharing or exchanging electrons between the absorbent and absorbate.^{23,24}

The mathematical derivation process of the mass flow rate equation on ZCN is shown in Section 2 in the [Supporting Information](#). The mass flow rate equation is expressed as [eq 10](#) and [11](#):

$$-\frac{dC}{dt} = k_f \times a(C - C_s) \quad (10)$$

$$C = b \exp[-ht] + C_0 - b \quad (11)$$

where C is the concentration of Sb (mg/L) in the bulk solution at any time t ; C_s is the concentration of Sb at interface (mg/L); h and b are the fitting parameters; and k_f is the mass transfer coefficient (cm/s).

[Figure 4b](#) shows the data fitted with the mass transfer model. The R^2 values obtained for ZCN on Sb(III) and Sb(V) adsorption are 0.991 and 0.970, respectively. The k_f for Sb(III) was 1.58×10^{-4} cm/s and it is higher than the k_f for Sb(V) which is 1.36×10^{-4} cm/s. These are reasonable values and this is mainly due to the molecular volume of Sb(V) which is bigger than Sb(III). Accordingly these results, adsorption kinetics for ZCN are external mass transfer limited.

Effect of pH. The pH is known to have an impact on the surface charge of the adsorbent and the adsorbate. The effect of pH on the adsorption capacity of Sb(III) and Sb(V) on ZCN is shown in [Figure 5](#). In [Figure 5](#), the adsorption capacity of both

Figure 5. Effect of pH on the adsorption capacity of Sb(III) and Sb(V) on ZCN. The initial Sb(III) and Sb(V) concentration was 200 mg/L; adsorbent dose was 1 g/L; the solution volume was 50 mL; the pH was 1.0–13.0; and the zeta potential of ZCN (inset figure).

Sb(III) and Sb(V) were relatively high and only fluctuated slightly over a wide range of pH values (from 1.0 to 13.0). The maximum adsorption capacity for both Sb(III) and Sb(V) were obtained when the pH value was approximately 7.0. These results show the great potential for treating drinking water as compared to other studies. Leng et al.¹⁴ used graphene as an adsorbent (the dose was 0.4 g/L) to remove Sb(III) from an aqueous solution. It can removal percentage almost 100% of Sb(III) at pH was 11.0 with initial concentration of 3 mg/L, while it can only remove nearly 40% of the Sb(III) when the pH was approximately 7. Zhao et al.¹⁶ developed a nanoscale zerovalent iron to remove Sb(III) and Sb(V), but they observed

Figure 6. XPS characterization of ZCN before and after Sb(III) and Sb(V) adsorption. (a) XPS survey spectra along with the spectra of (b) C 1s, (c) O 1s + Sb 3d (O_{latt} (lattice oxygen), O_{ad} (adsorb oxygen) and O_{H2O} (chemisorbed oxygen species, like H₂O)) and (d) Zr 3d.

a tremendous drop in the Sb(V) adsorption as the pH increased from 4 to 10.

The difference in adsorption efficiency in Sb(III) and Sb(V) may be due to electrostatic force differences that exist between the ZCN surface and Sb oxyanions present in the solutions. For Sb(III), Sb(OH)₃ is the most common species that exists over a wide pH range (2–10.4). For pH values above 10.4, the species that may be present are H₂SbO₃[−] or Sb(OH)₄[−]. Sb(OH)₆[−] is the dominate Sb(V) solution species that exists over the pH range 2.7–10.4.⁴⁸ Zeta-potential measurements (Figure 5 inset), show that untreated ZCN surfaces have net negative charge for pH values higher than the point of zero charge (pH_{pzc}) which is 7.3. This is the main reason for the decrease in adsorption capacity as the pH increases above 7.3.

The Performance ZCN in Tap Water. Tap water is a considerably more complex water matrix than deionized water because it includes various types of salts, organic matter, and possibly, microbes. The pH and TOC the raw tap water that we used was 7.32 and 0.39 mg/L, respectively. To simulate a Sb contamination in the tap water, the tap water was spiked with a stocked Sb solution, which had a concentration of 200 µg/L for both Sb(III) and Sb(V), prior to treatment. After 120 min of contact with ZCN, the residual Sb(III) and Sb(V) were 3.76 and 4.32 µg/L, respectively (Figure S6a), which was below the maximum contaminant level (MCL) of 6 µg/L. As a comparison, the same treatment with the deionized water was performed (Figure S6b). The residual concentration of Sb(III) and Sb(V) were 3.23 and 4.16 µg/L, respectively. The higher

Sb removal in deionized water than tap water is mainly attributed the impact of anion in the water (i.e., sulfate and phosphate). While the result from the tap water is still meet the requirement of the MCL of drinking water regulated by USEPA. These results demonstrated that the ZCN was an effective adsorbent for trace Sb removal not only in synthetic solutions but also in real tap water.

XPS Analyses. The chemical composition of ZCN after Sb adsorption was measured by XPS. As shown in Figure 6a, the peaks corresponding to Zr 3d, O 1s, C 1s, and Sb 3d are clearly identified in the survey scan spectrum. The presence of Sb in the resultant product further validates the adsorption of Sb onto ZCN. The peak at a binding energy of 284.8 eV is assigned to C 1s (Figure 6b),⁴⁹ and no change of C 1s have been identified after Sb adsorption. Two peaks at the binding energy of 530.7 and 540.0 eV are attributed to Sb 3d_{5/2} and Sb 3d_{3/2}. The appearance of the Sb 3d_{3/2} peak in Figure 6c indicates that both Sb(III) and Sb(V) are adsorbed on the ZCN.^{50,51} The proportion of O_{ad}/O_{latt} is increased from 14.8% to 16.0% and 16.9% after the Sb(III) and Sb(V) adsorptions, respectively. The higher proportion of O_{ad}/O_{latt} after Sb(V) adsorption than Sb(III) is primarily attributed to the fact that Sb(V) is bonded with five −OH, while Sb(III) is associated with three −OH. As displayed in Figure 6d, the Zr 3d peak can be decomposed into four peaks.⁵² The peaks approximately 182.1 and 184.6 eV correspond to Zr−O bonds and the peaks approximately 182.0 and 184.45 eV are the metallic Zr bonds (Zr−Zr). In addition, the binding energy of the Zr−O site is

Figure 7. Optimized (a) t-ZrO₂ (111) plane and (b) m-ZrO₂ (111) plane slab models for Sb(III) adsorption. The optimized (c) t-ZrO₂ (111) plane and (d) m-ZrO₂ (111) plane slab models for Sb(V) adsorption. Antimony atoms are purple, oxygen atoms are red, zirconium atoms are light blue, and hydrogen atoms are white. The actual adsorption sites as part of the slab is shown above the adsorbed Sb onto the plane slabs.

shifted to lower values after Sb(III) and Sb(V) adsorption. The core level shifts indicated an electron transfer in the valence band involving the reaction between Sb and ZrO₂. This finding indicates that the Zr–O site plays an indispensable role in Sb adsorption. All the XPS fitting results details, including peak positions and assignment, are shown in Table S5.

DFT Calculations. As shown in Figure 7a and b, the adsorption energy (E_{ad}) of Sb(III) onto t-ZrO₂ (111) (1.13 eV) is higher than the m-ZrO₂ (111) plane (0.76 eV). Apparently, t-ZrO₂ (111) provides a more stable adsorption site for Sb(III) than m-ZrO₂ (111) and this can be attributed to different more favorable bond lengths and atom net charges. Sb(III) is clearly forms an ionic bond to the surfaces of t-ZrO₂ (111) and m-ZrO₂ (111). The bond lengths between Sb–O and O–Zr depend the crystal phases. For the t-ZrO₂ (111) adsorption, the bond lengths of Sb–O and O–Zr are 2.42 and 2.10 Å, respectively. For m-ZrO₂ (111), the bond lengths of Sb–O and O–Zr are 2.35 and 2.27 Å. We calculated the net change in charge of the Sb(III) atom for adsorption onto t-ZrO₂ (111) plane and it was only +0.01. This result suggests that electron transfers from Sb to O are ionic for t-ZrO₂ (111) (See the value on the purple Sb(III) atom in Figure S7a). For the m-ZrO₂ (111) plane, we calculated a change of –0.08 for the Sb(III) atom (See the value on the purple Sb atom in Figure S7b).

Analogous results were obtained for the Sb(V) adsorption. In Figure 7c and d, the E_{ad} of Sb(V) on t-ZrO₂ (111) (6.07 eV) is higher than the m-ZrO₂ (111) plane (3.35 eV). Only the O–Zr bond is formed on the surface of t-ZrO₂ (111) and m-ZrO₂

(111). The O–Zr bond lengths in t-ZrO₂ (111) are 2.24 and 2.26 Å, respectively. For m-ZrO₂ (111), the O–Zr bond lengths are 2.07 Å, 2.25 and 2.40 Å, respectively. A weak H–O bond is also formed between Sb(V) and m-ZrO₂ (111). The different E_{ad} values contribute to the net charge change. The net charge of the Sb atom has changed after adsorbing to the surface of ZrO₂. For t-ZrO₂ (111), the change in charge for the Sb(V) atom is +0.02 (See the value on the purple Sb(V) atom in Figure S7c). While on the m-ZrO₂ (111), the change in charge for the Sb(V) atom is +0.09 (See the value on the purple Sb(V) atom in Figure S7d).

The E_{ad} of Sb(V) is much higher than E_{ad} of Sb(III) because Sb(V) is negatively charged and has a larger molecular volume than Sb(III). The different ring structure formed on the surface of t-ZrO₂ (111) plane and m-ZrO₂ (111) plane may have an influence on the E_{ad} as well. A four-membered ring is formed when Sb(III) atom is adsorbed onto the surface of the t-ZrO₂ (111) plane (Figure 7a inset), whereas a six-membered ring is formed on the surface of the m-ZrO₂ (111) plane (Figure 7b inset). In the Figure 7c inset, a similar four-membered ring structure is formed after Sb(V) is adsorbed on the surface of t-ZrO₂ (111) plane. An even more complicated structure (i.e., eight-membered ring) is formed on the m-ZrO₂ (111) plane after Sb(V) is adsorbed onto the surface.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02903.

Section S1–S2, Tables S1–S5 and Figures S1–S7 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is financially supported by the Major Program of the National Natural Science Foundation of China (No. 51290282) and National High Technology Research and Development Program of China (No. 2012AA062604). We also appreciate support from the Brook Byers Institute for Sustainable Systems, Hightower Chair and Georgia Research Alliance at Georgia Institute of Technology.

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