Adsorption behavior of arsenic onto protonated titanate nanotubes prepared via hydrothermal method

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ABSTRACT

A mesoporous material, titanate nanotubes (TNs) with different surface areas (197–312 m² g⁻¹) and pore size diameters (2–6 nm) was synthesized by alkaline hydrothermal method. Their adsorption abilities to arsenic, the notoriously poisonous inorganic contaminant in groundwater were evaluated. Batch experiments showed that the adsorption of arsenate [As (V)] was more favored in acid solution, while the uptake of arsenite [As (III)] was preferred in alkaline solution. The maximum uptake of As (V) and As (III) calculated by Langmuir equation was 208 mg g⁻¹ (pH 3.0) and 60 mg g⁻¹ (pH 7.0) respectively achieved on TN (180-1) adsorbent (312 m² g⁻¹, internal diameter, 5 nm), which was 33 and 10 times greater than those of nanosized titania particles (40–50 nm, 15 mg g⁻¹). Silicate anions, phosphate and sulfate had little effect on arsenic adsorption onto TNs. In several real water samples, TNs still showed high uptake efficiency to arsenic at pH 7.0. More than 80% of As (III) and 95% of As (V) adsorbed on TNs could be desorbed with 1.0 M NaOH solution within 1 h. Comparison study indicated that all the tubular titanate materials exhibited great adsorption capacity to arsenic regardless their surface areas. Since the equipment required for TNs synthesis is simple and cheap, and alkali solutions are reusable, TNs can be regarded as an efficient, low-cost adsorbent for the removal of arsenic.

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1. Introduction

Arsenic, a common constituent of the earth's crust, has been the concern of the world for many years for its high toxicity and carcinogenicity [1–3]. Arsenic exists in natural water predominantly as inorganic arsenate, As (V) and arsenite, As (III) [3–7]. Elevated concentrations of arsenic are found in groundwater in many regions around the world, which are caused by the release of arsenic from As-bearing sediments or anthropogenic sources [8–10]. The World Health Organization (WHO) has revised the guideline for arsenic in drinking water from 50 to 10 µg L⁻¹ considering its high toxicity.

Many different technologies have been developed to remove arsenic from water, such as adsorption, coagulation/precipitation, ion-exchange, and so on [3,6,7]. Among them, adsorption is considered to be one of the most promising technologies for its simplicity in operation and cost-effectivity [3]. Natural materials such as zeolite [11], natural iron ores [7,12,13], siderite [14] and red mud [15] have been examined intensively for arsenic removal. Although these materials are regarded as cheap and effective adsorbents,

there are several problems (their impurities, unknown stability and regeneration, low adsorption capacity and slow kinetics) associated with their use [4,13,16]. An ideal adsorbent should have suitable particle size or uniformly accessible pores, high surface area, and physical and/or chemical stability [4]. Recently, nano-scale metal oxides such as mesoporous alumina [4], TiO₂ [8], and zero-valent iron [5] have attracted the attention of researchers, and they have shown great advantage towards arsenic removal.

Lately, titanate nanotube (TNs) with small diameters (less than 10 nm) prepared by alkaline hydrothermal method is of particular interest for its potential application as hydrogen sensors, mesoporous catalyst supports, solar cell photosensitizers, ion-exchange materials and so forth [17,18]. This material can be easily fabricated by hydrothermal treatment of TiO₂ (anatase, rutile brookite or amorphous forms) in highly concentrated NaOH aqueous solution at moderate temperatures (90–180 °C). Compared with the template and sol-gel processes, this method is very simple with high quality and high yield (100% efficiency) [18]. The equipment required is simple and alkali solutions are reusable, showing that this method has potential for large-scale industrial production [19]. TNs have large surface area (300–400 m² g⁻¹), and possess more functional hydroxyl groups on the surface [20]. Moreover, almost all protons of these OH groups can be easily exchanged with alkali or transition metal cations in aqueous solution [18,21].

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Therefore, we assume that at $\text{pH} < \text{pH}_{\text{pzc}}$ (point of zero charge), TNs would have great adsorption potential to arsenic anions. Then the purpose of our study is to investigate the adsorption feasibility of TNs for arsenic, and provide a new, efficient and low-cost adsorbent for arsenic removal.

2. Experimental section

2.1. Chemical reagents

All chemicals were analytical grade and purchased from Beijing Chemical Co. (Beijing, China). The arsenite and arsenate stock solution were prepared with deionized (DI) water using NaAsO_2 and $\text{Na}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, respectively. Arsenic working solutions were freshly prepared by diluting stock solution with DI water. In some experiments, a tap water sample from our laboratory, a well water sample from the campus of China Agricultural University, and a river water sample from Jing Mi canal were used. The chemical compositions of water samples were summarized in Table S1. In all the samples the concentration of arsenic was below the detection limits (0.5 ng mL^{-1}) determined by hydride generation-atomic fluorescence spectroscopy.

2.2. Preparation of protonated titanate nanotubes

The raw materials for TNs preparation included nanosized titania particle (TP, 40–50 nm, $15 \text{ m}^2 \text{ g}^{-1}$) and sodium hydroxide. The surface area and pore size diameters of TNs were controlled by varying the reacting temperature and contact time of TP and 10 M NaOH solution. Generally, 3 g of titania was dispersed into 100 mL of 10 M NaOH solution, and remained in polytetrafluoroethylene autoclave to be heated at 110, 130, 150 °C for 24 h, or at 180 °C for 10 h or 48 h respectively [the products were coded as TN (110), TN (130), TN (150), TN (180-1) and TN (180-2) respectively]. The white products were washed with DI water to neutral, and then soaked in 0.5 M hydrochloric solution for 5 h. During the soaking of the nanotubes in acid solution, the interlayer sodium ions were anticipated to be exchanged for the protons. Then the protonated titanate nanotubes were washed to pH 7 with deionized water again. Finally, the products were dried at 100 °C.

2.3. Batch adsorption test

Batch experiments were performed to examine the adsorption behavior of arsenic on different adsorbents. Adsorption of arsenic as a function of pH onto protonated TNs was first examined in a series of experiments where the initial arsenic concentration was maintained constant (namely arsenate 5 mg L^{-1} and arsenite 25 mg L^{-1}) at varying pH values (pH 2–11) and then the optimum pH for adsorption was determined. But for TN (180-2) and TP, the initial concentration of arsenate and arsenite was 1 mg L^{-1} . Adsorption isotherm studies were conducted with initial arsenate or arsenite concentrations ranging in $1\text{--}500 \text{ mg L}^{-1}$ or $0.1\text{--}200 \text{ mg L}^{-1}$ at optimal pH in DI water. All batch tests were executed in 150 mL of glass bottles by taking 25 mg (dry weight) of TNs or TP adsorbent together with 25 mL of arsenic solution. Reactions proceeded for 24 h at 25 °C in a shaken water batch (200 rpm). The solution pH was adjusted with 1 M HCl and/or 1 M Tris, the ionic strength was controlled to 0.02 M with 1 M NaCl solution. However, for real water samples, the adsorption isotherms for arsenic species were carried out at pH 7.0 without control of ionic strength. In order to test the effects of coexisting anions, the adsorption isotherms were also studied with 5, 20 or 50 mg L^{-1} of NaH_2PO_4 , NaSiO_3 and Na_2SO_4 spiked into solution individually.

After mixing, the solid and solution were separated by centrifugation at 10,000 rpm for 10 min. Then a portion of supernatant was diluted to 5 mL with DI water and analyzed with hydride generation-atomic fluorescence spectroscopy (HG-AFS) with an AF-610A instrument (Beijing Ruili Analytical Instrument Co., Ltd. China). HCl solution (2%, V/V) was used as carrying fluid. All samples were analyzed within 24 h after collection. Duplicate adsorption experiments were conducted, and averaged results were reported.

Desorption tests were studied using alkaline solution to examine whether the adsorbent could be recycled. The desorption solution was adjusted by 6 M NaOH solution, and for arsenate the NaOH concentration was in the range of 0.01–1.0 M or pH 9.0; for arsenite NaOH concentration was varied from 0.01 M to 1.5 M. After adsorption of arsenic, the TNs were washed with 2 mL of DI water, then mixed with $2 \text{ mL} \times 3$ of desorption solution. The mixture was shaken for 4 h followed by a centrifugation at 10,000 rpm for separation. A kinetic study of desorption was conducted using 1.0 M NaOH solution.

2.4. Adsorbents characterization

An X-ray powder diffractometer (Rigaku III/B max) was used to analyze the crystalline structures of adsorbents. The radiation source was Cu K α . The applied current was 30 mA, and the voltage was 40 kV. During the analysis, the sample was scanned from 10° to 100° at a speed of $0.4^\circ/\text{min}$. Transmission electron micrograph (TEM) images were recorded on a H7500 transmission electron micrograph (Hitachi, Japan) operating at 120 kV. The points of zero charge of the materials were determined with zetasizer 2000 apparatus (Malvern, United Kingdom). The specific surface areas of adsorbents were determined by the BET method with N_2 gas (ASAP2000V3.01A; Micromeritics, Norcross, GA).

To detect the arsenic species adsorbed on the surface of the adsorbent after reaction with arsenite or arsenate, some selected samples were freeze-dried for further analysis using XPS collected on an ESCA-Lab-220i-XL spectrometer with monochromatic Al K α radiation (1486.6 eV). C1s peaks were used as an inner standard calibration peak at 284.7 eV. XPS data process and peak fitting was preformed using a nonlinear least-squares fitting program (XPSpeak software 4.1, Raymund W. M. Kwork).

3. Results and discussion

3.1. Characterization of protonated TNs and TP

TNs synthesized with hydrothermal method had well-defined and uniformly tubular morphology. Compared with carbon nanotubes, the titanate tubes were less adhesive to each other; the tube ends were released and kept open. As shown in Table 1 and Fig. 1, the surface areas ($197\text{--}312 \text{ m}^2 \text{ g}^{-1}$) and outer diameters of the TNs (5–13 nm) increased with the rising of heating temperature. However, for TN (180-2), the tubular structure disappeared, and nano-sized fibers formed instead, which was consistent with the results reported by Lee et al. [22], Yuan and Su [23] and Bavykin et al. [24]. XRD results of TP showed that the raw material was a mixture of rutile and anatase (Fig. 2). As reported by other researchers [22,25], though the TNs had been soaked in hydrochloric acid for a long time, sodium ions could not be substituted completely by protons. $\text{Na}_2\text{Ti}_6\text{O}_{13}$ peaks in the XRD patterns of TNs were observed, while for nanofiber [TN (180-2)], distinct $\text{Na}_2\text{Ti}_3\text{O}_7$ peaks were identified. The point of zero charge (PZC) of all materials was determined by their zeta potential in solution at different pH. Compared with TP (pH_{PZC} 6.3), the pH_{PZC} value for TNs had shifted to a lower pH range (pH 4.8–5.4), and the nanofiber possessed the lowest value of pH_{PZC} (pH 4.5). Since all the hydroxyl

Table 1

Points of zero charge, BET surface areas and size of raw materials (TP) and products (TNs).

Material	PZC value ^a	BET surface area (m ² g ⁻¹) ^b	External diameter (nm)	Internal diameter (nm)
TP	pH 6.3	15.63	30–50	
TN(110)	pH 5.4	197.05	5	2–3
TN(130)	pH 5.3	311.26	7	3–4
TN(150)	pH 5.1	279.78	11	5–6
TN(180-1)	pH 4.8	312.59	13	4.5–5.5
TN(180-2)	pH 4.5	37.83	44	

^a Points of zero charge of TP and TNs obtained by their zeta potentials in solution with 0.1 M NaCl at varied pH.^b Determined from the Brunauer Emmett Teller (BET) equation. **Fig. 1.** TEM image of (a) TP, (b) TN (180-2), (c) TN (180-1), (d) TN (150), (e) TN (130) and (f) TN (110).

groups on TNs surface could be deprotonized, the lower pH_{PZC} might mean more hydroxyl groups existing on the surface of nanofibers or TNs.

3.2. Adsorption behavior and mechanism of arsenic on protonated TNs

Arsenic adsorption reached equilibrium after 1 h of reaction with TP and TN (180-2). Possibly due to their tubular structure, longer contact time was demanded for the effective uptake of arsenic on TNs compared to TP and the nanofibers. The adsorption equilibrium of arsenic on all the tubular titanate was observed after 8 h of contact (Fig. 3). Arsenic adsorption was dependent on the initial solution pH (Fig. 4). All adsorbents showed similar adsorption trend towards arsenite and arsenate: the adsorption of arsenate was more favored in acid solution, and the uptake of arsenite was preferred in alkaline solution. The optimal pH ranges for arsenite and arsenate adsorption on TNs were pH 2.5–3.5 and pH 7.0–9.5 respectively, which were much wider than those of TP and TN (180-2). In the pH range of 6.0–7.5, the uptake of arsenate on TNs was greater than 70% with initial concentration of 25 mg L⁻¹. For arsenite, 70% of As (III) still could be adsorbed at pH 10.5. In the pH range of 2.5–11.5, the predominant arsenate species exist as H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$ [10]; and the main arsenite species is neutral H_3AsO_3 at pH < 9.2 [8]. The strong adsorption of arsenic at pH > pH_{PZC} might suggest that the arsenic species were

adsorbed on TNs through surface complexation, rather than electrostatic interactions. During the adsorption of arsenite and arsenate, the equilibrium pH decreased obviously with higher initial pH indicating the deprotonation of arsenic enhanced by their reaction with adsorbents, which were helpful for their adsorption.

Zeta potentials of TN (180-1) in both the presence and absence of 1 mg L⁻¹ arsenate or arsenite were described in Fig. 5. The adsorption of either arsenate or arsenite decreased the pH_{PZC} of TN (180-1) to approximately 4.3 and 4.0. It was reported that the formation of outer-sphere surface complexes could not shift the pH_{PZC} since there were no specific chemical reactions between the adsorbate and the surface that could change the surface charge. But the shift of pH_{PZC} to a lower pH range could be caused by the formation of anionic negatively charged surface complexes [8]. These results implied that the adsorption of arsenic would be based on the negatively charged inner-sphere complexes between As (V) or As (III) and TNs.

To further understand the adsorption mechanism of arsenic and investigate the oxidation state of arsenic species adsorbed on the surface of TNs, XPS data of TN (180-1) before and after reaction with arsenic were studied. After reaction with As (V) and As (III), the Ti atom content decreased by 16% and 9.5% respectively (shown in Supplementary data, Table S2); while the content of oxygen atom increased instead which was attributed to the introduction of arsenic oxyanions or water molecule [26]. The XPS spec-

Fig. 2. XRD patterns of the nanosized titania particles (TP) and products obtained from hydrothermal NaOH treatment of TP at 110, 130, 150 °C for 24 h, and 180 °C for 10 or 48 h respectively [the products were coded as TN (110), TN (130), TN (150), TN (180-1) and TN (180-2), respectively].

Fig. 3. Effect of contacting time on the adsorption of As (V) (a) and As (III) (b) onto different adsorbents.

Fig. 4. Effect of solution pH on the adsorption of As (V) and As (III) onto TN (180-2), TP (a) and TN (180-1) (b). Initial concentration of arsenic: 1 mg L⁻¹ for TN (180-2) and TP; for TN (180-1) As (V) 25 mg L⁻¹, As (III) 5 mg L⁻¹.

Fig. 5. Zeta potential of 0.6 g L⁻¹ TN (180-1) and TN (180-1) with 1 mg L⁻¹ of As (V) or As (III) in 0.1 M NaCl solution.

tra of O1s were illustrated in Fig. 6b, the peak of O1s spectra of surface complexes had shifted to a more negative binding energy for As (V) and As (III) adsorption (from 530.46 to 530.57 or 530.66 eV respectively). After reaction with As (V), no increase of intensity of O1s was observed; but 13% of enhancement of O1s intensity was seen after adsorption of As (III), indicating the strong

interactions between As (III) and O atoms [3,26]. In Fig. 6c and d, there was only one peak of As3d or As2p after uptake of arsenic, the binding energy of 44.6 eV and 46.0 eV should be ascribed to As (V)–O and As (III)–O respectively, which was accordant with the binding energy of arsenic after reaction with iron oxide [3]. It could be suggested that there was no As (III) oxidized into As (V) during the adsorption process.

3.3. Equilibrium study

The equilibrium adsorption isotherm data at different TNs adsorbents were analyzed using Freundlich and Langmuir models [4,14].

$$q = K_F C^{1/n} \quad (1)$$

$$q = \frac{q_m K_L C}{1 + K_L C} \quad (2)$$

where q_m (mg g⁻¹) is the maximum adsorption capacity, q (mg g⁻¹) is the amount of adsorbed As, C (mg L⁻¹) is the equilibrium solute (As) concentration, K_F (mL^{1/n} μg^{1-1/n}) and n are the Freundlich constants, and K_L is the Langmuir constant. The results of fitting Freundlich and Langmuir equations to isotherm curves were summarized in Table 2. Regression coefficients (R^2) for different conditions were larger than 0.94, indicating that both the models fit reasonably well with the arsenic adsorption. Compared with TP adsorbent, TNs exhibited good adsorption ability to arsenic. The adsorption capacity values obtained both from Langmuir and Freundlich equations showed that the adsorption capacity of TNs increased slightly with their surface area. The maximum adsorption of As (V) and As (III) were observed both on TN (180-1) adsorbent, and the maximal adsorption capacity for As (V) and As (III) calculated by Langmuir isotherm was 204.1 and 59.5 mg g⁻¹ respectively at 25 °C, which were 33 and 10 times greater than those of TP. Compared with the nanocrystalline titanium dioxide [2] and Hombikat UV100 suspension [27] (≥ 330 m² g⁻¹, <10 nm), the adsorption capacity of protonated titanate nanotubes was a little low, especially for As (III). It was reported that the interlayer distance of multi-layers was about 0.7–0.8 nm [18] which was close to the radius of arsenate and arsenite ions (HAsO₄²⁻ 0.397 nm, HAsO₄⁻ 0.416 nm, H₃AsO₄ 0.416 nm, HAsO₃⁻ 0.48 nm, H₃AsO₃ 0.48 nm) [4]. Therefore the hydroxyl groups on the multiple intralayers might not be accessible to arsenic anions, resulting in the decrease of adsorption capacity to arsenic. Due to the photocatalytic property, the As (III) was usually adsorbed in the form of As (V) as nanocrystalline titanium dioxide was used, which was favorable for the adsorption of As (III). But no As (III) was oxidized into As (V) during the adsorption process in our study. However, the adsorption capacity of protonated TNs to arsenic was still comparable to some reported adsorbents such as mesoporous alumina [4].

The adsorption density at a particular residual concentration was calculated using [4]

$$\Gamma = \frac{(C_i - C_e)V}{mS} \times 10^{-3} \quad (3)$$

where S is the surface area (m² g⁻¹) of TNs adsorbents, m is the amount (g) of TNs, V is the volume of solution (mL), and C_i is the initial concentration of adsorbate (mol L⁻¹), and C_e is the equilibrium concentration of adsorbate (mol L⁻¹). The maximum adsorption density (Γ_{max}) was obtained from the adsorption data. Interestingly, the adsorption density of arsenic on TNs and nanofibers decreased with the increase of surface area. The largest adsorption density for As (V) and As (III) was observed on either nanofiber TN (180-2) or TN (110), which might be caused by their different adsorption sites available on their surface. Although the surface area of TP was smaller than TN (180-2), this material still showed

Fig. 6. The XPS of (a) Ti3d, (b) O1s, (c) As3d and (d) As2p core level of original titanate nanotubes [TN (180-1)], and TNs after reaction with As (V) (pH 3.0) and As (III) (pH 7.0).

Table 2

Langmuir, Freundlich isotherms and adsorption density values for As (V) and As (III) onto TNs, TN (180-2) and TP^a.

Adsorbent		Langmuir			Freundlich			Adsorption density $\Gamma_{\max}^e$
		K^b	q_m^c	R^2	K_F^d	n	R^2	
As (V)	TN (110)	0.019	188.7	0.983	20.7	3.00	0.977	13.06
	TN (130)	0.027	204.1	0.997	25.2	3.09	0.977	8.94
	TN (150)	0.023	192.3	0.997	23.9	3.01	0.993	9.22
	TN (180-1)	0.019	204.1	0.994	23.0	2.97	0.995	8.89
	TN (180-2)	0.148	28.7	0.976	5.15	2.46	0.944	10.26
	TP	0.087	6.15	0.974	0.74	2.09	0.969	5.32
As (III)	TN (110)	0.11	41.2	0.994	3.87	1.65	0.978	2.82
	TN (130)	0.09	55.6	0.994	4.17	1.56	0.969	2.41
	TN (150)	0.06	56.8	0.995	3.82	1.60	0.983	2.75
	TN (180-1)	0.08	59.5	0.992	4.90	1.80	0.977	2.57
	TN (180-2)	0.09	16.4	0.973	2.35	2.37	0.993	3.77
	TP	0.04	6.32	0.993	0.45	1.81	0.984	1.94

^a As (V) at pH 3.0, As (III) at pH 7.0, adsorbent, 1 g L⁻¹, 25 °C.

^b K (L mg⁻¹).

^c q_m (mg g⁻¹).

^d K_F (mL^{1/n} μg^{1-1/n}).

^e $\Gamma_{\max}$ (mol m⁻²)E-6.

the lowest adsorption density for arsenic among these adsorbents, indicating the binding sites density on TP surface was lower than TN (180-2). Additionally, the affinity of As (V) to the surface site of all the adsorbents was found to be 3–5 times as large as that of As (III).

It is reported that the maximum ion-exchange capacity for sodium ions can be as high as 1.1, expressed as a ratio between sodium and titanium atoms in the nanotubes (Na/Ti ratio). For some of transition metals, the ratio is in the range of 0.069–0.09

[18]. In our study, the As/Ti ratio was about 0.098 or 0.048 for As (V) and As (III) on TN (180-1) respectively (determined by XPS and EDX, Table S2).

3.4. Effect of competing anions

In a representative test, the effects of individual anions (silicate anions, phosphate and sulfate) on the adsorption capacity of TN (180-1), nanofiber or TP for As (V) and As (III) were investigated.

And the spiked amount of each anion was coincident with their maximum concentration detected in water samples. Generally, the adsorption capacity of arsenate on TN (180-1) had decreased by 12.5%, 11% and 9% in the presence of phosphate, silicate anions and sulfate separately; while no evidently competitive effects on the adsorption of As (III) onto TN (180-1) were observed with these coexisting anions (Table 3). Similar result was reported by Bang [10] about the removal of arsenic by granular TiO_2 . But for TN (180-2) and TP, the adsorption capacity of arsenic was affected clearly in the presence of anions (Table S3). With the spiked phosphate, silicate anions, the adsorption capacities of As (III) on nanofiber and TP were dropped to 60–70% or 65–85% respectively; and for As (V), a decrease of 35–40% or 50–60% of adsorption capacity were observed on the two adsorbents separately. These results probably meant that TNs also had high adsorption ability to phosphate, silicate or sulfate under the condition in our experiment.

3.5. Desorption of arsenic

To test the feasibility of TNs adsorbents to be regenerated after adsorption of arsenic, desorption study was carried out on TN (180-1) adsorbent. It was expected that increased concentration of OH^- should compete greatly with the already adsorbed arsenate and arsenite on TNs, hence sodium hydroxide solution was used to desorb arsenic from adsorbent. Generally, desorption of the arsenic ions was more favored in strong alkaline solution. With 0.05 M NaOH solution, 90% of the adsorbed As (V) was desorbed, and desorption percent could arrive at 95% if the concentration of NaOH was higher than 0.1 M. With regard to As (III), satisfactory desorption (85%) of the adsorbed ions achieved with relatively higher concentration of NaOH (1.0 M NaOH) (Fig. 7). Since the TNs were produced in 10 M NaOH solution and the tubes were more stable in base solution, desorption could be conducted in extreme alkaline solution to attain total desorption of adsorbed arsenic ions without destroy of the tubular structure of adsorbents. A kinetic study of desorption of adsorbed arsenic on TN (180-1) was performed using 1.0 M of NaOH solution (Fig. 8). The desorption kinetics were much faster than the adsorption process. The desorption equilibrium for As (V) and As (III) was observed after contact 1 h and 3 h respectively with NaOH solution. Within 1 h, 80% of arsenic (III) and 95% of arsenic (V) adsorbed to TNs could be desorbed.

3.6. Adsorption of arsenic from water samples

Batch studies on the adsorption of arsenic were conducted on tap water, groundwater and river water samples. In these samples, the level of As (V) and As (III) was below the detection limits of HG-

Fig. 7. Effect of NaOH concentration on desorption of As (V) and As (III).

Fig. 8. Desorption kinetics for As (V) and As (III) with 1.0 M NaOH solution.

AFS, and the adsorption isotherms for arsenic were carried out at pH 7.0 without control of ionic strength. For comparison, the adsorption capacity of As (V) on TNs at pH 7.0 in DI water was also determined. Consequently, an clearly decreased adsorption capacity of As (V) (Langmuir adsorption capacity, 82 mg g^{-1}) was observed, but the reduced capacity was still comparable with those obtained by other metal oxide adsorbents, such as granular TiO_2

Table 3

Langmuir and Freundlich parameters for As (V) and As (III) adsorption on TN (180-1) in the presence of anions^a.

		Langmuir			Freundlich		
		K (L mg^{-1})	q_m (mg g^{-1})	R^2	K_F	n	R^2
As (III)	No PO_4 or SiO_2 or SO_4^{2-}	0.08	59.5	0.992	4.90	1.80	0.977
	PO_4^b	0.058	56.8	0.995	4.34	1.89	0.993
	SiO_2^c	0.049	57.8	0.998	4.37	1.95	0.999
	SO_4^{2-d}	0.056	57.5	0.999	4.40	1.90	0.994
As (V)	No no PO_4 or SiO_2 or SO_4^{2-}	0.019	204.1	0.994	23.0	2.97	0.995
	PO_4	0.015	178.6	0.998	9.01	2.03	0.988
	SiO_2	0.017	181.8	0.996	11.2	2.18	0.984
	SO_4^{2-}	0.030	185.2	0.998	16.2	2.32	0.999

^a As (V), pH 3.0; As (III), pH 7.0; TN (180-1), 1 g L^{-1} .

^b 5 mg L^{-1} .

^c 20 mg L^{-1} .

^d 50 mg L^{-1} .

Fig. 9. Langmuir isotherms for (a) As (V), and (b) As (III) adsorption on TN (180-1) in several real water samples, pH 7.0; TN (180-1), 1 g L⁻¹

[10] and metal modified MCM-41 [28] in neutral solution. In these environmental water samples, the adsorption efficiency of spiked As (V) and As (III) by TNs was as high as those obtained in DI water (Fig. 9) and the maximal uptake capacity for As (V) and As (III) was 81.3 and 60 mg g⁻¹ respectively. Meanwhile, arsenite, the more toxic species of arsenic, could be removed with 95–100% efficiency in water samples at an initial arsenite concentration of $\leq 500 \mu\text{g L}^{-1}$ with the residual arsenic concentration less than $10 \mu\text{g L}^{-1}$.

4. Conclusion

The titanate nanotubes with high surface area, open tube end and uniform tubular size have exhibited fast uptake rate and high adsorption capacity to inorganic arsenic. The coexisting anions in

solution show little competition effect on the adsorption of arsenic onto TNs. The adsorbed arsenic can be desorbed with NaOH solution efficiently and quickly. Moreover, TNs manifest reasonable uptake efficiency to arsenic at pH 7.0 in several real water samples. Anyway, the results presented here have suggested the potential of TNs as an efficient material for the treatment of arsenic. However, more experimental work is required to evaluate the possible use of TNs under continuous flow conditions, which is under progress in our lab.

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Appendix. Supplementary data

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