Groundwater arsenic removal using granular TiO_2 : integrated laboratory and field study

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Received: 27 August 2014 / Accepted: 4 December 2014 / Published online: 18 December 2014
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Abstract High concentrations of arsenic (As) in groundwater pose a great threat to human health. The motivation of this study was to provide a practical solution for As-safe water in As geogenic areas using granular TiO_2 (GTiO₂). The kinetics results indicated that the As (III/V) adsorption on GTiO₂ conformed to the Weber-Morris (WM) intraparticle diffusion model. The Langmuir isotherm results suggested that the adsorption capacities for As (III) and As (V) were 106.4 and 38.3 mg/g, respectively. Ion effect study showed that cationic Ca and Mg substantially enhanced As (V) adsorption, whereas no significant impact was observed on As (III). Silicate substantially decreased As (V) adsorption by 57 % and As (III) by 50 %. HCO_3^- remarkably inhibited As (V) adsorption by 52 %, whereas it slightly reduced As (III) adsorption by 8 %. Field column results demonstrated that ~700 $\mu\text{g/L}$ As was removed at an empty bed contact time (EBCT) of 1.08 min for 968 bed volumes before effluent As concentration exceeded 10 $\mu\text{g/L}$, corresponding to 0.96 mg As/g

GTiO₂. Two household filters loaded with 110 g GTiO₂ in the on-off operational mode can provide 6-L/day As-safe drinking water up to 288 and 600 days from the groundwater containing ~700 $\mu\text{g/L}$ As and ~217 $\mu\text{g/L}$ As, respectively. Integration of batch experiments and column tests with systematic variation of EBCTs was successfully achieved using PHREEQC incorporating a charge distribution multisite complexation (CD-MUSIC) model and one-dimensional reactive transport block.

Keywords Groundwater arsenic · Granular TiO_2 · Adsorption · Empty bed contact time · CD-MUSIC · PHREEQC · XANES

Introduction

High arsenic (As) in groundwater poses a severe health risk to 100 million people worldwide (Fendorf et al. 2010; Rodriguez-Lado et al. 2013). To provide As-safe drinking water, the groundwater in deep aquifers (>150 m) is suggested as an alternative source (Michael and Voss 2008). However, such large-scale exploitation could facilitate the downward migration of As-enriched shallow groundwater and ultimately contaminate the deep aquifers (Erban et al. 2013). Thus, the practical solution relies on effective and efficient As removal technologies in geogenic As areas.

As a cost-effective and user-friendly technique, adsorptive filtration is widely used in fixed bed columns without chemical addition (Ali et al. 2014; Dou et al. 2013; Kanematsu et al. 2012; Zeng et al. 2008). As summarized in Table S1 in the electronic supplementary material, iron-based adsorbents are some of the most commonly used media in As treatment. However, soluble iron may increase As toxicity (Chandrasekaran et al. 2010; Liu et al. 2013). Recently, a TiO_2 -based adsorbent demonstrated its advantage in As

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-3955-8) contains supplementary material, which is available to authorized users.

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removal due to its chemical stability and high specific affinity to As (Bang et al. 2005; Hristovski et al. 2008; Jing et al. 2009; Luo et al. 2010). Therefore, granular TiO_2 (GTiO₂) was adopted in our approach to remove high As in groundwater from geogenic areas.

Coexisting ion effects on As removal are usually evaluated using synthetic water. Cationic calcium (Ca^{2+}) and magnesium (Mg^{2+}) generally facilitate As (V) adsorption, while exhibiting a negligible or insignificant effect on As (III) (Kanematsu et al. 2013; Stachowicz et al. 2008). On the other hand, coexisting anions such as phosphate (P), silicate (Si), and bicarbonate (HCO_3^-) can suppress As adsorption (Meng et al. 2000; Stachowicz et al. 2008; Zhao and Guo 2014). Though the effect of coexisting ions has been widely studied in batch systems, the compounded influence on As removal in GTiO₂ columns is still not fully understood (Bang et al. 2005).

Extensive research has successfully employed adsorptive columns to remove As from groundwater (Table S1). However, three main challenges still remain that warrant further investigation. First, the As concentrations in previous studies averaged $98.6 \pm 152.2 \mu\text{g/L}$ ($n=82$, Table S1 and Fig. S1). Very few studies employed high groundwater As levels (~ 500 to $\sim 1000 \mu\text{g/L}$) (Luo et al. 2012; Zhao et al. 2014), which could rapidly saturate the capacity of adsorbents (Kanematsu et al. 2012; Li et al. 2012). Second, systematic study on the influence of variation of empty bed contact time (EBCT) has been limited, though EBCT can regulate As breakthrough curves (Zeng et al. 2008). Third, the parameters obtained from batch adsorption results should be used with caution when designing column experiments (Jeppu et al. 2012; Zhang and Selim 2006). These challenges motivate us to explore the effect of EBCT in treating elevated As groundwater and to integrate batch and column results.

The objective of this study was to evaluate As removal from elevated As groundwater using a series of EBCTs in GTiO₂ columns. Four major interfering ions were identified, Ca^{2+} , Mg^{2+} , Si, and HCO_3^- , and their effects on As removal were investigated under systematic variation of EBCTs using PHREEQC modeling. This geochemical model (Parkhurst and Appelo 2013), integrating batch adsorptive reactions with one-dimensional reactive transport, accurately predicts the As removal process in column experiments.

Materials and methods

Materials

Stock solutions were prepared with reagent grade NaAsO_2 , $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$, NaCl , $\text{Na}_3\text{SiO}_4 \cdot 9\text{H}_2\text{O}$, CaCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaHCO_3 , NaOH , and HCl (Sinopharm Chemical Reagent Co. Ltd., China). GTiO₂ was obtained using our reported method (Jing and Cui 2011). Geogenic groundwater

#1 from a rural well containing $\sim 700 \mu\text{g/L}$ As at $\text{pH } 8.20 \pm 0.06$ (Table S2) was used in batch and column experiments on site in Shanxi, China. The synthetic water (Table S3) was prepared using boiled deionized (DI) water with N_2 purging to remove dissolved O_2 . The synthetic water was adjusted to $\text{pH } 8.2$ according to groundwater #1.

Batch experiments

To study the kinetics of As adsorption, batch experiments were performed by mixing $800\text{-}\mu\text{g/L}$ As (III/V) solution at $\text{pH } 8.2$ with 0.2 g/L GTiO₂ in a 1-L beaker wrapped with aluminum foil. Samples were taken at designed time intervals and passed through a $0.22\text{-}\mu\text{m}$ membrane filter for soluble As analysis. The adsorption kinetics was simulated using Weber-Morris (WM) intraparticle diffusion model: $q_t = k_p t^{0.5} + b$, where q_t is the amount of adsorbed As (mg/g) at time t (h), k_p (mg/g/h^{0.5}) is the equilibrium rate constant for intraparticle diffusion, and b (mg/g) is the constant depicting the boundary layer effects (Dou et al. 2013).

To investigate As removal capacity on GTiO₂, adsorption isotherms were conducted by adding increasing amounts of As (III) and As (V) in 0.1 M NaCl at $\text{pH } 8.2$ with 1 g/L GTiO₂. The suspension samples were mixed on a rotator for 6 days based on kinetics results. The adsorption capacity of GTiO₂ was calculated using the Langmuir equation: $C_e/q_e = 1/q_m b + C_e/q_e$, where C_e (mg/L) is the equilibrium concentration of As (III) or As (V), and q_e (mg/g adsorbent) is the adsorbed amount of As (III) or As (V); q_m (mg/g) and b (L/mg) are the fitting parameters representing the maximum adsorption capacity and the adsorption affinity constant, respectively.

To investigate the effect of cations on As removal, a series of Ca^{2+} and Mg^{2+} concentrations were added with $800 \mu\text{g/L}$ As (III/V) in 0.1 M NaCl at a cation/As molar ratio varying from 0 to 1200. The solution was then mixed with 0.1 g/L GTiO₂ at $\text{pH } 8.2$ for 6 days. To explore anion effect, Si (8.9 mg/L) and HCO_3^- (388 mg/L) were added at similar levels as in groundwater #1 (Table S2). Ca^{2+} , Mg^{2+} , Si, and HCO_3^- were simultaneously added to investigate their coexisting effects on As removal.

The dose effect of GTiO₂ on As removal from groundwater #1 was performed in the field. Different dose of GTiO₂ was used to remove $800 \mu\text{g/L}$ As (III/V) in 0.1 M NaCl at $\text{pH } 8.2$ in the laboratory.

Field column studies and household pitcher application

The field column studies were performed using columns with diameter of 2.3 cm and length of 6.9 cm loaded with 26.2 g GTiO₂, resulting in a bed volume (BV) of 28.5 mL . The design parameters were determined according to the following equation: $\text{EBCT} = V_{\text{empty}}/Q$, where Q is the water flow rate (mL/min), V_{empty} is the volume of the empty bed (mL) (Zeng

et al. 2008). The designed EBCT was 0.11, 0.22, 0.32, 0.54, and 1.08 min, corresponding to a flow rate of 265.0, 132.5, 88.3, 53.0, and 26.5 mL/min, respectively. The upflow rate was controlled using a peristaltic pump (BT00-300 M, Longer, China).

To set up the column, groundwater was first slowly pumped into the column, and then, GTiO₂ was cautiously poured into the column to eliminate the trapping of air bubbles. Glass wool was packed in the ends of the column to guarantee no loss of the adsorbent. The columns were wrapped with aluminum foil to prevent light exposure. Samples of groundwater and effluent were collected periodically, passed through a 0.22- μ m membrane filter, and preserved in the dark with 5 % HCl at 4 °C (McCleskey et al. 2004). Random effluent sample was filtered through a speciation cartridge to separate As (III) and As (V) on site (Du et al. 2014a) and confirmed the absence of As speciation change during sample storage.

A cylindrical filter house (diameter=4.5 cm, length=8.5 cm) loaded with 110 g GTiO₂ was installed in a water pitcher to treat As-tainted groundwater #1 and #2 (containing ~200 μ g/L As in Table S2) from two wells. Generally, the water pitcher was used to filter 6 L of groundwater per day in an on-off operational mode.

Sample analysis

The As speciation and concentration were determined using high-performance liquid chromatography (HPLC) coupled with a hydride generation atomic fluorescence spectrometer (HG-AFS, Jitian, P. R. China). Briefly, online separation of As species was carried out with a Hamilton PRP-X100 anion exchange column, using 15 mM phosphate buffer at pH 6 as mobile phase at 1.0-mL/min flow rate. The detection limit was 1.7 μ g/L for As (V) and 0.7 μ g/L for As (III) (Cui et al. 2013). Concentrations of dissolved Ca, Mg, Na, Si, K, Al, Fe, and Mn were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8300, Perkin Elmer, US). Anions including F⁻, Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻ were measured using an ion chromatography system, DX-1100 (Dionex, US). Alkalinity was measured using the titration method.

Surface complexation and one-dimensional transport modeling

A charge distribution multisite complexation (CD-MUSIC) model with the triple plane option was used to describe the competitive As adsorption behaviors. The basic principles and modeling procedures have been well documented (Du et al. 2014b; Hiemstra and Van Riemsdijk 2006; Jing et al. 2012) and detailed in the electronic supplementary material.

The field column results were simulated using PHREEQC mode (version 3.0), which could integrate CD-MUSIC and transport block. Recently, PHREEQC has been applied in modeling pollutant adsorption and transport in one-dimensional columns importing well-founded thermodynamic database (Parkhurst and Appelo 2013). The water chemistry parameters, GTiO₂ surface properties, adsorptive reactions of As and coexisting ions, and transport parameter modeling are detailed in the electronic supplementary material with a PHREEQC input file with explanation notes (Table S4).

Characterization

The surface morphology of GTiO₂ was examined using a Hitachi S-3000 N scanning electron microscope (SEM) with an Oxford energy dispersive X-ray (EDS) analyzer. The BET surface area was determined using an automated surface area analyzer (Micromeritics ASAP 2000). X-ray powder diffraction (XRPD) data of GTiO₂ were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube and a graphite monochromator. The analyses of the XRPD patterns were performed using the PDF-2 reference database from the International Center for Diffraction Data database. The As speciation on spent GTiO₂ media in the field was analyzed using X-ray absorption near edge structure (XANES) spectroscopy at beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The sample preparation, data collection, and analysis are reported in the electronic supplementary material.

Results and discussion

Characterization of GTiO₂

The particle size of GTiO₂ was 60–80 mesh (0.18–0.25 mm) and is easier to be loaded in filtration columns than the nanoscale TiO₂ particles (Luo et al. 2010). The media exhibited a porous structure and coarse surface as evidenced by the SEM image (Fig. S2a) and a surface area of 196 m²/g. The XRD analysis indicated that GTiO₂ was in anatase form (Fig. S2b) according to the PDF-2 reference database.

As (III/V) adsorption results

The kinetics results indicated that a rapid As (III/V) uptake on GTiO₂ occurred for the first 5 h followed by a slow adsorption (Fig. 1a). The adsorption kinetics conformed to the intraparticle diffusion model as described by the WM equation. The plots of q_t versus $t^{0.5}$ implied the existence of two different processes from the steepness of the slope (Fig. 1b). The first step with a steep slope suggests external film

Fig. 1 As (III/V) adsorption on GTiO₂ as a function of time *t* (a) and *t*^{0.5} (b) based on Weber-Morris (WM) intraparticle model in synthetic water. The initial As concentration was 800 µg/L with 0.2 g/L GTiO₂ at pH 8.2. Solid lines represent WM model results

diffusion, whereas the second step with a flattened slope indicates that intraparticle diffusion is the rate-controlling process. The WM adsorption kinetics of GTiO₂ follows the behavior of porous media adsorption (Dou et al. 2013).

As (III) exhibited a little faster external and intraparticle diffusion kinetics from the WM model (0.583 and 0.218 mg/g/h^{0.5}, respectively, in Table S5) than As (V) (0.497 and 0.133 mg/g/h^{0.5}), consistent with a previous report using GTiO₂ (Bang et al. 2005).

The maximum adsorption capacities were 106.4 mg/g for As (III) and 38.3 mg/g for As (V), as calculated with the Langmuir model (Fig. 2). In comparison with the widely used granular adsorbent in previous reports (Table S6), GTiO₂ demonstrated a better As removal efficiency, especially for As (III).

Dose effect on As (III/V) removal using synthetic water and groundwater #1

Higher dose of GTiO₂ resulted in a better As removal in 0.1 M NaCl solution and real groundwater #1 (Fig. 3), which should be due to the increased adsorbent surface area (Ali et al. 2014). Nevertheless, groundwater matrices substantially inhibited As (V/III) adsorption in comparison with that in 0.1 M NaCl at the same dose. The inhibition should be attributed to the

competitive adsorption of Si and HCO₃[−] (Kanematsu et al. 2013; Stachowicz et al. 2008). Although phosphate (P) in groundwater has a significant negative effect on As adsorption (Kanematsu et al. 2013; Zeng et al. 2008), the low P concentration in groundwater #1 (<20 µg/L) and groundwater #2 (80 ±40 µg/L) could lead to neglected influence on As adsorption in comparison with Si. This hypothesis was justified by a previous study that Si (9.5 mg/L) exhibited a more negative effect than P when the P concentration (39 µg/L) is no higher than As (100 µg/L) (Kanematsu et al. 2012; Zeng et al. 2008).

The adsorption curves of As (III) and As (V) were well simulated using the CD-MUSIC model (Fig. 3). The modeling results indicated that in 0.1 M NaCl, the extended contact time of 6 days resulted in a logK value of 5.1 for As (III) and 26 for As (V). The logK values obtained with 6-day contact time were higher than those of 4.0 for As (III) and 23.3 for As (V), respectively, with a short contact time of 6 h. This observation is in agreement with a recent report that the logK of As (V) adsorption on ferrihydrite was linearly increased as a function of adsorption time (Swedlund et al. 2014). The change in logK value reflects the slow kinetics of As adsorption to reach equilibrium due to intraparticle diffusion in the porous adsorbent. In groundwater #1 at 6 h, the logK values of As (III) and As (V) adsorption were 6.6 and 21.8, respectively. These logK values are different from those in 0.1 M NaCl solution, which may be ascribed to the influence of coexisting ions.

The adsorption of coexisting Ca, Mg, and Si in groundwater on GTiO₂ was also well simulated using the CD-MUSIC model (Fig. S3). Their adsorption constants (Table S7) were employed in the simulation of As adsorption in 0.1 M NaCl solution with coexisting cations and anions.

Coexisting ion effect on As (III/V) adsorption

Increasing concentrations of Ca²⁺ and Mg²⁺ elevated As (V) adsorption on GTiO₂ (Fig. 4). The molar ratio of Ca²⁺/As (V) and Mg²⁺/As (V) in groundwater was 251 and 1116 (black dashed lines in Fig. 4), respectively, which enhanced As (V) adsorption by 37 and 42 %. The enhancement of As (V) by cationic ions should be caused by the electrostatic attraction (Kanematsu et al. 2013; Stachowicz et al. 2008). In contrast to

Fig. 2 Adsorption isotherms of As (III) (red square) and As (V) (black triangle) at pH 8.2 in 0.1 M NaCl with 1 g/L GTiO₂ for four replicates in 6 days. The solid lines represent the Langmuir model, and the parameters are inserted

Fig. 3 As (III/V) (800 µg/L) adsorption in 0.1 M NaCl with contact time of 6 h (square) and 6 days (diamond), and 595 µg/L As (III) and 149 µg/L As (V) adsorption in groundwater #1 with contact time of 6 h (triangle) under different dose of GTiO₂. The solid lines represent the CD-MUSIC model

As (V), As (III) adsorption was not affected in the presence of Ca²⁺ and Mg²⁺, which is in accordance with a previous study (Kanematsu et al. 2013).

Si substantially decreased the adsorption of As (III) by 50 % from 6.0 to 3.0 mg/g and that of As (V) by 57 % from 4.9 to 3.0 mg/g (Fig. 5). HCO₃⁻ significantly inhibited As (V) adsorption by 52 % from 5.0 to 2.4 mg/g. In contrast, As (III) adsorption declined by only 8 %, in line with a previous study (Maiti et al. 2013). The similar molecular structures of Si and HCO₃⁻ to As (III/V) anions enable their analogous adsorption behaviors, which is of crucial importance in As treatment practice (Kanematsu et al. 2013; Meng et al. 2000; Stachowicz et al. 2008).

The confounding effects of cations and anions on As adsorption were investigated, and the results demonstrate that the coexisting ions exhibited not a simple summation of individual ion effects but a compromise between them (Fig. 5). Such a postulation was justified by a previous study showing that the interference of Ca²⁺ or Mg²⁺ with HCO₃⁻ results in a lower effect on As adsorption/desorption on ferrihydrite than would be expected from their competitive effects alone (Saalfeld and Bostick 2010). Anions including Si and HCO₃⁻ in groundwater usually are neutralized with divalent cations such as Ca²⁺ and Mg²⁺, which would lead to positive influences in As treatment practice (Meng et al. 2000). Thus, this confounding observation suggested that the interference of one single ion could be masked or eliminated due to other

coexisting ions with stronger effects (Kanematsu et al. 2013; Zeng et al. 2008).

The adverse effects of anions on As adsorption were simulated using CD-MUSIC modeling and were in close agreement with the experimental observations (Fig. 5 and Table S7–8). Moreover, the simultaneous effect of Ca²⁺, Mg²⁺, Si, and HCO₃⁻ on As removal can be well modeled. For example, As (III) and As (V) loads of 3.51±0.06 and 2.67±0.26 mg/g were experimentally observed, respectively, whereas the corresponding model predictions were 3.51 and 2.69 mg/g. In the modeling process, though the adsorption constants of As and coexisting ions were employed from dose effect (Fig. 3 and Table S7), some fine-tuning of As charge distribution (f) to the TiO₂ surface has to be adapted (Table S8). The change should be affected by the coadsorbed ions, which could affect the electric double layer on TiO₂ surface. These satisfactory modeling results attest to the effective application of CD-MUSIC in predicting As adsorptive column breakthrough curves.

Field column results

To evaluate the effect of various EBCTs (0.11 to 1.08 min) on As removal efficiency, field column studies were conducted using ~700-µg/L As groundwater #1 (Fig. 6). Generally, extended As breakthrough was observed using high EBCT, consistent with previous reports (Hristovski et al. 2008; Zeng

Fig. 4 Ca²⁺ and Mg²⁺ effect on 800 µg/L As (III/V) adsorption on 0.1 g/L GTiO₂ in 0.1 M NaCl at pH 8.2. The dashed lines represent the ratios of Ca (Mg) versus As (III) (red) and As (V) (black) in groundwater #1

Fig. 5 Ion effects on 800 $\mu\text{g/L}$ As (III/V) adsorption on 0.1 g/L GTiO₂ at pH 8.2. “BK” represents 0.1 M NaCl. “Si” represents 8.9 mg/L Si in BK, “HCO₃⁻” represents 388 mg/L HCO₃⁻. “All” represents simultaneous addition of 8.92 mg/L Si, 388 mg/L HCO₃⁻, 39.1 mg/L Ca²⁺, and

104.3 mg/L Mg²⁺ in “BK.” The columns show the average of triplicate analysis with standard deviation. The blue diamonds represent CD-MUSIC modeling

et al. 2008). The number of BV before the effluent As concentration exceeded 10 $\mu\text{g/L}$ (BV₁₀) exhibited a clear linear increase as a function of EBCT ($R^2=0.997$, Fig. 7a).

The adsorbed As at BV₁₀, calculated from mass balance using the breakthrough curves, linearly increased from 0 to 0.96 mg/g with EBCT increasing from 0.11 to 1.08 min (Fig. 7b). The increasing of adsorbed As was also confirmed by EDS analysis of the spent GTiO₂ after column experiments (Fig. S4a). In agreement with our batch kinetics study (Fig. 1), this linear relationship confirms that extended contact time should facilitate the As mass transfer diffusion into GTiO₂ pores and its access to adsorption sites (Badruzzaman et al. 2004; Hristovski et al. 2008; Kanematsu et al. 2012).

The adsorbed As on GTiO₂ (0.96 mg/g) with EBCT=1.08 min ranks well in comparison with other groundwater treatment studies (Table S1). Previous column studies usually employed low As groundwater (98.6 $\pm$ 152.2 $\mu\text{g/L}$, $n=82$, median=51.5.0 $\mu\text{g/L}$, Table S1), resulting in an average adsorption load of 0.83 $\pm$ 1.13 mg/g with a median value of 0.40 mg/g. However, the BV₁₀ (968) at 1.08 min in our study was much lower than the average BV₁₀ in other studies (17,262 $\pm$ 16,032, median=11,250, Table S1). A recent column study reported that at EBCT=2 min, 10,500 BV groundwater can be treated when initial As is about 120 $\mu\text{g/L}$, whereas the BVs are appreciably reduced to 4300 with 410 $\mu\text{g/L}$ As in the raw water (Li et al. 2012). These consistent results highlight

Fig. 6 Breakthrough curves for As (III) and As (V) with EBCTs from 0.11 to 1.08 min for field columns. Solid lines are PHREEQC modeling results

Fig. 7 BV_{10} (a), adsorbed As concentrations (b), and adsorbed Si, Ca^{2+} , and Mg^{2+} concentrations (c) at BV_{10} as a function of EBCT. Solid lines represent linear fit results. The corresponding flow rate (Q , mL/min) for each EBCT is shown as the second x -axis

the challenge of treating groundwater with high As concentrations (>500 $\mu\text{g/L}$).

With increasing EBCT, both As (III) and As (V) exhibited lengthening of the breakthrough point at 10 $\mu\text{g/L}$, with a different extension (Fig. 6). For example, for EBCT=0.32 min, As (III) displayed a faster breakthrough ($BV_{10}=247$) than As (V) ($BV_{10}=741$), whereas for EBCT=1.08 min, As (III) showed a much slower breakthrough ($BV_{10}=2160$) than As (V) ($BV_{10}=1029$), though the adsorption of both was elevated. This observation indicates that more As (III) could be adsorbed on GTiO_2 than As (V), given sufficient time such as in the isotherm results.

Furthermore, As speciation analysis on spent GTiO_2 in the field column experiments using XANES revealed that 7–35 % of adsorbed As was in the As (III) form (Fig. 8), 6–52 % lower than the calculation from mass balance after filtration process (34–64 %). This difference indicates that the oxidation of adsorbed As (III) occurred during filtration due to trace amounts of dissolved oxygen in the groundwater (0.42 ± 0.61 mg/L , Table S2), which is consistent with our previous observations (Jing et al. 2009). The oxidation from As (III) to As (V) may facilitate As stabilization because As (V) usually has a higher affinity than As (III) (Guan et al. 2012).

During filtration, Ca^{2+} and Mg^{2+} were also adsorbed on GTiO_2 (Fig. S5a–b), and their loads increased with increasing EBCT from 0.11 to 1.08 min (Fig. 7c). The retention of Ca and Mg was evidenced by EDS analysis of the spent GTiO_2 surface (Fig. S4b–c). As a result, the adsorbed Ca^{2+} or Mg^{2+} may enhance As adsorption due to electrostatic attraction. Interestingly, the Ca^{2+} load (311 mg/g at EBCT=1.08 min)

was higher than Mg^{2+} (171 mg/g), though Ca^{2+} concentration (39.1 ± 2.1 mg/L , Table S2) was much lower than Mg^{2+} (104.3 ± 4.2 mg/L) in groundwater #1. In agreement with our observations, Ca^{2+} was bound more strongly than Mg^{2+} in a study of a column packed with Mn oxide-coated sand (Appelo and Postma 1999). Conversely, Ca^{2+} showed weaker affinity than Mg^{2+} on goethite (Stachowicz et al. 2008) and E33 (Kanematsu et al. 2013) in batch experiments. Although these two cations may exhibit distinct adsorption behaviors themselves, probably due to the variations in adsorbents and

Fig. 8 **a** As K-edge XANES spectra of the spent GTiO_2 after field column experiments using groundwater #1. Experimental spectra are displayed as black circles. The red lines are the LCF fitting results. **b** As (III) percentages in spent GTiO_2 by LCF fitting for XANES analysis and mass balance (MB) calculation from the breakthrough curves (electronic supplementary material)

experimental conditions, they generally lead to positive effects on As removal.

In addition, the Si adsorption was also a function of EBCT (Fig. 7c), but with an earlier breakthrough point than As under the same EBCT (Fig. S5c). This result implies that Si transports more quickly than As in the column, consistent with a previous report (Kanematsu et al. 2012). Consequently, the adsorbed Si (Fig. S4d) could occupy and block TiO_2 adsorption sites earlier than As, decrease the pH_{zpc} of TiO_2 , and significantly suppress As adsorption (Kanematsu et al. 2012).

One-dimensional reactive transport modeling for field column experiments

The groundwater chemistry, adsorptive reactions of As and coexisting ions, surface properties, and transport block parameters in the field columns can be included in the PHREEQC modeling (Table S4), and the As breakthrough curves can be calculated. As shown in Fig. 6, the general trend of the As modeling results agreed well with the experimental observations. This satisfactory agreement suggests that PHREEQC could successfully predict the As filtration process under a series of flow rates.

In these modeling runs, the transport properties of groundwater components and adsorption constants remained the same except for some fine-tuning of As adsorption parameters in the CD-MUSIC model (Table 1). The minute differences in the optimized adsorption constants (logK) among different columns reflect the slight variation in adsorption conditions. This fine-tuning approach is similar to previous studies where the parameters obtained from batch adsorption have to be modified to satisfactorily approximate the column data

(Hanna et al. 2010; Jing et al. 2009). For example, the surface area had to be decreased to simulate a gentisic acid transport process in hematite-coated sand column according to batch experiments due to inaccessibility of the reactive surface sites (Hanna et al. 2010).

Recently, As (III) breakthrough curves in a fixed bed with iron oxide-coated natural rock were well simulated using PHREEQC with the WATEQ4F database (Maji et al. 2012). On the other hand, the As transport process in an iron oxide-containing soil column could not be predicted using batch equilibrium adsorption parameters due to kinetic limitations (Williams et al. 2003). This limitation was mainly due to the fact that adsorption equilibrium at local micro-interfacial areas in a column is hard to reach without sufficient contact time (Zhang and Selim 2006). Thus, PHREEQC, derived from equilibrium conditions, could incorporate the kinetics block when elevating column modeling from batch experiments (Jeppu et al. 2012).

The CD-factor (f) is the charge distribution from the central As atom to the TiO_2 surface, reflecting the interfacial molecular structural information (Hiemstra and Van Riemsdijk 2006; Jing et al. 2009). The optimized f for As surface complexes was a function of EBCT (Table 1). For example, f increased from 0.50 to 0.66 for As (III), and from 0.40 to 0.50 for As (V) when EBCT increased from 0.11 to 1.08 min. This trend suggests the gradual transfer of As charge to the surface with increasing EBCT, which is attributable to the suppression of the electric double layer due to the increase of adsorbed ions with prolonged contact time.

Notably, when the effluent As (III/V) concentration exceeds 100 $\mu\text{g/L}$, the model may overestimate the effluent concentration (Fig. 6). This overestimation may be due to

Table 1 Optimized reaction parameters in PHREEQC modeling for field columns with a series of EBCTs

As adsorption reactions	0.11 min		0.22 min		0.32 min		0.54 min		1.08 min		LogK (Average $\pm$ std)
	f^*	logK	f^*	logK	f^*	logK	f^*	logK	f^*	logK	
$\text{H}_3\text{AseniteO}_3 + 2\text{Surf_sOH}^{-0.33} = (\text{Surf_sO})_2\text{AseniteOH}^{-0.66} + 2\text{H}_2\text{O}$	0.50	18.0	0.66	16.0	0.66	16.0	0.66	16.35	0.66	17.1	16.7 $\pm$ 0.9
$\text{H}^+ + \text{HAsO}_4^{-2} + 2\text{Surf_sOH}^{-0.33} = (\text{Surf_sO})_2\text{AsO}_2^{-1.66} + 2\text{H}_2\text{O}$	0.40	20.0	0.40	18.7	0.50	18.2	0.50	18.0	0.5	19.0	18.8 $\pm$ 0.8
$\text{H}_2\text{AsO}_4^- + 2\text{Surf_sOH}^{-0.33} = (\text{Surf_sO})_2\text{AsO}_2^{-1.66} + 2\text{H}_2\text{O}$	0.40	19.0	0.40	18.0	0.50	17.2	0.50	17.3	0.5	18.0	17.9 $\pm$ 0.7
$2\text{H}^+ + \text{HAsO}_4^{-2} + 2\text{Surf_sOH}^{-0.33} = (\text{Surf_sO})_2\text{AsOOH}^{-0.66} + 2\text{H}_2\text{O}$	0.40	30.0	0.40	30.0	0.50	29.0	0.50	29.0	0.5	28.0	29.0 $\pm$ 1.0
$\text{H}^+ + \text{H}_2\text{AsO}_4^{-2} + 2\text{Surf_sOH}^{-0.33} = (\text{Surf_sO})_2\text{AsOOH}^{-0.66} + 2\text{H}_2\text{O}$	0.40	25.6	0.40	26.2	0.50	24.6	0.50	24.0	0.5	24.0	24.9 $\pm$ 1.0
$\text{TiOH}^{-1/3}$ (strong site)	10.0	15.0	15.0	15.0	15.0	–	–	–	–	–	–
$\text{Ti}_2\text{O}^{-2/3}$ (weak site)	1.1	3.4	3.4	3.4	3.4	–	–	–	–	–	–
Cell length (m)	0.017	0.017	0.017	0.017	0.017	–	–	–	–	–	–
Time step (s)	1.0	1.9	2.9	4.8	9.7	–	–	–	–	–	–
Number of shifts	18567	40867	18946	10403	23343	–	–	–	–	–	–

f^* : f represents the charge distribution factor of the As atom to the TiO_2 surface

the unappreciated iron hydroxides generated in situ at circumneutral pH in the presence of iron in the raw groundwater. This explanation is justified by the fact that Fe was detected in the raw water (0.15 to 0.74 mg/L) but not in the effluent after filtration. These in situ formed iron surface sites could also contribute to As adsorption (Maiti et al. 2013). A similar observation was also reported in filtration experiments for groundwater As removal (Hug et al. 2008; Leupin et al. 2005).

Application: household pitcher

A household water pitcher with GTiO₂ was designed to treat As-contaminated groundwater from two wells. In groundwater #1 with ~700 µg/L As, 14,000 BVs (10.1 mg/g) were obtained before As breakthrough at 10 µg/L through 288 days (Fig. 9a). In groundwater #2 with ~217 µg/L As, 25,000 BV (7.8 mg/g) As-safe water was obtained for about 600 days (Fig. 9b). The much higher As adsorption in the household pitcher than that in field column results and literature reports (Table S1) could be attributed to its on-off operational mode. This on-off mode provides enough time for As to diffuse into the adsorbent pores and subsequently results in efficient As adsorption (Badruzzaman et al. 2004). This on-off operation matches the daily variability in household water demand. Nevertheless, the adsorbed As in the household filter is much lower than the adsorption capacity from the isotherm experiments. This difference should be attributed to the competition from coexisting anions in groundwater (Figs. 3 and 5) and the

short contact time in filters to reach adsorption equilibrium (Williams et al. 2003; Zhang and Selim 2006).

To evaluate the social acceptability of the household filter, the cost of the filtered water was calculated to be CNY 0.03–0.06 (USD 0.0048–0.0096) per liter. The cost is acceptable in rural areas in Shanxi, because the per capita net income was CNY 7154 for one rural resident in 2013 (Shanxi Statistical Bureau 2014).

Furthermore, to reduce the arsenic-laden waste and cost of As removal, spent GTiO₂ media was regenerated by immersing in 5 M NaOH for 1 h and subsequently washing to neutral pH according to our previous report (Luo et al. 2010). The media was reused, and the results showed satisfactory As removal in treating about 8000 BVs (Fig. 9c). The regenerated solution was collected and recovered as solid by heating at 70 °C (Luo et al. 2010), resulting in no secondary pollution.

Conclusions

This study used granular TiO₂ media to remove geogenic As (III) and As (V) from groundwater. Our kinetics study shows that As adsorption follows a fast external film diffusion and then a slow intraparticle diffusion process. Ca²⁺ and Mg²⁺ enhanced As (V) adsorption, while exhibiting a slight adverse impact on As (III). Si severely decreased As (III/V) adsorption, and HCO₃[−] significantly inhibited As (V) adsorption while slightly reducing As (III). Field systematic column studies show that longer EBCT may result in a higher As

Fig. 9 Performance of GTiO₂ (a) and regenerated GTiO₂ (b) for As removal in household filters using groundwater #1, and another filtration results of GTiO₂ using groundwater #2 as a function of bed volumes and filtration time (c). The horizontal lines represent the WHO guideline value (10 µg/L) for As in drinking water

removal efficiency, which is also confirmed by our kinetics results. The PHREEQC program well simulated systematic As breakthrough curves in field columns by integrating the CD-MUSIC model with one-dimensional reactive transport block. The household pitcher under on-off operational mode resulted in satisfactory As adsorption. Our approach provides a practical solution for supplying As-safe drinking water in As-contaminated areas.

Acknowledgments We thank Dr. David Parkhurst for the helpful discussion on PHREEQC modeling. We acknowledge the financial support of the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020201), the National Natural Science Foundation of China (41373123, 21337004), and RCEES (YSW2013A01).

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