Hydrous cerium oxides coated glass fiber for efficient and long-lasting arsenic removal from drinking water

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Abstract: A novel arsenic adsorbent with hydrous cerium oxides coated on glass fiber cloth (HCO/GFC) was synthesized. The HCO/GFC adsorbents were rolled into a cartridge for arsenic removal test. Due to the large pores between the glass fibers, the arsenic polluted water can flow through easily. The arsenic removal performance was evaluated by testing the equilibrium adsorption isotherm, adsorption kinetics, and packed-bed operation. The pH effects on arsenic removal were conducted. The test results show that HCO/GFC filter has high As(V) and As(III) removal capacity even at low equilibrium concentration. The more toxic As(III) in water can be easily removed within a wide range of solution pH without pre-treatment. Arsenic contaminated ground-water from Yangzong Lake (China) was used in the column test. At typical breakthrough conditions (the empty bed contact time, EBCT = 2 min), arsenic researched breakthrough at over 24,000 bed volumes (World Health Organization (WHO) suggested that the maximum contaminant level (MCL) for arsenic in drinking water is 10 mg/L). The Ce content in the treated water was lower than 5 ppb during the column test, which showed that cerium did not leach from the HCO/GFC material into the treated water. The relationship between dosage of adsorbents and the adsorption kinetic model was also clarified, which suggested that the pseudo second order model could fit the kinetic experimental data better when the adsorbent loading was relatively low, and the pseudo first order model could fit the kinetic experimental data better when the adsorbent loading amount was relatively high.

Keywords: hydrous cerium oxide (HCO); glass fiber cloth (GFC); column test; adsorption kinetics; adsorption mechanism

1 Introduction

Arsenic contamination of water bodies (ground/surface

water) could cause many human health problems, such as skin, lung, bladder, and kidney cancers as well as the neurological and cognitive dysfunction in children [1]. The World Health Organization (WHO) had classified arsenic as a carcinogen and recommended that the maximum contaminant level (MCL) for arsenic in

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drinking water should not be over 10 $\mu\text{g/L}$ [2]. Thus, it is important to remove excess arsenic species effectively from drinking water to guarantee the health of millions of people living near arsenic contaminated water bodies.

Several arsenic removal techniques have been established for arsenic removal from contaminated water sources, including precipitation/co-precipitation, ion-exchange, and adsorption [3]. Among them, the adsorption process is generally considered as a simple and cost-effective process to remove arsenic from drinking water when its contamination level is not very high [4]. With the rapid development of the synthesis and application of nanomaterials, various nanoadsorbents for arsenic removal had recently been developed, including hydrous TiO_2 nanoparticles [5], Fe_2O_3 nanoparticles [6], Fe_3O_4 nanoparticles [7], CuO nanoparticles [8], and nanostructured ZrO_2 sphere [9], which demonstrated promising arsenic removal performances from drinking water because of their large surface areas and suitable surface properties derived from their nanoscale nature [10]. However, most nanoadsorbents still have two major limitations which make it difficult for their applications in drinking water treatment practices. First, it is difficult to separate and reuse these nanoabsorbents after they are dispersed in arsenic contaminated water, and it is not feasible to use them in a fixed-bed or flow-through system due to the high particle attrition rate and the high pressure drop. Furthermore, some commonly used nanoadsorbents, for example nano-ferric oxides, have a leaching problem especially when the water pH varies, which could cause secondary pollution to drinking water.

Cerium oxide (CeO_2) is the most abundant and least expensive rare earth metal oxide. Due to its particular functionalities, it has been extensively investigated for various technical applications [11–13]. It possesses the lowest solubility against acid among the rare earth metal oxides, and does not elute during water treatment [14]. Thus, it had been studied as a potential adsorbent for the removal of various hazardous substances from water, including fluoride [15], bichromate [16], and arsenic species [17–19]. Although hydrous CeO_2 nanoparticles had demonstrated a superior arsenic adsorption performance for both As(III) and As(V) especially for drinking water treatment [20], their application in real practice is still rare because of their difficult separation from treated water and unfitness for fixed-bed or flow-through treatment systems from their

nanoscale feature as other nanoadsorbents. One feasible solution for this problem is to immobilize nano-sized CeO_2 onto macroscopic porous matrixes, which could be easily used in fixed-bed or flow-through treatment systems and avoid the nanomaterial separation issue. Several macroscopic porous matrixes had been developed for the loading of CeO_2 nanoparticles for arsenic removal, including porous resin [21], silica monolith [22], porous ceramic foam [23,24], and polymeric anion exchanger [25]. However, their synthesis processes were generally complex and time consuming, and they were quite expensive to be used for arsenic removal practices.

In this study, the glass fiber cloth (GFC) was chosen as the macroscopic porous matrix for hydrous CeO_2 nanoparticle loading to create a highly efficient, long-lasting adsorbent (HCO/GFC) for the removal of arsenic species from drinking water. The GFC matrix has the advantages of low cost, nontoxicity, and abundance of three-dimensional, interconnected large macropores which could facilitate both the flow-through of arsenic contaminated water with low pressure drop and their efficient contact with CeO_2 nanoparticles loaded on GFC. Furthermore, the nonwoven GFC used in this study was not fragile and it had a good flexibility for its assembly into a cartridge for being used in the flow-through apparatus. The HCO/GFC adsorbent demonstrated a good arsenic adsorption performance for both As(III) and As(V) in water, especially at low equilibrium arsenic concentrations, which suggested its application potential for drinking water treatment. The kinetics study demonstrated that the pseudo second order model could fit the kinetic experimental data better when the adsorbent loading was relatively low, whereas the pseudo first order model could fit the kinetic experimental data better when the adsorbent loading amount was relatively high. It could be easily rolled into cartridges for the use in the fixed-bed water treatment apparatus, which demonstrated a good arsenic removal performance in both lab-prepared and natural water samples with a large arsenic breakthrough bed volume, high regeneration capability, and good stability.

2 Experimental

2.1 Materials and chemicals

All the chemicals used in the synthesis process were of analytical reagent grade. $\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and NaOH

(Sinopharm Chemical Reagent Corporation, Shanghai, China) were used to synthesize HCO nanoparticles in ethanol solution. Sodium (meta) arsenite (NaAsO_2 , Shanghai Tian Ji Chemical Institute, Shanghai, China) and sodium arsenate heptahydrate ($\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, Fluka, USA) was used to prepare As(III) and As(V) stock solution. Concentrated hydrochloride acid (HCl , 32%–38%, Tianda Chemical Reagents Factory, Tianjin, China) was used to stabilize the arsenic species after treatment. As(III) and As(V) solutions used in the batch experiments were obtained by diluting the As(III) and As(V) stock solution to desired concentration with de-ionized (DI) water. The GFC was a non-woven fiber glass mat (Craneglas230, 0.015 nominal, fiber diameter of 16 μm) made by CRANE & CO (Stamford, CT, USA).

2.2 Synthesis of CeO_2 nanoparticle-loaded GFC

Hydrous CeO_2 nanoparticles were synthesized by the following process. 0.02 mol NaOH powder was dissolved in 100 mL absolute ethanol to prepare 0.2 M NaOH /ethanol solution. 0.005 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ powder was dissolved in 100 mL absolute ethanol to prepare 0.05 M $\text{Ce}(\text{NO}_3)_3$ /ethanol solution. The NaOH /ethanol solution was then added into the $\text{Ce}(\text{NO}_3)_3$ /ethanol solution at room temperature under vigorous stirring. With the mix of these two solutions, dark brown colloidal precipitates immediately formed. After being stirred continuously in air, the color of these colloidal precipitates changed from dark brown to gray yellow, and finally to bright yellow within 20 min. During this process, the main valence of cerium in precipitation changed from +3 to +4, and the cerium hydroxides transferred to hydrous CeO_2 . Finally, these precipitates were collected by the centrifugation, washed with DI water and absolute ethanol for several times, and dried in air at 100 °C for 12 h to obtain HCO nanoparticles.

To load hydrous CeO_2 nanoparticles on GFC, a piece of GFC was firstly dipped into 15% NH_4OH aqueous solution for 3 min to clean the glass fiber surface and improve the adhesion between CeO_2 and glass fiber. After drying at 85 °C for 5 min, it was immersed into an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.05 mol in 100 mL H_2O) for 3 min. The above process was repeated for two more times, and the obtained sample was then dried at 90 °C for 5 min, and washed with DI water for several times to removal NH_4^+ , NO_3^- , and CeO_2 nanoparticles that were not firmly loaded onto the GFC to obtain the desired HCO/GFC adsorbent sample. To prepare the HCO/GFC filter for a flow-through

apparatus with the down flow design as shown in Fig. 1, the HCO/GFC adsorbent was rolled into a cartridge (with the inner radius of 30 mm and volume of 100 mL) and put into a glass tube with two ends sealed to avoid any potential leakage of glass fibers. The loading amount percentage of HCO on GFC was calculated by Eq. (1):

$$\text{Loading amount (\%)} = \frac{W_2 - W_1}{W_2} \quad (1)$$

where W_1 is the weight of pure GFC and W_2 is the weight of GFC after the immobilization of HCO. The loading amount percentage of HCO/GFC adsorbent in this study was determined at ~18.3%.

2.3 Characterization of the HCO/GFC adsorbent

The morphology of the HCO/GFC adsorbent was examined by field emission scanning electron microscopy (FESEM). The crystal structure of nano-HCO nanoparticles was analyzed by X-ray powder diffractometer (D/MAX-2004-X-ray Rigaku Corporation, Tokyo, Japan). The surface element composition and chemical states of the samples were examined by X-ray photoelectron spectroscopy (XPS) measurements (Thermo Fisher Scientific Inc., Waltham, MA, USA). The isoelectric point of HCO nanoparticles was measured with electrophoretic spectroscopy (JS84H, Shanghai Zhongchen Digital Instrument Co., Ltd., Shanghai, China).

2.4 Arsenic adsorption methods

All the arsenic adsorption experiments were conducted at 25 °C and under common day-light illumination condition. In order to evaluate the intrinsic adsorption capacity of the hydrous CeO_2 nanoparticle, the As(III) and As(V) equilibrium adsorption isotherm study was carried out. The hydrous CeO_2 nanoparticles with the same material loadings (0.02 g/L) were added into the arsenic solutions with various initial concentrations (from 100 $\mu\text{g/L}$ to 5 mg/L) respectively and the suspensions were stirred magnetically for 24 h to disperse the

Fig. 1 Schematic diagram of the HCO/GFC filter cartridge and the column test setup.

samples. After appropriate time intervals, the sample was recovered by centrifugation at 2500 rpm for 10 min. The adsorption capacity at different equilibrium arsenic concentrations could then be calculated from the difference between the initial and the equilibrium concentrations. The arsenic removal kinetics of GFC immobilized with HCO nanoparticles was also investigated.

The column test was carried out using HCO/GFC cartridge described in Section 2.2. The setup contained a cartridge pump and a pre-prepared stock arsenic solution with DI water or arsenic contaminated ground-water. The flow rate of the arsenic solution was controlled by the pump. The arsenic concentration in the effluent was monitored by a atomic fluorescence spectrophotometer (AFS-9800, Beijing KeChuang-HaiGuang Instrument Inc., Beijing, China). The schematic diagram of the column test for arsenic removal is shown in Fig. 1. The empty bed volume of the HCO/GFC adsorbent is 100 mL. The weight percentage of HCO is 18.3% of the total filter. Both lab prepared (the initial As(III) concentration was ~ 84 $\mu\text{g/L}$ and the initial As(V) concentration was ~ 89 $\mu\text{g/L}$) and natural arsenic polluted water was tested in this study. The natural water was collected from ground-water of Yangzong Lake (China). The total arsenic concentration of natural water was 65 ppb, in which As(III) accounted for about 30%. The pH of the natural water was about 7.8. The water quality data was presented in Table 1.

3 Results and discussion

3.1 Characterization of the HCO/GFC adsorbent

Figure 2 shows the X-ray diffraction (XRD) analysis result of the obtained HCO/GFC adsorbent. The XRD peaks of cubic fluorite CeO_2 phase (JCPDS Number: 34-0394) could be observed in the XRD pattern, which

Fig. 2 XRD patterns of the HCO/GFC adsorbent.

clearly demonstrated that CeO_2 nanoparticles were successfully loaded on the GFC. The crystallite size (D) of CeO_2 nanoparticles was determined at ~ 4 nm from the strongest XRD peak (111) by the Scherrer's formula:

$$D = 0.9\lambda / (\beta \cos \theta) \quad (2)$$

where λ is the average wavelength of the X-ray radiation, β is the line-width at half-maximum peak position, and θ is the diffracting angle.

Figures 3(a)–3(c) show the FESEM observation results of the HCO/GFC adsorbent. Figure 3(a) shows the morphology of HCO/GFC adsorbents, which composed of GFC as a skeleton support and hydrous CeO_2 particles as the active sites. Figure 3(b) clearly demonstrated that hydrous CeO_2 nanoparticles were well dispersed onto the GFC. Because of the large macropores between glass fibers, the arsenic contaminated water could flow through the HCO/GFC adsorbent easily with low pressure drop. Figure 3(c) with a higher magnification demonstrates that these hydrous CeO_2 nanoparticles were aggregated into nanosized particles (100 nm or less) with a near-sphere shape, which formed a mesoporous structure of CeO_2 on the GFC. Figure 3(d) shows the N_2 adsorption/desorption isotherms of the HCO/GFC adsorbent, where P is the partial pressure of nitrogen and P_0 is the saturated vapor pressure of nitrogen at adsorption temperature. The N_2 adsorption followed the lower curve and the N_2 desorption followed the upper curve. From its isotherms, the Brunauer–Emmett–Teller (BET) specific surface area of the HCO/GFC adsorbent could be determined at ~ 184 m^2/g . The inset image in Fig. 3(d) shows the pore size distribution of the HCO/GFC adsorbent, where $D_v(d)$ represents the change of pore volume with different pore diameters. It is clearly demonstrated that most pores were mesoporous with an average pore diameter of ~ 37 nm. Thus, the arsenic contaminated water could

Table 1 Water quality data for ground-water samples of Yangzong Lake (China)

Ion species	Concentration (mg/L)	Ion species	Concentration (mg/L)
F^-	0.54	K^+	5
Cl^-	5.77	Ca^{2+}	24
NO_3^-	4.78	Mg^{2+}	29
HSO_4^-	365.73	Fe^{3+}	< 1
HCO_3^-	339.31	As(III)	0.021
Na^+	170	As(V)	0.044

Fig. 3 (a) FESEM image of the HCO/GFC adsorbent. (b) FESEM image of the HCO/GFC adsorbent with a higher magnitude. (c) FESEM image of HCO nanoparticles. (d) N_2 adsorption/desorption isotherms of the HCO/GFC adsorbent (note: the inset image shows its pore size distribution).

have a good contact with the active CeO_2 surface efficiently for the removal of arsenic species from their adsorption onto hydrous CeO_2 nanoparticles immobilized on the GFC.

3. 2 Arsenic adsorption capacity of the HCO/GFC adsorbent

Due to the toxic nature of arsenic, the MCLs for arsenic in both drinking water and safe contact water are both set at $10 \mu\text{g/L}$ [2]. Thus, the arsenic amount that an adsorbent could adsorb at low equilibrium concentration should have more practical significance than its maximum adsorption capability under very high equilibrium concentration for the estimation of its performance in arsenic removal practice. Figure 4(a) demonstrates the amount of arsenic adsorbed by HCO nanoparticles at low equilibrium arsenic concentration with the solution pH at ~ 7 . The adsorption data of both As(III) and As(V) could be best fitted with the Freundlich isotherm as given in Eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where q_e is the amount of As adsorbed at equilibrium (mg/g), C_e is the equilibrium arsenic concentration in water samples (mg/L), and K_F and n are the Freundlich constants. When the equilibrium arsenic concentration was $\sim 10 \mu\text{g/L}$, the adsorbed arsenic amount of the HCO adsorbent for As(III) and As(V) were ~ 5 and ~ 4 mg/g, and the HCO adsorbent generally demonstrated a better adsorption capability on the more mobile and toxic As(III) than on As(V). Usually, As(III) could not have high affinity to traditional adsorbents compared with charged As(V) due to its existence as nonionic H_3AsO_3 in natural water at near neutral pH environment [26]. The good adsorption of both As(III) and As(V) by the HCO adsorbent could eliminate the pre-treatment required by traditional arsenic adsorbents, which could largely simplify the arsenic removal process and lower the treatment cost. Table 2 compares the adsorption capabilities of some traditional arsenic adsorbents reported in Refs. [14,27,28] with that of the HCO adsorbent at near neutral pH environment. Usually, the As(III) adsorption capability was not reported in literature on these traditional arsenic adsorbents due to

Fig. 4 (a) Equilibrium adsorption isotherms of As(III) and As(V) on HCO nanoparticles with low equilibrium concentrations. (b, c) Adsorption kinetics of As(III) (the initial As(III) concentration $C_0 = 84$ μg/L) and As(V) ($C_0 = 89$ μg/L) on the GFC and the HCO/GFC adsorbent, respectively.

Table 2 Performance of various adsorbents at low equilibrium arsenic concentrations

Adsorbent	Surface area (m ² /g)	pH	Sorbate	Sorption capacity (mg/g)	
				$C_e = 10$ ppb	$C_e = 50$ ppb
Ferric hydroxide	240–300	6.5	As(V)	1.1	1.4
Aminated fiber	—	7.0	As(V)	1.7	—
ZrO ₂ sphere	32	7.3	As(V)	0.7	1.1

their lack of affinity to As(III) at near neutral pH environment. From the comparison, it was clear that the HCO adsorbent had a superior arsenic adsorption performance on both As(III) and As(V) than these traditional arsenic adsorbents.

Figures 4(b) and 4(c) show the As(III) and As(V) adsorption performances of the HCO/GFC adsorbent, respectively, compared with that of the pure GFC without HCO loading. The initial As(III) and As(V) concentrations were ~84 and ~89 μg/L, respectively, which were in the high end level of arsenic contamination in drinking water. The experiments were conducted in a batch reactor with the solution pH at ~7 and the adsorbent loading of 0.1 g/L. The results clearly showed that the pure GFC without HCO loading had no arsenic adsorption capability, whereas the HCO/GFC adsorbent demonstrated a good arsenic adsorption performance for both As(III) and As(V). After 120 min, the arsenic adsorption by the HCO/GFC adsorbent reached a plateau for either As(III) or As(V), and the corresponding equilibrium As(III) and As(V) concentrations were reduced to ~8.3 and ~4 μg/L, respectively, which were both within the MCL of arsenic in drinking water. These results suggested that HCO nanoparticles in the HCO/GFC adsorbent acted as the active component for arsenic removal as we designed and the GFC served as the supporting matrix to immobilized HCO nanoparticles and facilitate the flow-through of arsenic contaminated water with low pressure drop during water treatment process.

3.3 Kinetic model fitness evaluation of arsenic adsorption on the HCO/GFC adsorbent

In a solid–liquid system, the adsorption kinetics could be commonly fitted with both the pseudo-first-order and pseudo-second-order kinetic models [29–32]. In order to evaluate the fitness of these two adsorption kinetic models on arsenic adsorption on the HCO/GFC adsorbent, kinetic tests were carried out with a series of the HCO/GFC adsorbent dosages (0.1, 0.5, 1.0, and 1.5 g/L) in a representative 500 mL arsenic aqueous solution with the initial concentrations of ~124 μg/L for As(III) and ~91 μg/L for As(V) at pH ≈ 7 as shown in Figs. S1(a) and S1(b) in the Electronic Supplementary Material (ESM), respectively. The kinetic experimental data were further fitted with both the pseudo-first-order and pseudo-second-order kinetic models as shown in Fig. S2 in the ESM for As(III) adsorption and Fig. S3 in the ESM for As(V) adsorption, respectively. Figures 5(a) and 5(b) show the relationship between the adsorbent dosage and the corresponding correlation coefficient (R^2) data for As(III) adsorption and As(V) adsorption with both models, respectively. It clearly demonstrated that with the increase of the adsorbent loading, the R^2 of the pseudo-first-order model fitting gradually increased towards 1, while the R^2 of the pseudo-second-order model fitting gradually decreased away from 1. Thus, the fitness of kinetic models changed with the increase of the adsorbent loading. When the adsorbent loading

Fig. 5 Correlation coefficients (R^2) of the pseudo-first-order and the pseudo-second-order kinetics models with four different adsorbent dosages for (a) As(III) adsorption and (b) As(V) adsorption.

was relatively low, the pseudo-second-order model could fit the kinetic experimental data better, whereas the pseudo-first-order model could fit the kinetic experimental data better when the adsorbent loading amount was over ~ 0.6 g/L for As(III) and ~ 0.3 g/L for As(V), respectively.

With the increase of the adsorbent loading in the arsenic solution of the same volume, the ratio of adsorbent to arsenic species increased and there could be sufficient surface adsorption site to adsorb arsenic species even in the later stage of the adsorption process. Thus, a fast adsorption kinetics should be observed and a low exponential rate equation (pseudo-first-order kinetic model) should be more suitable to describe it. On the contrary, if the adsorbent loading was small, the ratio of adsorbent to arsenic species was relatively low, and the already adsorbed arsenic species could occupy a considerable part of active sites on the surface of hydrous CeO_2 nanoparticles. Thus, arsenic species had to overcome the diffusion resistance to adsorb onto the inner pores of the hydrous CeO_2 nanoparticle agglomerates in the later stage of the adsorption process. Then, the intraparticle diffusion could be the limiting mass transfer step and control the adsorption kinetics [29]. So the adsorption rate in the later stage of the adsorption process would decrease, and a high

exponential rate equation (pseudo-second-order kinetic model) should be more suitable to describe it. This analysis was clearly consistent with the experimental data shown in Figs. 5(a) and 5(b).

3.4 Chemical states of arsenic species on the HCO/GFC adsorbent

Figure 6 shows the high-resolution XPS scans over As 3d peak on the HCO/GFC adsorbent surface after the As(III) and As(V) adsorptions, respectively. Both the As(III)–HCO/GFC sample and As(V)–HCO/GFC sample demonstrated a single peak for As 3d. The binding energy of As(III)–HCO/GFC was ~ 44.1 eV, and the binding energy of As(V)–HCO/GFC was ~ 45.2 eV. It had been reported in literature that the binding energy of As(V) 3d adsorbed on CuO was at ~ 45.2 eV and the binding energy of As(III) 3d was usually about 1 eV lower than that of As(V) [33,34]. Thus, it could be concluded that the oxidation states of both As(III) and As(V) did not change after their adsorptions onto the HCO/GFC adsorbent surface, and the removal of arsenic species from water by the HGO/GFC adsorbent mainly involved the adsorption process.

3.5 Continuous flow column tests of the HCO/GFC cartridge with lab-prepared arsenic solutions

Continuous flow column tests of the HCO/GFC cartridge were conducted firstly with lab-prepared As(III) and As(V) solutions of a series of pH values, respectively, to examine its arsenic removal performance for potential applications. Figures 7(a) and 7(b) show the breakthrough curves of As(III) and As(V), respectively. The initial As(III) concentration was ~ 84 $\mu\text{g/L}$, the initial As(V) concentration was ~ 89 $\mu\text{g/L}$, and the empty bed contact time (EBCT) was fixed at 4 min. The results demonstrated that the HCO/GFC cartridge could

Fig. 6 High-resolution XPS scans on As 3d peak of As(III)–HCO and As(V)–HCO nanoparticles.

Fig. 7 Arsenic removal of (a) As(III) ($C_0 = 84$ µg/L) and (b) As(V) ($C_0 = 89$ µg/L) on the HCO/GFC adsorbent at different pH values.

successfully remove both As(III) and As(V) well below the MCL of arsenic species in drinking water (10 µg/L) for large amounts of water compared to its bed volume. When the arsenic concentration in the effluent reached 10 µg/L, for example, its breakthrough bed volume (BV) for As(III) was ~27,000 BV at pH 6.5, and that for As(V) was ~23,700 BV at pH 7.0. It was found that the pH dependences of the HCO/GFC cartridge to As(III) and As(V) were different. Figure 7(a) demonstrates that no significant pH dependence was observed for the As(III) removal performance of the HCO/GFC cartridge. When the As(III) solution pH changed largely from 4.5 to 10.5, its As(III) breakthrough curves were generally similar and its As(III) breakthrough bed volume just slightly decreased from ~29,000 to ~27,000 BV. For As(V), however, the adsorption performance of HCO/GFC cartridge demonstrated a clear pH dependence as shown in Fig. 7(b). When the As(V) solution pH changed largely from 4.0 to 10.8, its As(V) breakthrough bed volume decreased obviously from ~29,000 to ~21,500 BV.

This phenomenon could be related to the difference existence states of As(III)/As(V) and surface charge states of HCO nanoparticles in water under different pH conditions. The isoelectric point (IEP) of active HCO nanoparticles for arsenic adsorption was at $\text{pH} \approx 2.7$,

and the glass fiber had little effect on the IEP of HCO nanoparticles. For the pH range we investigated (from 4 to 11), the surface of HCO nanoparticles was negatively charged, and the negative charge increased with the increase of the solution pH. When the As(III) solution pH was less than 9.2, As(III) existed predominately as non-charged H_3AsO_3 [35], and no repulsive force existed between the negatively-charged HCO nanoparticle surface and As(III) or adsorbed As(III) and As(III) still in water. Only when the As(III) solution pH was over 9.2, As(III) existed mainly as H_2AsO_3^- and now the negatively-charged HCO nanoparticle surface could begin to have the coulomb repulsive force to As(III) to induce the observed slight decrease of the As(III) removal performance of the HCO/GFC cartridge. When the As(V) solution pH value was at (~4)–(~11), As(V) existed mainly in the forms of H_2AsO_4^- and HAsO_4^{2-} . Thus, there always existed an electric repulsion between As(V) and the negative-charged HCO nanoparticle surface, and the repulsion increased with the increase of the solution pH. Furthermore, the adsorption of these negatively-charged As(V) species could also cause the coulomb repulsive effect between adsorbed As(V) and As(V) still in water. Thus, the As(V) removal performance of the HCO/GFC cartridge continued to decrease with the increase of the solution pH.

3.6 Continuous flow column tests of the HCO/GFC cartridge with natural water

To examine the arsenic removal performance of the HCO/GFC cartridge in the real water body environment, continuous flow column tests were conducted on it with an arsenic-contaminated natural water sample from Yangzong Lake (China), which was contaminated by industrial pollution. Table 1 summarizes the water quality data of the natural water sample. It demonstrated that various ion species existed in the natural water sample with concentrations much higher than that of arsenic species (total arsenic concentration of ~65 ppb), which could have strong competition effects on the arsenic removal performance of the HCO/GFC cartridge. Figure 8(a) shows the breakthrough curves of the total arsenic species in the natural water sample with a series of EBCTs of 2, 4, and 6 min, respectively, which demonstrated that the HCO/GFC cartridge had a very good arsenic removal performance even for the treatment of arsenic-contaminated natural water. For EBCTs of 2, 4, and 6 min, the arsenic breakthrough bed volumes of

Fig. 8 (a) Column test of the HCO/GFC adsorbent with natural water from Yangzong Lake (China). (b) Regeneration performance and Ce content examination in the treated water effluent during the continuous flow column test of the HCO/GFC adsorbent.

the HCO/GFC cartridge were ~24,000, ~30,000, and ~33,000 BV, respectively, when the arsenic concentration in the effluent reached 10 μg/L. The arsenic breakthrough bed volume of the HCO/GFC cartridge decreased with the decrease of EBCT as expected, which could be attributed to the less contact time effect.

The regeneration and reuse of an arsenic adsorbent are critical for its potential applications. After the arsenic concentration in the effluent reached 10 μg/L, the HCO/GFC cartridge was disassembled from the flow-through apparatus, soaked in 0.1 M NaOH aqueous solution for 2 h for arsenic desorption, washed by DI water for several times until the water pH reached ~7, and reassembled into the flow-through apparatus for the next continuous flow column test. Figure 8(b) compares the breakthrough curves of the total arsenic species in the natural water sample with EBCT of 2 min for the pristine HCO/GFC cartridge and the HCO/GFC cartridge after one time regeneration. When the arsenic concentration in the effluent reached 10 μg/L, the arsenic breakthrough bed volume of the pristine HCO/GFC cartridge was ~24,000 BV, while that after its first-time regeneration was ~20,500 BV. From this comparison, the HCO/GFC cartridge retained over

85% of its original arsenic removal performance after regeneration. Thus, it could be regenerated and reused to remove arsenic species from contaminated natural water efficiently, which could largely reduce the material cost for apparatus based on the HCO/GFC cartridge and be beneficial for its potential applications.

The concentration of cerium in the effluent was also examined during the continuous flow column test with the arsenic-contaminated natural water sample to evaluate the stability of the HCO/GFC adsorbent during the long time operation. Figure 8(b) shows the Ce content in the treated water effluent during the continuous flow column test for the natural water sample with EBCT of 2 min. It was always lower than 5 ppb during the whole treatment process, which showed that the HCO/GFC cartridge was stable in water and its use as the arsenic adsorbent did not cause secondary pollution to drinking water. These arsenic removal experiments with arsenic contaminated natural water samples showed that the HCO/GFC cartridge had a good arsenic removal performance in natural water with a large arsenic breakthrough bed volume, high regeneration capability, and good stability, which demonstrated its application potential for drinking water treatment.

4 Conclusions

This study offered a low-cost and simple method for the synthesis of hydrous CeO₂ nanoparticles attached on glass fiber adsorbents which have good arsenic removal performance and the potential industrial applicability. The HCO/GFC adsorbent was rolled into a cartridge for arsenic removal test. The arsenic removal performance was evaluated by equilibrium adsorption isotherm test, adsorption kinetic test, and flow through column test. The pH effects on column test were conducted. The test results show that HCO/GFC cartridge has the advantages of high arsenic removal capacity, easy handling, and low cost. The more toxic As(III) in water can be easily removed within a wide range of solution pH without pre-treatment. The arsenic contaminated ground-water from Yangzong Lake (China) was used in the column test. At EBCT of 2 min, the breakthrough bed volume was over 24,000 when the arsenic concentration in the effluent reached 10 ppb. The Ce content in the treated water was lower than 5 ppb during the column test, which showed that the use of the HCO/GFC material as an adsorbent did

not cause secondary pollution. The application conditions of the pseudo-first and pseudo-second models of adsorption kinetics are also clarified. When the ratio of As/HCO is low, the low exponential rate equation (first-order equation) is more suitable. When the ratio of As/HCO is higher, the high exponential rate equation (secondary equation) is more suitable.

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Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-020-0435-0>.

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