Simultaneous removal of As(V) and Cr(VI) from water by macroporous anion exchanger supported nanoscale hydrous ferric oxide composite

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ABSTRACT

As(V) and Cr(VI) are both highly toxic anionic pollutants and commonly co-exist in some industrial effluents and contaminated waters. In this study, simultaneous removal of them was efficiently achieved by employing a composite adsorbent (HFO-201) fabricated by immobilizing nanoscale hydrous ferric oxide (HFO) within a macroporous anion exchanger D201. The HFO-201 composite possesses two types of adsorption sites, i.e. the quaternary ammonium groups fixed on the D201 matrix and the embedded HFO nanoparticles. In the binary solution, the adsorption kinetic processes of both As(V) and Cr(VI) by HFO-201 were well fitted with the pseudo-first order kinetic model. Furthermore, HFO-201 exhibited a significantly higher adsorption capacity toward As(V) than D201 and an identical adsorption capacity toward Cr(VI) to D201. During the removal process, As(V) was captured by both the electrostatic attraction from the fixed quaternary ammonium groups and the formation of inner-sphere complex with the embedded HFO nanoparticles. Whereas, Cr(VI) was primarily adsorbed by the fixed ammonium groups. Fixed-bed treatment of As(V)/Cr(VI) binary synthetic water by HFO-201 resulted in elimination of As (from 1.0 to below 0.01 mg/L) and Cr (from 5.0 to below 0.05 mg/L), with the treatment capacity of 1700 bed volume (BV). Moreover, the exhausted HFO-201 was amenable to efficient in situ regeneration with a binary NaOH-NaCl solution for repeated use without any significant capacity loss.

Keywords: Adsorption, Ion exchange, Arsenate, Hexavalent chromium, Simultaneous removal, Nanocomposite.

1. Introduction

Both arsenic and chromium are highly toxic chemicals associated to serious problems of environmental pollution as well as several diseases. The high arsenic concentrations in the environment result from natural sources and human activities such as waste chemicals, the smelting of arsenic bearing minerals, the burning of fossil fuels, and the application of arsenic compounds in many products ([Mudhoo et al., 2011](#)). On the other hand, chromium species are mainly present in wastewater from different industries such as metal plating, paints and pigments, leather tanning, textile dyeing, and printing inks and also in additives for wood preservation ([El Nemr et al., 2008](#)). In aqueous solution, chromium and arsenic species are present mainly as oxyanions depending on the pH. The arsenic species present in water are mainly arsenate, As(V), and arsenite, As(III) ([Ratna Kumar et al., 2004](#)). Chromium exist mainly as hexavalent and trivalent species (Cr(VI) and Cr(III) respectively) ([Oh et al., 2007](#)). The maximum contaminant level in drinking water for Cr(VI) is 50 µg/L and that for arsenic is 10 µg/L recommended by the World Health Organization (WHO) ([WHO 2001, 1993](#)). More importantly, As(V) and Cr(VI) coexist in many cases, such as in the vicinity of mineral deposits, in the wastewater of timber preservative manufacture, and in the mining effluents. Since As(V) and Cr(VI) both have adverse health impacts, effective remediation technology is in great demand to simultaneously remove both pollutants. Till now, various strategies have been proposed to mitigate As(V) and Cr(VI) in wastewaters and source waters, including ion exchange ([Badruddoza et al., 2013](#)), precipitation ([Bazrafshan et al., 2013](#)), electrochemical treatment ([Janin et al., 2009](#)) and membrane separation ([Bodzek and Konieczny, 2011](#)). However, the most widely used techniques for the removal of As(V) and Cr(VI) have many limitations and cannot satisfy the increasingly stringent regulation.

For instance, the arsenic removal efficiency by membrane technologies can be greatly influenced by source water parameters and membrane types. The membrane fouling is still an obstacle for application ([Brandhuber and Amy, 1998](#)). The ion exchange method conducted by traditional ion exchangers usually disturbed by the influence of competing ions in wastewater ([Baciacchi et al., 2005](#); [Choong et al., 2007](#)). The physical processes are expensive and inefficient and chemical precipitation suffered from high costs, sludge handling and operational difficulties. The removal of As(V) by the electrochemical treatment is highly pH dependent ([Lakshmanan et al., 2010](#)). Thus, new efficient techniques are urgently required to enhance As(V) and Cr(VI) simultaneous removal from water.

Adsorption is regarded as an attractive technology for the removal of arsenic and chromium oxyanions, owing to its simplicity, easy handling, sludge-free operation, and cost effectiveness ([Dubey et al., 2009](#); [Capasso and De Martino, 2013](#)). Varieties of adsorbents have been investigated for the removal of As(V) and Cr(VI) including activated carbon ([Wu et al., 2009](#)), agricultural residues ([Dubey et al., 2009](#)), biomass ([Kamala et al., 2005](#)), and zeolite ([Figueiredo and Quintelas, 2014](#)). Of particular interest are the nanosized metal (hydr) oxides (NMOs) ([Onnby et al., 2014](#); [Pinakidou et al., 2016](#)). In comparison with the bulk counterparts, NMOs have a much larger surface area to accommodate far greater number of active sites for adsorption interaction. Furthermore, NMOs can selectively capture the target heavy metal anions by formation of inner-sphere complexes with surface hydroxyl groups (-OH). Furthermore, the saturated NMOs after adsorption can be regenerated with acidic or alkaline solution. Various kinds of nano materials such as iron oxide, aluminum oxide, zirconium oxide, and titanium oxide have shown high adsorption affinity for

oxyanions including arsenate and chromium ([Bang et al., 2005](#); [Badrudodoza et al., 2013](#)). Nevertheless, field application of nano-adsorbents for heavy metal removal is still a challenging issue, because of their ultrafine nature and poor mechanical strength, which greatly limited their prolonged use in water treatment. It is considered an effective approach to solve this issue to encapsulate the NMOs inside the channels of porous hosts with larger particle size and better mechanical strength. Among the numerous porous hosts, polymeric ion-exchanger with cross-linked structure is one of the most promising choices due to its durability, mechanical strength, and appropriate pore structure to embed the NMOs. In particular, the covalently bonded functional groups with electrostatic charges would greatly favor the dispersion of the NMOs as well as adsorption enhancement of the anionic pollutants on the basis of Donnan principle ([Nilchi et al., 2011](#); [Sarkar et al., 2011](#)).

Hydrated ferric oxides (HFOs) have high affinity for both As(III) and As(V) because of the functional surface groups, FeOH_2^+ and FeOH ([German et al. 2014](#)). Hydrous ferric oxide (HFO) could be prepared by precipitation of ammonia with ferric chloride or nitrate solutions in carbonate-free environment by purging with N_2 ([Fan et al., 2005](#)). In the past decades, many researchers have focused on doping particulate hydrated ferric oxides within the traditional adsorbents of larger pore size ([Cumbal et al., 2003](#); [DeMarco et al., 2003](#); [Blaney et al., 2007](#)).

A nanocomposite adsorbent named HFO-201, which was fabricated by confined growth of hydrated ferric oxide (HFO) nanoparticles inside the pore channels of polymeric anion exchanger D201, has exhibited preferable removal of phosphate or arsenic from synthetic and field water ([Zhang et al., 2008a](#); [Pan et al., 2009](#)). effect of solution chemistry on Struvite-based phosphorus recovery from the concentrated

bioeffluent was studied by using HFO-201 (Zhang et al., 2015). Also, the stability of HFO-201 was well demonstrated in acidic or alkaline pHs (Wang et al., 2011; Hua et al., 2013). Given that As(V) and Cr(VI) are both present in anionic forms, plus their coexistence in many cases, it can be anticipated that HFO-201 has great potential for simultaneous removal of both contaminants from water. However, the synchronous elimination of both pollutants by HFO-201 has never been reported. Hence, the objectives of this study are to investigate the adsorption of As(V) and Cr(VI) by HFO-201, and to elucidate the mechanism of their simultaneous removal. Batch adsorption experiments were carried out to explore the performance and mechanism of As(V) and Cr(VI) adsorption by HFO-201. Furthermore, fixed-bed adsorption and in situ regeneration experiments were conducted to evaluate the cyclic applicability of HFO-201 for the treatment of effluent containing both pollutants.

2. Materials and Methods

2.1. Materials

Disodium hydrogen arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was obtained from Sigma-Aldrich. Other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification. Stock solutions of As(V) and Cr(VI) were separately prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and K_2CrO_4 into deionized water (DI water) for further experiment. D201, a macroporous strongly basic anion exchanger of polystyrene matrix and chloride type, was obtained from Zhengguang Resin Co. Ltd. (Hangzhou, China). It was present as spherical beads ranging from 0.7 to 0.9 mm in diameter, with ammonium groups covalently bonded to the matrix. Prior to use, D201 was subjected to extraction with ethanol in a Soxhlet apparatus to remove the possible residue

impurities, and dried in vacuum at 313 K. In this study, D201 was also employed for comparison purpose because it is also utilized as a typical adsorbent to remove anionic pollutants from water.

2.2.Preparation of nanocomposite adsorbents

The HFO-201 nanocomposite was fabricated according to our previous study (Pan et al., 2009). In brief, the D201 beads were added into mixed solution of FeCl_3 , NaCl and HCl, followed by continuous agitation for 12 h. Then, the Fe(III)-loaded D201 beads were introduced into NaOH solution with continuous stirring, where Fe(III) was immobilized inside the pore channels of D201. Then, the resin beads were rinsed with DI water until neutral pH. Finally, the resulting beads were washed with ethanol and then were heated at 60 °C for 24 h to obtain the hybrid adsorbent HFO-201. Prior to use, the OH-type HFO-201 was transformed to Cl^- type by immersing the beads into 1.0 M NaCl solution, and then rinsed by DI water to approach neutral pH.

2.3.Batch adsorption experiments

Adsorption experiments were conducted through a batch equilibrium method. Briefly, a known amount of adsorbent was added in a 250 mL flask containing 100 mL binary solution of As(V) and Cr(VI), which was adjusted to designated pH with HCl or NaOH. The sealed flasks were then shaken in a thermostatic incubator at 180 rpm for 24 h to ensure the equilibrium. The preliminary kinetic experiments indicated that 6 h was sufficient to reach the adsorption equilibrium onto D201 and HFO-201. The amount of As(V) and Cr(VI) adsorbed were determined on the basis of mass

balance. For the kinetic experiments, 0.10 g of adsorbent was added into 500 mL solution containing As(V) and Cr(VI). Then, a 0.2-mL aliquot was sampled at a series of time intervals to determine As and Cr concentrations.

2.4.Fixed-bed adsorption and regeneration

Fixed-bed adsorption and regeneration experiments were conducted in a glass column (12 mm in diameter and 130 mm in height) equipped with a water bath to maintain a constant temperature at 298 K. Synthetic feeding solution containing As(V), Cr(VI), and coexisting anions (Cl^- , NO_3^- , and SO_4^{2-}) flowed through the fixed bed packed with 5 mL of HFO-201 or D201 beads. The flow rate was controlled by a digital peristaltic pump (Lange-850), and an automatic fraction collector was employed to collect the effluent samples. The empty bed contact time (EBCT) was 4 min. After adsorption, the laden adsorbent was insitu regenerated with a binary NaOH-NaCl solution (both 5% in mass), followed by rinsing with DI water until pH of the effluent approached neutral. Then, the regenerated adsorbent was employed for the next cycle of operation.

2.5.Analysis

The concentration of Cr(VI) was determined with an atomic adsorption spectrometer (AA7000, Shimadzu, Japan), while that of As(V) with an atomic fluorescence spectroscope equipped with an online reducing unit (AF-640A, China). The amount of Fe loaded within HFO-201 was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer, USA) after being digested in $\text{HNO}_3\text{--HClO}_4$ solution. N_2 adsorption-desorption analysis was carried out

at 77 K to determine the specific surface and pore size distribution using a Micromeritics ASAP-2010C Instrument (Norcross, GA, USA). The morphology of HFO particles dispersed in the pore channels of D201 was observed with transmission electron microscopy (TEM, H-800, Hitachi, Japan), and the mineralogy of the encapsulated HFO nanoparticles was analyzed by X-ray diffraction (XRD, XTRA, Switzerland) with $\text{CuK}\alpha$ radiation (40 kV, 25 mA). Scanning electron microscope (SEM, JEM-200CX, Hitachi, Japan) equipped with energy dispersive X-rayspectroscopy (EDX) was employed to further reveal the structural characteristics of HFO-201.

3. Results and discussion

3.1.Characterization of HFO-201

The fabricated nanocomposite HFO-201 was in the form of spherical beads (Fig. 1a). The TEM images of HFO-201 (Fig. 1b) revealed that HFO was immobilized within D201 as nanoparticles or nano-aggregates with size of 5-20 nm. SEM-EDX analysis indicated that Fe element distributed uniformly along the radial direction of HFO-201 beads (Fig. 1c). The uniform distribution of Fe will make more fully utilization of the inner space of the adsorbent and avoid clogging on the exterior of the bead. Statistically, ~75% of the embedded HFO nanoparticles had a size ranged from 10 to 30 nm (Fig. 1d). According to the XRD pattern of HFO-201 (Fig. 1d), the HFO nanoparticles encapsulated inside D201 was amorphous in nature, possibly due to the relatively low temperature ($<100^\circ\text{C}$) during the thermal treatment process (Yoldas, 1986).

The salient properties of D201 and HFO-201 are summarized in Table 1. ICP-

MS measurement of the resultant solid beads after acidic digestion showed that the Fe content in the HFO-201 composite was 19.1% in mass. Due to the pore blockage induced by HFO encapsulation, both the average pore diameter and pore volume of HFO-201 was smaller than that of the host material D201. However, the specific surface area significantly increased from 17.3 to 51.0 m²/g after the HFO loading, which could be attributed to the presence of the nanosized HFO particles with larger surface areas.

3.2. Effect of initial concentrations on the adsorption of As(V) and Cr(VI)

The effect of the initial Cr(VI) concentration on the adsorption of Cr(VI) and As(V) was presented in [Fig. 2](#). It can be seen from [Fig. 2a](#) that the uptake of Cr(VI) on both HFO-201 and D201 increased with the increase of Cr(VI) concentration. The capacity of D201 towards Cr(VI) was higher than that of HFO-201, which could be explained by the decrease in available ion-exchange sites of HFO-201 as a result of the pore blockage due to the immobilized hydrated metal oxide nanoparticles ([Zhang et al., 2008b](#)). In contrast, the uptake of As(V) onto both adsorbents decreased with the increase of the initial Cr(VI) concentration ([Fig. 2b](#)). Nevertheless, the decline in As(V) uptake by HFO-201 was relatively insignificant compared with D201. Particularly, at the initial Cr(VI) concentration of 30 mg/L, the uptake of As(V) by HFO-201 (17.5 mg/g) was more than twice of D201 (8.5 mg/g). Given that the HFO-201 composite is composed of the host anion exchanger D201 and the impregnated HFO nanoparticles, the positively charged quaternary ammonium groups of D201 matrix could sequester As(V) anions through nonspecific electrostatic attraction, while the entrapped HFO nanoparticles could further immobilize the target

As(V) anions by formation inner-sphere complex. Therefore, HFO-201 maintained a higher adsorption capacity toward As(V) than D201 at various initial Cr(VI) concentrations.

The effect of initial As(V) concentration on the adsorption of As(V) and Cr(VI) was depicted in Fig. 3. Similarly, the uptake of As(V) from binary solution by both adsorbents increased with the initial As(V) concentration increased from 0 to 30 mg/L (Fig. 3a). The capacity for As retention of HFO-201 was significantly higher than that of D201, owing to extra adsorption sites provided by the HFO nanoparticles loaded in the pore channels of the D201 host. The uptake of Cr(VI) by D201 remained unchanged regardless of the variation of initial As(V) concentration, while the uptake of Cr(VI) onto HFO-201 decreased very slightly (Fig. 3b). The above observations suggested that the quaternary ammonium groups had stronger affinity for Cr(VI) than the HFO nanoparticles. Therefore, Cr(VI) and As(V) preferentially occupied different kinds of adsorption sites during the simultaneous removal by HFO-201. Specifically, the HFO-201 has two types of active sites that worked on the simultaneous removal of Cr(VI) and As(V). According to the experimental result, As(V) mainly favored the inner-sphere complexation with the surface OH groups of HFO, whereas, Cr(VI) was sequestered primarily via the anion-exchange sites provided by the quaternary ammonium groups of the host material D201. The proposed mechanism was consistent with the previous studies concerning the simultaneous and separate adsorption of Cr(VI) and As(V) (Badruddoza et al., 2013; Fernandez-Calvino et al., 2014).

3.3. Effect of pH on the simultaneous adsorption of As(V) and Cr(VI)

The effect of solution pH on As(V) and Cr(VI) uptake from binary solution was examined, and the results were listed in Fig. 4a and b, respectively. During the given pH range, the zeta potential of HFO-201 was consistently higher than 15 mV (Fig. S1, Supporting information) and was favor of adsorption towards As(V) and Cr(VI) anions. The uptake of As(V) by HFO-201 and D201 increased gradually with pH increasing from 2.7 to 7.7 and from 2.7 to 7.1, respectively, and then decreased with further increase of pH from 7.7 to 8.8 and from 7.1 to 8.4, respectively (Fig. 4a). As(V) is present as the anionic species throughout the investigated pH range (Fig. S2, Supporting information). With pH increases, the more negatively charged species (H_2AsO_4^- and HAsO_4^{2-}) becomes predominant, which could augment the electrostatic attraction with the host D201. Thus, the uptake of As(V) by both adsorbents increased with the solution pH in the approximate range of 3-7. On the other hand, as for HFO-201, the surface of HFOs is gradually deprotonated and more negatively charged with further increase of pH approximately from 7 to 9. Therefore, the unfavorable As(V) uptake at high pH could be attributed to the repulsion between As(V) and HFO, as well as the competition between As(V) and the increasing OH^- for adsorption sites. As for D201, the unfavorable As(V) uptake at high pH could be only attributed to the competition between As(V) and the increasing OH^- for adsorption sites. As shown in Fig. 4b, the capacity of HFO-201 and D201 toward Cr(VI) decreased gradually with the equilibrium pH was increased from 3 to 9. Cr(VI) exists in various species in aqueous solution such as H_2CrO_4 , HCrO_4^- , and CrO_4^{2-} depending on the solution pH (Singh and Tiwari, 1997) (Fig. S3). The larger capacity of Cr(VI) adsorption at lower pH by HFO-201 and D201 may be attributed to the higher degree of surface protonation of the adsorbents. The increased of pH resulted in competitive

adsorption between OH^- and CrO_4^{2-} . Generally, the uptake of As(V) and Cr(VI) exhibited significantly different pH dependence. The adsorbed amount of As(V) had a peak at about pH 7.1-7.7, while the that of Cr(VI) gradually decreased with increasing pH. The above observation agreed well with those reported in the previous studies for As(V) and Cr(VI) adsorption ([Seki et al., 2005](#); [Memon and Bhatti, 2014](#)).

3.4. Adsorption kinetics

The kinetics of adsorption processes toward As(V) and Cr(VI) was studied in binary solutions, and the results were presented in [Fig. 5](#). The data of all four adsorption kinetic curves were well fitted ($r^2 > 0.98$) with pseudo first-order kinetic model.

The derived parameters were listed in [Table S1 \(Supporting information\)](#). Both the adsorptive rates of As(V) and Cr(VI) were rapid at initial process and then gradually decreased until equilibrium. For the adsorption of As(V), the equilibration time of D201 was 100 min while that of HFO-201 was about 150 min. The equilibrium capacity of HFO-201 toward As(V) was significantly higher than that of D201. This result implied that the HFO nanoparticles embedded in the pore channels provided large quantities of adsorption sites for As(V). According to our previous research on HFO loaded resin, adsorption of arsenic onto HFO loaded hybrid sorbents involved the following steps: (I) bulk diffusion; (II) boundary layer diffusion around HFO particles; (III) intraparticle diffusion within HFO particles; (IV) final equilibrium stage. Smaller HFO nanoparticles possess more exterior active sites. The intraparticle diffusion was primary limitation for adsorption rate when the average pore diameter of adsorbent was larger than 4.2 nm ([Wang et al., 2011](#)). But when the

average pore diameter of HFO-201 was decreased caused by impregnation of HFO nanoparticles (Table 1), the uptake rate of As(V) onto HFO-201 was predominantly controlled by HFO adsorption. For the adsorption of Cr(VI), the equilibrium capacity as well as the equilibrium time of Cr(VI) onto HFO-201 and D201 were quite similar, which revealed that Cr(VI) anions were primarily adsorbed by the ammonium groups via ion-exchange process.

3.5.Fixed-bed adsorption and regeneration

Fix-bed column adsorption experiments were conducted to evaluate the potential of the adsorbents in practical application. In addition to As(V) and Cr(VI), the feeding solutions also contained various coexisting ions to simulate the contaminated waters. The maximum contaminant level of Cr(VI) and As(V) was 50 and 10 $\mu\text{g/L}$ as recommended by drinking water guideline of WHO, respectively. The break through profiles of As(V) and Cr(VI) with high and low initial concentrations are depicted in Fig. 6 and Fig. 7, respectively. It can be seen from Fig. 6 that HFO-201 showed similar performance with D201 in the removal of Cr(VI) with working capacity of ~ 1700 bed volume (BV). However, the working capacity of HFO-201 (~ 1700 BV) was significantly superior to D201 (~ 250 BV) in terms of As(V) removal. In contrast, at relatively low initial concentrations (Fig. 7), the working capacity of HFO-201 was larger than D201 for both As(V) and Cr(VI). The capacity of Cr(VI) was mostly contributed by quaternary ammonium groups. But at low initial concentration of Cr(VI), the coexist anions were at relative higher concentration and they occupied most number of quaternary ammonium groups. So only a small part of Cr(V) was provided by HFO. Therefore, at low initial concentration the capacity of Cr(V) onto

HFO-201 exhibited higher than onto D201. Specifically, the effective treatment volume by HFO-201 for As(V) was ~4500 BV, which was orders of magnitude higher than that of D201 (~250 BV) (Fig. 7a). Moreover, the treatment volume by HFO-201 for Cr(VI) was ~4200 BV, which was also larger than that of D201 (~3300 BV) (Fig. 7b). Noticed that HFO-201 showed better (low concentration) or similar (high concentration) performance for Cr(VI) removal than D201, in contrast with results of batch experiment without co-existing anions. Associated with the results of batch experiments, it can be concluded that the Cr(VI) adsorption was primarily drove by non-specific ion exchange towards amino groups binding to matrix of resin instead of specific coordination towards hydroxyl on the surface of loaded HFO nanoparticles when there were no competing anions co-existed. The above observations demonstrated that HFO-201 was more competent for the efficient treatment of effluents containing both As(V) and Cr(VI) in comparison with the host material D201, which substantially broadened the applicability of the anion exchangers after the loading of HFO nanoparticles.

Upon the completion of the fixed-bed adsorption, the laden composite HFO-201 was subjected to in situ regeneration. As illuminated by the fact that HFO can be deprotonated and negatively charged under alkaline pH conditions, a binary solution of NaOH-NaCl (both 5% in mass) was used as the regenerant. The results in Fig. 8 indicated that the regeneration efficiency exceeded 90% for As(V) and 98% for Cr(VI) within only 10 BV of the regenerant. Furthermore, HFO-201 exhibited stable removal capability for both contaminants in the adsorption-regeneration cycles (Fig. 6 and Fig. 7) with only negligible capacity loss. The above observations showed that HFO-201 had great potential for sustainable utilization in fixed-bed reactors, which is

essential for the practical application in water treatment processes.

4. Conclusions

In the current study, we impregnated nanosized hydrated ferric oxide (HFO) into a polymeric anion exchanger D201 to obtain a hybrid sorbent (HFO-201) for synchronous elimination of As(V) and Cr(VI) from water. Compared with D201, HFO-201 exhibits superior performance of As(V) and Cr(VI) removal especially in the fixed-bed adsorption experiments that varieties of other anions co-existed. The adsorption of the two anionic contaminants by HFO-201 relied on different mechanisms. The removal of As(V) was mainly attributed to the Donnan membrane effect exerted by the host D201 as well as the specific interaction with the loaded HFO nanoparticles, while Cr(VI) was mainly adsorbed via ion-exchange onto the quaternary ammonium groups bonded to the matrix. The exhausted HFO-201 is amenable to effective regeneration with the binary NaOH-NaCl solution for cyclic utilization without significant capacity loss. This study showed that HFO-201 is a promising composite adsorbent for simultaneous removal of As(V) and Cr(VI) from water.

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Figures and tables

Fig. 1. Characterization of the resultant HFO-201: (a) SEM image of HFO-201, (b) TEM image of HFO-201, (c) distribution of Fe along the diameter on the cross section of HFO-201 bead, (d) particle size distribution of the embedded HFO nanoparticles, XRD pattern of HFO powders and HFO-201.

Fig. 2. Effect of the initial Cr(VI) concentration on the adsorption of (a) Cr(VI) and (b) As(V) in the binary system by D201 and HFO-201 at 298 K, pH = 7.0, initial As(V) 5 mg/L, adsorbent dosage 0.2 g/L, contact time 6 h.

Fig. 3. Effect of the initial As(V) concentration on the adsorption of (a) As(V) and (b) Cr(VI) in the binary system by D201 and HFO-201 at 298 K, pH = 7.0, initial Cr(VI) 20 mg/L, adsorbent dosage 0.2 g/L, contact time 6 h.

Fig. 4. Effect of solution pH on the adsorption of (a) As(V) and (b) Cr(VI) in binary system at 298 K. Initial As(V) 5 mg/L, initial Cr(VI) 20 mg/L, adsorbent dosage 0.2 g/L, contact time 6 h.

Fig. 5. Adsorption kinetics of (a) As(V) and (b) Cr(VI) in binary solution at 298 K. Initial As(V) 5 mg/L, initial Cr(VI) 20 mg/L, adsorbent dosage 0.2 g/L, pH = 7.0.

Fig. 6. Breakthrough curves of (a) As(V) and (b) Cr(VI) sorption from simulated mining waters onto HFO-201 and D201 at 298 K. Feed solution compositions: As(V) = 1 mg/L, Cr(VI) = 5 mg/L, SO_4^{2-} = 50 mg/L, NO_3^- = 10 mg/L, Cl^- = 10 mg/L; pH = 7.0 ± 0.1 ; The empty bed contact time (EBCT) = 4.0 min.

Fig. 7. Breakthrough curves of (a) As(V) and (b) Cr(VI) sorption from simulated natural waters onto HFO-201 and D201 at 298 K. Feed solution compositions: As(V) = 0.2 mg/L, Cr(VI) = 1.0 mg/L, SO_4^{2-} = 50 mg/L, NO_3^- = 10 mg/L, Cl^- = 10 mg/L; pH = 7.0 ± 0.1 ; The empty bed contact time (EBCT) = 4.0 min.

Fig. 8. Regeneration of the HFO-201 packed in fixed-bed at 298 K. Regenerant: binary NaOH-NaCl solution (both 5% in mass).

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Table 1.

Physicochemical properties of two polystyrene-based adsorbents

Adsorbent	D201	HFO-201
Matrix	polystyrene	
Functional sites	R-N ⁺ (CH ₃) ₃	R-N ⁺ (CH ₃) ₃ , HFO
BET surface area (m ² /g)	17.3	51.0
Pore volume (cm ³ /g)	0.2240	0.0446
Average pore diameter (nm)	51.8	3.50
Fe content (wt%)	--	19.1

GRAPHICAL ABSTRACT

In As-Cr binary solution, Cr(VI) was primarily adsorbed by quaternary ammonium groups fixed on the matrix of HFO-201, while As(V) was preferentially captured by the embedded HFO nanoparticles.