Fabrication, Characterization, and Application of a Composite Adsorbent for Simultaneous Removal of Arsenic and Fluoride

Chuanyong Jing,*† Jinli Cui,† Yuying Huang‡ and Aiguo Li‡

†State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
‡Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201214, China

Supporting Information

ABSTRACT: Coexisting arsenic (As) and fluoride (F) in groundwater poses severe health risks worldwide. Highly efficient simultaneous removal of As and F is therefore of great urgency and high priority. The purpose of this study was to fabricate a novel composite adsorbent and explore the mechanism for concurrent removal of As(V) and F at the molecular level. This bifunctional adsorbent with titanium and lanthanum oxides impregnated on granular activated carbon (TLAC) exhibits a pronounced As(V) and F adsorption capacity over commercially available iron- and aluminum-based adsorbents for synthetic and real contaminated groundwater samples. Synchrotron-based X-ray microfluorescence analysis demonstrates that La and Ti were homogeneously distributed on TLAC. Extended X-ray absorption fine structure spectroscopic results suggest that As(V) formed bidentate binuclear surface complex as evidenced by an averaged Ti−As bond distance of 3.34 Å in the presence of F. Adsorption tests and Fourier transform infrared spectroscopy analysis indicate that F was selectively adsorbed on lanthanum oxides. The surface configurations constrained with the spectroscopic results were formulated in the charge distribution multisite complexation model to describe the competitive adsorption behaviors of As(V) and F. The results of this study indicate that TLAC could be used as an effective adsorbent for simultaneous removal of As(V) and F.

KEYWORDS: arsenic, fluoride, simultaneous removal, synchrotron-based techniques, molecular level mechanisms

INTRODUCTION

Arsenic (As) and fluoride (F) are naturally occurring groundwater contaminants around the world, and have been the focus of extensive research efforts in the past few decades.1−3 Coexistence of As and F in groundwater is commonly found in many countries including Argentina,4 China,5 Mexico,5 and Pakistan,7 with concentrations up to 5300 μg of As/L and 29 mg of F/L in the same groundwater sample.4 The synergistic adverse effects are observed in mouse liver and kidney even at low As and F concentrations.6 The neuropsychological tests demonstrate that coexposure to As and F could exacerbate children’s performance.7 The drinking water standards for As and F are 10 μg/L and 1.5 mg/L, respectively, as suggested by the World Health Organization (WHO).8 However, this WHO standard is still a worldwide challenge, especially in rural villages without proper treatment.1

Among various As and F removal technologies, adsorption is most attractive because it is highly efficient, cost-effective, and suitable for single families and small communities.11,12 Many adsorptive media have been successfully developed to remove As or F. For example, TiO2 has been recently used for As removal from drinking water11 and from wastewater.13 Metal impregnation on porous materials has demonstrated promising results. The iron impregnated granular activated carbon (GAC) has an As adsorption capacity of 6.6 mg/g.14 To selectively adsorb F, researchers have impregnated rare earth elements on various carrier materials, such as La on chitosan beads15 and Zr on collagen fiber.16

However, few studies have paid attention to developing effective adsorbents for simultaneous removal of As(V) and F.17,18 Rather low adsorption capacities for As(V) (0.9 mg/g) and F (0.5 mg/g) are reported when goethite are applied to remove coexisting As(V) and F in a groundwater sample.17 Modified cellulose fibers result in an appreciable decrease of F removal from 82 to 28% in the presence of 1 mg/L As.18 A fundamental understanding of As and F adsorption mechanisms at the molecular level should improve our ability to design such a composite adsorbent for simultaneous As and F removal. Arsenic predominantly forms bidentate binuclear inner-sphere surface complexes by ligand exchange with hydroxyl groups at oxide surfaces.11,19 Ligand exchange between surface hydroxyl group and F is also the predominant

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F adsorption mechanism. Nevertheless, limited knowledge is available about the local coordination environment of As(V) surface complexes in the presence of F. The lack of this crucial information may inhibit the design of effective adsorbent for As(V) and F simultaneous removal.

The objective of this study was to develop a composite adsorbent with titanium and lanthanum oxides impregnated on granular activated carbon (TLAC) for simultaneous effective removal of As(V) and F. The effectiveness of TLAC was evaluated using batch experiments with a comparison to commercially available adsorbents. Synchrotron-based X-ray microfluorescence ($\mu$-XRF) was used to study the elemental distribution. The local coordination environments of As and F obtained with extended X-ray absorption fine structure (EXAFS) spectroscopy and Fourier transform infrared (FTIR) spectroscopy were employed as the molecular-level constraints in surface complexation modeling. The results of the study should further our understanding of simultaneous removal mechanisms of As(V) and F.

# EXPERIMENTAL SECTION

## Materials

All solutions were prepared using analytical grade chemicals and deionized (DI) water (Mill-Q, USA). Sodium arsenate (Na$_3$AsO$_4$·12H$_2$O), sodium fluoride (NaF), sodium perchlorate (NaClO$_4$), titanium sulfate (Ti(SO$_4$)$_3$), sodium arsenite (NaAsO$_2$), and lanthanum nitrate (La(NO$_3$)$_3$) were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). A Suwannee River Humic Acid solution (Guangfu, China) was used in the experiment without further purification. The stock solutions of 1,000 mg/L As(V), As(III), and F$_2$O$_7$·2H$_2$O, NaAsO$_2$, and NaF in DI water, respectively, and stored in refrigerator at 4 °C. A background electrolyte of 0.04 M NaClO$_4$ was used in the experiments.

**TLAC Synthesis.** The TLAC was prepared by impregnating Ti and La oxides on GAC. GAC was boiled for 30 min, then washed with DI water, and dried at 104.5 °C. About 12.0 g of cleaned GAC was added in 40 mL of 187.1 g/L Ti(SO$_4$)$_2$ solution and sonicated for 4 h before drying at 104.5 °C. The obtained material was transferred into 40 mL of 467.9 g/L La(NO$_3$)$_3$ solution and sonicated for another 4 h to impregnate La. Then, TLAC was roasted at 400 °C for 6 h, washed with DI water three times, and dried at 104.5 °C. The details of the TLAC optimization are shown in the Supporting Information, and the properties of E33p, Al$_2$O$_3$, and TLAC are shown in Table S1 in the Supporting Information.

**Characterization.** The surface morphology was examined using a Hitachi S-3000N scanning electron microscope (SEM) with an Oxford energy dispersive X-ray (EDX) analyzer. The BET surface area was determined using an automated surface area analyzer (Micromeritics ASAP 2000). X-ray powder diffraction (XRPD) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu target tube and a graphite monochromator. Scans were made in the 2θ range of 5° to 70° with a step size of 0.01° and a count time of 2 s per step. The analyses of the XRPD patterns were performed using the PDF-2 reference database from the International Center for Diffraction Data database.

**Batch Adsorption Experiments.** Kinetic experiments were carried out by reacting 30 mg/L As(V) and 10 mg/L F in 0.04 M NaClO$_4$ solution containing 0.1 g of TLAC, E33p, and Al$_2$O$_3$. The solution contained increasing amounts of As(V) and F at pH 7 with 0.04 M NaClO$_4$ as ionic strength. The suspension was mixed on a rotator for 24 h.

To compare the adsorption efficiency of TLAC, E33p, and Al$_2$O$_3$ for real contaminated groundwater, we conducted batch adsorption experiments in triplicate for each adsorbent with 1 h mixing. Groundwater with 0.73 mg/L As(III), 0.69 mg/L As(V), 2.01 mg/L F, and 7.5 mg/L TOC at pH 8.0 was obtained from a tubewell in Shanxi, China. Synthetic groundwater samples containing 1.7 mg/L As(III), 3.5 mg/L As(V), 10 mg/L F, and 2.5 mg/L HA in 0.04 M NaClO$_4$ at pH 7.0 were used as a comparison. The HA concentration was determined by UV spectroscopy at $\lambda = 245$ nm.

Adsorption envelope experiments were performed to determine the adsorption edge, which is the percentage of As(V) and F adsorbed as a function of the final solution pH. Suspension samples containing 1 and 30 mg/L As(V), 10 mg/L F, and 1 g/L TLAC were adjusted to desired pH values in the range of 4–12 with NaOH and HClO$_4$. The samples were mixed on a rotator for 24 h.

**EXAFS Analysis.** The EXAFS samples were prepared with 30 mg/L As(V), 50 mg/L F, and 1 g/L TLAC in 0.04 M NaClO$_4$. The spent TLAC adsorbent was freeze-dried and deposited onto Kapton tape. The monochromator was set at 14 keV to collect $\mu$-XRF maps at angles 15U at Shanghai Synchrotron Radiation Facility (SSRF), China. The beam was 5 × 5 μm$^2$, the dwell time per pixel was 0.3 s, and the step size was 5 μm. The peak intensities for As, Ti, and La were collected at each pixel of $\mu$-XRF maps with 0.4 × 0.4 mm$^2$ in size.

**ATR-FTIR Study.** Infrared spectra were collected with a Nicolet 6700 FTIR spectrometer equipped with a horizontal 45° ZnSe crystal as an attenuated total reflectance (ATR) attachment (Pike Technologies, USA). Spectra were obtained at a resolution of 2 cm$^{-1}$ with coaddition of 1000 scans using a liquid N$_2$ cooled mercury–cadmium–telluride (MCT) detector.

The adsorption samples for FTIR analysis were prepared by mixing F@As(V) and F solution containing 0.04 M NaCl with 30 g/L TLAC at pH 7.0 for 24 h. Then the solid and the solution were separated by centrifuging at 8,000 rpm, and the supernatant was filtered through a 0.22-μm membrane to remove any residual solid particles. Infrared spectra of adsorbed species of As(V) and F on TLAC were obtained by measuring wet paste and the corresponding supernatant as reference. The spectrum of blank TLAC was also collected as a control. The sample on the ZnSe crystal was covered with a lid to prevent water evaporation during the measurement. The subtraction of supernatant spectra from the wet paste spectra should yield the spectra of adsorbed As(V) and F on TLAC. The baseline correction of the ATR-FTIR spectra was performed without manipulating the magnitude of the peak or peak position shift.

**Surface Complexation Modeling.** A charge distribution multisite complexation (CD-MUSIC) model was used to describe the adsorption edges of As(V) and F on TLAC. The CD-MUSIC model has previously been employed to describe As adsorption behavior on TiO$_2$ and F adsorption on goethite. Details of CD-MUSIC modeling are reported in the Supporting Information.
RESULTS AND DISCUSSION

Adsorbent Characterization. The SEM images of GAC and TLAC are presented in Figure 1. Compared with the pristine GAC, TLAC exhibited even distribution of metal oxide particles in the porous structure and on the coarse surface. The EDX analysis of 14 different locations on TLAC suggested that the Ti and La contents were 14.7 ± 2.7% and 11.9 ± 1.5%, respectively, on a weight basis. In agreement with a previous report, the XRD pattern of GAC showed two broad peaks at 2θ = 24 and 43°, attributing to the activated carbon structure (Figure 1IV). With the coexistence of As(V) and F, the maximum adsorption capacity of As(V) on TLAC decreased from 30.3 to 25.1 mg/g (a reduction of 17%), and that of F from 27.8 to 17.0 mg/g (a reduction of 39%). The observed unequal decrease in As(V) and F adsorption capacity suggested that As(V) had a higher surface affinity than F. The TLAC media exhibited a pronounced advantage over E33p, Al2O3, and the modified cellulose fibers in As(V) and F removal on a weight basis (see Table S2 in the Supporting Information). The As(V) adsorption on E33p and Al2O3 did not significantly decrease in the presence of F (Figure 2), whereas the F adsorption in the presence of As(V) decreased by 64% (from 2.3 to 0.8 mg of F/g) on E33p and 25% (from 4.8 to 3.6 mg of F/g) on Al2O3 (see Table S2 in the Supporting Information). Modified cellulose fibers could achieve 27.93 mg of As/g and 8.59 mg of F/g adsorption capacity. TLAC resulted in much higher adsorption capacities of As(V) and F (see Table S2 in the Supporting Information).

Particle size is an important factor in adsorption. For example, the size effect of TiO2 on As adsorption has been previously reported by Xu and Meng, and they found the adsorption capacity of TiO2 for As increased linearly with the BET surface area, which is inversely related to the particle size. As shown in Table S2 in the Supporting Information, the direct comparison of adsorbed As(V) quantities per m2 surface area of various adsorbents indicated that E33p had the highest surface-area-based adsorption capacity. Because TLAC was a composite adsorbent with GAC as the supporting material for TiO2 and

that LaOOH was not transferred to La2O3 at 400°C. The BET surface area was slightly reduced from 681 of GAC to 538 m2/g of TLAC because the impregnation of Ti and La oxides may block some porous structure of GAC.

Simultaneous Adsorption of As(V) and F on TLAC, E33p, and Al2O3. Adsorption isotherms of As(V) and F (Figure 2) followed Langmuir equation: 

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}
\]

where \(C_e\) (mg/L) is the equilibrium concentration of As(V) or F, and \(q_e\) (mg/g adsorbent) is the amount of As(V) or F adsorbed; \(q_m\) (mg/g) and \(b\) (L/mg) are fitting parameters representing the maximum adsorption capacity and the adsorption affinity constant, respectively. The parameters of Langmuir isotherms for TLAC, E33p, and Al2O3 are listed in Table S2 in the Supporting Information. The maximum adsorption capacities of single As(V) (30.3 mg/g) and F (27.8 mg/g) on TLAC were significantly higher than those on E33p (18.0 mg-As/g and 2.3 mg-F/g) and Al2O3 (7.3 mg-As/g and 4.8 mg-F/g). With the coexistence of As(V) and F, the maximum adsorption capacity of As(V) on TLAC decreased from 30.3 to 25.1 mg/g (a reduction of 17%), and that of F from 27.8 to 17.0 mg/g (a reduction of 39%). The observed unequal decrease in As(V) and F adsorption capacity suggested that As(V) had a higher surface affinity than F. The TLAC media exhibited a pronounced advantage over E33p, Al2O3, and the modified cellulose fibers in As(V) and F removal on a weight basis (see Table S2 in the Supporting Information). The As(V) adsorption on E33p and Al2O3 did not significantly decrease in the presence of F (Figure 2), whereas the F adsorption in the presence of As(V) decreased by 64% (from 2.3 to 0.8 mg of F/g) on E33p and 25% (from 4.8 to 3.6 mg of F/g) on Al2O3 (see Table S2 in the Supporting Information). Modified cellulose fibers could achieve 27.93 mg of As/g and 8.59 mg of F/g adsorption capacity. TLAC resulted in much higher adsorption capacities of As(V) and F (see Table S2 in the Supporting Information).

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![Figure 1. SEM images of pristine (I) GAC and (II) TLAC, (III) EDX spectrum for TLAC with inset showing an average Ti and La content at 14 various locations, and (IV) the XRD patterns of GAC and TLAC.](image1)

![Figure 2. Adsorption isotherms for (I) As(V) and (II) F on TLAC (square), E33p (triangle), and Al2O3 (diamond) in 0.04 M NaClO4 solution at pH 7.0. Open and closed symbols represent the presence of single adsorbate and coexisting As(V) and F, respectively.](image2)
LaOOH, its BET surface area was mainly attributed to pristine GAC. GAC with its superior surface area, however, did not contribute to As(V) adsorption as indicated in Figure S1 in the Supporting Information. This observation may suggest that surface area is an important parameter when comparing the adsorption capacity of the same material with various sizes. Nevertheless, the surface area alone may not be a proper parameter to compare different media because the adsorption mechanisms may not be the same for various adsorbents.

In this study, the adsorption capacity of As (30.3 mg/g) on TLAC was comparable with that on nanocrystalline TiO2 (37.5 mg/g) reported in a previous study under the same experimental condition where As(V) in a 0.04 M electrolyte solution was adsorbed on 1 g/L TiO2 at pH 7.26 The particle size and aggregation state of impregnated TiO2 on TLAC should be more stable during the adsorption process than that of nanocrystalline TiO2. The different physical states of TLAC and nanocrystalline TiO2 may lead to the discrepancies in As adsorption capacity.

The effectiveness of TLAC, E33p, and Al2O3 on simultaneous As and F removal was compared using synthetic and real contaminated groundwater samples and the results are shown in Figure 3. TLAC was superior to the commercial media in the removal of As (III), As(V), and F in synthetic samples even at elevated contamination levels (Figure 3I). The same conclusion can be drawn using real groundwater samples (Figure 3II). Over 80% As(V) and As(III) was adsorbed on TLAC, which was the highest removal efficiency among the three media. To compare the removal efficiency of TLAC with commercial media, 1 g/L adsorbent was used in batch adsorption experiments. In the practice of water treatment, the adsorptive filtration process is generally adopted where contaminated water flow through the media in a fixed bed.27 The enhanced solid to liquid ratio in the filter house could provide sufficient surface sites for adsorption, resulting in satisfactory water quality.

The F adsorption in groundwater sample was reduced compared with that in synthetic water (Figure 3). The groundwater sample had a complex matrix including 110 mg/L sulfate and 412 mg/L carbonate, which can have a negative impact on F adsorption.28 Sulfate can form both outer-sphere and inner-sphere complexes on metal oxides,29 whereas carbonate primarily forms inner-sphere surface complex.30 Therefore, the competition from the coexisting anions would compete with As and F for the available adsorption sites.31 The adverse effect was much more pronounced for F than for As, indicating As has a higher affinity to adsorbent than F. In addition, no soluble La and Ti was detected in solution, suggesting that LaOOH and TiO2 would not leach out during the adsorption.

Adsorption Kinetics of As(V) and F on TLAC. The adsorption rates of As(V) and F were rapid during the initial 15 min, and the As(V) and F concentration kept relatively constant thereafter (Figure 4). A pseudosecond-order kinetics model has been applied previously to describe the adsorption of As(V) on TiO2,33 and F on lanthanum hydroxide32 and was used in the present study. The equation is expressed as $t/q = t/\text{qe} + 1/k\text{qe}^2$, where $q_e$ and $q_t$ are the amount (mg/g) of As(V) or F adsorbed at time $t$ and equilibrium, respectively, and $k$ (g/(mg h)) is the rate constant. The model described the experimental data pretty well (Figure 4) with calculated parameters shown in Table S3 in the Supporting Information. F had a negligible effect on As(V) adsorption kinetics. Although the equilibration time of F adsorption was not affected by the presence of As(V), the adsorption capacity of F decreased from 9.4 to 7.4 mg/g with coexisting As(V). This observation also confirmed a higher affinity of As(V) to TLAC than F.

Element Distribution on TLAC. The SEM-EDX (see Figure S4 in the Supporting Information) and μ-XRF (Figure S) analyses of spent TLAC media showed that As(V) was associated with the impregnated Ti and La oxides. The highly correlated Ti and La demonstrated that TiO2 and LaOOH were evenly impregnated on GAC in μm size resolution provided by μ-XRF. To investigate our hypothesis that As(V) and F adsorb on TiO2 and LaOOH, respectively, the molecular level study including EXAFS and FTIR should be performed.

![Figure 3](image1.png) Adsorption efficiency using 1 g/L TLAC, E33p, and Al2O3 (I) for a synthetic water sample containing 1.7 mg/L As(III), 3.5 mg/L As(V), 10 mg/L F, and 2.5 mg/L HA in 0.04 M NaClO4 at pH 7.0, and (II) for a real groundwater sample containing 0.73 mg/L As(III), 0.69 mg/L As(V), 2.01 mg/L F, and 7.5 mg/L TOC at pH 8.0.

![Figure 4](image2.png) Adsorption kinetics of (I) 30 mg/L As(V) and (II) 10 mg/L F on TLAC in 0.04 M NaClO4 solution at pH 7.0. Open and closed symbols represent the presence of single adsorbate and coexisting As and F, respectively.
Arsenic K-edge EXAFS Analysis. EXAFS spectroscopy was employed to determine the As(V) local coordination environment on TLAC in the presence of increasing amounts of F. The \( k^3 \)-weighted EXAFS spectra and Fourier transform (FT) versus radial distance are shown in Figure 6. The optimal structure parameters obtained by fitting the theoretical paths to the experimental spectra are shown in Table S4 in the Supporting Information. The FT of the EXAFS spectra isolated the contributions of coordination shells, and the peak positions correspond to the interatomic distances. However, these peak positions in Figure 6 were uncorrected for the phase shift, so they deviated from the true distance by 0.3–0.5 Å.

The EXAFS analysis showed that the first and strongest peak in the FT curve was contributed by 4 oxygen atoms at an average distance of 1.69 Å for all samples, which is in agreement with previous reports.\textsuperscript{22,33,54} The result confirmed that the tetrahedral \( \text{AsO}_4 \) structure did not change under the competition of F. The second peak in the FT was attributed to 1.3–1.6 Ti atoms at an interatomic distance of 3.33–3.35 Å. In line with our previous study,\textsuperscript{11} the As–Ti distances and coordination numbers suggested that As(V) formed bidentate binuclear inner-sphere complexes on TiO\textsubscript{2}. In the presence of F with a concentration up to 1000 mg/L F (F/As = 131, molar ratio), the structure of adsorbed As(V) remained unchanged.

ATR-FTIR Analysis. In order to understand which metal oxide is responsible for F adsorption, the ATR-FTIR spectra of adsorbed As(V) and F were collected as shown in Figure 7. All spectra exhibited a broad peak at around 1100 cm\(^{-1} \) which can be attributed to TLAC. In the presence of 0.01 M As(V) (Figure 7-b), a strong peak at 849 cm\(^{-1} \) was observed that corresponded to the As–O vibration.\textsuperscript{35} With the addition of 0.26 and 0.65 M F, this As–O peak did not shift. The lack of change in As(V) peak position under an extremely high F/
As(V) molar ratio of 65 indicates that F may be adsorbed to a different surface site other than TiO₂. Single F adsorption resulted in a peak at 920 cm⁻¹ (Figure 7e).

To further validate the assumption that F selectively adsorbed on LaOOH, we compared the F adsorption on TLAC, LaOOH, La₂O₃, TiO₂, and GAC. Less than 5% F was adsorbed on GAC and TiO₂ (Figure 8). In stark contrast, LaOOH and TLAC resulted in more than 89% F adsorption, indicating that F preferentially adsorbed on LaOOH surfaces. TLAC resulted in a higher F removal than La₂O₃, most probably because the amorphous LaOOH in TLAC may have a larger BET surface area than that crystal form of La₂O₃.

Surface Complexation Modeling. To link the macroscopic As(V) and F adsorption behaviors with the molecular level adsorption mechanisms, we employed a CD-MUSIC model to simulate the As(V) and F adsorption pH edges. The model adopted TiOH surface for As(V) adsorption and LaOH surface for F.

Two As(V) concentration levels, 1 and 30 mg/L, were used to study the effect of 10 mg/L F competition. The results showed that over 90% As(V) was adsorbed in environmental relevant pH range of 5 to 9 for low and high initial As(V) concentrations (Figure 9). The adsorption percentage at pH > 10 was decreased due to the competitive adsorption with hydroxides, and a higher initial As(V) concentration resulted in a greater decrease in adsorption. F had negligible effect on As(V) pH edge curves.

The adsorption percentage of F increased slightly from 81.5% at pH 3.24 to 91.2% at pH 5.35, and then decreased slowly to 15.1% at pH 11.1 (Figure 9II). This observation is consistent with F adsorption on metal oxides and metal-impregnated adsorbents. The adsorption of F decreased with the addition of As(V), and the decrease was evident with increasing As(V) concentrations from 1 to 30 mg/L. The zeta potential of the double layer on surface would decrease appreciably to negative values in environmental pH range upon As(V) adsorption. As a consequence, F adsorption would be inhibited. On the other hand, F adsorption by ligand exchange of a surface OH⁻ by F⁻ suggests that the charge and potential of the surface should not change upon F adsorption. Therefore, F adsorption caused negligible changes in As(V) adsorption. If the adsorbents were mixed with TiO₂ impregnated GAC and LaOOH impregnated GAC, coexisting As(V) and F would also compete for the surface hydroxyl groups because this ligand exchange is the mechanism of adsorption of anions.

**CONCLUSION**

Highly efficient simultaneous As and F adsorptive media is under urgent need to reduce the coexposure risks. Our results show that TLAC has a higher As(V) and F adsorption capacity than that of widely used E33p and Al₂O₃ media, and could be used as an effective adsorbent for simultaneous removal of As(V) and F. TiO₂ and LaOOH evenly distributed on the surfaced of the TLAC, which preferably form inner-sphere surface complexes with As(V) and F, respectively. In addition, the advantage of GAC in removing dissolved organic matter makes TLAC more attractive. Applicability of TLAC for long-term real groundwater treatment merits further investigation.

**ASSOCIATED CONTENT**

Supporting Information
Description of TLAC optimization and characterization, LaOOH synthesis and PZC determination, SEM-EDX, and EXAFS analysis; tables showing comparison of media, parameters for isotherms, kinetics, EXAFS, and CD-MUSIC modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: cyjing@rcees.ac.cn.

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