Original article

Adsorption of arsenate on lanthanum-impregnated activated alumina: *In situ* ATR-FTIR and two-dimensional correlation analysis study

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ARTICLE INFO

Article history:

Received 30 September 2014
Received in revised form 15 November 2014
Accepted 1 December 2014
Available online 16 December 2014

Keywords:

Arsenic
Adsorption
Lanthanum-impregnated activated alumina
Two-dimensional (2D) correlation

ABSTRACT

Lanthanum modified materials have been widely used for the removal of hazardous anions. In this study, *in situ* ATR-FTIR and two-dimensional correlation analysis were employed to investigate the adsorption mechanism of arsenate (As(V)) on lanthanum-impregnated activated alumina (LAA). Our results showed that electrostatic interaction attracted As(V) anions to the LAA surface, and then As(V) could form monodentate configuration on the LAA surface at pH 5–9. The result of 2D-COS showed that two coexistent adsorbed As(V) species, H_2AsO_4^- and HAsO_4^{2-} , were adsorbed on the LAA surface without specific sequence at different pH conditions, indicating a negligible role of the incorporated protons of As(V) on the adsorption affinity to LAA surface. The results of this study reveal insights into LAA surface complexes on the molecular scale and provide theoretical support to new metal oxides design for efficient arsenic removal.

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1. Introduction

Naturally occurring arsenic (As) in groundwater has drawn great attention due to its hypertoxicity and extensive distribution [1,2]. The World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) have successively proposed a more restricted guideline for As in drinking water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ [3]. Thus, new technologies and materials for efficient removal of As from water are urgently demanded.

Since lanthanum (La)-impregnated silica gel was first designed as an adsorbent for water treatment in 1996 [4], extensive La loading materials have been widely studied for hazardous anion removal, especially for fluoride [5], phosphate [6], and arsenate (As(V)) [7], due to their selectivity and high removal efficiency without producing harmful by-products. While many La-based materials were synthesized for adsorption, however, research efforts have primarily focused on the promotion of anion removal efficiency, while studies on the adsorption mechanisms at the liquid/solid interface are still scarce, which has seriously limited the development of the adsorbents.

Due to the high sensitivity needed to reflect the molecular structure changes at interfaces without interferences by the

signals from the liquid phase, *in situ* ATR-FTIR spectroscopy has been widely used to probe the liquid/solid interfaces at the molecular level [8,9]. Besides, two-dimensional correlation spectroscopy (2D-COS) has been successfully applied to investigate the dynamics of adsorption, diffusion, and biological processes [10,11]. One major advantage of 2D-COS is that it can probe the specific sequence of spectral intensity changes corresponding to external perturbations, such as the changes in pH, time, and concentration. Therefore, 2D-COS is especially suitable for the data analysis following the *in situ* ATR-FTIR spectroscopy.

The objective of this work is to explore the adsorption process and mechanisms of As(V) on lanthanum impregnated, activated alumina (LAA) at the molecular level. The *in situ* ATR-FTIR technique and 2D-COS analysis are employed to gain important insights into the As(V) adsorption at different pH and then determine the surface As species and structures. The results would further improve our understanding of the interactions between As(V) and metal oxides.

2. Experimental

2.1. Materials synthesis

LAA was synthesized as reported in our previous study [5]. Briefly, 14.5 g activated alumina (AA, Keyuan, China) was

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Fig. 1. High resolution transmission electron microscope image of LAA powder (a) with inset picture of high magnification of region 2; EDS of region 1a is shown in (b) and region 2a is shown in (c); XRD patterns (d) of LAA (blue) and AA (black) (▼: χ - Al_2O_3 , PDF No. 13-0373).

impregnated with 10 mL 0.9 mol/L $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution. Then the synthesized material was calcinated at 300 °C for 4 h. After the material was cooled to room temperature, it was washed with deionized (DI) water and air-dried. The obtained LAA was powdered and characterized for surface morphology and element distribution using a high resolution transmission electron microscopy (HRTEM) and an Oxford energy dispersive X-ray spectroscopy (EDS) analyzer (Tecnai G2 F20, FEI, U.S.). X-ray powder diffraction (XRD, X'Pert PRO MPD, PANalytical, The Netherlands) data were recorded on a Rigaku D/Max-2500 diffractometer using a Cu-target tube ($\lambda = 1.5418$). Scans were made in the 2θ range of 5–90° with a step size of 0.01° and a count time of 2 s per step. Analysis of the XRD patterns was performed using the PDF-2 reference database from the International Center for Diffraction Data (ICDD) database.

2.2. In situ ATR-FTIR experiments

ATR-FTIR measurements were performed using a Thermo-Nicolet Nexus 6700 FTIR spectrometer equipped with a horizontal attenuated total reflectance (HATR) cell (PIKE Tech) and a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. A multibounce ZnSe ATR crystal with 45° beveled faces (infrared angle of incidence, θ) was used and the infrared spectra were collected using 256 scans per spectrum at a resolution of 4 cm^{-1} .

A 20 mg/L As(V) solution was prepared in 0.01 mol/L NaCl background electrolyte at the designed pH values. The FTIR measurements of As(V) sorption were similar to those described in our previous publications [12,13]. Briefly, the film was deposited on the ZnSe crystal by applying 500 μL of the well-diffusion (using ultrasonic method) LAA suspension (5 g/L) and dried in the room temperature. Prior to use, the film was rinsed with DI water to remove loosely deposited particles. The 0.01 mol/L NaCl solution at a predetermined pH was passed through the flow cell at a rate of 0.4 mL/min until there was no further change in the spectra. A

background spectrum comprised of the absorbance of the ZnSe crystal and deposited adsorbents was collected. Spectra were recorded as a function of time until the sorption reached equilibrium (at least 4 h). All of the samples were purged with N_2 in dark during the spectra collection.

2.3. 2D-COS

After essential smoothing and baseline corrections performed using the Omnic 8.2 software, FTIR spectra collected with an increment of 8 min during adsorption process were selected for 2D correlation analysis using the 2Dshige software (Shigeaki Morita, Kwansei-Gakuin University, 2004–2005). The method was detailed in the previous report [12].

3. Results and discussion

The surface morphology of synthesized LAA was characterized by HRTEM. As shown in Fig. 1a, nanosheets were found on the surface of particles, which was in agreement with our previous field emission scanning electron microscope (FE-SEM) results [9]. The element distribution of regions 1 and 2 (Fig. 1a) was further investigated by EDS. The main composition of region 1 was alumina and region 2 was lanthanum oxides (Fig. 1b and c, respectively). The appearance of a peak due to Cu in the EDS spectra was due to the drop of samples on Cu grid for HRTEM characterization. No obvious lattice was found in the high-magnification of region 2 (Fig. 1a inset), indicating the lanthanum oxides were in the amorphous phase. In addition, the XRD spectra of LAA showed no significant difference from those of AA. The only observation of χ - Al_2O_3 phase in LAA indicated the formation of amorphous phase lanthanum oxides, which agreed well with our HRTEM results.

Fig. 2. In situ ATR-FTIR spectra of As(V) adsorbed on LAA at pH 5, 6, 7, 8, and 9; arsenate concentration = 20 mg/L, ionic strength = 0.01 mol/L NaCl, room temperature.

The ATR-FTIR spectra of adsorbed As(V) on LAA films at different pH values as a function of time are presented in Fig. 2. The striking spectral changes mainly occurred at 1000–700 cm^{-1} region, which was the focus in this study. With the increasing of time, the peak at $\sim 830 \text{ cm}^{-1}$, corresponding to the vibration of As–O bond adsorbed on LAA, was progressively increased. The peak position agreed well with our previous results [14] and the report of other researchers [15]. Meanwhile, the peak intensity, which correlated with the amount of As(V) adsorbed on LAA, changed over the pH values. Furthermore, the peak positions also shifted from 839 cm^{-1} to 819 cm^{-1} from pH 5 to 9. Because the spectroscopic method alone was not sensitive enough to reveal the dynamics of the sorption process, kinetics modeling and 2D-COS were employed for the further study.

To further understand the processes of the As(V) adsorbed on LAA, the peaks centered at 839, 831 and 819 cm^{-1} in spectra at pH 5–9 (the maximum peak in each spectrum) were selected as indexes of adsorbed As(V) on LAA, respectively. The increase in the peak intensity of those selected peak was further fitted using *pseudo*-second-order equation:

$$Q = \frac{Q_e K_1 t}{1 + Q_e K_1 t}$$

where Q_e and Q_t are the absorption of adsorbed arsenate (Abs) at equilibrium and at any time t (min), respectively. K_1 (Abs min^{-1}) is the equilibrium rate constant for the *pseudo*-second-order model. The related kinetics parameters were summarized in Table 1. The high correlation coefficients ($R^2 > 0.980$) showed that the adsorption processes were well-described using *pseudo*-second-order kinetics model. The parameters of this model, including the calculated adsorbed As(V) amount at equilibrium (Q_e), are shown in Table 1. The Q_e of LAA decreased gradually in the order of pH 6 > pH 5 > pH 7 > pH 8 > pH 9. Because the point of zeta charge (pH_{pzc}) of LAA was 8.9 as we measured, the electrostatic attraction between the positive surfaces of LAA and As(V) anions existed at most of the studied pH conditions. This nonspecific interaction is attributed to the adsorption trend as the As(V) adsorption capacity decreased with increasing pH from 6 to 9. The exceptional low adsorption capacity at pH 5 was due to the La leaching from LAA at pH < 6 as shown in our previous study [5] (Fig. 3).

The second derivative spectra were always used to distinguish the overlapped IR sub peaks. In our study, as shown in Fig. 4, the IR spectra were further studied through their negative second derivative performances. The results showed peaks appeared at 869, 838, 798, and 788 cm^{-1} , and peaks at lower peak positions ($< 780 \text{ cm}^{-1}$) were also observed in the spectra. The appearance of more than four peaks in the IR spectra indicated that other than one species of As(V) adsorbed on the LAA surface. However, the ratio of signal/noise in this area was not adequate to acquire

Fig. 3. Kinetics of peak intensity as a function of time acquired at different pH values, As(V) concentration = 20 mg/L, ionic strength = 0.01 mol/L NaCl (839, 839, 839, 831, and 819 cm^{-1} at pH = 5, 6, 7, 8, and 9, respectively).

information of those As(V) species. This low resolution further motivated us to analyze the IR spectra using 2D-COS techniques.

As mentioned above, 2D-COS was also employed to discern the As(V) adsorption process at different pH, and the results are shown in Fig. 5. The synchronous spectra indicated the direction of variations in peak intensity during the adsorption. For example, the peak intensity of the 839 cm^{-1} bands at pH 5–9 increased with increasing time (Fig. 2), so a positive synchronous cross peak was resolved.

As shown in Fig. 5, the prominent auto-peaks on the diagonal were observed at 839, 839, 839, 831 and 819 cm^{-1} in synchronous spectra, respectively, suggesting the spectral intensities of As–O stretching bands have distinctly changed during the adsorption process. Similar to the results of ATR-FTIR spectra, with increasing pH, the peak positions markedly shifted toward lower wavenumbers, which was attributed to the change of incorporated proton number on the adsorbed AsO_4^{3-} at different pH conditions [16]. Specifically, with the increasing of pH from 5 to 9, the dominate species of As(V) changed from H_2AsO_4^- to HAsO_4^{2-} ($\text{pK}_{\text{a}2} = 6.76$). Then, the same conversion from adsorbed H_2AsO_4^- to HAsO_4^{2-} occurred on the LAA surface and further caused the peak shift.

Furthermore, the peak shift followed a simple rule to determine the coordinate mode of arsenate. The transformation of a monodentate-coordinated metal–arsenate complex from two to one incorporated proton leads to the shift of the As–O stretching bands to lower frequency, while for a bridging bidentate complex, the result is the opposite [17]. The different band shift trends are caused by different symmetries and As–O band intensities of coordinated arsenate surface complexes. In our study, the peak position shifted from 838 cm^{-1} at pH 5 to 819 cm^{-1} at pH 9, which was due to the increasing peak intensity at lower wavenumber from pH 5 to 9. Furthermore, the lower wavenumber at high pH indicated that the As–O stretch of HAsO_4^{2-} was weaker than

Table 1

Parameters of *pseudo*-second-order model for arsenate adsorbed on LAA at different pH values.

pH	<i>Pseudo</i> -second-model		
	K_1 ($10^{-3} \text{ Abs}^{-1} \text{ min}^{-1}$)	Q_e (Abs)	R^2
5	0.093	0.172	0.998
6	0.054	0.238	0.992
7	0.119	0.142	0.985
8	0.109	0.077	0.984
9	0.285	0.029	0.980

Fig. 4. Negative second derivative FTIR spectra of As(V) adsorbed on LAA at different pH conditions.

Fig. 5. Synchronous (top) and asynchronous (bottom) contour plots obtained from the time dependent spectra of arsenate adsorbed on LAA at different pH values. The shaded and unshaded areas in the 2D spectra represent negative and positive peaks, respectively.

Table 2

The 2D-COS results on the assignment and sign of each cross-peak in synchronous (Φ) and asynchronous (Ψ , in the parentheses) maps of arsenate adsorbed on LAA at pH 7.

pH 7	869	838	800	788
788		(+)		^a
800		+	^a	
838	(-)	^a	+	(-)
869	^a	(+)		

^a Denotes the synchronous autpeak.

that of H_2AsO_4^- adsorbed on LAA. This phenomenon agreed well with the monodentate configuration on metal oxide surfaces, indicating that the As(V) adsorbed on LAA in monodentate configurations in the pH range 5–9.

Two-dimensional asynchronous spectra could identify the specific order in surface interactions taking place under external perturbations [12]. An asynchronous cross peak arises when the intensity of two peaks change independently out of phase. The sequential order of intensity changes between band ν_1 and ν_2 could be obtained from the sign of synchronous correlation peak Φ (ν_1 , ν_2) and asynchronous correlation peak Ψ (ν_1 , ν_2) under the well-established principles [11]. In brief, the change in the spectral intensity at ν_1 band occurs prior to that at ν_2 if Φ (ν_1 , ν_2) and Ψ (ν_1 , ν_2) have the same sign, while the order is reversed if Φ (ν_1 , ν_2) and Ψ (ν_1 , ν_2) have the opposite sign. The changes at ν_1 and ν_2 occur simultaneously if Ψ (ν_1 , ν_2) is zero. The order is indeterminate if Φ (ν_1 , ν_2) is zero.

On the basis of this rule, correlation analysis was performed for the spectra at pH 5–9 in this study. As shown in Fig. 5 and Table 2 (take pH 7 as an example), the analysis resolved several cross peaks at different pH. For example, the sub peaks at 869, 838, 800, 788 cm^{-1} were observed at pH 7, which were in agreement with our second derivative spectra. Furthermore, the positive Φ values of auto peaks in the synchronous indicated the arising As(V) amount in the adsorption processes. However, most cross peaks in asynchronous maps were not observed in the synchronous maps, indicating the specific order in surface interactions was indeterminate. It implied that the adsorption sequence of H_2AsO_4^- and HAsO_4^{2-} was irregular, depending on the solution condition. This result suggested that protons incorporated on As(V) played a negligible role on As(V) adsorption affinity to LAA.

4. Conclusion

Both ATR-FTIR and 2D-COS were used to explore the adsorption process of As(V) on LAA in this study. The ATR-FTIR result and adsorption kinetics study confirmed that the electrostatic attraction between the positive surfaces of LAA and As(V) anions existed. The results of 2D-COS demonstrated that the As(V) was adsorbed on LAA as a monodentate configuration in the pH range 5–9. In addition, the coexistent adsorbed species, H_2AsO_4^- and HAsO_4^{2-} , were adsorbed on LAA surface without specific sequence at different pH, indicating a negligible role of the incorporated protons of As(V) on the adsorption affinity to LAA surface. The results of this study gained insights into LAA surface complexes on the molecular scale and provided theoretical support to new metal oxides design for efficient removal of arsenic.

Acknowledgments

This work is supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB14020201), the National Basic Research Program of China (No. 2014CB441102), the National Natural Science Foundation of China (No. 21477144), and the Young Scientists Fund of RCEES, RCEES-QN-20130017F.

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