

ARSENIC SPECIATION AND IDENTIFICATION ON ACTIVE IRON ADSORBENT SITES BY XAFS TECHNOLOGY

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ABSTRACT: Nano-sized Fe species were formed as layered FeO(OH) and as Fe-montmorillonites, which were identified by X-ray absorption fine structure (XAFS) spectroscopy, XRD and BET techniques, and applied for As removal from test solutions of 0.20 – 16 mg_{As}/L. Adsorption efficiency was better for these nano-materials compared to traditional bulk iron oxyhydroxides. The performance of layered FeO(OH) was best when it was washed with ethanol prior to its use for arsenic sorption. Layered FeO(OH) and Fe-montmorillonites exhibited nearly equivalent performance for arsenic uptake on an adsorbent weight basis. On an iron weight basis, the latter was ≥ 4 times better than the former. To detect very low concentrations of As (0.13 – 0.48 wt%) in the high concentrations of heavy elements (*i.e.* Fe), As K-edge XAFS was combined with high-energy-resolution fluorescence spectrometry. The inflection point energy of adsorbed arsenite shifted close to the arsenate reference compound, indicating oxidation of As^{III} upon adsorption from test solutions of 0.20 – 16 mg_{As}/L.

INTRODUCTION

As Contamination and Novel Materials for its Removal. High risks to human health due to the consumption of As in drinking water have prompted reduction of the maximum contaminant level (MCL) of As from 50 µg/L to 10 µg/L (Smith et al., 2002). Depending upon solution pH, As exists in water as As^{III} and As^V oxyanions (Munoz et al., 2002). As^{III} is more toxic and more mobile.

Novel materials and methods are required to cope with modern regulations, especially for the binding and control of As^{III} species. As affinity for Fe-based materials is well known (Raven et al., 1998, Farquhar et al., 2002); however, its removal from dilute solutions of less than 1 mg/L (especially As^{III}) is difficult. Adsorbent materials where the active adsorption sites are dispersed on a nano-level are promising for As removal. Nano-sized Fe^{III} species were prepared from surfactant-assisted, layered FeO(OH) and also intercalated between montmorillonite layers. As prepared, layered FeO(OH) was hydrophobic. A soft removal method (washing in ethanol at 333 K) was used to eliminate surfactant while maintaining structure and avoiding aggregation of particles. Na-montmorillonite (Na-Mont) was utilized to stabilize the Fe^{III} nano particles. For both the adsorbents, no characteristic peaks of crystalline Fe oxides appeared in their XRD patterns.

XAFS Combined with Fluorescence Spectrometry. XAFS spectroscopy is a state-of-the-art technique for short-range order bonding studies. For environmental applications, the local structure studies of adsorbent-adsorbate

systems will help to optimize adsorbent materials. Molecular level studies of environmental contaminants using XAFS are attracting much attention as a means of understanding their fate, but it still has limitations for dilute contaminants (~0.1 wt%), especially in the presence of other heavy elements. XAFS in combination with a fluorescence spectrometer was able to detect the speciation of trace-levels of Pb adsorbed under environmental conditions by utilizing the advantage of extremely high signal/background ratio for XAFS data acquisition (Izumi et al., 2002). The fluorescence spectrometer has a high energy-resolution (0.3 eV at 6 keV) and has allowed monitoring As K-edge XANES for low concentrations (0.13 – 0.48 wt%) of adsorbed As.

MATERIALS AND METHODS

Layered FeO(OH) and Fe-Montmorillonite Synthesis. Layered FeO(OH) was synthesized from 0.1 M FeCl₂ (100 mL) and 0.07 M sodium dodecyl sulfate (20 mL). First, a colloidal suspension was formed to which 3 wt% H₂O₂ (20 mL) was added quickly with vigorous stirring. The reaction mixture was stirred for 30 min, and the solid and liquid phases were separated by filtration (Wirnsberger et al., 2001). The surfactant was extracted by re-suspension of the precipitates in ethanol, swirling the mixture at 333 K for 2.5 h, and following with filtration. The extraction process was repeated five times to completely eliminate the surfactant from the solid. The material obtained was air-dried under ambient conditions, and then calcined at 423 K for 2 h in air.

Fe-montmorillonite (Fe-Mont) was prepared by two step interaction; (1) interaction of 3 mmol Fe³⁺ with Na⁺ and Ca²⁺ of montmorillonite (1 g; 0.5 wt% aqueous suspension), (2) subsequent reaction with NaOH of double the molar amount (6 mmol) of Fe³⁺ introduced. The reaction mixture was aged at 290 K for 12 h, filtered and washed several times with Millipore water until the pH of the filtrate was more than 6.8. The solid obtained was dried on a glass plate under ambient conditions and ground to powder. The maximum amount of Fe intercalated was 14.0 wt% of the dried mass.

Characterization. XRD patterns of powdered samples were measured by Multiflex-S diffractometer (Rigaku). N₂ adsorption-desorption isotherms were measured at 77 K using BELSORP mini (Bell, Japan).

Fe and As K-edge XAFS Studies. Reference compounds, α -Fe₂O₃ and α -FeO(OH), and the samples were mixed with boron nitride (BN) and pressed into disks (diameter 20 mm). Fe K-edge XAFS spectra were measured at 290 K in transmission mode at beamline 10B (KEK-PF). An Si(311) monochromator was used. N₂ and a mixture of N₂/Ar (85/15) were used, respectively, in ionization chambers measuring I_0 and I signal counts. The rising K-edge energy of Fe metal foil was calibrated to 7111.2 eV.

As metal (As⁰), As₂O₃ (As^{III}) and KH₂AsO₄ (As^V) were mixed with BN to contain 2 wt% of As and pressed into disks (diameter 20 mm). As adsorbed, air-dried samples were also pressed into the same sized disks. As K-edge XANES spectra were measured at 290 K at Undulator beamline 10XU (SPring-8). An Si(111) monochromator was used. Fluorescence X-rays emitted from the sample

were analyzed by a homemade Rowland-type spectrometer. A cylindrically-bent Johansson-type Ge(555) crystal and a scintillation counter were positioned on the Rowland circle ($R = 220$ mm) and controlled by computer. The sample was set on a flat plane, nearly horizontal, tilted 6° towards the incident X-rays and 7° towards the center of Ge(555) crystal (Izumi et al., 2002). With the excitation energy of 11885.0 eV, As $K\alpha_1$ emission spectrum was measured. Then, the spectrometer was tuned to the center of the As $K\alpha_1$ peak, and XANES spectra were measured. The rising K-edge energy of As⁰ was calibrated at 11865.0 eV.

As Adsorption Test. 1.0 g/L As^{III} and As^V stock solutions were prepared from As₂O₃ and KH₂AsO₄, respectively. 1, 2, 4, 8 and 16 mg/L dilutions were used for the adsorption tests. The pH of starting solutions was in the range of 5.7 – 6.0 (As^{III}) and 5.7 – 6.4 (As^V). Layered FeO(OH) washed with ethanol, Fe-Mont, α -FeO(OH) ($S_{BET} = 16$ m²/g), and Na-Mont were used for adsorption. For As batch adsorption tests, 50 mg of adsorbent was immersed in 20 mL of As solution. The mixture was shaken for 12 h at 298 K, followed by separation using 0.4 μ m cellulose membranes. The aqueous phase As concentrations were measured by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy; Vista-Pro, Seiko-Varian Instruments).

RESULTS AND DISCUSSION

High Surface Area Layered Materials. For the as-prepared, layered FeO(OH), the characteristic XRD peak appeared at 2.6 degree, demonstrating a regularity of 34 Å (Figure 1-A-a). After template extraction with ethanol, the peak shifted toward 3.1 degree, indicating a $d(001)$ -spacing of 28 Å (Figure 1-A-b). High specific surface area (166 m²/g) and pore volume (154 mm³/g) was achieved for the ethanol washed sample compared to as-prepared, layered FeO(OH) (Table 1).

TABLE 1. XRD and BET Results of Layered FeO(OH) and Montmorillonites

	Layered FeO(OH)		Na-Mont	Fe-Mont
	as-prepared	Ethanol washed		
$d(001)$ -spacing (Å)	34	28	12.2	15.7
S_{BET} (m ² /g)	2.8	166	25	118
Pore Vol. (mm ³ /g)	8.3	154	33	67

For Fe-Mont, the layered structure was retained after Fe intercalation as shown by XRD patterns (Figure 1-B-b), and with the intercalation of Fe species the $d(001)$ -spacing increased from 12.2 Å to 15.7 Å (Table 1). Specific surface area (25 m²/g) and pore volume (33 mm³/g) also increased to 118 m²/g and 67 mm³/g, respectively, after intercalation of Fe species (Table 1).

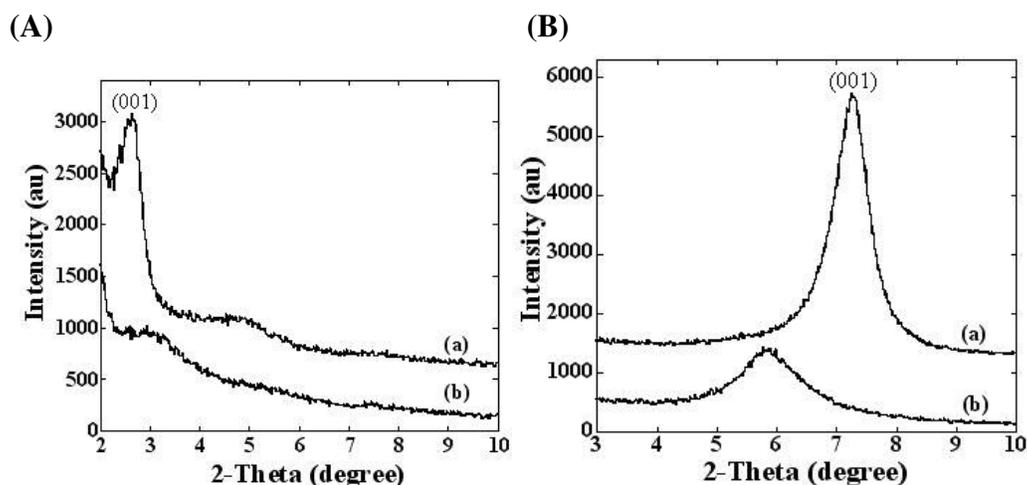


FIGURE 1. XRD patterns of layered FeO(OH) (A); as prepared (a), ethanol washed (b), and montmorillonites (B); Na-Mont (a), and Fe-Mont (b).

Nano-sized Fe Species. Fe species in both the materials (layered FeO(OH) and Fe-Mont) were lacking any long-range order, as no iron oxide characteristic peaks appeared in XRD patterns. The local structure of Fe was studied by extended X-ray absorption fine structure (EXAFS). In the Fourier transforms of as prepared layered FeO(OH) and Fe-Mont the magnitudes of Fe-Fe peaks were $\leq 20\%$ compared to goethite (bulk α -iron oxyhydroxide) indicating nano-size of Fe species.

As Speciation. As low as 0.13 wt% As adsorbed from 200 $\mu\text{g/L}$ As^{III} solution under flow setup on the adsorbent containing high amount of Fe 15.3 wt% (total), Si 21 wt% and Al 8 wt% was measured successfully by XAFS combined with fluorescence spectrometry. For the As^{V} adsorbed sample the inflection point energy was similar to As^{V} reference showing no change in oxidation state. But, the inflection point energies of As^{III} adsorbed samples (11871.9 eV; 0.13 wt% As adsorbed from 200 $\mu\text{g/L}$ As^{III} solution, and 11872.0 eV; 0.48 wt% As adsorbed from 16 mg/L As^{III} solution) were close to As^{V} reference (11872.1 eV) rather than the As^{III} reference (11868.5 eV), revealing the oxidation of adsorbed As species. This oxidation phenomenon is environmentally important regarding the binding and control of the more toxic As^{III} species.

As Removal. As adsorption isotherms followed by the adsorbents were of the Langmuir type (Figure 2-A). Saturated As adsorption (a) and equilibrium constant (K) values obtained by fitting the adsorption isotherms to first order Langmuir equation are reported in Table 2. As adsorption from As^{V} solution was higher as compared to adsorption from As^{III} solution (Figure 2-A, Table 2). Adsorption of $\text{As}^{\text{III,V}}$ by Na-Mont was negligible (isotherms not shown). So, in

the case of Fe-Mont, the intercalated nano-sized Fe species were totally responsible for As adsorption.

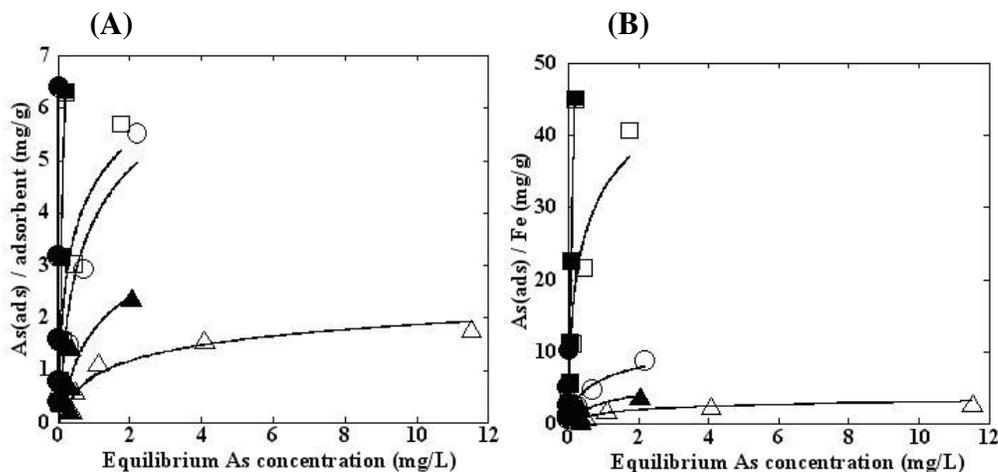


FIGURE 2. As adsorption isotherms; adsorbent weight basis (A), Fe weight basis (B) for ethanol washed layered FeO(OH); As^{III} (○), As^V (●), Fe-Mont; As^{III} (□), As^V (■), and goethite; As^{III} (Δ), and As^V (▲).

TABLE 2. Saturated As Adsorption (*a*) and Equilibrium Constant (*K*) Values

	As ^{III}		As ^V	
	<i>a</i> (mg _{As} /g _{adsorbent})	<i>K</i> (mL/g _{As})	<i>a</i> (mg _{As} /g _{adsorbent})	<i>K</i> (mL/g _{As})
Ethanol washed layered FeO(OH)	9.5	6.2 x 10 ⁵	12.8	1.3 x 10 ⁸
Fe-Mont	8.0	1.4 x 10 ⁶	75.0	4.3 x 10 ⁵
Goethite	1.9	1.4 x 10 ⁶	2.7	3.2 x 10 ⁶

As^{III,V} adsorption efficiencies of nano-size iron species in ethanol-washed, layered FeO(OH) and Fe-Mont were comparable on adsorbent weight basis, and were much better than bulk iron oxyhydroxide (Figure 2-A). Next, for the Fe-Mont (Fe 14.0 wt%) the amount of As adsorbed per g Fe was ≥ 4 times higher than the ethanol-washed, layered FeO(OH) (Fe 62.9 wt%), and ≥ 10 times higher than the bulk iron oxyhydroxide (Fe 62.9 wt%) (Figure 2-B). Highly dispersed nano-sized Fe species in the hybrid material had more active adsorption sites. Especially for the removal of more toxic and highly mobile As^{III} species, the Fe-Mont even with low Fe contents (14.0 wt%), but with more active adsorption sites was the best adsorbent material (Figure 2, Table 2).

CONCLUSIONS

Adsorption active nano-sized Fe species were identified by XAFS and the environmentally important phenomenon of As^{III} oxidation was monitored and demonstrated successfully by the XAFS combined fluorescence spectrometry.

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