Supporting Information

Adsorption Thermodynamics of p-Arsanilic Acid on Iron (oxyhydr)Oxides: In-situ ATR-FTIR Studies

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Supporting Information (7 pages, 2 Tables):

1. Fe-(oxyhydr)oxide Film Preparation. The deposition methods described herein of Fe-(oxyhydr)oxide films on the ATR crystal were modified from the literature. The criterion used to test the suitability of a given method is the stability of the deposited film in contact with water throughout the experimental time, which ranged from 6 to 8 hours. We have verified that the deposition procedure described below yielded reproducibly films in good and uniform contact with the ATR crystal by measuring the baseline-corrected heights of the bands below 1000 cm^{-1} assigned to the Fe-O-Fe in the bulk of the Fe-(oxyhydr)oxide materials (*1*). α-Fe_2O_3 films were prepared by making a slurry of 14 mg sample in an 1.5 mL water/ethanol mixture (1 : 0.4 (v/v)), which was ultrasonicated for 1 hr. All of the solution was then spread over a clean and dry ZnSe ATR crystal and allowed to dry overnight in air at room temperature. γ-Fe_2O_3 films were prepared as described above using a 10 mg sample. Goethite (α-FeOOH) slurry was prepared using a 16 mg sample of ground goethite (Wig-L-Bug, 1 min), in a 0.75 mL ethanol. The slurry was ultrasonicated for 1 hour and then deposited on a clean and dry ZnSe ATR crystal and allowed to dry overnight in air at room temperature. An ATR-FTIR spectra of the dry films were acquired at the beginning of every experiment. Water adjusted to the desired pH and ionic strength was then injected in excess amounts into the flow cell containing the dry deposited films to remove the loosely bound particles, which were visible on a white KimWipe (VWR). Most of these particles were from the top layers of the film, and not those probed by the evanescent wave. For the goethite films, however, wetting was done by holding the flow cell (with the cover removed) at an angle and allowing a gentle stream of water adjusted to the desired pH and ionic strength to drain down. Excess water containing loosely bound particles was absorbed by a KimWipe at the other end of the film. The process was repeated till no particles were seen on the white KimWipe. The thickness of the deposited films was measured using surface profilometry to be 11(2), 9.7(1) and 18(4) μm for α-Fe_2O_3, γ-Fe_2O_3, and α-FeOOH, respectively (see Table S1). These measurements were done on films deposited on glass slides with the same exposed area as the ZnSe ATR crystal.

2. Collection and Processing of ATR Single Beam Spectra. For collection of solution phase absorbance spectra, single beam spectra of pH-adjusted liquid water and the standard solutions of p-AsA were measured. The former was used as the background spectrum to obtain the absorbance spectra of p-AsA(aq). We determined that the detection limit for p-AsA(aq) is 8mM at pH 7. For the adsorption experiments on the Fe-(oxyhydr)oxide-coated ZnSe crystal, pH-adjusted liquid water was allowed to equilibrate with the film for 15min before a single beam file was collected (SB#1). Liquid water was then removed from the flow cell using a syringe. Standard solutions of p-AsA were then injected into the flow cell starting with the lowest concentration (1μM), and allowed to equilibrate with the film for 15min before a single beam file was collected (SB#2). The "reacted" solution was then removed before the injection of the subsequent p-AsA solution. The absorbance spectra (SB#3) containing signal of adsorbed p-AsA was obtained by referencing SB#2 to SB#1. All "reacted" solutions with concentrations above the detection limit were collected and their ATR absorbance spectra (SB#4) were measured on an uncoated ZnSe crystal. SB#4 were then subtracted from SB#3 to yield the spectra of adsorbed p-AsA. This way, the contribution of p-AsA(aq) is eliminated from the spectra collected in the presence of Fe-(oxyhyr)oxides films. The difference spectra were used to quantify the surface coverage of p-AsA by assuming that the baseline-corrected height of the broad band assigned to ν(As—O) at 837±2cm^{-1} is proportional to the surface concentration of p-AsA.

3. Calculations of the Refractive Index of Porous Fe-(oxyhydr)oxide Films. The effective pathlength (d_e) using liquid water as a sample is found to be 1.6±0.2μm, which was determined from the baseline-corrected absorbance at 1641 cm^{-1}, $A(\lambda)$, the molar extinction coefficient, $\varepsilon(\lambda)$ at 1641 cm^{-1} (1.74×10^4 cm^2mol^{-1}) (*2*), and concentration, c, of water (55.5 M) using the Beer's relation: $A(\lambda) = \varepsilon(\lambda)cd_e$ (*3, 4*). The depth of penetration per reflection (d_p) approximately equals to d_e/N, where N is the total number of reflections. Hence, from the d_e value above, the actual angle of incidence, θ, and number of reflections, N, were calculated to be 73.3° and 3, respectively (*5*).

The enhancement in the detection limit of p-AsA in the presence of Fe-(oxyhydr)oxide films is due to the increase in the value of d_e. Bulk hematite and maghemite have higher refractive indices (n_2) than ZnSe (2.9 and 2.6 compared to 2.4)(*6*), which means that the condition for the internal reflection $\sin^2(\theta)-(n_2/n_1)^2 \geq 0$ is not fulfilled for these two materials. This condition is also not fulfilled using goethite as a sample ($n_2 = 2.3$) (*6*). However, internal reflection is observed experimentally using the above Fe-(oxyhydr)oxides, which suggests that the refractive indices of the porous films of these materials, n'_2, are less than that for ZnSe. n'_2 is defined as the volume-weighed average of the refractive index of the particles and the aqueous phase in the pores, which can be calculated using eq. (1):(*7*)

$$n'_2 = F_v \cdot n_{par} + (1 - F_v) \cdot n_{H_2O(l)}, \quad \text{where } F_v = \frac{m(\mathrm{g})}{a(\mathrm{cm}^2) \cdot h(\mathrm{cm}) \cdot \rho_t(\mathrm{gcm}^{-3})} \tag{1}$$

The variable F_v is the volume fraction of the solid, which is basically the ratio of the bulk density, ρ_b, of the deposited Fe-(oxyhydr)oxides films to the true density, ρ_t. The bulk density is calculated from the deposited mass (*m*), area covered ($a = 5.0\ cm^2$) and measured thickness of the films (*h*). Table S1 below summarizes the calculations of d_e at 1641 cm^{-1} for the Fe-

(oxyhydr)oxides materials in the presence of liquid H_2O using $\theta = 73.3°$. To verify the accuracy of these calculations, the net absorbance of the bending mode of water at 1641 cm^{-1} in contact with the films is calculated to be 0.3, 0.22, and 0.18 for α-Fe_2O_3, γ-Fe_2O_3 and α-FeOOH, respectively. These values are in excellent agreement the experimental values obtained from the spectra of water in contact with Fe-(oxyhydr)oxide films: 0.24, 0.20 and 0.17, respectively.

Table S1: Calculations of the Effective Pathlength of IR Light for a ZnSe IRE Coated with Fe-(oxyhydr)Oxide Films in Contact with Liquid Water at 298 K

Material	Mass, *m* (mg)	Measured thickness, *h* (cm)	True density, ρ_t (g cm^{-3}) (*6*)	Volume Fraction, F_v	Volume-weighed n_2 (n'_2)	Effective pathlength, ($d_e^{1641cm^{-1}}$, cm)	Effective pathlength, ($d_e^{837cm^{-1}}$, cm)
α-Fe_2O_3	14.4(0.4)	11(2.4)×10^{-4}	5.3	0.49(0.2)	2.1(0.9)	3.1(1)×10^{-4}	6.1(3)×10^{-4}
γ-Fe_2O_3	10.3(0.4)	9.7(1.3)×10^{-4}	4.9	0.43(0.1)	1.9(0.4)	2.3(0.5)×10^{-4}	4.4(0.9)×10^{-4}
α-FeOOH	16.5(0.3)	18(4.0)×10^{-4}	4.3	0.43(0.1)	1.7(0.7)	1.9(0.8)×10^{-4}	3.7(0.5)×10^{-4}

Notes: F_v and n'_2 are calculated using eq. (1), and d_e using $d_e(\lambda) \approx N \cdot d_p(\lambda) = (l/t)\cot\theta \cdot \lambda/[2\pi n_1\sqrt{\sin^2\theta - (n_2/n_1)^2}]$, where l is the length of the IRE (80 mm), t is the thickness of the IRE (4 mm). n_1 and n_2 are the refractive indices of IRE (2.4 for ZnSe) and the sample, $\theta = 73.3°$, and N=3. Numbers in parentheses are $\pm\sigma$. Compare d_e values to 1.6(0.2)×10^{-4} cm calculated at 1641 cm^{-1} from the measured spectra of liquid water ($n_2 = 1.3$) in contact with the ZnSe IRE (no Fe-(oxyhydr)oxide coating present).

4. Determination of p-AsA Surface Coverage on Fe-(oxyhydr)oxides from Batch Experiments using ICP-AES. Batch adsorption experiments were conducted by reacting ca. 0.5 g of α-Fe_2O_3, γ-Fe_2O_3 and α-FeOOH particles with 10 mL of 0.47 mM p-AsA standard solution (35.6 ppm As) adjusted to pH 7 and I = 0.01 M (KCl). At this solution concentration, a monolayer of p-AsA forms on the surface of Fe-(oxyhydr)oxide. Particles suspensions were shaken for 24 hours using a vortex mixture, followed by centrifugation. Supernatants were filtered in 0.45 μm syringe filters once and collected for analysis of total arsenic using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Table S2 summarizes the results of the batch experiments. Total arsenic content in the p-AsA standard was also analyzed as a reference and the value was found to be 33.1 ppm.

Table S2: Total Arsenic Content from Batch Experiments on p-AsA Binding to Fe-(oxyhydr)oxides at pH 7 and I = 0.01 M KCl

Substrate	[As] in supernatants (mg/L)	[As] adsorbed[a] (mg/L)	As/Fe molar ratio (mmol/mol)	p-AsA surface density (molecules/cm^2)
α-Fe_2O_3	0.010	33.09	0.67	2.7×10^{13}
γ-Fe_2O_3	0.340	32.76	0.70	2.0×10^{13}
α-FeOOH	0.009	33.09	0.79	2.5×10^{13}

[a] The amount adsorbed was calculated by subtracting [As] in supernatants from p-AsA standard solution (33.1 ppm As as measured by ICP-AES) added to ca. 50 g/L of each substrate.

5. Literature Cited

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