Supporting Information

Photochemical transformation of iron(III)–arsenite complex in acidic aqueous solution

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Determination of stability constants and absorption coefficients of Fe(III)-As(III) complexes

In aqueous solution at pH < 4, three main equilibria have to be taken into account:

$Fe^{3+} + H_2O \Leftrightarrow FeOH^{2+} + H^+$, p$K_g$;

$Fe^{3+} + HL \Leftrightarrow = FeL^{2+} + H^+$, p$K_1$;

$FeL^{2+} + HL \Leftrightarrow = FeL_2^+ + H^+$, p$K_2$.

Where the abbreviation "HL" stands for H_3AsO_3, K_g is the hydrolysis constant of Fe^{3+}, and K_n (n = 1, 2) is the stability constants of 1:1 and 1:2 Fe(III)–As(III) complexes. The following expressions may be written for equilibrium constants and material balance:

$K_g = [FeOH^{2+}][H^+]/[Fe^{3+}]$; (1)

$K_1 = [FeL^{2+}][H^+]/[Fe^{3+}][HL]$; (2)

$K_2 = [FeL_2^+][H^+]/[FeL^{2+}][HL]$; (3)

$C_L = [HL] + [FeL^{2+}] + 2[FeL_2^+]$ (4)

$C_{Fe} = [Fe^{3+}] + [FeOH^{2+}] + [FeL^{2+}] + [FeL_2^+]$ (5)

Where C_L and C_{Fe} is the total concentration of the ligand and iron, correspondingly. Combining Eqs. (1)–(5) yields Eqs. (6)–(10):

$$[\mathrm{Fe}^{3+}] = \frac{C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \quad (6)$$

$$[\mathrm{Fe}OH^{2+}] = \frac{(Q-1)C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \quad (7)$$

$$[\mathrm{FeL}^{2+}] = \frac{K_1^{'}[HL]C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \quad (8)$$

$$[\mathrm{FeL_2}^{+}] = \frac{K_1^{'}K_2^{'}[HL]^2 C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \quad (9)$$

$$C_L = [H\mathrm{L}] + \frac{K_1^{'}K_2^{'}[HL]C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} + \frac{2K_1^{'}K_2^{'}[HL]^2 C_{Fe}}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \quad (10)$$

Where Q = 1 + $K_g/[H^+]$ = 7.3 at pH 3, $K_1' = K_1/[H^+]$, $K_2' = K_2/[H^+]$. Eq. (10) could be transformed into

Eq. (11):

$$a[HL]^3 + b[HL]^2 + c[HL] + d = 0 \tag{11}$$

Where

$a = K_1^{'}K_2^{'}$,

$b = K_1^{'} + 2K_1^{'}K_2^{'}C_{Fe} - K_1^{'}K_2^{'}C_L$,

$c = Q + K_1^{'}C_{Fe} - K_1^{'}C_L$,

$\mathrm{d} = -C_L Q$.

Optical density at region of wavelengths where only Fe(III) species absorb can be expressed as:

$$\mathrm{A} = \varepsilon_{\mathrm{Fe^{3+}}}[\mathrm{Fe^{3+}}]l + \varepsilon_{\mathrm{FeOH^{2+}}}[\mathrm{FeOH^{2+}}]l + \varepsilon_{\mathrm{FeL}}[\mathrm{FeL^{2+}}]l + \varepsilon_{\mathrm{FeL2}}[\mathrm{FeL_2}^{+}]l \tag{12}$$

Where A is an optical density at the selected wavelength, l is the path length of the quartz cell, ε is a molar absorption coefficient of the corresponding Fe(III) species at the selected wavelength. Combining Eqs. (6)–(9) with Eq. (12) yields Eq. (13):

$$\mathrm{A/C_{Fe}}l = \frac{\varepsilon_{\mathrm{Fe^{3+}}} + \varepsilon_{\mathrm{FeOH^{2+}}}(Q-1) + \varepsilon_{\mathrm{FeL}}K_1^{'}[HL] + \varepsilon_{\mathrm{FeL2}}K_1^{'}K_2^{'}[HL]^2}{Q + K_1^{'}[HL] + K_1^{'}K_2^{'}[HL]^2} \tag{13}$$

With all of the necessary equations in hand, a script can be written in the nonlinear curve fitter of Origin 8.0 program to numerically solve Eq. (11) for [HL] while fitting the data using Eq. (13). This script, shown below, fits a set of titration data in which parameter $\mathrm{A/C_{Fe}}l$ (y in the script) is recorded as a function of $\mathrm{C_L}$ (x in the script). Values for x and y are read from a standard data file by the program.

```
A=10^lgK1*10^lgK2;
B=10^lgK1+2*M*10^lgK1*10^lgK2-10^lgK1*10^lgK2*x;
C=7.3+10^lgK1*M-10^lgK1*x;
D=-7.3*x;
for (L=x, step=1; abs(step)>1e-15; L=L-step){step=(A*L^3+B*L^2+C*L+D)/(3*A*L^2+2*B*L+C);};
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y = (E0+E1*10^lgK1*L+E2*10^lgK1*10^lgK2*L^2)/(7.3+10^lgK1*L+10^lgK1*10^lgK2*L^2)

Where L is [HL], M is C_{Fe}, E0 is $\varepsilon_{\mathrm{Fe}^{3+}} + \varepsilon_{\mathrm{FeOH}^{2+}}(Q-1)$ and it is a fixed parameter, E1, E2, K1, K2 – absorption coefficients and stability constants of 1:1 and 1:2 Fe(III)–As(III) complexes and they are varied parameters.

More information about fitting procedure used and the application of Newton’s iterative optimization method could be found in the original paper [1].

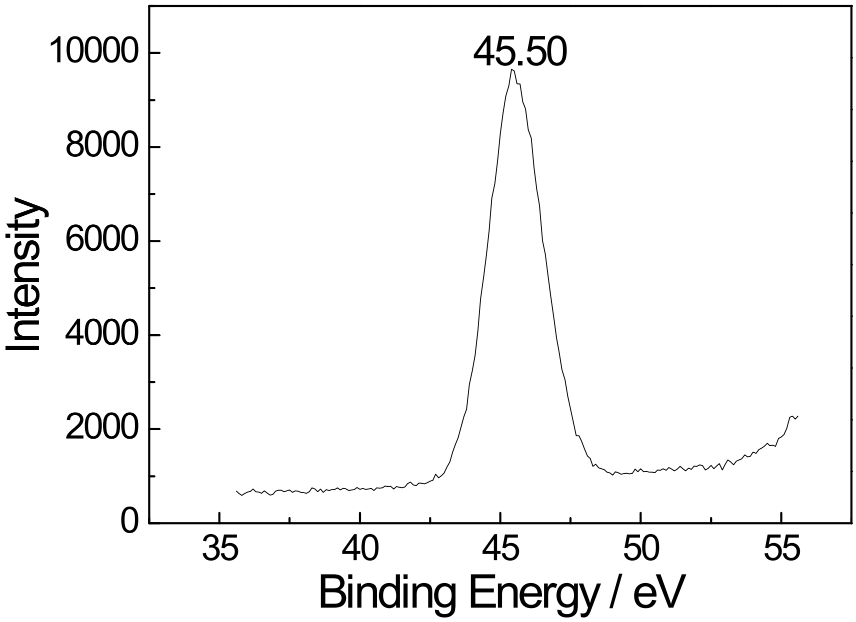

Fig. S1 As 3d XPS spectrum of the precipitate of the Fe(III)–As(V) complex formed by direct mixing of Fe(III) and As(V) at pH 1. Experimental conditions: [Fe(III)(ClO_4)$_3$] = 177 mM, [As(V)] = 59 mM.

Langmuir et al. [2] has reported that the solubility of ferric arsenate at pH 1.9 was about 3.7 mM. So 0.047 g of solid Fe(III)–As(V) complex was dissolved in 200 mL of $HClO_4$ solution at pH 1. The concentration of Fe(III) and As(V) in solution were 0.73 mM and 0.71 mM respectively determined by spectrophotometry and HG–AFS. This indicated that the ratio of Fe(III)/As(V) in Fe(III)–As(V) complex was around 1:1.

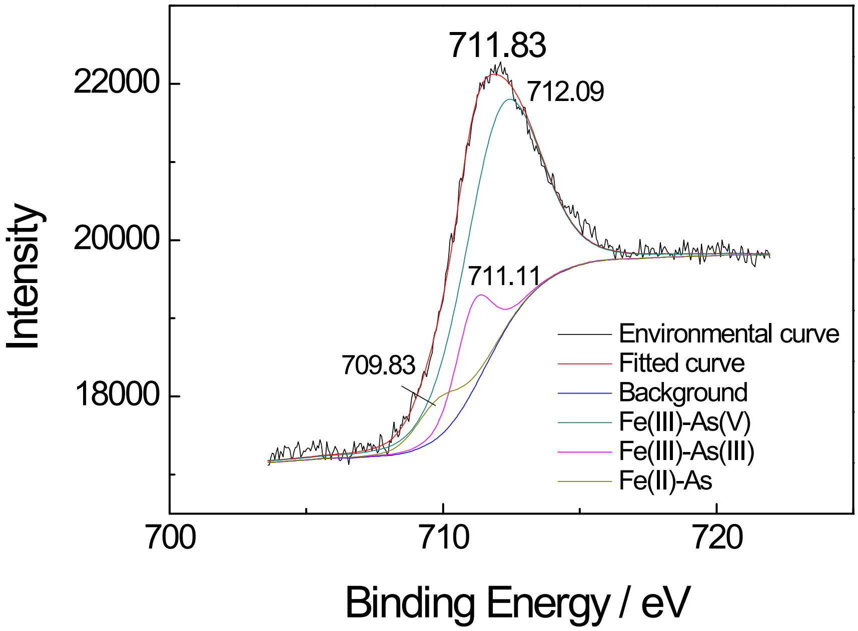

Fig. S2 Fe $2p_{3/2}$ XPS spectrum of solid Fe(III)–As(III) complex formed by direct mixing of Fe(III) and As(III) at pH 1 with ethanol. Experimental conditions: [Fe(III)(ClO_4)$_3$] = 59 mM, [As(III)] = 177 mM.

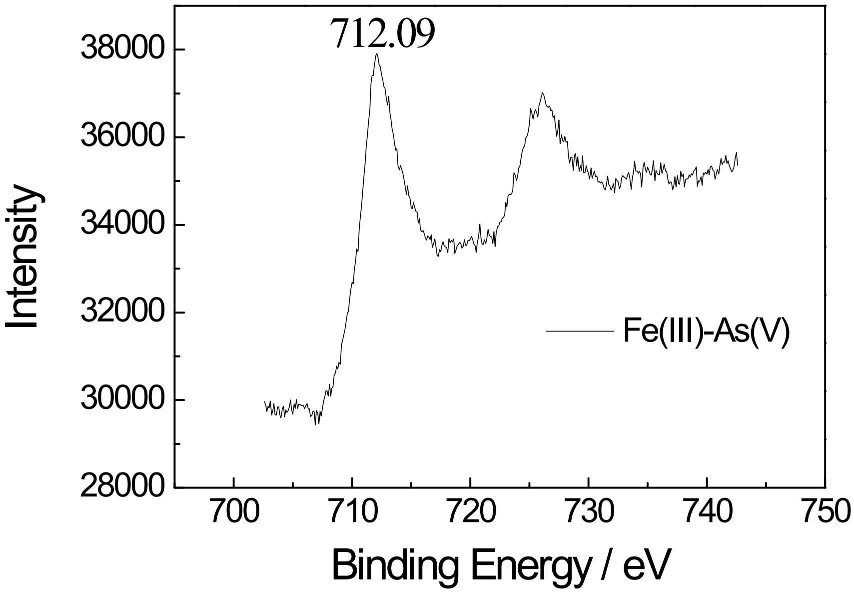

Fig. S3 Fe $2p_3$ XPS spectrum of the precipitate of Fe(III)–As(V) complex formed by direct mixing of Fe(III) and As(V) at pH 1. Experimental conditions: [Fe(III)(ClO_4)$_3$] = 177 mM, [As(V)] = 59 mM.

The XPS spectrum of Fe 2p can be fitted by three species with the energy at 709.83, 711.11 and 712.09 eV.

The binding energies of Fe–O in different species have been reported such as 710.6 eV (Fe_2O_3), 708.3 eV (FeO) [3]. And Ding et al. [4] have reported that the electronegativity value of As(III) has an obvious influence on the charge distribution of Fe–O(formation of Fe–O–As). As a result, binding energy of Fe–O is shifted much higher. So in Fig. S2, the binding energy of Fe–O(Fe_2O_3) is shifted from 710.6 eV to 711.11 eV and 712.09 eV respectively. Comparison the results with these in Fig. S3, 712.09 eV was attributed to Fe(III)–O–As(V) and 711.11 eV was assigned to Fe(III)–O–As(III), respectively. The formation of Fe(II)–O–As shifts the binding energy of Fe–O (FeO) to 709.83 eV, because the electron transfer from arsenic to iron [4]. Feeble signal of Fe(II)–O–As makes it hard to distingush the As(III) and As(V). Daniels and Weiss [5] have proposed that production of As(IV) occurred during the oxidation of As(III) by the action of X-rays in solution. The good photoactivity of Fe(III)–O–As(III) results in As(III) oxidation during the measurement of XPS.

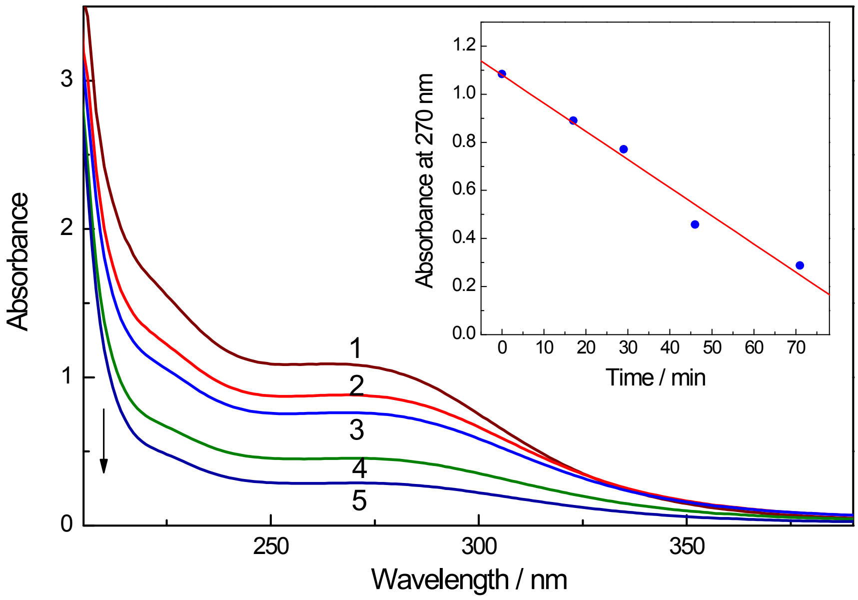

Fig. S4 Steady-state photolysis (308 nm) of Fe(III)–As(III) system at pH 3. (1–5) Spectra after 0 (1), 17 (2), 29 (3), 46 (4), and 71 min (5) of irradiation, respectively. Experimental conditions: Initial volume 2 mL, [Fe(III)(ClO_4)$_3$] = 0.27 mM, [As(III)] = 15 mM, incident light intensity = 1.4×10^{16} quanta/s or 0.56 mM/min. Inset : changes in optical density at 270 nm during photolysis.

Fig. S5 Photos of the white colloids formed by directly mixing Fe(III) and As(V) (A) ([Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(V)] = 0.34 mM) and during photolysis of Fe(III)–As(III) complex (B) ([Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(III)] = 17 mM) at pH 3.

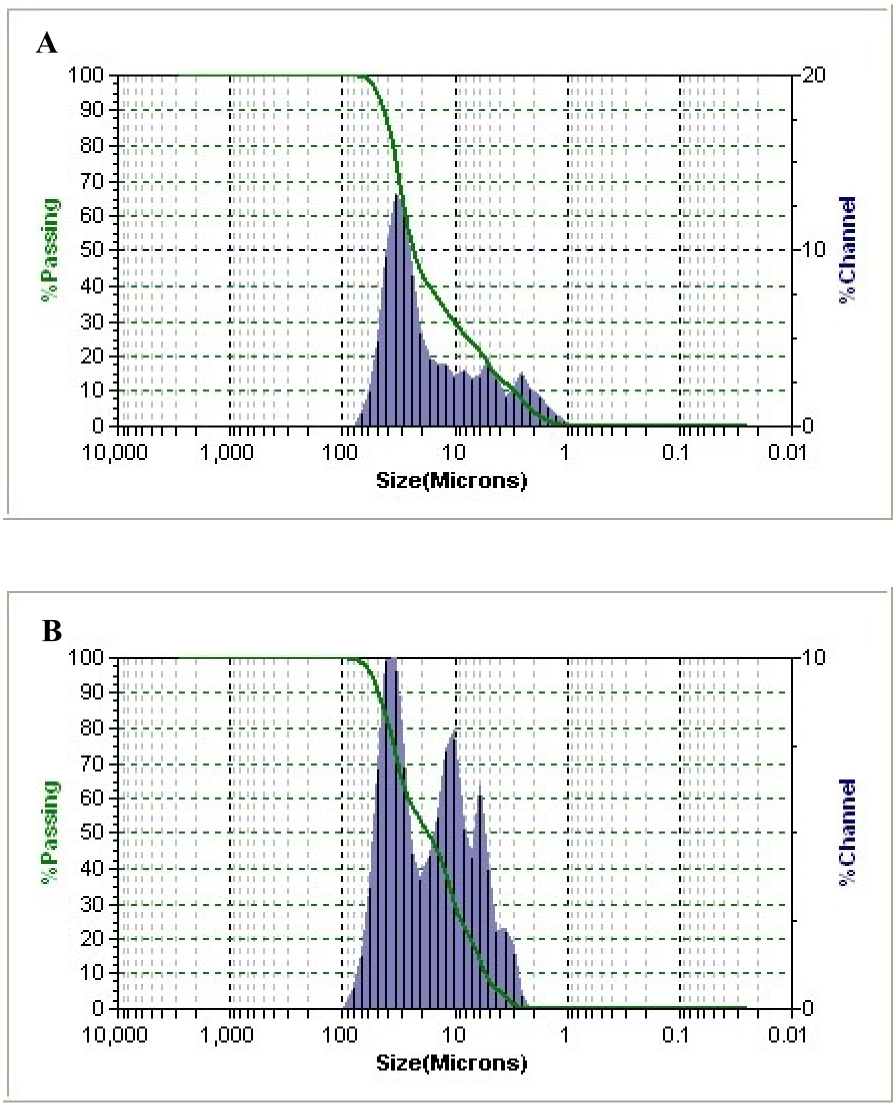

Fig. S6 Particle size distribution of the colloids, the size of the colloidal particles: (A) Colloids formed by direct mixing of Fe(III) and As(V), [Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(V)] = 0.34 mM, pH 3; (B) Colloids formed after photolysis, [Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(III)] = 17 mM, pH 3.

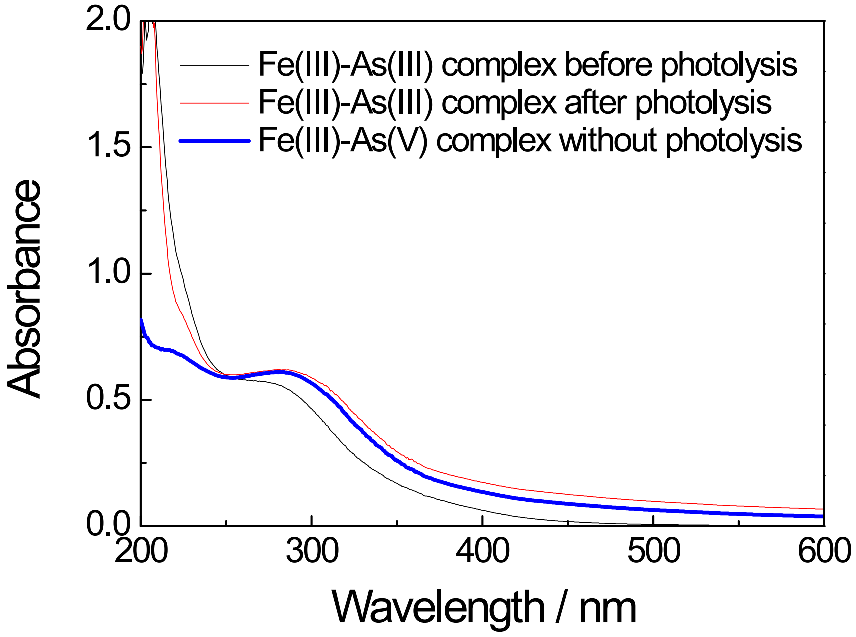

Fig. S7 UV/Vis spectra of the colloidal solutions at pH 3. Black: spectrum of Fe(III)–As(III) complex solution without illumination, [Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(III)] = 17 mM. Red: spectrum of Fe(III)–As(III) complex solution after illumination (λ ≥ 220 nm), [Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(III)] = 17 mM. Blue: spectrum of Fe(III)–As(V) complex solution without illumination, [Fe(III)(ClO_4)$_3$] = [As(V)] = 0.34 mM.

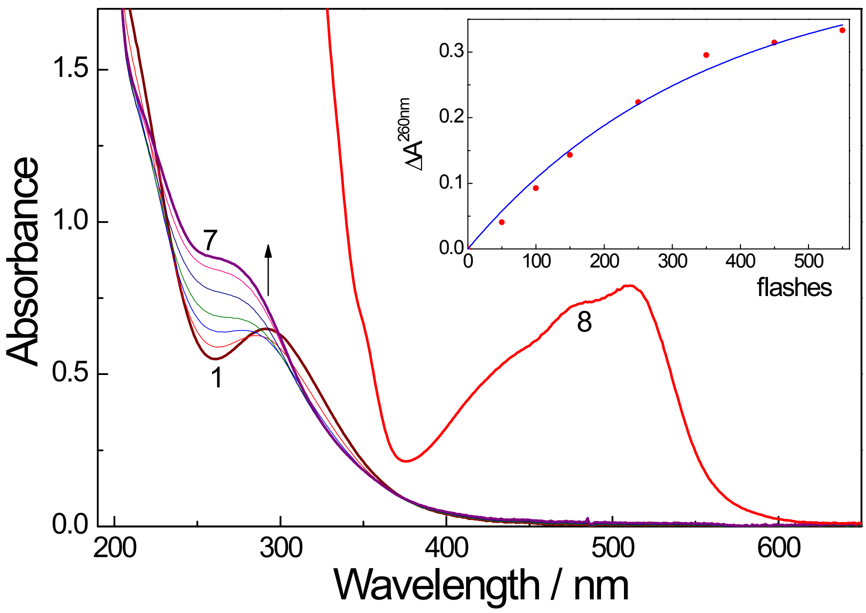

Fig. S8 Steady-state photolysis (266 nm) of Fe(III)–As(III) system at pH 3, [Fe(III)(ClO_4)$_3$] = 0.34 mM, [As(III)] = 1.1 mM. (1–7) Spectra after 0 (1), 50 (2), 100 (3), 150 (4), 250 (5), 350 (5) and 550 pulses (7), respectively. (8) Spectrum of solution irradiated by 550 pulses after addition of o-phenanthroline. Inset: changes of optical density at 260 nm during photolysis.

Table S1. Calculation of the ratio of Fe/As in Fe(III)–As(III) complex formed by direct mixing of 59 mM Fe(III) and 177 mM As(III) at pH 1 with ethanol in Fig. 3.

Parameter	Category		
Total concentration	As(III) 11.68 wt%	Fe(III) 6.23 wt%	
The ratios of the products in Fig. 3 (in terms of As mole ratio)	As_2O_3	Fe(III)–O–As	
		Fe(III)–O–As(V)	Fe(III)–O–As(III)
	34.50%	54.00%	11.50%
The ratio of As coordinated to Fe(III)	= 1 – 34.5% = 65.5%		
Concentration of As coordinated to Fe(III)	= 11.68 wt% × 65.5% = 7.65 wt%		
Fe/As molar ratio of solid Fe(III)–As(III) complex	= 6.23 wt%/55.8:7.65 wt%/74.9 = 1:0.92		

By area estimation from XPS spectra, the ratios of As_2O_3, Fe(III)–As(V), and Fe(III)–As(III) (in terms of As mole ratio) were found to be 34.5%, 54.0%, and 11.5%, respectively. Fe(III) and As(III) concentrations were 6.23% and 11.68%, respectively determined by spectrophotometry and HG–AFS.

Reference

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