# Species-specific uptake of arsenic on confined metastable 2-line ferrihydrite: A combined Raman-XPS investigation of the adsorption mechanism

Chennu Sudhakar,<sup>†</sup> Avula Anil Kumar,<sup>†</sup> Radha Gobinda Bhuin,<sup>†</sup> Soujit Sen Gupta,<sup>†</sup> Ganapati Natarajan<sup>†</sup> and Thalappil Pradeep<sup>\*,†</sup>

<sup>†</sup>DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

\* Corresponding author

Thalappil Pradeep: pradeep@iitm.ac.in

Thalappil Pradeep, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

Tel.: +91-44 2257 4208; Fax: +91-44 2257 0545/0509

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**Figure S1.** Aqueous Raman spectra. A) As(III)), B) As(V) speciation under various pH conditions. pH values are indicated on the right.



**Figure S2.** Time dependent Raman spectra for the interaction of MAG with A) As(III), B) As(V) and C) As(mix). Peaks have been fitted with their components.



**Figure S3.** Time dependent Raman spectra for the interaction of HEM with A) As(III), B) As(V) and C) As(mix). Peaks have been fitted with their components.



**Figure S4.** Representation of data presented in Figure 3 in terms of area under the peak (A) and concentration of species (B).

Adsorption kinetics can be expressed by using pseudo-second-order equation:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad \text{Equation (1)}$$

Where,  $q_t$  is the adsorption capacity of given material at time t,  $q_e$  is the adsorption capacity of the material at equilibrium and k is the pseudo-second-order rate constant, where initial rate is h =  $kq_e^2$ . Integration of equation (1) with limits t = 0 to t and applying boundary conditions  $q_t = 0$  at t = 0 gives,

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right)t + \frac{1}{k{q_e}^2}$$
 Equation (2)

The values of k and  $q_e$  can be calculated by plotting  $t/q_t$  versus t.

#### Conversion of concentration of solution (mM) into $q_t$ :

Concentration of solution  $(x) \rightarrow xM_{wt} \approx C_t$ 

 $M_{wt}$  is the molecular weight of arsenic species present in solution.

$$q_t = \left(\frac{C_0 - C_t}{m}\right) V \qquad \text{Equation (3)}$$

Where,  $C_0$  (mg/g) is the concentration of solution at time t = 0,  $C_t$  (mg/g) is the concentration of solution at time t, V is the volume of solution in liters (L) and m is the mass of material used in grams (g).



**Figure S5.** Representation of data presented in Figure S2 in terms of area under the peak (A) and concentration of species (B).



**Figure S6.** Representation of data presented in Figure S3 in terms of area under the peak (A) and concentration of species (B).



**Figure S7.** A) and B) Raman spectra for the various concentrations of pure As(III) and As(V) solutions at pH 7. C) Representation of data presented in A and D) Representation of data presented in B in terms of area under the peak Vs concentration of the species. Peaks have been fitted with their components.

#### The correlation between area under the peak and concentration of solution:

$$y = mx + c$$
 Equation (4)

Equation 4 can be applied for both As(III) and As(V) solutions.

Where, y is area under the peak, x is concentration of the solution (mM), c is the y intercept and m is slope of line of the plot of y versus x. For calculating the unknown concentrations of solution, the (x, y) data points of line in Figure S7C and FigureS7D were taken as reference for As(III) and As(V), respectively.

#### To find unknown concentration of solution $(x_u)$ :

$$x_u = \left(\frac{y_m - C}{m}\right)$$
 Equation (5)

 $y_m$  is area under the peak of unknown solution multiplied with laser intensity correction factor (K). K values vary with Raman measurement parameters during experiment. The each set of experimental data have different K value. K defined based on reference (*x*, *y*) data and the initial concentration of solution data ( $x_0, y_0$ ).



**Figure S8**. XPS spectrum of A) As 3d and B) Fe 2p. As 3d region of Aa) NaAsO<sub>2</sub> (red trace) and Na<sub>2</sub>HAsO<sub>4</sub>.7H<sub>2</sub>O (blue trace). Comparison of the positions may be noted. b) As(III), c) As(V) and d) As(mix) adsorbed on HEM. Spectra are fitted for the  $3d_{5/2}$  and  $3d_{3/2}$  features. Ba) HEM before adsorption, b), c) and d) are Fe 2p after adsorption, as before. Peaks have been fitted with their components.



Figure S9. XRD pattern of CM2LF. Specific lines are labeled.



**Figure S10.** Schematic representation of the (010) plane of 2-line ferrihydrite surface under different conditions. A) Singly/doubly coordinated oxygens involving in protonation or deprotonation according to the solution pH. The singly coordinated surface oxygens ( $H_2O^+$ -/- $O^-$ /-OH) are shown in dotted rectangular boxes. B) The labile nature of singly coordinated oxygens of the cluster, Fe<sub>2</sub>O<sub>10</sub>Hy (y = 9/8/7) involved in the ligand exchange mechanism with As(III) and As(V) under different conditions. In each case, the preference of complexation is in the order, 3

> 2 > 1. As(III) gives complex 1 (<sup>1</sup>V), while As(V) results in complex 2 (<sup>1</sup>V) and complex 3 (<sup>1</sup>V), respectively (<sup>1</sup>V: Monodentate mononuclear complex). The 2-line ferrihydrite is composed of Fe1 and Fe2 centers which differ in the octahedral environment (FeO<sub>6</sub>) but, Fe3 center is in tetrahedral environment (FeO<sub>4</sub>) as shown in Figure 8A.



**Figure S11.** The influence of competing ions on arsenic adsorption for CM2LF, MAG and HEM with an input concentration of 1.0 mg  $L^{-1}$  for both A) As(III) and B) As(V), separately. 100 mL arsenic contaminated deionized water was taken with 25 mg of CM2LF/MAG/HEM and the incubation time was kept as 150 min. The individual ion concentration taken was 1 mM, before spiking arsenic in water.

# Supporting Table 1

Energy levels (eV)	CM2LF	MAG	HEM				
	Before As treatment						
As 3d	$NaAsO_2: 44.2 \qquad Na_2HAsO_4.7H_2O: 44.8$						
Fe 2p <sub>3/2</sub>	710.1	Main peak : 710.4 Fe(II) : 709.5 Fe(III) : 711.2	710				
Fe 2p <sub>1/2</sub>	723.2	Main peak : 724.0 Fe(II) : 723.1 Fe(III) : 724.8	723.1				
	After As(III) treatment						
As 3d	45.1	44.3	44.7				
Fe 2p <sub>3/2</sub>	710.0	Main peak : 710.4 Fe(II) : 709.6 Fe(III) : 711.3	709.8				
Fe 2p <sub>1/2</sub>	723.1	Main peak : 724.0 Fe(II) : 723.2 Fe(III) : 724.9	722.9				
	After As(V) treatment						
As 3d	45.3	45.5	46.5				
Fe 2p <sub>3/2</sub>	712.2	Main peak : 710.7 Fe(II) : 709.5 Fe(III) : 711.2	709.8				
Fe 2p <sub>1/2</sub>	725.3	Main peak : 724.3 Fe(II) : 723.1 Fe(III) : 724.8	722.9				

**Table S1.** XPS data of before and after arsenic adsorption.