

Supporting Information Cover Sheet

Iron(III) Modification of *Bacillus subtilis* Membranes Provides Record Sorption Capacity for Arsenic and Endows Unusual Selectivity for As(V)

Ting Yang,^a Ming-Li Chen,^a Lan-Hua Liu,^a Jian-Hua Wang,^{a*} and Purnendu K.

Dasgupta^{b*}

^a Research Center for Analytical Sciences, Box 332, Northeastern University, Shenyang

110819, China; ^bDepartment of Chemistry and Biochemistry, University of Texas at

Arlington, Arlington, TX 76019-0065, USA.

Submitted to *Environmental Science & Technology*

Number of pages: 13

Number of figures: 8

Number of tables: 2

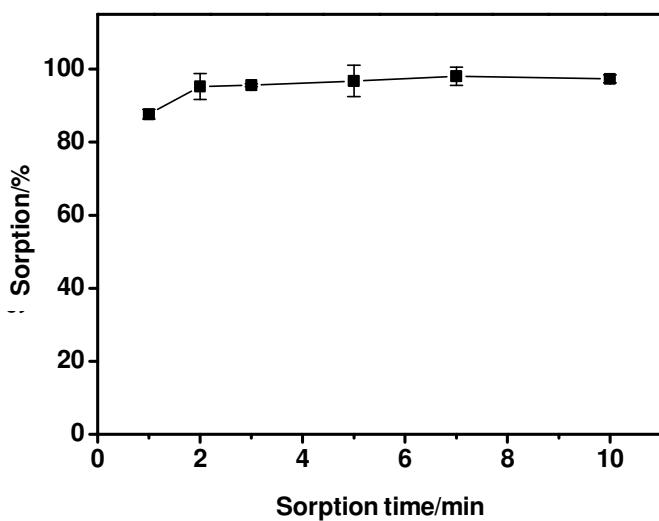


Figure S1. The dependence of sorption efficiency of As(V) on the sorption time. Sample volume: 200 μL , 20 $\mu\text{g L}^{-1}$ As(V); Biomass weight: 2.2 mg; Eluent (0.8 mol L^{-1} HNO_3): 100 μL ; Elution time: 2 min.

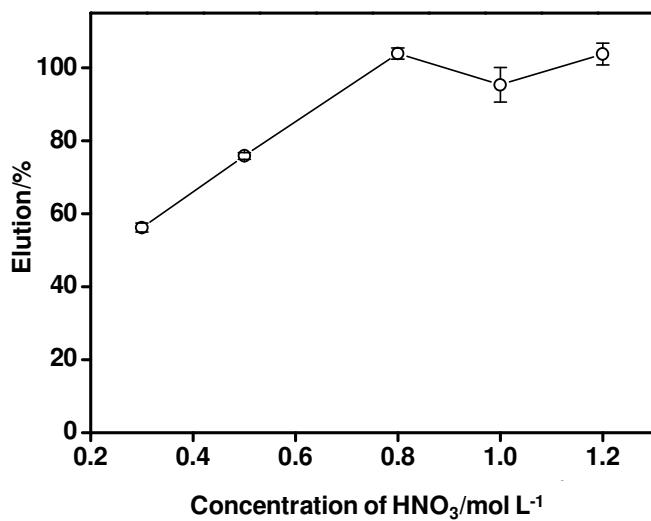


Figure S2. The dependence of elution efficiency of As(V) on the concentration of eluent (HNO_3). Sample volume: 200 μL , 20 $\mu\text{g L}^{-1}$ As(V); Biomass weight: 2.2 mg; Sorption time: 3 min; Eluent (HNO_3 with various concentrations): 100 μL ; Elution time: 2 min. Note that the % elution refers to the original amount of As(V) taken, 96% is retained in the preconcentration process.

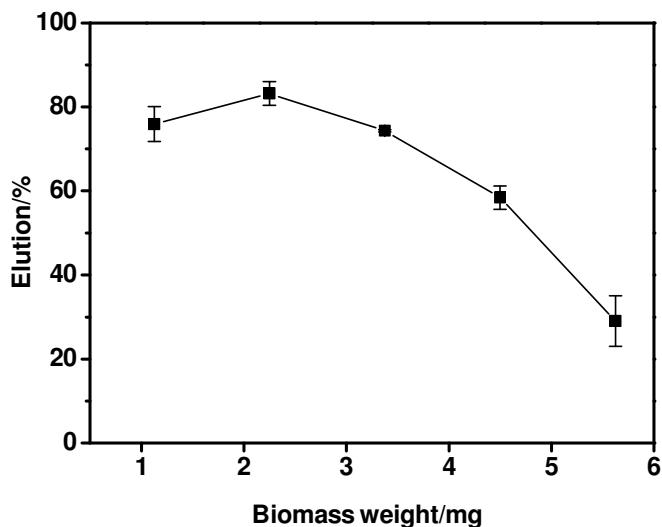


Figure S3. The dependence of elution efficiency of As(V) on the biomass weight. Sample volume: 1000 μL , 1.0 $\mu\text{g L}^{-1}$ As(V); Sorption time: 3 min; Eluent (0.8 mol L^{-1} HNO_3): 100 μL ; Elution time: 2 min. Note that the elution/% refers to the original amount of As(V) taken, 96% is retained in the preconcentration process.

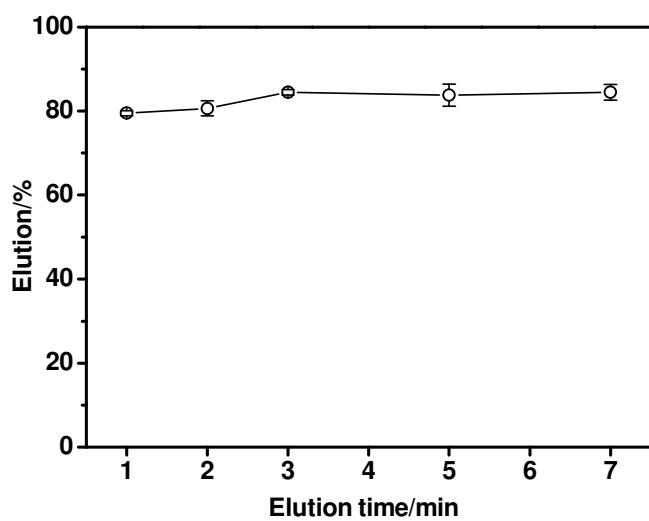


Figure S4. The dependence of elution efficiency of As(V) on the elution time. Sample volume: 1000 μL , 1.0 $\mu\text{g L}^{-1}$ As(V); Biomass weight: 2.2 mg; Sorption time: 3 min; Eluent (0.8 mol L^{-1} HNO_3): 100 μL . Note that the elution/% refers to the original amount of As(V) taken, 96% is retained in the preconcentration process.

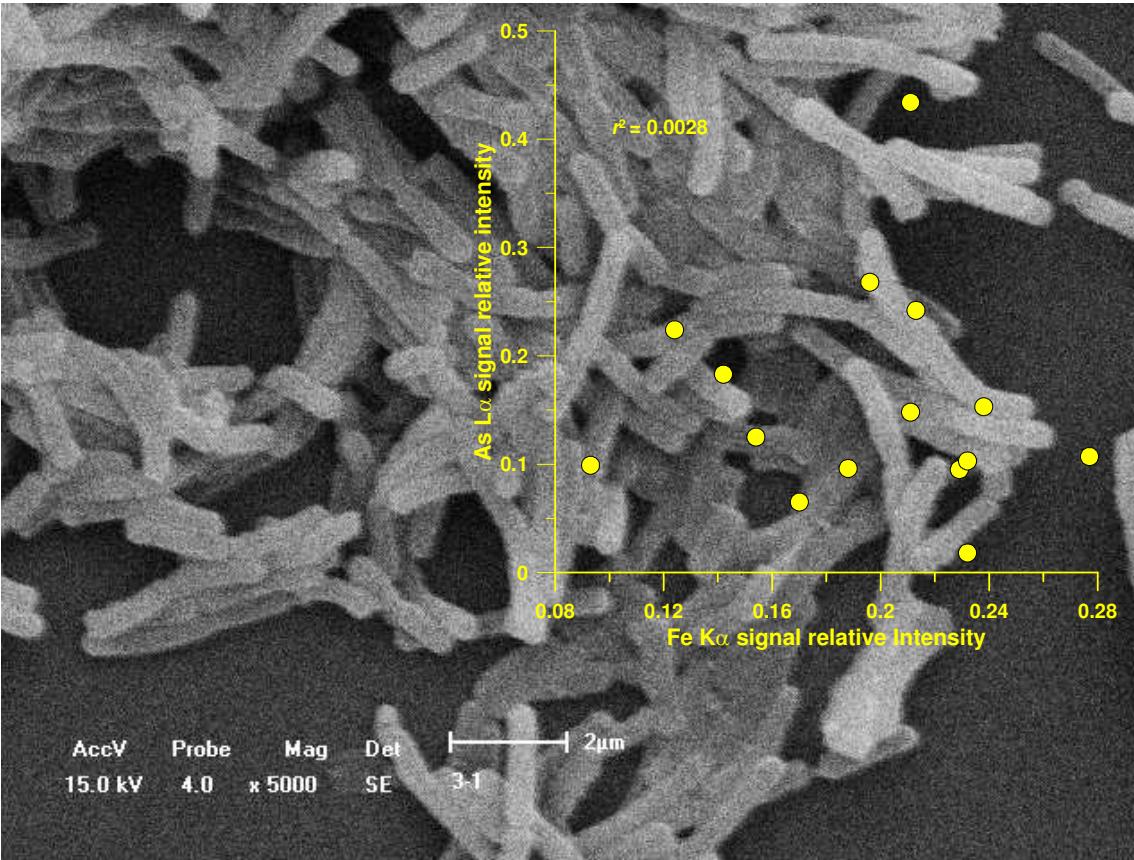


Figure S5. Fe and As X-ray intensities were measured in randomly chosen $30 \times 40 \mu\text{m}$ viewing frames (each frame containing hundreds of bacteria); the As and Fe signals showed no correlation whatsoever ($r^2 = 0.0028$, $n = 15$). As a reference, the background micrograph has a frame size of $30 \times 40 \mu\text{m}$

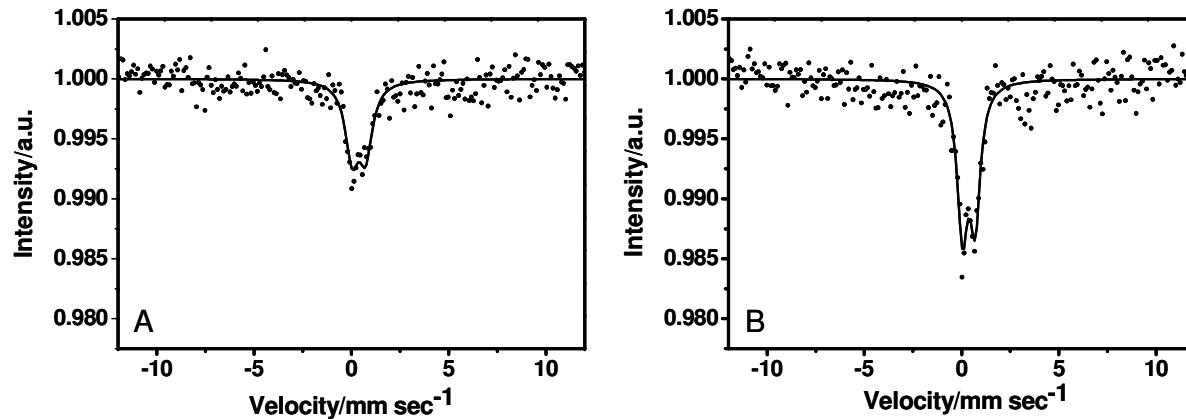


Figure S6. Room temperature ^{57}Fe Mössbauer spectra. (A) Fe(III) loaded *Bacillus subtilis* (*Fe-bac*); (B) *Fe-bac-As(V)*. For (A), the Fe(III) concentration is 8 mM. For (B), the *Fe-bac* is pre-treated with 200 mg L $^{-1}$ As(V) solution (pH 3.0) under vigorous agitation for 60 min to facilitate adsorption. The parameters for Fe-bac related to α -Fe are an isomer shift (IS) of 0.3854 mm s $^{-1}$, a quadrupole split (QS) of 0.7007 mm s $^{-1}$, with a half-line width of the spectra of 0.4188 mm s $^{-1}$. On the other hand, the corresponding parameters for *Fe-bac-As(V)* are: IS of 0.3715 mm s $^{-1}$, QS of 0.6501 mm s $^{-1}$ with a half-line width of 0.3250 mm s $^{-1}$. The error limits of IS and QS are 0.001 mm s $^{-1}$ and 0.002 mm s $^{-1}$, respectively.

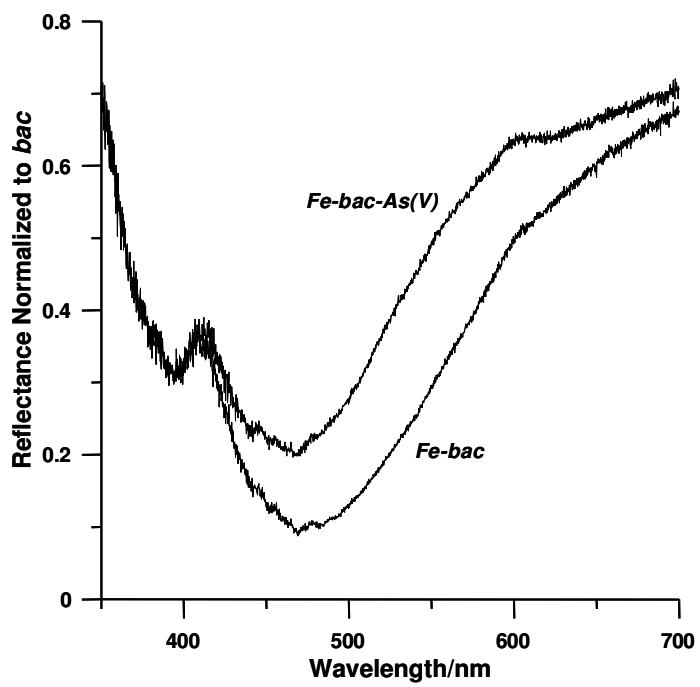


Figure S7. Reflectance spectra of *Fe-bac* and *Fe-bac-As(V)* referenced to *native Bacillus subtilis*. Upon binding of arsenic, the color is similar but there is a decrease in visible absorption. This is also observed in solution. See Figure S8.

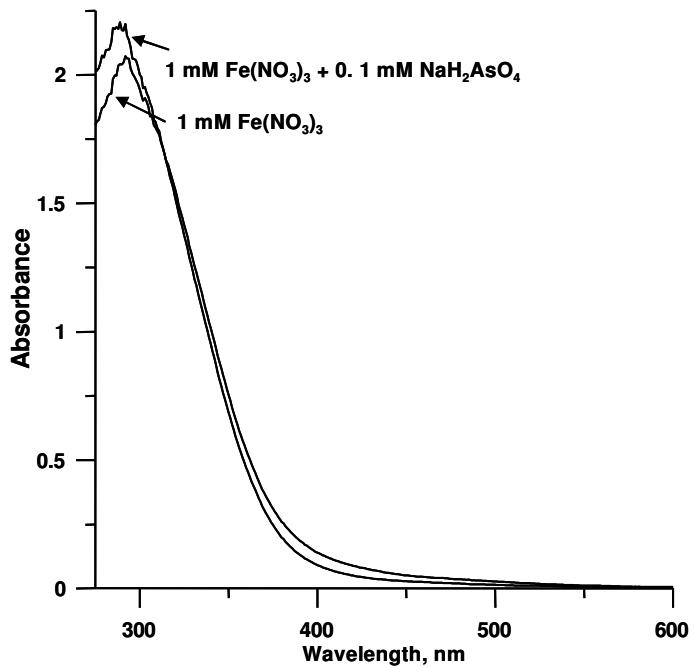


Figure S8. When small amounts of arsenate (not sufficient to cause precipitation) is added to ferric nitrate solution, the UV absorption increases slightly and the absorption maximum blue shifts slightly. More importantly the visible absorption decreases, very slightly but perceptibly. These spectra were obtained on an Agilent 8453 diode array spectrometer.

Table S1. Arsenic sorption/removal capacities of different iron-bearing sorbents per unit iron content.

Sorbent	Sorption capacity mol As/mol Fe		Ref.	Sorbent	Sorption capacity mol As/mol Fe		Ref.
	As(III)	As(V)			As(III)	As(V)	
Iron oxide coated cement	0.002		1	HFO on granular activated carbon	0.2	9	
Goethite	0.016	0.016	2	Fe(III) loaded sponge	0.24	1.83	10
Goethite	0.026	0.005	3	HFO	0.31	0.24	2
Goethite		0.0059	4	Fe modified activated carbon	0.26	0.3	11
Cr(OH) ₃ /Fe(OH) ₃		0.028	5	Fe(OH) ₃ on polyacrylamide		0.34	12
HFO	0.041	0.01	3	Iron oxide loaded melted slag	0.35	1.04	13
Crystal FePO ₄	0.032	0.018	6	Fe(III) loaded chelating resin	0.88	0.78	14
Amorphous FePO ₄	0.042	0.02	6	Ferrihydrite	0.6	0.25	15
Iron oxide coated cement		0.02	7	HFO loaded fibrous		0.94	16
HFO on cellulose	0.16	0.053	8	Fe loaded <i>Bacillus subtilis</i>	1.4	1.9	This work

Table S2. Assignments of the IR bands (refs. 17-20).

Wavenumber (cm^{-1})				← → Formatted: Centered
<i>Bacillus subtilis</i> bacteria	<i>Fe-bac</i>	As loaded <i>Fe-bac</i>	IR band assignment	
1640	1640	1641	C=O stretching in amide (amide I)	
1538	1517	1516	N-H bending and C-N stretching in amide (amide II)	
1455	1451	1455	CH ₂ scissoring	
1398	1386	1386	COO ⁻ symmetric stretching	
1217	1212	1211	P=O stretching (phosphate)	
1054	1058	1042	Asymmetric/symmetric stretching of PO ₂ ⁻ and P(OH) ₂ in phosphate; vibrations of C-OH and C-C in polysaccharides.	
--	--	818	As-O stretching vibration of Fe-O-As groups	

REFERENCES

- (1) Kundu, S.; Gupta, A. K. As(III) removal from aqueous medium in fixed bed using iron oxide-coated cement: Experimental and modeling studies. *Chem. Eng. J.* **2007**, *129*, 123-131.
- (2) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182-4189.
- (3) Lenoble, V.; Bouras, O.; Deluchat, V.; Serpaud, B.; Bollinger, J. C. Arsenic adsorption onto pillared clays and iron oxides. *J. Colloid Interf. Sci.* **2002**, *255*, 52-58.
- (4) Lakshmipathiraj, P.; Narasimhan, B. R. V.; Prabhakar, S.; Raju, G. B. Adsorption of arsenate on synthetic goethite from aqueous solutions. *J. Hazard. Mater.* **2006**, *136*, 281-287.
- (5) Namasivayam, C.; Senthilkumar, S. Removal of arsenic(V) from aqueous solution using industrial solid waste: Adsorption rates and equilibrium studies. *Ind. Eng. Chem. Res.* **1998**, *37*, 4816-4822.
- (6) Lenoble, V.; Laclautre, C.; Deluchat, V.; Serpaud, B.; Bollinger, J. C. Arsenic removal by adsorption on iron(III) phosphate. *J. Hazard. Mater.* **2005**, *123*, 262-268.
- (7) Kundu, S.; Gupta, A. K. Adsorptive removal of As(III) from aqueous solution using iron oxide coated cement: Evaluation of kinetic, equilibrium and thermodynamic models. *Sep. Purif. Technol.* **2006**, *51*, 165-172.
- (8) Guo, X. J.; Chen, F. H. Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater. *Environ. Sci. Technol.* **2005**, *39*, 6808-6818.
- (9) Gu, Z. M.; Fang, J.; Deng, B. L. Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environ. Sci. Technol.* **2005**, *39*, 3833-3843.
- (10) Munoz, J. A.; Gonzalo, A.; Valiente, M. Arsenic adsorption by Fe(III)-loaded open-celled cellulose sponge. Thermodynamic and selectivity aspects. *Environ. Sci. Technol.* **2002**, *36*, 3405-3411.
- (11) Chen, W. F.; Parette, R.; Zou, J. Y. Arsenic removal by iron-modified activated carbon. *Water Res.* **2007**, *41*, 1851-1858.
- (12) Shigetomi, Y.; Hori, Y.; Kojima, T. The removal of arsenate in waste water with an

- adsorbent prepared by binding hydrous iron(III) oxide with polyacrylamide. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1475-1476.
- (13) Zhang, F. S.; Itoh, H. Iron oxide-loaded slag for arsenic removal from aqueous system. *Chemosphere* **2005**, *60*, 319-325.
- (14) Matsunaga, H.; Yokoyama, T.; Eldridge, R. J.; Bolto, B. A., Adsorption characteristics of arsenic(III) and arsenic(V) on iron(III)-loaded chelating resin having lysine-N-alpha, N-alpha-diacetic acid moiety. *React. Funct. Polym.* **1996**, *29* (3), 167-174.
- (15) Jain, A.; Raven, K. P.; Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: Surface charge reduction and net OH⁻ release stoichiometry. *Environ. Sci. Technol.* **1999**, *33*, 1179-1184.
- (16) Vatutsina, O. M.; Soldatov, V. S.; Sokolova, V. I.; Johann, J.; Bissen, M.; Weissenbacher, A. A new hybrid (polymer/inorganic) fibrous sorbent for arsenic removal from drinking water. *React. Funct. Polym.* **2007**, *67*, 184-201.
- (17) Wei, J.; Saxena, A.; Song, B.; Ward, B. B.; Beveridge, T. J.; Myneni, S. C. B., Elucidation of functional groups on gram-positive and gram-negative bacterial surfaces using infrared spectroscopy. *Langmuir* **2004**, *20* (26), 11433-11442.
- (18) Goldberg, S.; Johnston, C. T., Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *J. Colloid Interface Sci.* **2001**, *234* (1), 204-216.
- (19) Parikh, S. J.; Chorover, J., ATR-FTIR spectroscopy reveals bond formation during bacterial adhesion to iron oxide. *Langmuir* **2006**, *22* (20), 8492-8500.
- (20) Jia, Y. F.; Xu, L. Y.; Wang, X.; Demopoulos, G. P., Infrared spectroscopic and X-ray diffraction characterization of the nature of adsorbed arsenate on ferrihydrite. *Geochim. Cosmochim. Acta* **2007**, *71* (7), 1643-1654.