

ZINC ADSORPTION EFFECTS ON ARSENITE OXIDATION KINETICS AT THE  
BIRNESSITE-WATER INTERFACE

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Number of pages (including this one): 5

Number of tables: 3

Number of figures: 2

**Table 1.** Percent As(III)(aq) during As(III) oxidation at the birnessite-water interface as a function of initial As(III) concentrations, various Zn(II) additions (i.e., no Zn(II), Zn(II) pre-sorbed prior to the As(III) addition, and As(III)/Zn(II) simultaneous addition) at pH 4.5.

Time (h)	% As as [As(III)](aq) <sup>1</sup>					
	[As(III)] <sub>i</sub> = 100 μM			[As(III)] <sub>i</sub> = 300 μM		
	No Zn	Pre-sorbed	Simultaneous	No Zn	Pre-sorbed	Simultaneous
0	100.0	100.0	100.0	100.0	100.0	100.0
0.33	68.5	93.9	91.6	84.3	96.6	92.7
0.67	44.1	89.0	83.4	68.4	90.1	87.1
1	28.0	83.1	74.0	56.2	81.6	76.8
2	2.7	64.5	44.9	36.3	62.9	54.8
4	0.0	32.0	5.9	20.0	39.9	30.9
6	0.0	18.0	0.0	14.6	28.0	19.7
8	0.0	9.6	0.0	8.1	25.2	18.5
10	0.0	2.0	0.0	NA	19.0	NA
24	0.4	5.0	0.0	0.4	11.3	0.8

<sup>1</sup>NA = Not Available

**Table 2.** Percent As(III)(aq) during the As(III) oxidation at the birnessite-water interface as a function of initial As(III) concentrations and various Zn(II) additions (i.e., no Zn(II), Zn(II) pre-sorbed prior to the As(III) addition, and As(III)/Zn(II) simultaneous addition) at pH 6.

Time (h)	% As as [As(III)](aq) <sup>1</sup>					
	[As(III)] <sub>i</sub> = 100 μM			[As(III)] <sub>i</sub> = 300 μM		
	No Zn	Pre-sorbed	Simultaneous	No Zn	Pre-sorbed	Simultaneous
0	100.0	100.0	100.0	100.0	100.0	100.0
0.33	79.8	98.6	92.5	90.3	98.0	97.1
0.67	68.5	96.3	92.2	82.9	97.7	95.6
1	55.3	93.3	88.8	80.9	97.7	94.2
2	42.6	90.8	85.2	73.6	94.4	91.4
4	19.5	80.5	75.7	62.9	88.7	87.8
6	16.3	77.8	71.3	55.5	83.7	79.7
8	NA	70.0	62.3	46.7	77.8	74.2
10	NA	65.9	52.8	NA	71.9	68.9
24	3.5	19.6	18.8	25.7	46.8	45.3

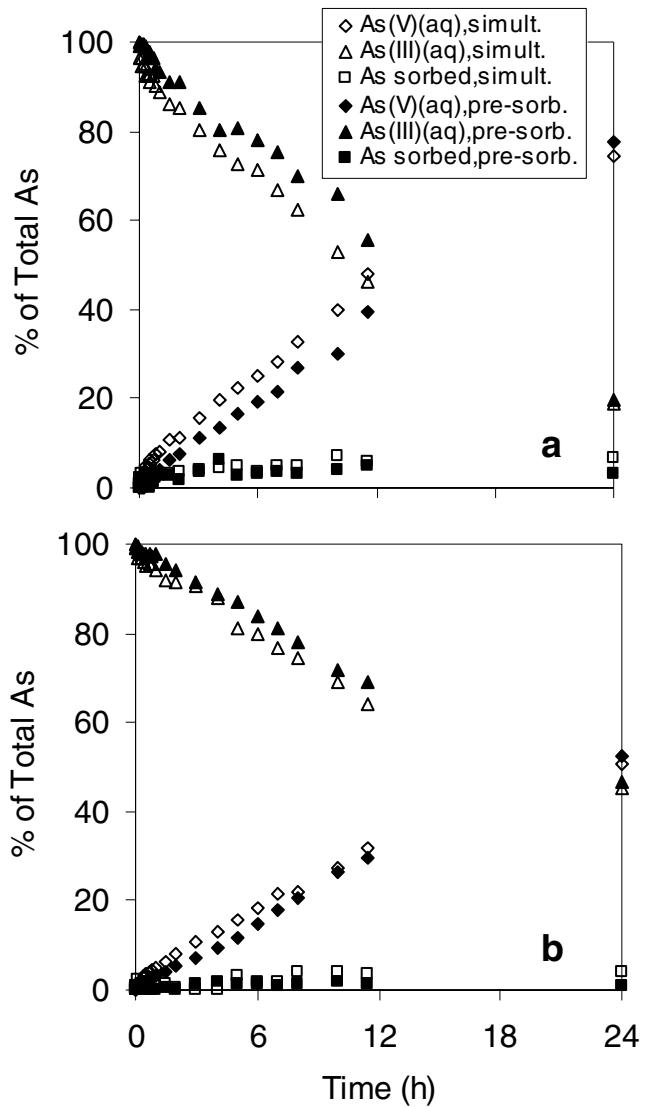
<sup>1</sup>NA = Not Available

**Table 3.** Log of Ion Activity Product (IAP) and Log of Solubility Product (Log K) for Mn(II)- and Zn(II)-arsenate precipitates during the As(III) oxidation kinetic experiments on birnessite.

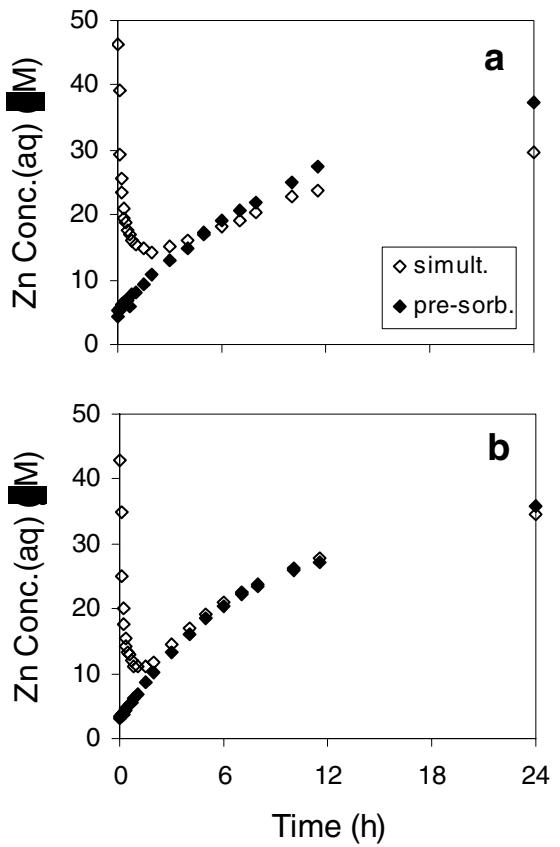
Time (h)	-log(IAP)													
	Mn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	Mn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>	Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O <sup>a</sup>	Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O <sup>b</sup>	pH6	pH4.5	pH6	pH4.5	pH6	pH4.5	pH6	pH4.5
<i>[As(III)]<sub>i</sub> = 100 μM</i>														
0.67	13.4	NA	13.1	48.0	14.3	14.7	15.4	12.9	13.6	12.7	14.7	10.9		
2	11.9	12.5	11.6	9.3	12.9	13.2	13.9	11.3	12.4	12.5	13.4	10.6		
4	11.7	11.0	11.4	7.8	12.1	12.2	13.2	10.4	11.8	11.8	12.9	10.0		
8	11.8	10.3	11.5	7.1	11.8	11.1	12.9	9.3	11.7	11.0	12.7	9.2		
12	11.8	9.9	11.5	6.7	11.8	10.5	12.8	8.6	11.7	10.5	12.7	8.7		
24	11.8	9.7	11.5	6.5	11.7	9.5	12.8	7.7	11.7	9.8	12.7	8.0		
<i>[As(III)]<sub>i</sub> = 300 μM</i>														
0.67	11.8	17.6	11.4	14.4	13.2	13.9	14.2	12.1	12.7	12.6	13.8	10.8		
2	9.9	10.4	9.6	5.2	11.6	12.6	12.7	10.7	11.3	12.0	12.4	10.2		
4	9.2	8.9	8.9	4.4	11.1	11.5	12.1	9.6	10.9	11.1	11.9	9.3		
8	8.9	7.8	8.6	3.7	10.9	10.3	11.9	8.5	10.7	10.2	11.7	8.4		
12	8.8	7.4	8.4	3.5	10.7	9.8	11.8	8.0	10.6	9.7	11.6	7.9		
24	8.6	6.9	8.2	3.0	10.7	8.9	11.7	7.1	10.5	9.0	11.5	7.2		

For comparison -log(K<sub>sadiq</sub>) for Mn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> = -8.5, -log(K<sub>mineq<sup>+</sup></sub>) for Mn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O = -28.9, -log(K<sub>sadiq</sub>) for Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> = -8.2, and -log(K<sub>mineq<sup>+</sup></sub>) for Zn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O = -27.6. <sup>a</sup>Pre-sorbed Zn(II) for 24 h prior to the As(III) addition.

<sup>b</sup>Zn(II) and As(III) simultaneous addition.



**Figure 1.** Effects of pre-sorbed Zn(II) vs Zn(II)/As(III)-simultaneous treatment on the As(III) oxidation kinetics on birnessite surfaces (pH 6, suspension density =  $0.1 \text{ g L}^{-1}$ , I = 0.01 M NaCl, total Zn(II) concentrations:  $[\text{Zn}]_t = 100 \mu\text{M}$ , and  $\text{N}_2$  atmosphere). Percent As(III) depletion, As(V) release, and total As adsorption are shown as a function of time (h). (a) initial As(III) concentrations:  $[\text{As(III)}]_i = 100 \mu\text{M}$ ; (b)  $[\text{As(III)}]_i = 300 \mu\text{M}$ .



**Figure 2.** Effects of the pre-sorbed Zn(II) vs Zn(II)/As(III)-simultaneous treatment on the aqueous profiles of Zn(II) during the As(III) oxidation kinetics on birnessite surfaces (pH 6, suspension density = 0.1 g L<sup>-1</sup>, I = 0.01 M NaCl, total Zn(II) concentrations: [Zn]<sub>t</sub> = 100 μM, and N<sub>2</sub> atmosphere). (a) Initial As(III) concentrations: [As(III)]<sub>i</sub> = 100 μM; (b) [As(III)]<sub>i</sub> = 300 μM.