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SUPPLEMENTAL INFORMATION

Aerobic Oxidation of Arsenite to Arsenate by Cu(II)-chitosan/O₂ in Fenton-like Reaction, a XANES Investigation

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Figure S1. Comparison of phosphate removal by Cu(II)-chitosan (0.4 g $Cu(NO_3)_2$ -3H₂O / g chitosan) and Cu(II)-chitosan (0.1 g $Cu(NO_3)_2$ -3H₂O / g chitosan). Starting concentrations were 16 ppm P and 25 mM acetate buffer pH6, and 4 ppm As(III) where indicated. Incubation was done in the dark in oxic conditions. Results indicate that copper loading strongly controls phosphate sorption potential.

Modeling Isotherms via Langmuir and Freundlich Equations

The Langmuir equation is as follows:

$$q_e = q_{max} \left(\frac{bC_e}{1 + bC_e}\right)$$

with q_e as the equilibrium adsorption capacity (mg As removed / g adsorbent), *b* as the Langmuir adsorption constant (L/mg), C_e as the equilibrium concentration in solution (ppm), and q_{max} as the maximum adsorption capacity of the adsorbent (mg/g). The Freundlich equation is as follows: $q_e = K_f C^{1/n}$

with q_e as the equilibrium adsorption capacity (mg arsenic removed / g adsorbent), C as equilibrium concentration, and K_f and n as empirical constants.



S(V) Daik	AS(V) + P	AS(III) UV	AS(III) + P	AS(III) Dark	AS(III) + P	A5(III)
	Dark		UV		Dark	Anoxic Dark
12.8	12.3	17.9	6.11	1.54	0.516	1.56
0.497	0.486	0.078	0.373	1.83	4.55	0.303
1.33	0.311	0.459	0.510	0.161	0.074	0.014
4.14	3.83	1.51	1.77	0.812	0.332	0.467
0.490	0.505	0.712	0.445	0.313	0.237	0.428
0.100	1.60	0.400	1.69	0.158	0.092	0.007
	12.8 0.497 1.33 4.14 0.490 0.100	I2.8 I2.3 0.497 0.486 1.33 0.311 4.14 3.83 0.490 0.505 0.100 1.60	I2.8 I2.3 I7.9 0.497 0.486 0.078 1.33 0.311 0.459 4.14 3.83 1.51 0.490 0.505 0.712 0.100 1.60 0.400	Joark As(ii) Fr As(iii) Fr As(iii) Fr Dark UV 12.8 12.3 17.9 6.11 0.497 0.486 0.078 0.373 1.33 0.311 0.459 0.510 4.14 3.83 1.51 1.77 0.490 0.505 0.712 0.445 0.100 1.60 0.400 1.69	Joark As(iii) ov As(iii) ov As(iii) ov As(iii) ov As(iii) ov 12.8 12.3 17.9 6.11 1.54 0.497 0.486 0.078 0.373 1.83 1.33 0.311 0.459 0.510 0.161 4.14 3.83 1.51 1.77 0.812 0.490 0.505 0.712 0.445 0.313 0.100 1.60 0.400 1.69 0.158	Jark Jark Juv Jark Juv Juv<

Figure S2. Langmuir (solid line) and Freundlich (dashed line) adsorption isotherms and fitting parameters for arsenic removal of Cu(II)-n-TiO₂-chitosan A (0.4 g Cu(NO₃)₂-3H₂O, 0.3 g n-TiO₂ per 1 g chitosan). Initial concentrations were 50 ppb, 500 ppb, 1 ppm, 4 ppm, 6 ppm, 8 ppm, 12 ppm, and 20 ppm As and 0.25 mM acetate buffer pH 6. Phosphate concentration was 16 ppm when present. UV light, 8 W, 365 nm was suspended within the incubator 18" above samples where indicated. Anoxic incubation was done in a N atmosphere. Figure adapted with permission from Pincus et al., (2018).[1]



	As(V) Dark	As(V) + P	As(III) UV	As(III) + P	As(III) Dark	As(III) + P	As(III)
		Dark		UV		Dark	Anoxic Dark
Langmuir							
q Max (mg/g)	35.0	37.2	0.959	0.964	0.930	0.964	0.310
b (L/mg)	0.063	0.022	0.380	0.144	0.304	0.144	0.266
Chi-square	1.25	0.390	0.013	0.001	0.063	0.001	0.001
Freundlich							
K _f	2.48	0.730	0.290	0.145	0.263	0.024	0.082
1/n	0.698	0.975	0.451	0.608	0.438	1.340	0.427
Chi-square	2.52	0.287	0.007	0.001	0.038	0.012	0.003

Figure S3. Langmuir (solid line) and Freundlich (dashed line) adsorption isotherms and fitting parameters for arsenic removal of Cu(II)-n-TiO₂-chitosan B ($0.36 \text{ g Cu}(NO_3)_2$ - $3H_2O$, $0.60 \text{ g n-TiO}_2 \text{ per 1 g chitosan}$). Initial concentrations were 4 ppm, 6 ppm, 8 ppm, and 12 ppm As for As(V) and 1, 4, 8, and 12 ppm As for all other systems conditions and 0.25 mM acetate buffer pH 6. Phosphate concentration was 16 ppm when present. UV light, 8 W, 365 nm was suspended within the incubator 18" above samples where indicated. Anoxic incubation was done in a N atmosphere. Figure adapted with permission from Pincus et al., (2018).[1]

References:

[1] L.N. Pincus, F. Melnikov, J.S. Yamani, J.B. Zimmerman, Multifunctional photoactive and selective adsorbent for arsenite and arsenate: Evaluation of nano titanium dioxide-enabled chitosan crosslinked with copper, J. Hazard. Mater. 358 (2018) 145–154. https://doi.org/10.1016/j.jhazmat.2018.06.033.