

Supporting Information: Copper doping improves hydroxyapatite sorption for arsenate in simulated groundwaters

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This document includes: XRD patterns (Figure S1), FTIR spectra (Figure S2), and the infrared band assignments (Table S1) for HAP and CuHAP; relation between phosphorus release and arsenate sorption to unit area of HAP or CuHAP (Figure S3); effect of copper doping level on residual copper concentration in the SGW after arsenate sorption to HAP and CuHAP (Figure S4); stability constants for Cu^{2+} - CO_3^{2-} complexation and hydrolysis of AsO_4^{3-} and CO_3^{2-} (Table S2); and effect of calcium on zeta potential of HAP and CuHAP (Figure S5).

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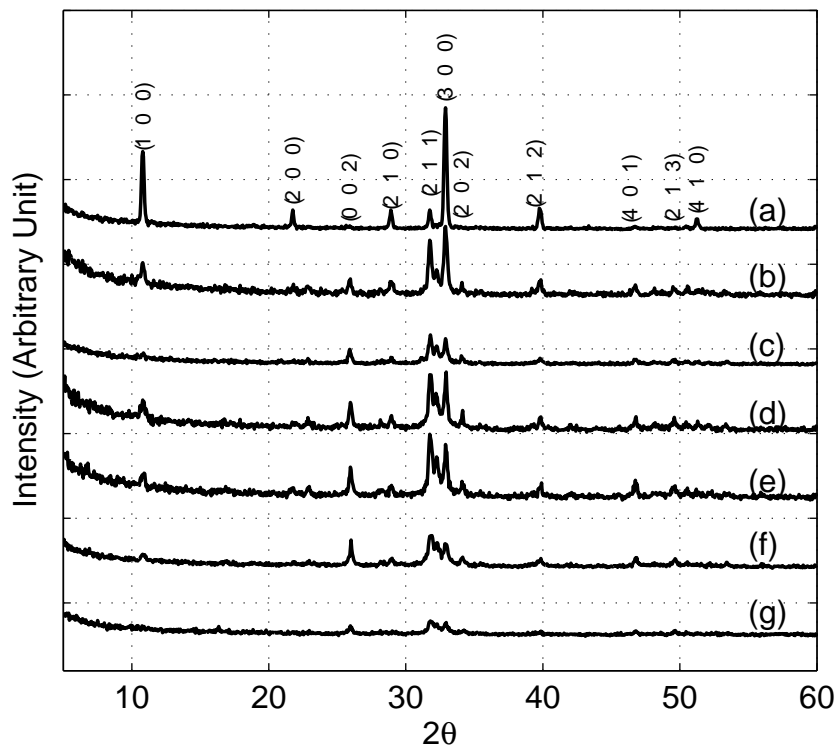


Figure S1: XRD patterns of HAP and CuHAP at $X_{Cu/Cu+Ca}$ of (a) 0, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.04, (f) 0.05, (g) 0.08.

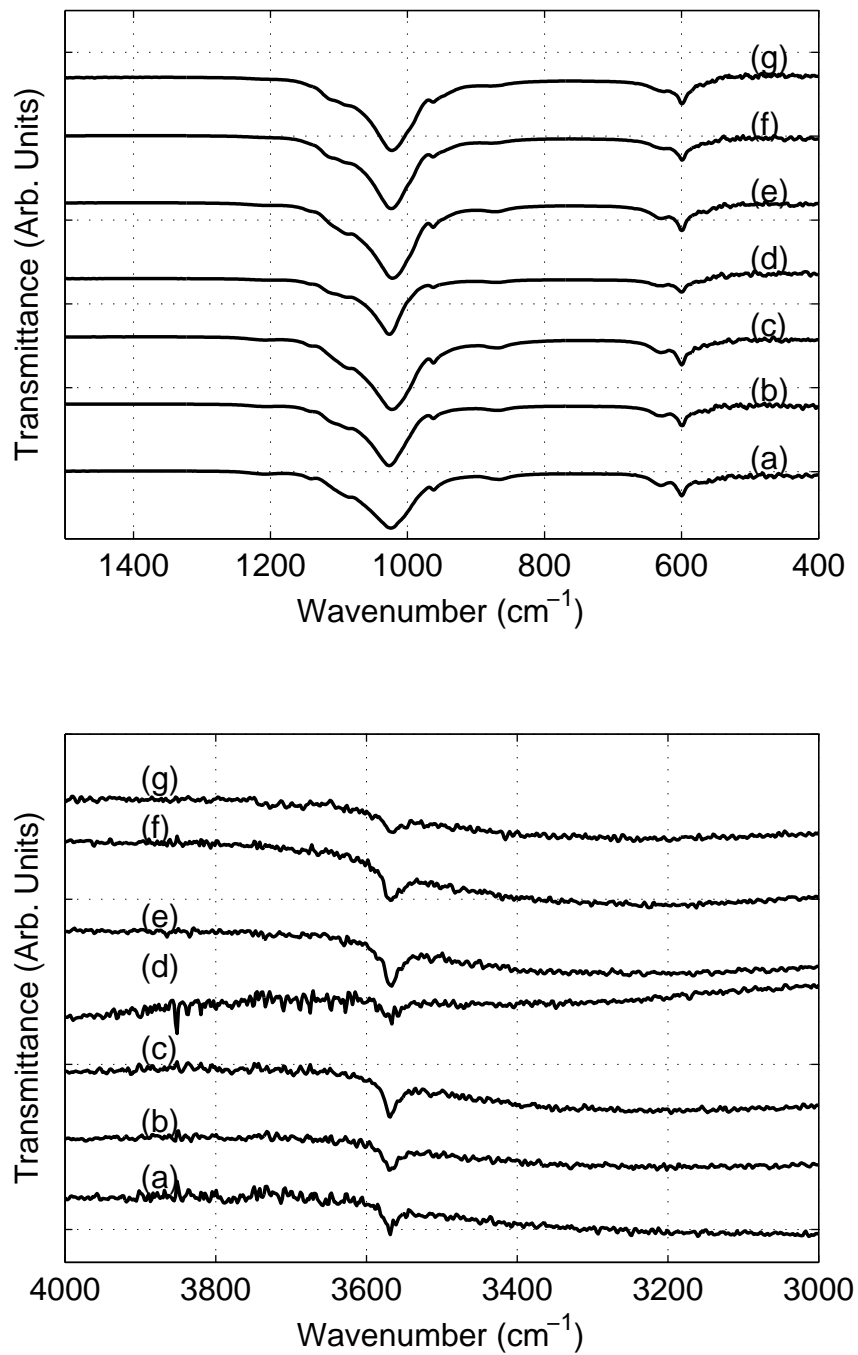


Figure S2: FTIR spectra of HAP and CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of (a) 0, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.04, (f) 0.05, (g) 0.08.

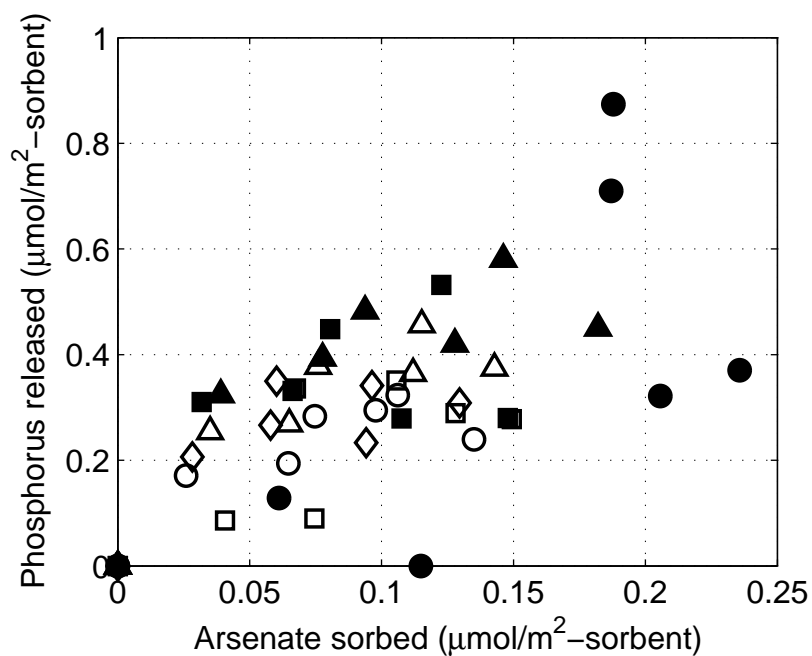


Figure S3: Relation between the amount of phosphorus released from and the amount of arsenic sorbed to unit area of HAP (●) and CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.01 (□), 0.02 (◇), 0.03 (■), 0.04 (△), 0.05 (○), and 0.08 (▲) in the SGW. Sorbent concentration, 0.3 g/L; mixing time, 24 hours; pH, 7.7–8.0.

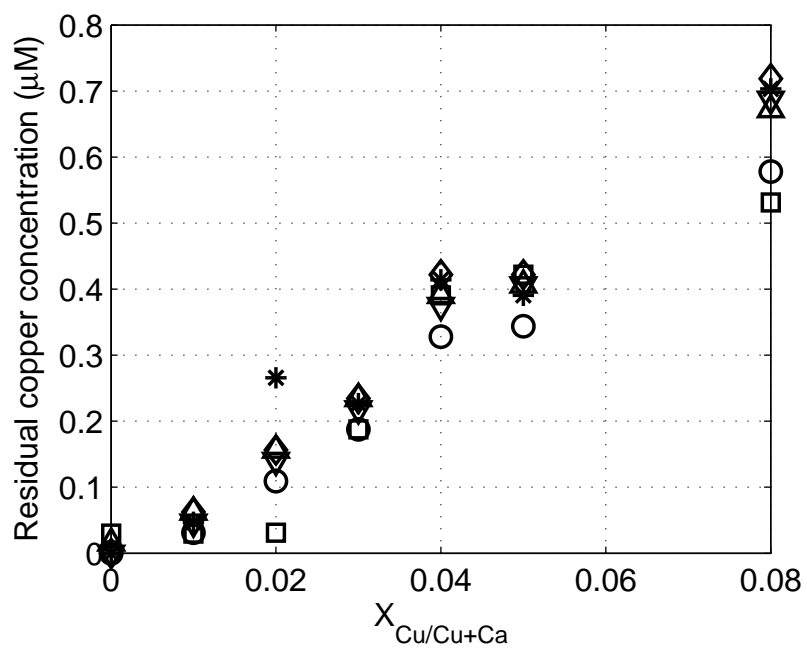


Figure S4: Effect of copper doping level on residual copper concentration in the SGW after arsenate sorption. Initial arsenate concentration was 2.14 (○), 4.35 (□), 6.26 (*), 8.81(▽), 10.4 (◇), 10.8 (△) μM. Sorbent concentration, 0.3 g/L; mixing time, 24 hours; pH, 7.7–8.0.

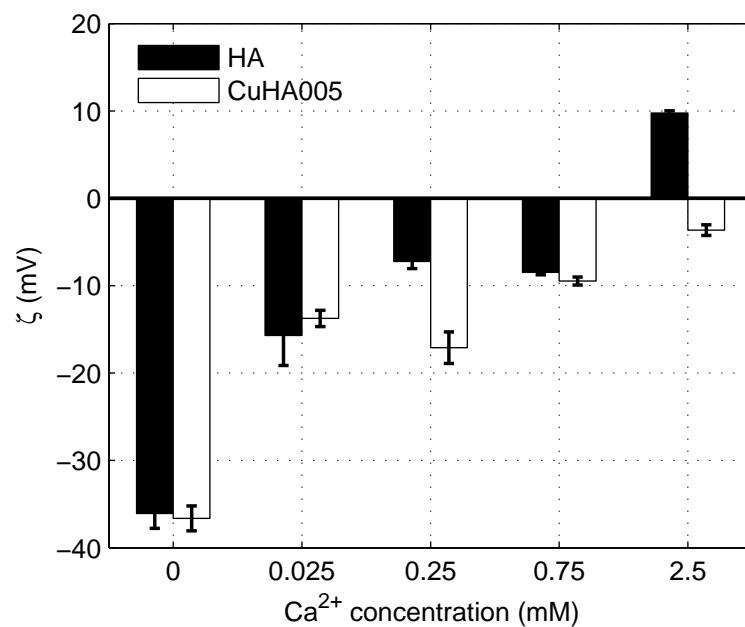


Figure S5: Effect of calcium concentration on ζ potential of HAP and CuHAP at $X_{Cu/Cu+Ca}$ of 0.05 (CuHAP005) in the NBS. Sorbent concentration, 0.3 g/L; mixing time, 24 hours; pH, 8.2–8.4. Error bars represent the standard deviation for triplicate measurements.

Table S1: Assignments of observed vibrational frequencies of synthesized HA and CuHA at various $X_{Cu/Cu+Ca}$

Assignments	Observed vibration frequencies (cm^{-1})							
	$X_{Cu/Cu+Ca}$	0	0.01	0.02	0.03	0.04	0.05	0.08
PO ₄ bend (ν_4)		600	600	600	600	600	600	600
Structural OH		631	629	630	628	630	626	626
PO ₄ bend (ν_1)		962	963	963	963	963	963	963
PO ₄ bend (ν_3)		1024	1026	1022	1026	1022	1024	1026
PO ₄ bend (ν_4)		1084	1084	1084	1086	1086	–	–
Structural OH		3568	3570	3568	3566	3566	3568	3565

Table S2: Stability constants for Cu^{2+} - CO_3^{2-} complexation and hydrolysis of AsO_4^{3-} and CO_3^{2-}

No.	Reaction	logK	Ref.
1	$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CuCO}_3^0 (\text{aq})$	6.77	(1)
2	$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-}$	10.2	(1)
3	$\text{Cu}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CuHCO}_3^+$	12.13	(1)
4	$\text{AsO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{HAsO}_4^{2-}$	11.29	(2)
5	$\text{AsO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{AsO}_4^-$	18.05	(2)
6	$\text{AsO}_4^{3-} + 3\text{H}^+ \rightleftharpoons \text{H}_3\text{AsO}_4^0$	20.31	(2)
7	$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$	10.33	(2)
8	$\text{CO}_3^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3^*$	16.68	(2)

References

- (1) Smith, R.; Martell, A.; Motekaitis, R. *NIST Critically Selected Stability Constants of Metal Complexes Database*; National Institute of Standards and Technology Standard Reference Data Program, 1998.
- (2) Perrin, D.D. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution, Second Edition*; Pergamon, Oxford, 1982.