

Copper Doping Improves Hydroxyapatite Sorption for Arsenate in Simulated Groundwaters

GUOJING LIU,^{*,†} JEFFREY W. TALLEY,^{*,‡} CHONGZHENG NA,[†] STEVE L. LARSON,[§] AND LAWRENCE G. WOLFE[†]

Department of Civil Engineering and Geological Sciences, Notre Dame, Indiana 46556; Department of Environmental and Civil Engineering, Dallas, Texas 75205; and U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi 39180

Received May 29, 2009. Revised manuscript received December 1, 2009. Accepted December 14, 2009.

Hydroxyapatite (HAP) has been widely used to immobilize many cationic heavy metals in water and soils. Compared with its strong sorption for metal cations, the abilities of HAP to sorb metal anions, such as arsenic, are less significant. Improving HAP sorption for anionic arsenic species is important for expanding its application potential because the presence of arsenic in the environment has raised serious health concerns and there is need for cost-effective remediation methods. In this work, we report an innovative method of copper doping to improve a synthetic HAP sorption for arsenate, which is a primary aqueous arsenic species, in simulated groundwaters. The undoped HAP and copper doped HAP (CuHAP) were characterized with XRD, FTIR, N₂ adsorption, and SEM, and then evaluated as sorbents for arsenate removal tests. The experimental results suggest that copper doping changed the morphology and increased the surface area of HAP. The CuHAP sorbed 1.6–9.1× more arsenate than the undoped HAP did in a simulated groundwater at pH of 7.7–8.0. The improved arsenate sorption is presumably due to the increase in surface area of HAP as a result of copper doping. In addition to the copper doping level, the arsenate sorption to HAP and CuHAP can also be increased with increasing water pH and calcium concentration. The experimental data indicate that sorbent dissolution is an important factor governing arsenate sorption to HAP and CuHAP.

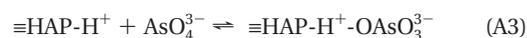
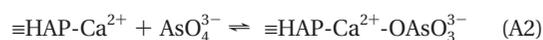
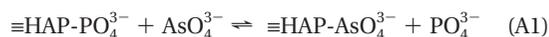
Introduction

Hydroxyapatite [HAP, Ca₁₀(PO₄)₆(OH)₂], which is the principle component of biological hard tissues and phosphate mineral rocks, has been long recognized as an excellent sorbent for many divalent metal cations (1–5). Because HAP is inexpensive, effective for a variety of metals, and readily available in the natural environment (1–5), it has been widely used to immobilize a wide range of heavy metals in water and soils, including lead, cadmium, zinc, uranium, copper, and nickel (6–9). The stabilization mechanisms of these heavy metals on HAP include ion-exchange, surface complexation,

coprecipitation, and dissolution–precipitation, with dissolution–precipitation dominating in the immobilization of lead and uranium (3, 4, 9–15). Compared with its strong sorption for metal cations, the ability of HAP to sorb metal anions, such as arsenic, is less significant (5, 16). Improving HAP sorption for anionic arsenic species is important for expanding its application potential because the presence of arsenic in the environment has raised serious health concerns and there is need for cost-effective remediation methods (17–19).

Arsenic pollution in groundwater, for example, is an issue of concern in many countries throughout the world. Studies have shown that there are over 100 million people in the world who are consuming groundwater with arsenic concentration up to 10× higher than the World Health Organization regulated safe level (17). Traditional technologies for arsenic remediation in groundwater include pump-and-treat methods and *in situ* treating the contaminated water with reactive materials such as zerovalent iron (ZVI) (6, 19–23). The *in situ* method is preferred because of its low costs for operation and maintenance (6, 20). As a matter of fact, the remediation expense is a major factor confining the application of a technology in addition to the effectiveness because many arsenic-associated calamities occur in underdeveloped countries (17–19). Compared with ZVI and many other arsenic-sorption media (e.g., granular activated carbon (GAC), activated alumina, and other iron compounds), HAP is less expensive and has been utilized in practice for *in situ* immobilization of many other heavy metals in groundwater (6, 8, 9). Therefore, HAP can be an economically and practically benign candidate for *in situ* remediation of arsenic in groundwater, provided that its sorption efficiency for arsenic is satisfactory.

Arsenic exists in water primarily as trivalent arsenite and pentavalent arsenate, with arsenate prevailing in many groundwater systems (18). The mechanisms responsible for the limited arsenate sorption to HAP include ion-exchange (Reaction A1) and adsorption (Reactions A2 and A3) (24, 25). Hence, the arsenate sorption to HAP could be improved by (i) replacing phosphate by another functional group that can be more easily substituted by arsenate, or (ii) replacing calcium with another cationic element that has a stronger affinity for arsenate. The element substitution in HAP lattices can be achieved through a doping technique, which is a technique of adding impurities to nanostructures, to modify their physical–chemical properties (24, 26–28). A previous study shows that doping silicate on a biogenic HAP surface increased the ion-exchangeability of the HAP for arsenate, thus resulting in a significant increase in arsenate removal from geothermal water (24). However, few studies have been performed on how the substitution of calcium by another metal cation affects HAP sorption for arsenic in groundwater.



In this work, we report to improve the sorption efficiency of a synthetic HAP for arsenate in simulated groundwaters by copper doping. We hypothesize that copper doping can improve HAP sorption for arsenate because copper has a stronger affinity for arsenate than calcium (29). The sorptions of arsenate to the undoped HAP and copper-doped HAP

* Corresponding author e-mail: liuguojing@gmail.com; jtalley@lyle.smu.edu.

† University of Notre Dame.

‡ Southern Methodist University.

§ U.S. Army Engineer Research and Development Center.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 01 DEC 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Copper Doping Improves Hydroxyapatite Sorption for Arsenate in Simulated Groundwaters				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center, Vicksburg, MS, 39180				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

TABLE 1. Chemical Compositions of the SGW and NBS Used in Batch Arsenate Sorption Experiments

chemical	SGW	NBS
pH	8.0	8.4
calcium	100 mg/L	0 mg/L
magnesium	19.2 mg/L	0 mg/L
sodium	46 mg/L	46 mg/L
carbonate	120 mg/L	120 mg/L
chloride	243 mg/L	177.5 mg/L

(CuHAP) in simulated groundwaters were tested. The effects of the copper doping level and water composition parameters, including pH and calcium concentration, on arsenate sorption were examined. The mechanisms behind these observed effects were discussed.

Materials and Methods

Chemicals. All chemicals used were analytical grade or better. Milli-Q water with a resistivity of 18 Ω -cm was used to prepare all solutions. Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 99%), sodium bicarbonate (NaHCO_3 , 99.5%), DL-lactic acid ($\text{CH}_3\text{CHOHCOOH}$, 90%), and copper oxide (CuO , 99%) were obtained from Sigma-Aldrich. Phosphoric acid (H_3PO_4 , 85%), calcium hydroxide (Ca(OH)_2 , 98%), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were from Fisher Scientific Inc.

Preparation of HAP and CuHAP. The HAP synthesis method was adopted from Roeder et al. (30) with a slight modification. Briefly, a solution that contains 0.1 M of lactic acid and 0.03 M of phosphoric acid was first made. A certain amount of Ca(OH)_2 powder was then added to the premade lactic-phosphoric acid solution to reach a Ca(OH)_2 concentration of 0.05 M. The mixture was constantly stirred at 4 $^\circ\text{C}$ for about 2 h until the added Ca(OH)_2 powder was completely dissolved. The resulting solution was purged with high purity N_2 for 10 min, and then transferred to a Teflon-lined reaction vessel (Parr Instrument Co.). The reactant was sealed and heated in an isotherm oven at 200 $^\circ\text{C}$ for 3 h, after which the vessel was removed from the oven and allowed to cool in air. After cooling, the HAP precipitates were collected on filter paper (Whatman, No.5) followed by washing with 500 mL of Milli-Q water. The precipitates were then oven-dried at 90 $^\circ\text{C}$ for 12 h.

The CuHAP was synthesized following a similar procedure to that for HAP, except that a small amount of CuO was first dissolved in the mixed solution of lactic acid and phosphoric acid before the addition of Ca(OH)_2 powder. The molar ratio of $\text{Cu}/\text{Cu}+\text{Ca}$ in the reactant (i.e., $X_{\text{Cu}/\text{Cu}+\text{Ca}}$) ranged from 0.01 to 0.08, and the total concentration of $\text{Cu}+\text{Ca}$ remained 0.05 M.

HAP and CuHAP Characterization. The synthesized HA and CuHA were characterized for crystal structures, functional groups, surface morphology, and surface area by a Scintag XGEN-4000 X-ray diffractometer (Scintag Inc., Cupertino, CA), an Illuminat Fourier transform infrared spectrometer (SensIR Technologies, Danbury, CT), a LEO EVO 50 electron microscope (Carl Zeiss SMT, Germany), and a Beckman Coulter SA3100 surface area analyzer (Fullerton, CA), respectively. The ζ potential of HA and CuHA in different water samples was determined using a BIC ZetaPlus ζ potential analyzer (BrookHaven Instruments Corporation, Holtsville, NY).

Arsenate Sorption Experiments. Arsenate sorption experiments were conducted in a simulated groundwater (SGW), or in a NaHCO_3 -buffered solution (NBS). The chemical compositions of the SGW and NBS are presented in Table 1. The SGW was used to study the effects of pH and initial arsenate concentration on arsenate retention by HA and CuHA, while

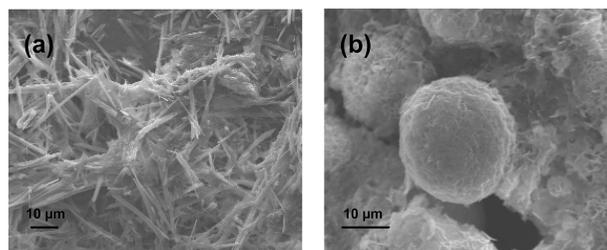


FIGURE 1. SEM image of synthesized HAP (a) and CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.08 (b). Pictures were taken at EHT (Electrical High Tension) voltage of 20 kV. Samples were sputter coated with gold.

the NBS was used to study the effect of calcium on arsenate sorption. To avoid arsenate transformation to arsenite, both SGW and NBS were filtered with a 0.2- μm Gelman FP-Verical membrane before aliquots of concentrated arsenate solution (13.3 mM) were spiked into the obtained filtrates (31). The pH of the arsenic-containing SGW or NBS was then adjusted to desired values using concentrated HCl and/or NaOH prior to arsenic spiking. The suspensions of HAP or CuHAP and the arsenic-containing waters were mixed in the dark for 24 h, within which the sorption of arsenate to HAP or CuHAP can reach steady state (32). At the end of the reaction, the pHs of the suspensions were measured and recorded, and the suspensions were filtered through 0.45- μm PTEF syringe filters (Fisher). The filtrates were analyzed for total arsenic, phosphorus, and copper concentration with a Perkin-Elmer optima 2000 DV inductively coupled plasma optical emission spectrometer (ICP-OES). The detection limits of the ICP-OES for arsenic, copper, and phosphorus were 25, 5, and 50 $\mu\text{g}/\text{L}$, respectively. The relative standard deviation for each triplicate measurement of the same sample was within 5% for arsenic and copper, and within 15% for phosphorus. All sorption experiments were performed in duplicates and the average is presented.

Results and Discussion

HAP and CuHAP Characterization. XRD and FTIR spectra of HAP and CuHAP at various $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ suggest that copper doping did not significantly affect the crystalline and surface structure of HAP (see Figures S1, S2, and Table S1, of the Supporting Information). These results are consistent with a previous report by Wakamura et al. (27). The copper doping, however, resulted in a change of morphology and specific surface area of HAP. Figure 1 displays the SEM images of HAP and CuHAP. Without doping, the HAP particles were needle-like whiskers, whereas after doping, the CuHAP particles were spherical clusters. The BET surface 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 were determined to be 6.63, 29.0, 52.0, 53.7, 63.3, 73.3, 77.5 m^2/g , respectively. The BET surface area correlates well with $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ with a linear correlation coefficient of 0.81. Since the ionic radius of divalent copper ion (Cu^{2+} ; 0.072 nm) is relatively smaller than that of calcium ion (Ca^{2+} ; 0.100 nm), the substitution of calcium with copper could form strains in the HAP lattice, causing an increased surface area. The change of morphology and specific surface area of HAP by copper doping implies that the sorption properties of HAP for arsenate could also be changed.

Arsenate Sorption to HAP and CuHAP.

Arsenate Sorption Isotherms. Figure 2(a) presents the sorption isotherms of arsenate to HAP and CuHAP in the SGW. The initial arsenate concentration ranged from 2.16 to 12.8 μM . The sorption data were fitted with a linear sorption equation (eq 1). The model fitted data are shown as solid lines in Figure 2(a), and the resulting solid-water distribution coefficients are presented in Table 2.

$$[\text{As}]_{\text{sorbed}} = K_d[\text{As}]_{\text{aq}} \quad (1)$$

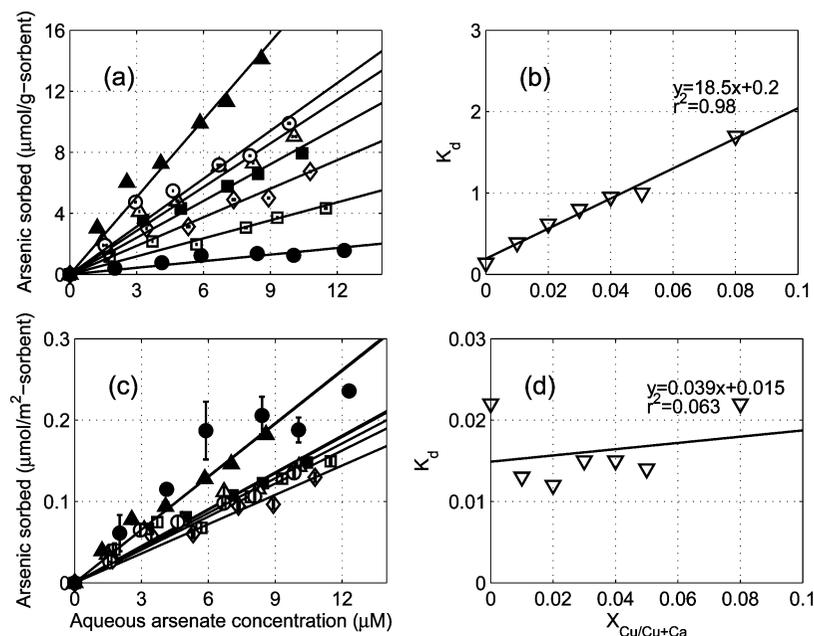


FIGURE 2. Sorption isotherms for arsenate to HAP (●) and CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.01 (□), 0.02 (◇), 0.03 (■), 0.04 (△), 0.05 (○), and 0.08 (▲) in the SGW (a). Correlation of $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ with solid-water distribution coefficients (K_d) obtained from the linear modeling of arsenate sorption isotherms (b). Normalized arsenate sorption isotherms with the BET surface area of HAP and CuHAP at various $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ (c); symbols are same with (a). Correlation of $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ and K_d values obtained from the linear modeling of the normalized arsenate sorption isotherms (d). Sorbent concentration, 0.3 g/L; mixing time, 24 h; pH, 7.7–8.0. Error bars represent the range of the data for duplicate samples.

TABLE 2. Linear Sorption Isotherm Parameters for Arsenate Sorption to HAP and CuHAP in the SGW before and after Normalized with the BET Surface Area of the Sorbent

sorbent	$X_{\text{Cu}:\text{Cu}+\text{Ca}}^a$	$X_{\text{Cu}:\text{Cu}+\text{Ca}}^{b,c}$	BET surface area (m ² /g)	$[\text{As}]_{\text{sorbed}} = K_d \cdot [\text{As}]_{\text{aq}}$		$([\text{As}]_{\text{sorbed}})/(\text{SA}_{\text{BET}}) = K_d \cdot [\text{As}]_{\text{aq}}$	
				K_d (L/g-sorbent)	r^2	K_d (L/g-sorbent)	r^2
HAP	0	0	6.63	0.14	0.84	0.022	0.84
CuHAP001	0.01	0.01	29.0	0.39	0.94	0.013	0.94
CuHAP002	0.02	0.03	52.0	0.62	0.96	0.012	0.96
CuHAP003	0.03	0.03	53.7	0.80	0.97	0.015	0.97
CuHAP004	0.04	0.06	63.3	0.95	0.95	0.015	0.95
CuHAP005	0.05	0.08	73.3	1.0	0.95	0.014	0.95
CuHAP008	0.08	0.08	77.5	1.7	0.97	0.022	0.97

^a Molar ratio of Cu:(Cu+Ca) in the reactant for synthesizing HAP or CuHAP. ^b Molar ratio of Cu:(Cu+Ca) in the synthesized HAP or CuHAP powder. ^c Data from one-time measurement.

where, $[\text{As}]_{\text{sorbed}}$ is the amount of arsenic sorbed to HAP or CuHAP, $\mu\text{mol/g-sorbent}$; $[\text{As}]_{\text{aq}}$ is the residual arsenate concentration in SGW at sorption steady state, μM ; and K_d is solid-water distribution coefficient, L/g-sorbent. For HAP, the amount of arsenic sorbed ranged from 0.4 to 1.6 $\mu\text{mol/g-sorbent}$. The uptake of arsenic by CuHAP was 1.6–9.1× higher than that observed for the undoped HAP. The amount of arsenic sorbed to CuHAP increased with increasing the copper doping level ($X_{\text{Cu}/\text{Cu}+\text{Ca}}$). For either HAP or CuHAP, the sorption data fitted the linear sorption equation well (Table 2). The solid-water distribution coefficients (K_d) for HAP and CuHAP correlated well with $X_{\text{Cu}/\text{Cu}+\text{Ca}}$, with a linear correlation coefficient of 0.98 [Figure 2 (b)]. The experimental results and model analyses suggest that copper doping improved the sorption ability of HAP for arsenate in the SGW. The observed improvement was hypothesized to be due to three reasons: (i) copper doping increased the surface area of HAP; (ii) copper doping increased the adsorption affinity or ion exchangeability of HAP for arsenate; and (iii) copper doping introduced the precipitation of Cu_3AsO_4 on HAP surface.

To elucidate how the surface area of HAP and CuHAP affected arsenate sorption, we normalized the sorption data

shown in Figure 2(a) with the BET surface area of each sorbent and re-established the sorption isotherms using the normalized data. The results are presented in Figure 2(c). The normalized arsenate sorption to the CuHAP appeared to be lower than to HAP when $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ ranged from 0.01 to 0.05. When $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ was 0.08, the amount of arsenic sorbed to unit area of CuHAP was similar to that of HAP. The normalized sorption data also fitted the linear sorption equation well (Table 2). Unlike the K_d values obtained from the unnormalized data, the normalized K_d values for HAP and CuHAP no longer correlated with $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ [Figure 2(d)], implying that the increase in surface area of HAP as a result of copper doping is a major reason causing the improved arsenate sorption. By increasing the surface area, copper doping could also facilitate HAP dissolution (Reaction A4), resulting in a decrease of sorbent mass and an elevated phosphate concentration in the SGW. The decrease of sorbent mass and increase of phosphate concentration in the SGW can subsequently suppress arsenate sorption through common ion effects and phosphate competition with arsenate for adsorption sites (Reactions A1–A3, A5, and A6). Therefore, the normalized sorption data can result in a lower K_d for CuHAP than for HAP (Table 2). An evidence for phosphate

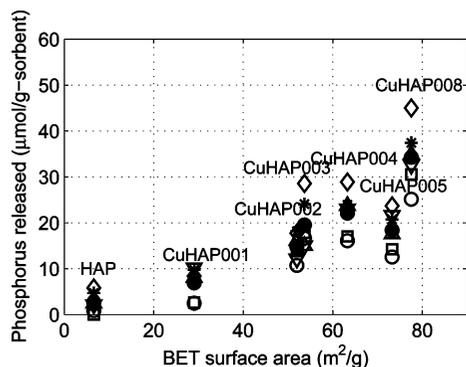
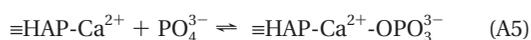
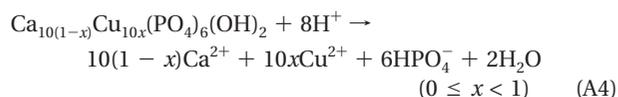


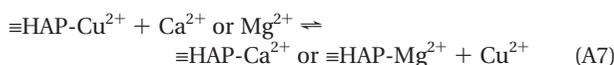
FIGURE 3. Relation between sorbent surface area and the amount of phosphorus released during arsenate sorption to HAP and CuHAP in the SGW; filled circles (●) represent the averaged phosphorus release for six samples with using same sorbent but different initial arsenate concentrations of 2.14 (○), 4.35 (□), 6.26 (*), 8.81 (▽), 10.4 (◇), 10.8 (△) μM . Sorbent concentration, 0.3 g/L; mixing time, 24 h; pH, 7.7–8.0.

release under the experimental conditions is the detection of elevated phosphorus concentration in water at the end of the sorption experiments. As shown in Figure 3, the amount of phosphorus released during arsenate sorption to HAP and CuHAP is positively correlated with the BET surface area of each sorbent. If the observed phosphorus release was completely from the 1:1 ion-exchange of phosphate by arsenate in the SGW (Reaction A1), then the phosphorus released from unit area of sorbent should be equal to that of arsenic sorbed. However, our experimental data show that the phosphorus released from unit area of sorbent were 1.2–9.8 times higher the arsenic sorbed (see Figure S3 of the Supporting Information), indicating that most of the phosphorus was released due to sorbent dissolution instead of the phosphate-arsenate exchange on HAP or CuHAP surface.



If copper doping did not increase the association affinity or ion-exchangeability of HAP for arsenate, then the normalized arsenate sorption to HAP and CuHAP should decrease when $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ increased, since increasing copper doping level can facilitate sorbent dissolution and subsequently inhibit arsenate sorption. However, our experimental data show that the CuHAP with $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.08 resulted in the same normalized K_d value as HAP did, although the former was more subjected to dissolution than the latter (Figure 3). From Reaction A4, CuHAP dissolution can introduce Cu^{2+} to water in addition to phosphate species. Cu^{2+} can also enter the aqueous phase from CuHAP surface through the ion-exchange by Ca^{2+} and Mg^{2+} ions in the SGW (Reaction A7). It is possible that the released Cu^{2+} reacted with unhydrolyzed arsenate (AsO_4^{3-}) in the SGW to form Cu_3AsO_4 precipitate thus increased the apparent arsenic sorption. To verify this, we examined the residual copper concentration in the SGW at the end of the sorption experiments. The results confirm that increasing the copper doping level can increase the residual copper concentration in the SGW after arsenate sorption (see Figure S4 of the Supporting Information). For all CuHAP tested, the maximum residual copper concentration in the SGW was 0.72 μM . Due to the complexation of Cu^{2+} with carbonate and the hydrolysis of AsO_4^{3-} (see Table

S2 of the Supporting Information), the ionic product of Cu^{2+} and AsO_4^{3-} in the SGW was estimated to be less than $10^{-39.2}$, which is about 5 orders lower than the solubility product of $\text{Cu}_3(\text{AsO}_4)_2$ ($K_{\text{sp}} = 10^{-35.1}$). Therefore, precipitation of $\text{Cu}_3(\text{AsO}_4)_2$ was unlikely to occur under the experimental conditions. The speciation calculation of copper in the SGW also indicate that no other copper precipitates, such as CuCO_3 or $\text{Cu}(\text{OH})_2$, had formed. As a result, the fact that CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.08 had the same normalized K_d as HAP under the condition that the former released 8–30 \times more phosphorus than the latter (Table 2, Figure 3), indicates that copper doping could improve the association affinity or ion-exchangeability of HAP for arsenate.



The examination of arsenate sorption isotherms suggests that copper doping increased the sorption ability of HAP for arsenate in the SGW, presumably due to the increase in surface area. The surface area normalized sorption data imply that sorbent dissolution inhibits arsenate uptake by HAP and CuHAP. Through common ion effects, water composition parameters such as pH and calcium concentration can affect arsenate adsorption (Reactions A2 and A3), as well as HAP or CuHAP dissolution (Reaction A4). Therefore, the sorption efficiency of HAP and CuHAP for arsenate can vary with water pH and calcium level. To test this, we examined the effects of pH and calcium concentration on arsenate removal by HAP and CuHAP sorption.

Effect of pH. The effect of pH on arsenate removal by HAP or CuHAP was examined in the SGW. Prior to adding the sorbent, we adjusted the initial pH of the SGW to 4.0–10.0. The water pH changed to 5.5–9.1 at the end of the sorption processes owing to the buffering effects of HAP (25, 33).

Figure 4(a) demonstrates the effect of pH on arsenate removal from the SGW. For either HAP or CuHAP, the arsenate removal increased dramatically with increasing pH and then leveled off when water pH approached 8.0. Over the pH range tested, the arsenate removal efficiency by HAP ranged from 0.68 to 9.36%, while it was from 5.75 to 42.0% by CuHAP. At all pH levels, the removal of arsenate by CuHAP was higher than by HAP, which is consistent with the observations shown in Figure 2(a). The uptake of arsenate by CuHAP increased with increasing $X_{\text{Cu}/\text{Cu}+\text{Ca}}$, and the effect of copper doping level was more significant at high pH than at low pH. The effects of pH on arsenate removal by HAP or CuHAP suggest that electrostatic attraction is not a major mechanism responsible for the arsenate sorption under our experimental conditions, otherwise the apparent arsenate sorption would decrease with increasing pH (Reaction A3). Instead, the observed effects should be due to sorbent dissolution. As discussed previously, sorbent dissolution can result in a decrease of sorbent mass and an increase of phosphate concentration in water, both of which can inhibit arsenate sorption. As suggested by Reaction A4, lowering pH can favor the dissolution HAP and CuHAP, and thus suppress arsenate sorption. Copper doping increased the surface area of HAP, which facilitated arsenate sorption as well as HAP dissolution (Figure 2(a) and Figure 3). When water pH decreased, the inhibition effects of sorbent dissolution on arsenate sorption became more and more significant. As a result, the improved arsenate sorption by copper doping was more compromised at low pH than at high pH. Therefore, the effect of the copper doping level on arsenate removal by HAP and CuHAP appeared less significant at low pH than at high pH.

The examination of pH effects on arsenate sorption to CuHAP reveals that the CuHAPs have appreciable arsenate

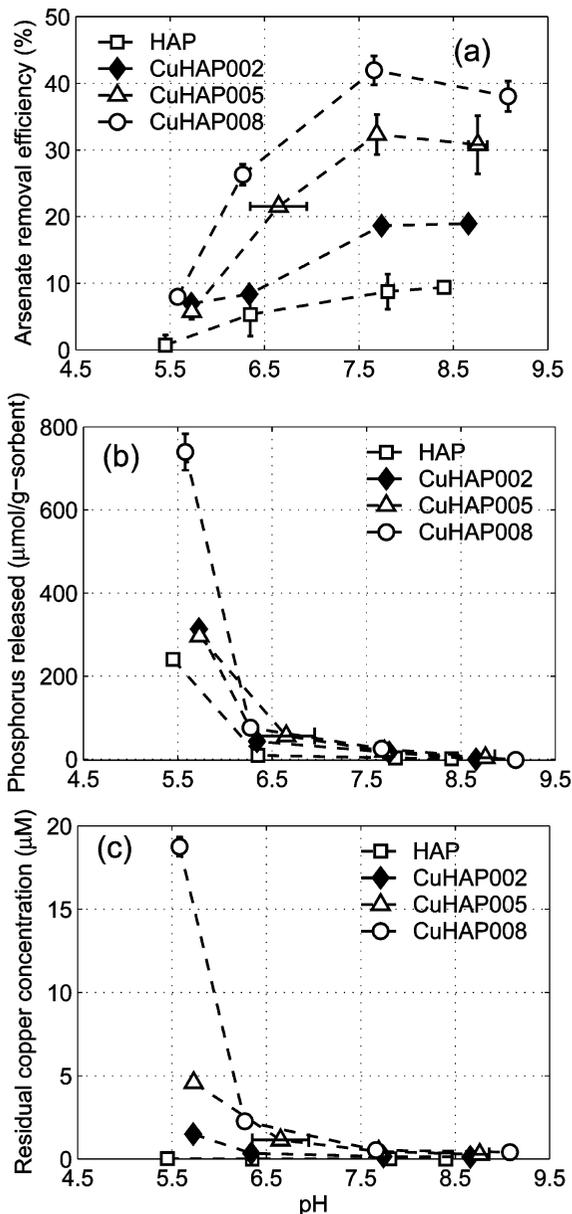


FIGURE 4. Effect of pH on arsenate removal (a), phosphorus released (b), and residual copper concentration (c) in the SGW during the sorption of arsenate to HAP or CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.02 (CuHA002), 0.05 (CuHA005), and 0.08 (CuHA008). Initial arsenate concentration, 4 μM ; sorbent concentration, 0.3 g/L; mixing time, 24 h. Error bars represent the range of the data for duplicate samples.

removal efficiencies under alkaline conditions. This is different from ZVI and other iron compounds, the most widely used arsenic sorbents, which have high efficiencies for arsenate removal only at low pH values (19). As a comparison, we tested the arsenate removals from the SGW with an initial water pH of 9.0 by using the CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.08 and an iron-coated sand (34). The results show that the arsenate removal efficiency for the CuHAP was 2.7 \times higher than that for the iron-coated sand (56.7% versus 20.7%) under the same experimental condition, implying that CuHAP can be advantageous over iron-based sorbents for arsenate removal in alkaline waters.

As shown in Figure 4(b), up to 727 $\mu\text{mol/g-sorbent}$ of phosphorus was released from from HAP or CuHAP during arsenate sorption. For each sorbent, the phosphorus release decreased with increasing water pH, but increased with increasing the copper doping level. Unlike the arsenate

removal efficiency, the effect of copper doping on phosphorus release was less significantly at high pH than at low pH. If the phosphorus was released from the ion-exchange of arsenate for phosphate on HAP or CuHAP surface, then the trend for phosphorus release with pH would follow that for arsenate removal efficiency. This is opposite from our observation. Therefore, the phosphorus detected was most likely released from sorbent dissolution.

In accordance with the trend for phosphorus release with pH, the residual copper concentration in the SGW was also found to decrease with increasing water pH and increase with increasing the copper doping level [Figure 4(c)]. When the initial water pH ranged from 6.0 to 10.0, the residual copper concentration was within the range of 0.31–2.3 μM (equivalent to 0.02–0.15 mg/L), which was 1–2 orders lower than the U.S. Environmental Protection Agency (USEPA) regulated maximum contamination level (MCL) for copper in drinking water. When the initial pH of the SGW was 4.0, the maximum residual copper concentration was 18.75 μM (equivalent to 1.2 mg/L), still lower than the regulated MCL of 1.3 mg/L (35). In addition to CuHAP dissolution, copper could also be released from CuHAP through the ion-exchange of Cu^{2+} by Ca^{2+} or Mg^{2+} in the SGW. However, based on a speciation calculation of calcium and magnesium in the SGW, the amounts of Ca^{2+} and Mg^{2+} ions did not change over the pH range tested. Therefore, the observed pH effects on residual copper concentration in the SGW should mainly reflect the variation of CuHAP dissolution with pH. The observed copper doping effects on phosphorus release and residual copper concentration shown in Figures 4(b) and (c) suggest that CuHAP was more soluble than HAP, especially in the acidic SGW.

The fact that lowering pH favors HAP dissolution was also noticed by Valsami-Jones et al. and Sneddon et al. (25, 33). Our experimental data further imply that pH is also an important factor controlling the solubility of CuHAP. Though sorbent dissolution inhibits arsenate sorption to HAP, it can promote the retentions of lead and uranium, which rely on HAP dissolution and reprecipitation of additional phosphate mineral phases (3, 4, 9, 11, 15). As indicated by Figures 3 and 4(b),(c), CuHAP is more soluble than HAP. Therefore, the copper doping technique can be used to improve HAP sorption efficiencies for cationic heavy metals in addition to that for arsenic.

Effect of Calcium Concentration. Figure 5(a) presents the effect of calcium concentration on arsenate removal by HAP and CuHAP in the NBS. For all sorbents tested, increasing calcium level appeared to assist arsenate sorption. The effect of calcium concentration on arsenate sorption to CuHAP is more significant than to HAP. For example, when calcium concentration increased from 0 to 2.5 mM, the arsenate removal efficiency increased from 2.4% to 5.4% by using HAP, whereas it increased from 15.3% to 45.3% when CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ was used. The calcium effects on arsenate sorption to HAP and CuHAP are thought to be due to two reasons. First, according to Reaction A4, increasing calcium concentration in water can inhibit HAP and CuHAP dissolution, which can inhibit arsenate sorption to the sorbents. The common ion effect of calcium on HAP or CuHAP dissolution was verified by the observations for the phosphorus release, which appeared to decrease with the increase of calcium concentration in the NBS [Figure 5(b)]. The suppression of HAP dissolution by large amount of calcium in solution was also reported in literature (25, 36). Second, Ca^{2+} in water can complex with phosphate on HAP surface, resulting in an increase of sorption sites and subsequently an increase of arsenate sorption (Reaction A8). The measurement of the ζ potential of HAP and CuHAP suggests that the

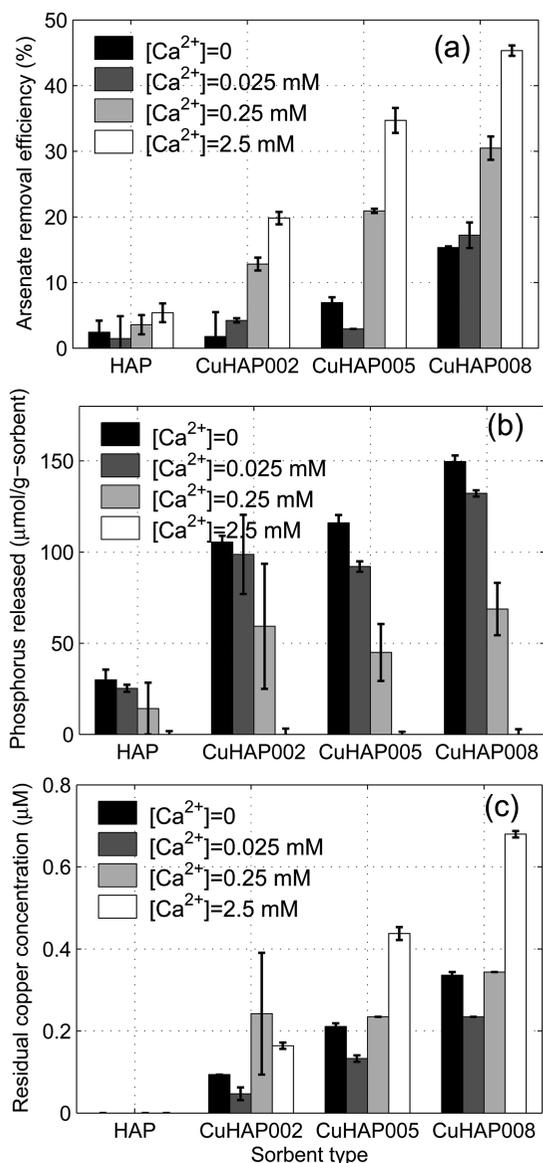
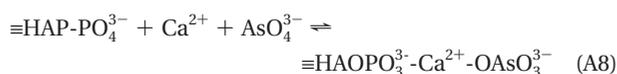


FIGURE 5. Effect of calcium concentration on arsenate removal (a), total phosphorus released (b), and residual copper concentration (c) in the NBS during the sorption of arsenate by HAP and CuHAP at $X_{\text{Cu}/\text{Cu}+\text{Ca}}$ of 0.02 (CuHAP002), 0.05 (CuHAP005), and 0.08 (CuHAP008). Initial arsenate concentration, 4 μM ; sorbent concentration, 0.3 g/L; mixing time, 24 h; pH, 8.2–8.4. Error bars represent the range of the data for duplicate samples.

sorbents were negatively charged in the calcium-free NBS. The surface charge of the sorbents became less negative as calcium concentration increased (see Figure S5 of the Supporting Information), which implies that Ca^{2+} formed complex with the HAP or CuHAP surface (37).



Different from the phosphorus release, the residual copper concentration in the NBS decreased first and then increased with increasing calcium concentration [Figure 5(c)]. It is because in addition to CuHAP dissolution, the residual copper concentration in water is also governed by the Ca^{2+} – Cu^{2+} ion exchange the CuHAP surfaces, which is favored at high calcium level (Reaction A7). The experimental data shown in Figure 5(c) thus reflect a combined results of sorbent dissolution and ion-exchange of Cu^{2+} by Ca^{2+} in solution.

The examination of calcium effects on arsenate removal by HAP and CuHAP further proves that sorbent dissolution was a major mechanism controlling arsenate sorption under the experimental conditions.

Implications. Arsenic pollution in groundwater has raised health concerns throughout the world. Remediating arsenic contaminated groundwater requires the employment of low-cost approaches (19). *In situ* treatment of groundwater with HAP can offer an economically and practically benign method for arsenic remediation, provided that the sorption efficiency of HAP for arsenic is satisfactory. By using an innovative copper doping method, we improved a synthetic HAP sorption for arsenate, which is a primary arsenic species in groundwaters, in simulated groundwater by up to $9.1 \times$. Such an improvement is attributed to the increase in surface area of HAP as a result of copper doping. Our experimental data also reveal that the CuHAP can result in appreciable arsenate removals within a pH range of 6.0–9.0 and a calcium concentration range of 0–2.5 mM, which is representative for average groundwater conditions. As a result, the CuHAP can be advantageous for arsenate sorption under alkaline conditions over the iron-based sorbents, which are the most commonly used arsenic-sorption media and have high sorption efficiencies only in acidic waters (19). The CuHAP has a larger surface area and appeared to be more soluble than HAP, especially when water pH was low. It indicates that the copper doping technique also has the potential to promote the sorptions of heavy metals including cadmium, zinc, lead, and uranium, whose removals are dependent on the surface area and solubility of HAP (3, 4, 9, 11, 14, 15).

Acknowledgments

We thank the Center of Environmental Science and Technology (CEST), the Environmental Molecular Scientific Institute (EMSI), and the Environmental Mineralogy and Crystal Structures Lab at the University of Notre Dame for providing the necessary instrumentation for this study. C.N. thanks the generous support by the University of Notre Dame Faculty Scholarship Award Program.

Supporting Information Available

XRD patterns (Figure S1), FTIR spectra (Figure S2), and the infrared band assignments (Table S1) of 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); effect of calcium on zeta potential of HAP and CuHAP (Figure S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Suzuki, T.; Hatsushika, T.; Hayakawa, Y. Synthetic hydroxyapatites employed as inorganic cation-exchangers. *J. Chem. Soc. Faraday Tras.* **1981**, *77*, 1059–1062.
- (2) Suzuki, T.; Hatsushika, T.; Hayakawa, Y. Synthetic hydroxyapatites employed as inorganic cation-exchangers, Part 2. *J. Chem. Soc. Faraday Tras.* **1982**, *78*, 3605–3611.
- (3) Ma, Q.; Logan, T.; Traina, S. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environ. Sci. Technol.* **1995**, *29*, 1118–1126.
- (4) Chen, X.; Wright, J.; Conca, J.; Feurrung, L. Evaluation of heavy metal remediation using mineral apatite. *Water Air Soil Pollut.* **1997**, *98*, 57–78.
- (5) Seaman, J. C.; Arey, J. S.; Bertsch, P. M. Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *J. Environ. Qual.* **2001**, *30*, 460–469.

- (6) Naftz, D. L., Morrison, S. J., Davis, J. A., Fuller, C. C., Eds. *Handbook of Groundwater Remediation Using Permeable Reactive Barrier: Applications to Radionuclides, Trace metals, and Nutrients*; Academic Press: San Diego, CA, 2002.
- (7) Larson, S.; Tardy, B.; Beverly, M.; Hearn, A.; Thompson, M.; Williams, G. *Topical Application of Phosphate Amendments to Lead-Contaminated Small Arms Firing Range Soils*; U.S. Army Engineer Research and Development Center; U.S. Army Corps of Engineers: Vicksburg, MS, 2004.
- (8) Conca, J. L.; Wright, J. An Apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb, and Cd. *Appl. Geochem.* **2006**, *21*, 1288–1300.
- (9) Simon, F. G.; Biermann, V.; Peplinski, B. Uranium removal from groundwater using hydroxyapatite. *Appl. Geochem.* **2008**, *23*, 2137–2145.
- (10) Xu, Y.; Schwartz, F.; Tralna, S. Sorption of Zn²⁺ and Cd²⁺ on hydroxyapatite surfaces. *Environ. Sci. Technol.* **1994**, *28*, 1427–1480.
- (11) Chen, X.; Wright, J.; Conca, J.; Peurrung, L. Effect of pH on heavy metal sorption on mineral apatite. *Environ. Sci. Technol.* **1997**, *31*, 624–631.
- (12) Mandjiny, S.; Matis, K.; Zouboulis, A. Calcium hydroxyapatites: evaluation of sorption properties for cadmium ions in aqueous solution. *J. Mater. Sci.* **1998**, *33*, 5433–5439.
- (13) Lusvardi, G.; Malavasi, G.; Menabue, L.; Saladini, M. Removal of cadmium ions by means of synthetic hydroxyapatite. *Waste Manage.* **2002**, *22*, 853–857.
- (14) Peld, M.; Tonsuaadu, K.; Bender, W. Sorption and desorption of Cd²⁺ and Zn²⁺ ions in apatite-aqueous systems. *Environ. Sci. Technol.* **2004**, *38*, 5626–5631.
- (15) Krestou, A.; Xenidis, A.; Panias, D. Mechanism of aqueous uranium(VI) uptake by hydroxyapatite. *Miner. Eng.* **2004**, *17*, 373–381.
- (16) Boisson, J.; Ruttens, A.; Mench, M.; Vangronsveld, J. Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils. Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation. *Environ. Pollut.* **1999**, *104*, 225–233.
- (17) Kinniburgh, D. G., Smedley, P. L., Eds. *Arsenic Contamination of Groundwater in Bangladesh, Vol. 2: Final Report*; BGS Technical Report WC/00/19; British Geological Survey: Keyworth, UK, 2001.
- (18) Mandal, B.; Suzuki, K. Arsenic round the world: a review. *Talanta* **2002**, *58*, 201–235.
- (19) Mohan, D.; Pittman, C. Arsenic removal from water/wastewater using adsorbents--a critical review. *J. Hazard. Mater.* **2007**, *142*, 1–53.
- (20) U.S. Environmental Protection Agency, *Permeable Reactive Barrier Technologies for Contaminant Remediation*; EPA: Washington, DC, 1998.
- (21) Su, C.; Puls, R. Arsenate and arsenite removal by zero valence iron: kinetics, redox transformation, and implications for *in situ* groundwater remediation. *Environ. Sci. Technol.* **2001**, *35*, 1487–1492.
- (22) Nikolaidis, N. P.; Dobbs, G. M.; Lackovic, J. A. Arsenic removal by zero-valent iron: field, laboratory and modeling studies. *Wat. Res.* **2003**, *37*, 1417–1425.
- (23) Lien, H.-L.; Wilkin, R. T. High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **2005**, *59*, 377–386.
- (24) Nakahira, A.; Okajima, T.; Honma, T.; Yoshioka, S.; Tanaka, I. Arsenic removal by hydroxyapatite-based ceramics. *Chem. Lett.* **2006**, *35*, 856–857.
- (25) Sneddon, I.; Garelick, H.; Valsami-Jones, E. An investigation into arsenic(V) removal from aqueous solutions by hydroxyapatite and bone-char. *Mineral. Mag.* **2005**, *69*, 769–780.
- (26) Misono, M.; Hall, W. Oxidation–reduction properties of copper- and nickel- substituted hydroxyapatites. *J. Phys. Chem.* **1973**, *77*, 791–800.
- (27) Wakamura, M.; Kandori, K.; Ishikawa, T. Surface composition of calcium hydroxyapatite modified with metal ions. *Colloids Surf, A* **1998**, *142*, 107–116.
- (28) Qi, J.; Chen, W.; Wang, H.; Li, L.; Chan, H. Low temperature sintering behavior of B₂O₃ vapor in BaTiO₃-based PTCR thermistors. *Sens. Actuators* **2004**, *116*, 215–218.
- (29) Robins, R. The aqueous chemistry of arsenic in relation to hydrometallurgical processes. *Proceedings, Impurity Control and Disposal. CIM Annual Meeting*, Vancouver, Canada, pp1/1–1/26, 1985.
- (30) Roeder, R.; Converse, G.; Leng, H.; Yue, W. Kinetic effects on hydroxyapatite whisker synthesized by the chelate decomposition method. *J. Am. Ceram. Soc.* **2006**, *89*, 2096–2104.
- (31) Liu, G.; Zhang, X.; Jain, J.; Talley, J.; Neal, C. Stability of inorganic arsenic species in simulated raw waters with the presence of NOM. *Wat. Sci. Technol.: Wat. Supply* **2006**, *6*, 175–182.
- (32) Liu, G.; Larson, S.; Talley, J. Iron or copper doped hydroxyapatite shows improved As(V) removal from water. *Abstracts of Papers of the American Chemical Society, 236th National Meeting*; American Chemical Society: Philadelphia, PA, 2008.
- (33) Valsami-Jones, E.; Ragnarsdottir, K.; Putnis, A.; Bosbach, D.; Kemp, A.; Gressey, G. The dissolution of apatite in the presence of aqueous metal cations at pH 2–7. *Chem. Geol.* **1998**, *151*, 215–233.
- (34) Ams, D.; Fein, J.; Dong, H.; Maurice, P. Experimental measurement of the adsorption of *Bacillus subtilis* and *Pseudomonas mendocina* onto Fe-oxyhydroxide-coated and uncoated quartz grains. *Geomicrobiol. J.* **2004**, *21*, 511–519.
- (35) U.S. Environmental Protection Agency, *National Primary Drinking Water Regulations*; EPA: Washington, DC, 2002.
- (36) Czerniczyniec, M.; Farias, S.; Magallanes, J.; Cicerone, D. Arsenic(V) adsorption onto biogenic hydroxyapatite: solution composition effects. *Water Air Soil Pollut.* **2007**, *180*, 75–82.
- (37) Doss, S. Surface properties of hydroxyapatite: 1. the effect of various inorganic ions on the electrophoretic behavior. *J. Dent. Res.* **1976**, *55*, 1067–1075.

ES9015734