

## KINETICS, CATALYSIS, AND REACTION ENGINEERING

**Kinetics of Bacterial As(III) Oxidation and Subsequent As(V) Removal by Sorption onto Biogenic Manganese Oxides during Groundwater Treatment****Ioannis A. Katsoyiannis,<sup>†</sup> Anastasios I. Zouboulis,<sup>\*,†</sup> and Martin Jekel<sup>‡</sup>**

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In groundwaters, indigenous iron- and manganese-oxidizing bacteria are able to catalyze the oxidation of dissolved manganese [Mn(II)], which can subsequently be removed by filtration of the insoluble products (hydrous manganese oxides). This process results in the creation of a natural coating on the surface of the filter medium, and if arsenic is simultaneously present in the groundwater, it can subsequently be removed by sorption. The results indicate that this method can serve as an alternative treatment option for the removal of low-level arsenic concentrations [35 and 42  $\mu\text{g/L}$  for As(III) and As(V), respectively]. Rapid oxidation of As(III) was observed prior to removal by sorption onto the biogenic manganese oxide surfaces. The rates of As(III) oxidation were estimated, yielding an apparent first-order constant of  $0.23 \text{ min}^{-1}$  (half-life of 3 min). A comparison of these values with the respective data obtained from the literature indicated that the rate of oxidation of As(III) was significantly higher than the rates reported for abiotic As(III) oxidation by manganese oxides, supporting the indication that bacteria play an important role in both the oxidation of As(III) and the generation of reactive manganese oxide surfaces for the removal of As(III) and As(V) from solution. The following sequence of reactions have been found to occur in the treatment system: (a) oxidation of Mn(II) to Mn(IV) and Fe(II) to Fe(III), (b) oxidation of As(III) to As(V), (c) precipitation of manganese(IV) oxides, (d) abiotic oxidation of As(III) by manganese(IV) oxides, and (e) As(V) sorption by manganese(IV) oxides, where steps a and b are biotic and steps c–e are abiotic. The presence of phosphates at concentrations of around 600  $\mu\text{g/L}$  had an adverse effect on As(III) removal (competitive adsorption), reducing the overall removal efficiency by 50% (from 80 to 30%), although it did not affect the oxidation of As(III).

**Introduction**

Arsenic is a ubiquitous element in earth's crust, and its presence in groundwaters<sup>1</sup> has received increased concern, because of its high toxicity to humans, causing both acute and chronic adverse health effects, including cancer.<sup>2,3</sup> The predominant forms of arsenic in water sources are the inorganic arsenate [As(V)] and arsenite [As(III)] species,<sup>4</sup> with the latter being more toxic.

Under oxidizing conditions, the most probable form of arsenic is As(V), which exists mainly as the oxyanions of arsenic acid ( $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ). On the contrary, under reducing conditions (i.e., anaerobic groundwaters), As(III) species are also present and exist as the undissociated molecule of arsenious acid ( $\text{H}_3\text{AsO}_3$ ), at the pH values usually encountered in most natural water sources.<sup>4,5</sup> The maximum contaminant level (MCL) of arsenic in drinking water was revised in March 1998 by the European Commission. According

to directive 98/83/EEC, all drinking water supply systems within the European Union were required to comply by Dec 25, 2003, with the new limit, which was reduced from 50 to 10  $\mu\text{g/L}$ .<sup>6</sup> Recently, the U.S. EPA decided to move forward in implementing the same standard for arsenic in drinking water.<sup>7</sup>

The removal of arsenic from water sources is generally accomplished by the application of conventional treatment methods such as coagulation, adsorption on activated alumina or granular ferric hydroxide, adsorptive filtration, membrane processes, and ion exchange.<sup>8–12</sup> Most of these technologies are not sufficiently efficient in the removal of As(III), so a preliminary oxidation step is usually applied to achieve finished waters with total arsenic concentrations below 10  $\mu\text{g/L}$ .

The oxidation of As(III) is usually carried out by the addition of chemical reagents such as ozone, hydrogen peroxide, chlorine, or potassium permanganate.<sup>8,13,14</sup> However, the use of chemical reagents in drinking water treatment is not recommended and should be avoided, because it often leads to undesirable byproducts such as trihalomethanes (THMs).<sup>15</sup>

As an alternative to chemical oxidation, bacterially catalyzed As(III) oxidation can be applied. Several

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**Table 1. Physicochemical Characteristics of the Groundwater from the Wells of the Research Institute of the Federal Environmental Agency, (Marienfelde), Berlin, Germany<sup>a</sup>**

property	value
conductivity	1125 $\mu\text{S}/\text{cm}$
pH	7.2
total hardness	5.6 $\text{mol}/\text{m}^3 \text{CaCO}_3$
[Fe]	2.8 $\text{mg}/\text{L}$
[Mn]	0.6 $\text{mg}/\text{L}$
[As]	<1 $\mu\text{g}/\text{L}$
ORP	-150 mV

<sup>a</sup> Iron was removed prior to the experiments.

species of bacteria have been found to mediate this process,<sup>4,16–18</sup> although, to date, only a few studies applying the biological arsenic oxidation directly in continuous groundwater treatment have been reported.<sup>19–21</sup>

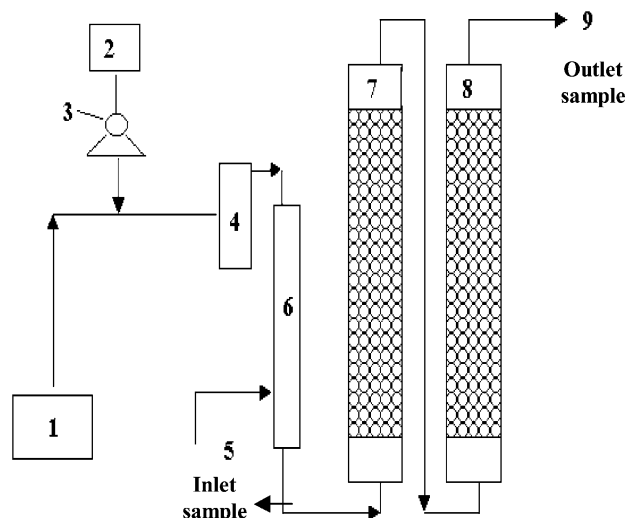
According to the latter publications, As(III) can be oxidized to As(V) by dissolved oxygen, and this reaction was found to be mediated by specific bacteria that are indigenous in groundwater sources, the so-called “iron- and manganese-oxidizing bacteria”. Iron and manganese exert a strong influence on arsenic concentrations in groundwaters. The application of biological iron or manganese oxidation results in the formation of insoluble products (iron or manganese oxides), which are subsequently removed from water by filtration.<sup>22</sup> If arsenic is simultaneously present, it can be removed by sorption onto the produced oxides, which progressively creates a natural (biogenic) coating of the filter medium. Therefore, the application of this method for the removal of arsenic has been termed “biological adsorptive filtration”.<sup>20</sup>

In the present article, the kinetics of bacterial As(III) oxidation and the subsequent removal of arsenic by sorption on biogenic manganese oxides have been investigated. The research on the removal of arsenic by chemical oxidation and sorption onto manganese oxides is well-documented;<sup>23–31</sup> however, most of these papers have not addressed the combination of bacterial As(III) oxidation with subsequent As(V) sorption onto biogenic hydrous manganese oxides.

## Experimental Section

**Materials.** The experiments were performed using groundwater from the wells of the Federal Environmental Agency in Berlin (Research Site Marienfelde), Germany. The characteristics of the groundwater are reported in Table 1. To examine the removal of arsenic by sorption onto manganese oxides and to avoid interference from iron, the groundwater was first treated for biological iron removal in a full-scale biological treatment plant, and the experimental apparatus was subsequently fed with the partially treated groundwater. During this treatment stage, the initial concentration of manganese was reduced by around 20%; therefore, the manganese concentration of the water entering the plant was about 0.4–0.5  $\text{mg}/\text{L}$ , whereas the concentration of iron was below 0.1  $\text{mg}/\text{L}$ .

Arsenic(III or V) was added to the influent after iron removal, to investigate its removal on manganese oxides. As(III) stock solutions were prepared by dissolving arsenic oxide ( $\text{As}_2\text{O}_3$ , AnalaR) in deionized water, using 10  $\text{mL}/\text{L}$  of HCl acid (37% proanalysis, Merck), and then heating the solution to accelerate dissolution; this procedure was performed in a hood. As(V) stock solu-



**Figure 1.** Schematic representation of the experimental setup for arsenic removal during biological oxidation of dissolved manganese from groundwaters. (1) Continuous flow of groundwater, (2) arsenic stock solution, (3) peristaltic (feeding) pump, (4) influent mixing vessel, (5) air injection, (6) aeration column, (7, 8) filtration columns, (9) effluent. Column characteristics: active height, 1 m; inner diameter, 68 mm; surface area, 0.0036  $\text{m}^2$ ; bed volume, 3.6 L; total bed porosity, 0.37.

tions were prepared by dissolving  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Merck) in deionized water.

**Methods.** The treatment process was based on a fixed-bed upflow filtration unit, as shown in the schematic representation of Figure 1 and has been described in detail elsewhere.<sup>21</sup> The apparatus consisted of two (PVC) columns, which were filled with appropriate filtration media (polystyrene beads of mean diameter 3 mm). The continuous oxidation of manganese (and residual iron) resulted in the formation of a natural coating on the filter media, where the iron- and manganese-oxidizing bacteria were entrapped, accelerating the oxidation procedures.<sup>22,32</sup> The bacteria responsible for the reactions occurring in the treatment system were identified during previous studies.<sup>20</sup> The observed species were the *Gallionella ferruginea* and *Leptothrix ochracea*.

In the present treatment system, *Leptothrix ochracea* is the main microorganism, responsible for the bacterial oxidation of manganese. However, several other species of bacteria have been reported to oxidize manganese, belonging mainly to the *Leptothrix* or *Sphaerotilus* groups.<sup>22,32</sup> These bacteria, which are indigenous in most groundwaters, require relatively stringent conditions to oxidize the soluble forms of manganese. In particular, they demand an aerobic environment [i.e., dissolved oxygen (DO) > 3  $\text{mg}/\text{L}$ ] and redox (Eh) values between 300 and 400 mV. Occasionally, to accelerate the initiation of the manganese oxidation procedure, the filter medium (i.e., sand or polystyrene beads) can be coated with synthetic  $\text{MnO}_2$ .<sup>22</sup>

The groundwater inflow was continuous. The groundwater stream was spiked with arsenic stock solution (10–30  $\text{mg}/\text{L}$ ) after iron removal was accomplished. The aeration was performed in a separate column prior to filtration, to control the dissolved oxygen concentration and to avoid the collision of bubbles with the deposited sludge, which could cause a disturbance of the system and increased iron and manganese concentrations in the effluent. The collection of the inlet sample was performed after the aeration and before the (sorp-

filtration stage. No removal of arsenic prior to the inlet sampling was detected. The outlet samples were collected after the filtration stage and corresponded to the fully treated water. All of the collected samples were analyzed for total arsenic [As(III) + V], As(III), iron, and manganese concentrations.

The treatment columns were subjected to backwashing, to remove the excessive biomass and manganese oxide solids from the filters. Following this action, there was an adaptation period, during which the oxidation, precipitation, and removal of manganese were not efficient enough to enable the removal of arsenic. When the removal of manganese was reestablished (usually after the treatment of 50–100 L of water), the beds were considered to have reached the so-called “ripe stage”. Subsequently, the experiments with As(III) or As(V) were restarted. Triplicate samples were collected and analyzed, and the average values are presented in the figures. The repeatability of the experimental results was sufficient, as it corresponded to less than 5% variability. The volume of water treated was calculated using the appropriate volumetric flow rate.

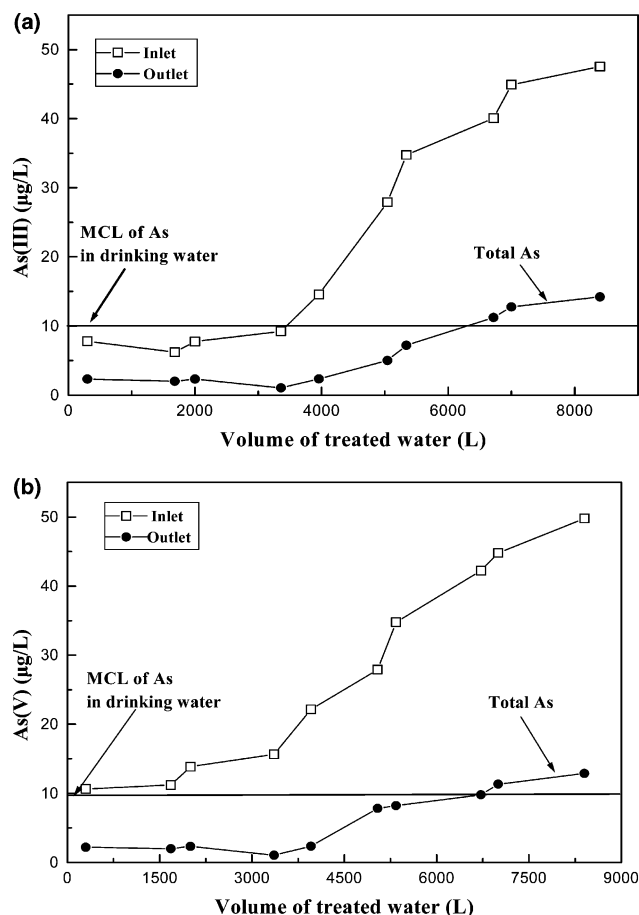
**Analytical Determinations.** The determination of arsenic was performed by hydride generation atomic absorption spectrometry, according to a modification of the Driehaus and Jekel method.<sup>33</sup> To selectively determine the concentration of As(III) (speciation), the samples were pretreated with acetic acid, in place of the pretreatment with hydrochloric acid and potassium iodide in ascorbic acid solution used for the determination of total arsenic. This method allows for the rapid determination of inorganic arsenic species at concentrations down to 1  $\mu\text{g/L}$ . The determination of the iron, manganese, and phosphate concentrations was performed by colorimetric methods using a Hitachi U-2000 photometer. In particular, iron was measured by the phenanthroline colorimetric method (detection limit = 10  $\mu\text{g/L}$ ) at 510 nm, manganese with the respective colorimetric test (detection limit = 30  $\mu\text{g/L}$ ) at 535 nm, and phosphates with the ascorbic method (detection limit = 150  $\mu\text{g/L}$ ) at 880 nm.<sup>34</sup>

The oxidation–reduction potential (ORP) was continuously measured (Metrohm, E396 B) using two electrodes (Ag/AgCl and Pt). A dissolved oxygen meter (Consort, Z 521) was employed for the respective measurements.

## Results and Discussion

**Removal of Arsenic by Sorption onto Biogenic Manganese Oxides.** The removal of manganese was very efficient during the whole period of investigations; the treatment of a Mn(II) concentration of 0.4 mg/L resulted in a residual of below 0.05 mg/L,<sup>35</sup> which is the maximum contaminant level for manganese in drinking water.<sup>6</sup> The resulting oxidation products were totally amorphous manganese oxides.<sup>35</sup>

Arsenic(III or V) removal was examined using different initial arsenic concentrations, and the results are presented in Figure 2. Two different experimental runs were performed, the first by spiking only As(III) (Figure 2a) and the second by spiking only As(V) (Figure 2b). For each different inlet arsenic concentration, inlet and outlet samples were collected and analyzed to determine the removal of arsenic. Afterward, the inlet concentration of arsenic was increased step-by-step, and several samples were again collected to determine the removal of arsenic at the higher inlet concentration.



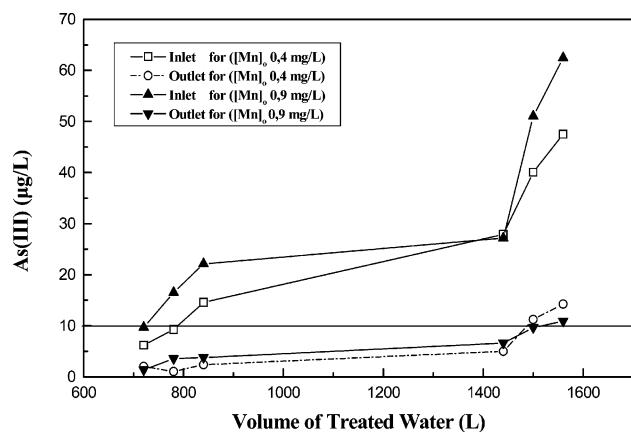
**Figure 2.** Removal of arsenic during the biological oxidation of dissolved manganese from groundwaters: (a) As(III) removal, (b) As(V) removal. Conditions:  $[\text{Mn(II)}]_0$ , 0.4 mg/L; pH, 7.2; DO, 3.8 mg/L; ORP, 330–340 mV; linear velocity, 7 m/h.

It can be observed that around 80% removal can be achieved for both forms of inorganic arsenic. Residual arsenic concentrations below the MCL of 10  $\mu\text{g/L}$  were achieved when the initial concentrations were 35 and 42  $\mu\text{g/L}$  for As(III) and As(V), respectively, meaning that the two species of arsenic showed almost the same removal behavior. This provides a primary indication of As(III) oxidation to As(V), as it is well-demonstrated that, when As(III) is treated without preliminary oxidation, it is removed from the water less efficiently than As(V).<sup>8,9,12</sup>

The obtained results indicated lower efficiencies than those obtained during the biological oxidation of iron from groundwaters.<sup>20</sup> During iron oxidation, the percentage removal of arsenic was more than 90%, and the MCL (10  $\mu\text{g/L}$ ) could be achieved even from initial arsenic concentrations of 230  $\mu\text{g/L}$ .

The difference in the removal efficiency can be attributed to the fact that iron oxides are well-established to be efficient adsorbents for arsenic removal, presenting a strong tendency to create surface complexes with arsenic ions,<sup>36</sup> whereas the use of manganese oxides is not equally effective. Manganese oxides usually have points of zero charge (PZCs) between 2 and 4.5.<sup>37</sup> Therefore, at the pH value at which these experiments were carried out (7.2), the net surface charge of manganese oxides was expected to be negative. In this pH range, arsenate [As(V)] is present as an oxyanion, and arsenite [As(III)] is present mainly as the undissociated molecule of arsenious acid.<sup>4</sup> Therefore, the sorption of





**Figure 3.** Effect of initial manganese concentration on the removal of trivalent arsenic from groundwaters. Conditions: pH, 7.2; DO, 3.8 mg/L; ORP, 330–340 mV; linear velocity, 7 m/h.

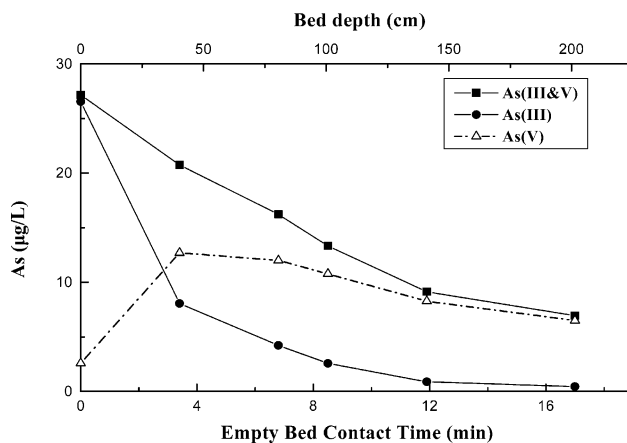
arsenic on manganese oxides can be attributed to chemical interactions through specific adsorption, because Coulombic interactions do not favor the sorption.

These results are consistent with findings of previous studies regarding arsenic removal by sorption onto manganese oxides.<sup>24</sup> Previous studies have indicated the formation of a bidentate binuclear complex between manganese oxides and arsenic.<sup>30</sup>

To investigate the possible effect of the initial manganese concentration in untreated groundwater on the removal of arsenic, the groundwater stream was spiked with dissolved Mn(II), and the obtained results are presented in Figure 3. The same experiments were performed twice, once with 0.4 mg/L inlet manganese concentration and the other time with 0.9 mg/L. For both manganese concentrations, the removal of arsenic(III) was examined for similar initial arsenic concentrations. It was found that, when the initial concentration of manganese was increased from 0.4 to 0.9 mg/L, the removal of arsenic was influenced only slightly; therefore, the manganese concentration does not appear to be a critical factor for the efficient removal of arsenic, for the range of initial arsenic concentrations examined (25–50 µg/L).

The contamination of groundwaters with elevated concentrations of manganese and arsenic, but relatively low concentrations of iron (i.e., <0.1 mg/L), is not a common case; however, it can be met in certain cases, such as the groundwaters in the greater area of Thessaloniki, Greece.<sup>38</sup>

Therefore, this technology appears to be well-suited for the treatment of manganese-containing waters that are weakly contaminated with arsenic and can be applied without the additional use of chemical reagents for the oxidation of Mn(II) or As(III). This renders the method quite economical, and the fact that the filters can be used for long-term runs without the filter medium being replaced reinforces this statement. Furthermore, because the bacteria that mediate the oxidative processes are classified as nonpathogens, the method does not pose any health risk.<sup>22</sup> This method (for the removal of iron and manganese) has been used for many years in European countries without any health problems being reported. However, for safety reasons, the treated water can be subjected to disinfection. In this way, if any pathogens slough into the treated water, they will be destroyed. Furthermore, under optimized



**Figure 4.** Depletion of arsenic concentration during the filtration of groundwater, throughout the bed (column) depth. Speciation of dissolved As(III)/As(V) and total As(III + V). Conditions: pH, 7.2; DO, 3.8 mg/L; ORP, 330–340 mV; linear velocity, 7 m/h.

operating conditions, the arsenic-contaminated biofilm cannot be sloughed off into the treated water, because most of it is periodically removed during backwashing steps. It can be also noticed that the arsenic content cannot slough off into the water, as it is strongly bound by adsorption onto the manganese oxides.<sup>30</sup> In addition, biological processes are well-documented to achieve relatively high reaction rates, which allow for the application of higher linear velocities; hence, the method could fall within the realm of viable commercial application.

**Mechanism of Arsenic Removal.** The removal of arsenic was monitored by collecting several samples throughout the bed (column) depth. The samples were then subjected to analytical determination (hydride generation) of total arsenic, as well as selective determination of As(III), so that information about the mechanism of arsenic removal could be derived. The results are presented in Figure 4, in relation to the bed depth (total bed depth of the two columns = 200 cm) and the empty-bed contact time (EBCT) of the solution in the bed columns. The EBCT was considered as the time that the water needs to fill the empty column and was calculated according to the following common equation

$$\text{EBCT} = \frac{\text{column height (m)}}{\text{linear velocity (m/h)}}$$

At the beginning of the process, only As(III) was spiked into the influent stream. However, as the process progressed, the reduction of the As(III) concentration was faster than the reduction of the total arsenic concentration, indicating the oxidation of As(III) during this treatment stage; as a result, As(V) was released into the water stream. The subsequent depletion of total arsenic can be attributed to the sorption of As(V) onto the biogenic manganese oxides that were continuously produced and deposited on the filter medium, comprising the major solid phase in the filters.

The oxidation of trivalent arsenic can be attributed either to the dissolved oxygen content or to the presence of manganese oxides, which have been well-demonstrated to oxidize trivalent arsenic. However, abiotic oxidation of As(III) by dissolved oxygen has been found to exhibit very slow kinetics, on the order of several days;<sup>14,39</sup> thus, this process could not occur in such a

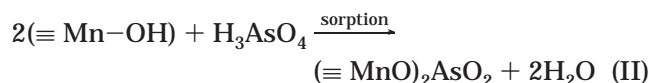
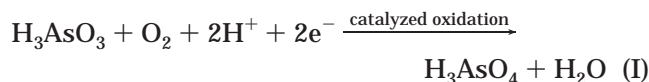
**Table 2. As(III) Depletion Rates Reported in the Literature, as Compared to Those Obtained in the Present Study**

As(III) oxidation process	kinetic constant, $k$ (min <sup>-1</sup> )	half-life, $t_{1/2}$ (min)	ref
As(III) oxidation during biological Mn(II) oxidation	0.23	3	this study
microbial oxidation	0.038	18	47
	1.2	0.58	48
abiotic oxidation by MnO <sub>2</sub>	0.067 (pH 4)	10.2	28
	0.035 (pH 7)	19.8	26
	0.0096 (pH 7.5)	72	27
oxidation by dissolved oxygen (abiotic)	$2.2 \times 10^{-4}$	3168	14
oxidation by dissolved air (abiotic)	$9.7 \times 10^{-5}$	7056	14
oxidation by ozone	0.15	4.5	14

short period of time. As shown in Figure 4, the oxidation of As(III) was almost complete after a 12-min EBCT.

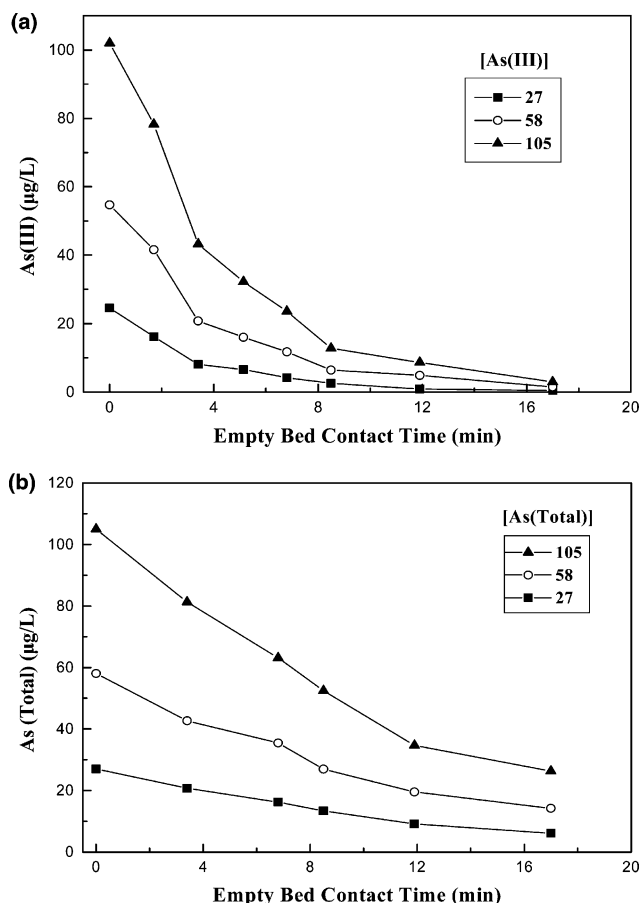
The kinetics of abiotic As(III) oxidation by manganese oxides are also slower than the rates observed in the present study (Table 2). However, the freshly precipitated manganese (hydr)oxides could have much greater specific surface areas than the well-crystallized hexagonal birnessite studied by Tournassat et al.,<sup>31</sup> with correspondingly higher As(III) oxidation rates.

A possible oxidation mechanism would be the reaction of As(III) with dissolved oxygen, mediated by the heterotrophic manganese-oxidizing bacteria, most probably by *Leptothrix ochracea*, according to the proposed scheme of reactions



It has been proposed that, during the biological oxidation of manganese, *Leptothrix ochracea* releases a catalase, which acts as a peroxidase, catalyzing the formation of hydrogen peroxide.<sup>22</sup> Hydrogen peroxide is a strong oxidant and could contribute to the oxidation of As(III);<sup>13</sup> however, Pettine et al.<sup>40</sup> have shown that, at pH value of 7.5, the kinetics of As(III) oxidation by H<sub>2</sub>O<sub>2</sub> are on the order of hours. Therefore, the reaction of As(III) oxidation (reaction I) should be catalyzed, to proceed on a time scale of few minutes. Voegelin and Hug<sup>41</sup> recently studied the oxidation of As(III) by H<sub>2</sub>O<sub>2</sub> in the presence of ferrihydrite. They found that this reaction can be catalyzed on the surface of ferrihydrite, even though no oxidation was observed within minutes to hours prior to H<sub>2</sub>O<sub>2</sub> addition.

The oxides of manganese could probably catalyze the reaction of As(III) by H<sub>2</sub>O<sub>2</sub> in a way similar to that proposed by Voegelin and Hug for the case of ferrihydrite. The rapid oxidation in such a system can be attributed to the fact that adsorbed As(III) is assumed to be oxidized more readily than the undissociated species in solution, while the decomposition of hydrogen peroxide on the manganese oxides surfaces<sup>42</sup> might also lead to As(III) oxidation.<sup>41</sup> Therefore, the great importance of the presence of electron donors such as Mn(II) becomes obvious, because such species are necessary for the growth of the bacteria and for the formation of the biogenic solid surfaces, enabling the subsequent removal of oxidized arsenic by sorption.

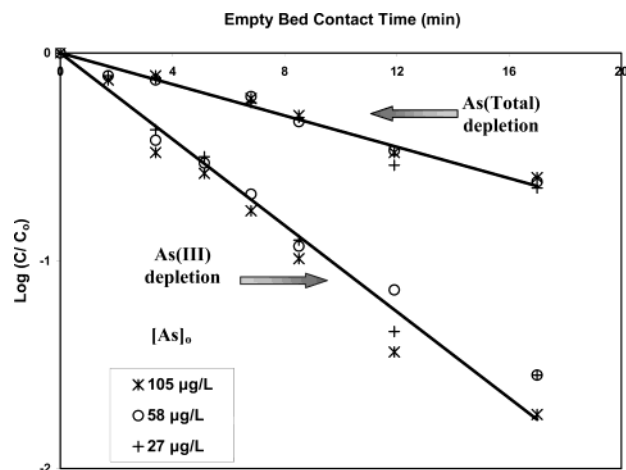


**Figure 5.** Depletion of As concentration, applying different initial As concentrations, in relation to the empty bed contact time of the solution in the filter columns: (a) As(III) depletion, (b) total As depletion. Conditions: pH, 7.2; DO, 3.8 mg/L; ORP, 330–340 mV; linear velocity, 7 m/h.

**Kinetics of Bacterial As(III) Oxidation and of As-(Total) Depletion.** Arsenic removal was also studied for different influent As concentrations (Figure 5). The residual As(III) concentration was very low (Figure 5a), although in all cases, the corresponding residual total arsenic concentration was significantly higher (Figure 5b). To investigate the kinetics of As(III) oxidation, the apparent first-order rate equation for the depletion of As(III) was considered.

A plot of  $\log([\text{As(III)}]_t/[\text{As(III)}]_0)$  versus time (Figure 6) will be linear and independent of the initial As(III) concentration if the oxidation of As(III) follows a first-order reaction rate. The slope of such a plot is  $-k/(\ln 10)$ , and the half-life of As(III) oxidation can be calculated from the relationship  $t_{1/2} = -(\ln 2)/k$ . The results in Figure 6 imply that As(III) oxidation can be described by a first-order reaction. Relevant values regarding the first-order oxidation of As(III) by other chemical reagents are summarized in Table 2.

It can be seen that the oxidation of As(III) using the specific treatment system discussed here is much faster than that observed with the other methods (physico-chemical) usually applied. The higher rates of As(III) oxidation support the conclusion that As(III) oxidation was probably catalyzed by the bacteria, probably the same microorganisms that mediate Mn(II) oxidation. Furthermore, the oxidation of As(III) (half-life of 3 min) was found to proceed almost in parallel with the bacterial manganese oxidation for this specific treat-



**Figure 6.** First-order fit for (a) As(III) oxidation rate, (b) total As depletion rate [as a result of As(III) oxidation].

ment unit, because the kinetic analysis of Mn(II) oxidation yielded a half-life of 3.98 min.<sup>35</sup>

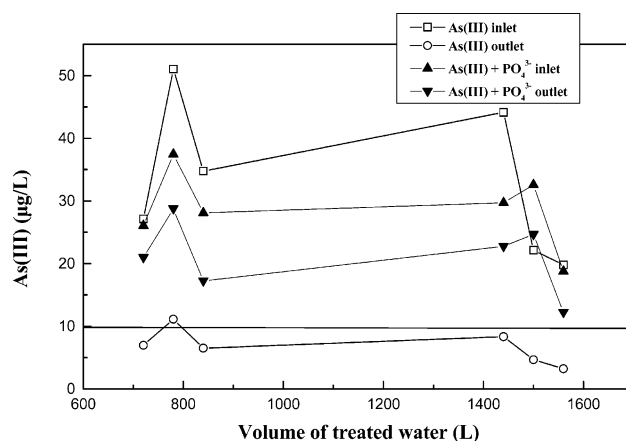
Assuming that the removal of arsenic from the groundwater stream was mainly due to the specific interaction with the deposited manganese oxides, the kinetics of total arsenic depletion could be calculated by plotting  $\log([As(Total)]_t/[As(Total)]_0)$  versus time (Figure 6). The calculated kinetic constant  $k$  for the depletion of total arsenic from the solution was found to be  $0.083 \text{ min}^{-1}$ , indicating the sequence of reactions responsible for the removal of As(III) in such a system.

**Effect of Phosphates on the Removal of As(III) during Biological Oxidation of Manganese from Groundwaters.** Among the anions that are usually present in aquatic sources and can inhibit the sorption of arsenic are phosphates. The effect of phosphates on the removal of arsenic by sorption onto iron oxides is well-documented.<sup>43</sup> It has been found that, when the phosphates concentration is low ( $<200 \text{ µg/L}$ ), the effect on arsenic removal is not significant; however, at higher concentrations (i.e.,  $>400 \text{ µg/L}$ ), the removal of arsenic is not efficient, at least for an initial arsenic concentration  $50 \text{ µg/L}$ .<sup>44</sup>

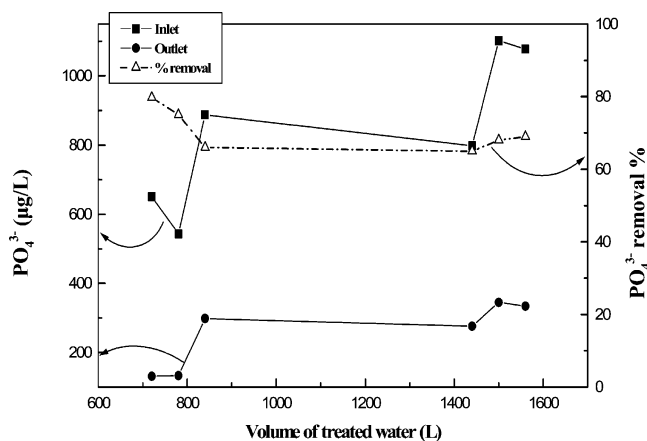
Relevant information about the effect of phosphates on arsenic removal by sorption on manganese oxides is limited. Therefore, in the following experiments, the groundwater stream was spiked with phosphates to a final inlet concentration of  $600 \text{ µg/L}$ , corresponding to  $6.3 \text{ µM PO}_4^{3-}$ , while the As(III) concentration was varied from 0.3 to  $0.7 \text{ µM}$ . The results are presented in Figure 7.

It is clearly demonstrated in this figure that the presence of phosphates, in this concentration range, inhibits arsenic(III) removal, which drops from 80% removal efficiency (in the absence of phosphates) to around 30%. Phosphates compete with arsenic for the available sorption sites on the surface of the manganese oxides. It has been reported that the sorption of phosphates on manganese oxides is a very efficient and rapid process.<sup>45,46</sup> The manganese oxides present a high affinity for creating surface complexes with phosphates, with a  $\log K$  value of 29.<sup>45</sup> These results are consistent with the present experiments, as shown in Figure 8. The removal of phosphates is sufficient, as it accounts for around 80%, even when high initial phosphates concentrations ( $\sim 1 \text{ mg/L}$ ) are applied.

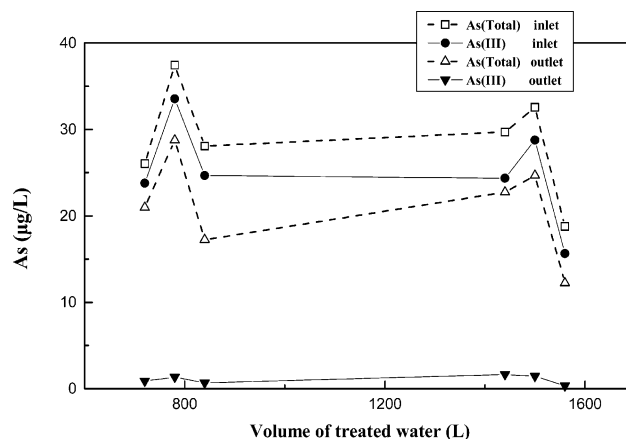
However, it was questionable whether the presence of phosphates would have an adverse effect on the



**Figure 7.** Impact of phosphates on the removal of arsenic by sorption on biogenic manganese oxides. Conditions:  $[Mn(II)]_0$ ,  $0.6 \text{ mg/L}$ ; pH, 7.2; DO,  $3.8 \text{ mg/L}$ ; ORP, 330–340 mV; linear velocity,  $7 \text{ m/h}$ ;  $[PO_4^{3-}]_0$ ,  $600 \text{ µg/L}$ .



**Figure 8.** Removal of phosphates by sorption on biogenic manganese oxides, with the simultaneous presence of arsenic in the groundwater stream. Conditions:  $[Mn(II)]_0$ ,  $0.6 \text{ mg/L}$ ;  $[As(Total)]_0$ ,  $\sim 50 \text{ µg/L}$ ; pH, 7.2; DO,  $3.8 \text{ mg/L}$ ; ORP, 330–340 mV; linear velocity,  $7 \text{ m/h}$ .



**Figure 9.** Effect of phosphates on the oxidation of As(III) in groundwater treatment. Conditions:  $[Mn(II)]_0$ ,  $0.6 \text{ mg/L}$ ; pH, 7.2; DO,  $3.8 \text{ mg/L}$ ; ORP, 330–340 mV; linear velocity,  $7 \text{ m/h}$ ;  $[PO_4^{3-}]_0$ ,  $600 \text{ µg/L}$ .

oxidation of As(III). Therefore, samples of the effluent were analyzed for the selective determination of As(III), to observe the possible effect of phosphates on the behavior of arsenic in the current treatment system (Figure 9). The results clearly indicate that the presence of phosphates, despite inhibiting the overall arsenic



removal through competitive adsorption, did not have any impact on the oxidation of As(III). It is illustrated in Figure 9 that, although the effluent concentration of total arsenic was around 20  $\mu\text{g/L}$ , As(III) accounted for only 1–2  $\mu\text{g/L}$ . The fact that As(III) is essentially 100% oxidized in the presence of excess phosphates adsorption provides strong evidence for the biotic oxidation of As(III).

In conclusion, it was found that the application of biological treatment methods for the removal of dissolved manganese from groundwater sources can serve as an efficient method for the simultaneous removal of low-level arsenic concentrations. During this treatment, the removal of arsenic is equally efficient for both forms of inorganic arsenic. It was found that As(III) is oxidized, and the kinetic constant for this oxidation was calculated. From these results and a comparison with available literature data, it was assumed that As(III) oxidation was carried out by  $\text{H}_2\text{O}_2$ , catalyzed by the manganese oxide surfaces, while bacteria are believed to play an important role in accelerating these processes.

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### Literature Cited

- (1) Nordstrom, D. K. Worldwide occurrences of arsenic in groundwater. *Science* **2002**, *296*, 2143.
- (2) Pontius, F. W.; Brown, K. G.; Chen, C. J. Health implications of arsenic in drinking water. *J. Am. Water Works Assoc.* **1994**, *86* (9), 52.
- (3) Hughes, M. F. Arsenic toxicity and potential mechanisms of action. *Toxicol. Lett.* **2002**, *133*, 1.
- (4) Cullen, W. R.; Reimer, K. J. Arsenic speciation in the environment. *Chem. Rev.* **1989**, *89*, 713.
- (5) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517.
- (6) Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption; Drinking Water Directive 98/83/EEC; European Commission: Brussels, Belgium, 1998.
- (7) Implementation Guidance for the Arsenic Rule; Report EPA-816-D-02-005; Office of Groundwater and Drinking Water, U.S. Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, 2002 (also available at [www.epa.gov/safewater/ars/implement.html](http://www.epa.gov/safewater/ars/implement.html), accessed Mar 2002).
- (8) Jekel, M. R. Removal of arsenic in drinking water treatment. In *Arsenic in the Environment. Part 1: Cycling and Characterization*; Nriagu, J. O., Ed.; New York, 1994; pp 119–130.
- (9) Kartinen, E. O.; Martin, C. J. An overview of arsenic removal processes. *Desalination* **1995**, *103*, 79.
- (10) Driehaus, W.; Jekel, M.; Hildebrandt, U. Granular ferric hydroxide—A new adsorbent for the removal of arsenic from natural water. *J. Water SRT-Aqua* **1998**, *47*, 30.
- (11) Zouboulis, A. I.; Katsoyiannis, I. A. Removal of arsenates from contaminated water by coagulation-direct filtration. *Sep. Sci. Technol.* **2002**, *37* (12), 2859.
- (12) Zouboulis, A. I.; Katsoyiannis, I. A. Arsenic removal using iron oxide loaded alginate beads. *Ind. Eng. Chem. Res.* **2002**, *41*, 6149.
- (13) Molnar, L.; Vircikova, E.; Lech, P. Experimental study of As(III) oxidation by hydrogen peroxide. *Hydrometallurgy* **1994**, *35*, 1.
- (14) Kim, M. J.; Nriagu, J. Oxidation of arsenite in groundwater using ozone and oxygen. *Sci. Total Environ.* **2000**, *247*, 71.
- (15) Gallard, H. U.; von Gunten, U. Chlorination of natural organic matter: Kinetics of chlorination and of THM formation. *Water Res.* **2002**, *36*, 65.
- (16) Battaglia-Brunet, F.; Dictro, M.-C.; Garrido, F.; Crouzet, C.; Morin, D.; Dekeyser, K.; Clarens, M.; Baranger, P. An arsenic(III) oxidizing bacterial population: Selection, characterization and performance in reactors. *J. Appl. Microbiol.* **2002**, *93*, 656.
- (17) Weeger, W.; Lievreumont, D.; Perret, M.; Lagarde, F.; Hubert, J.; Leroy, M.; Lett, M. Oxidation of arsenite to arsenate by a bacterium isolated from an aquatic environment. *Biometals* **1998**, *12*, 141.
- (18) Santini, J. M.; Sly, L. I.; Schnagl, R. D.; Macy, J. M. A new chemolithotrophic arsenite-oxidizing bacterium isolated from a gold mine: Phylogenetic, physiological and preliminary biochemical studies. *Appl. Environ. Microbiol.* **2000**, *66*, 92.
- (19) Seith, R.; Jekel, M. 1997. Biooxidation of As(III) in fixed bed bioreactors. *Vom Wasser* **1997**, *89*, 283.
- (20) Zouboulis, A. I.; Katsoyiannis, I. A. Removal of arsenic from contaminated groundwaters using combined chemical and biological treatment methods. In *Chemical Water and Wastewater Treatment*; Hahn, H., Hoffmann, E., Odegaard, H., Eds.; IWA Publishing: London, 2002; pp 119–130.
- (21) Katsoyiannis, I.; Zouboulis, A.; Althoff, H. W.; Bartel, H. As(III) removal from groundwater using fixed bed upflow bioreactors. *Chemosphere* **2002**, *47*, 325.
- (22) Mouchet, P. From conventional to biological removal of iron and manganese in France. *J. Am. Water Works Assoc.* **1992**, *84* (4), 158.
- (23) Edwards, M. Chemistry of arsenic: Removal during coagulation and Fe–Mn oxidation. 1994. *J. Am. Water Works Assoc.* **1994**, *86* (9), 64.
- (24) Driehaus, W.; Seith, R.; Jekel, M. Oxidation of As(III) with manganese oxides in water treatment. *Water Res.* **1995**, *29* (1), 297.
- (25) Bajpai, S.; Chaudhuri, M. Removal of arsenic from groundwater by manganese dioxide coated sand. *J. Environ. Eng.* **1999**, *125* (8), 782.
- (26) Oscarson, D. W.; Huang, P. M.; Liaw, W. K.; Hammer, U. T. Kinetics of oxidation of arsenite by various manganese dioxides. *Soil. Sci. Soc. Am. J.* **1983**, *47*, 644.
- (27) Moore, J. N.; Walker, J. R.; Hayes, T. H. Reaction scheme for the oxidation of As(III) by birnessite. *Clays Clay Miner.* **1990**, *38* (5), 549–555.
- (28) Scott, M. J.; Morgan, J. J. Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. *Environ. Sci. Technol.* **1995**, *29* (8), 1898.
- (29) Nesbitt, H. W.; Canning, G. W.; Bancroft, G. M. XPS study of reductive dissolution of 7A birnessite by  $\text{H}_3\text{AsO}_3$  with constraints on the reaction mechanism. *Geochim. Cosmochim. Acta* **1998**, *62*, 2097.
- (30) Manning, B. A.; Fendorf, S. E.; Bostick, B.; Suarez, D. L. Arsenic(III) and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* **2002**, *36*, 976.
- (31) Tournassat, C.; Charlet, L.; Bosbach, D.; Manceau, A. Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate. *Environ. Sci. Technol.* **2002**, *36*, 493.
- (32) Chekalla, C.; Mevius, W.; Hanert, H. Quantitative removal of iron and manganese by microorganisms in rapid sand filters (in situ investigations). *Water Supply* **1985**, *3*, 111.
- (33) Driehaus, W.; Jekel, M. Determination of As(III) and total inorganic arsenic by on-line pretreatment in hydride generation atomic absorption spectrometry. *Fresenius' J. Anal. Chem.* **1992**, *343*, 352.
- (34) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; APHA-AWWA-WPCF: Washington, DC, 1989.
- (35) Katsoyiannis, I. A. Arsenic Removal from Groundwaters Applying Combined Treatment Methods. Ph.D. Thesis, Department of Chemistry, Laboratory of General and Inorganic Chemical Technology, Aristotle University of Thessaloniki, Thessaloniki, Greece, 2002 (in Greek, with extended English summary).
- (36) Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* **1993**, *57*, 2251.
- (37) Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*; Wiley International: New York, 1996.

- (38) Voutsas, D.; Samara, C.; Kouimtzis, Th. Groundwater quality in the major industrial area of Thessaloniki, Greece. Part II: Heavy metal distribution—source identification. *Toxicol. Environ. Chem.* **1994**, *45*, 105.
- (39) Tallman, D. E.; Shaikh, A. U. Redox stability of inorganic arsenic(III) and arsenic(V) in aqueous solution. *Anal. Chem.* **1980**, *52*, 199.
- (40) Pettine, M.; Campanella, L.; Millero, F. J. Arsenite oxidation by  $H_2O_2$  in aqueous solutions. *Geochim. Cosmochim. Acta* **1999**, *63*, 2727.
- (41) Voegelin, A.; Hug, S. J. Catalyzed oxidation of arsenic(III) by hydrogen peroxide on the surface of ferrihydrite: An in situ ATR-FTIR study. *Environ. Sci. Technol.* **2003**, *37*, 972.
- (42) Petigara, B. R.; Blough, N. V.; Mignerey, A. C. Mechanism of hydrogen peroxide decomposition in soils. *Environ. Sci. Technol.* **2002**, *36*, 639.
- (43) Meng, X.; Korfiatis, G. P.; Bang, S.; Bang, K. W. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol. Lett.* **2002**, *133* (1), 103.
- (44) Katsoyiannis, I. A.; Zouboulis, A. I. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Res.* **2002**, *36*, 5141.
- (45) Yao, W.; Millero, F. J. Adsorption of phosphate on manganese dioxide in seawater. *Environ. Sci. Technol.* **1996**, *30*, 536.
- (46) Ouvrard, S.; Simonnot, M. O.; Sardin, M. Reactive behavior of natural manganese oxides towards the adsorption of phosphate and arsenate. *Ind. Eng. Chem. Res.* **2002**, *41* (11), 2785.
- (47) Wilkie, J. A.; Hering, J. G. Rapid oxidation of geothermal arsenic(III) in steamwaters of the eastern Sierra Nevada. *Environ. Sci. Technol.* **1998**, *32*, 657.
- (48) Langner, H. W.; Jackson, C. R.; McDermott, T. R.; Inskeep, W. P. Rapid oxidation of arsenite in a hot spring ecosystem, Yellowstone national park. *Environ. Sci. Technol.* **2001**, *35*, 3302.

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