

# Anoxic Oxidation of Arsenite Linked to Denitrification

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Arsenic (As) contamination of groundwater and surface water is a worldwide problem. Exposure to arsenic in drinking water is an important and current public health issue, which contributes to non-cancer and cancer diseases. The U.S. Environmental Protection Agency (USEPA) has recently enacted a stricter drinking water standard for arsenic that lowers the maximum contaminant level (MCL) from 50 to 10  $\mu\text{g/L}$  (USEPA 2001). The most commonly detected forms of inorganic As are arsenate [As(V)], which dominates under aerobic conditions, and arsenite [As(III)], that predominates in reducing environments. As(III) is generally considered more mobile than As(V), because the former tends to be less tightly adsorbed onto the surface of minerals containing aluminum. The main objective is to determine whether the microbial oxidation of As(III) coupled to denitrification could be sustained for long periods of time in upward flow anaerobic sludge bed reactors, in which biomass is immobilized as granular bio-films. Also it is important to illustrate if the microorganisms could acclimate to high As(III) concentration by step-to-step increase of feeding of As(III).

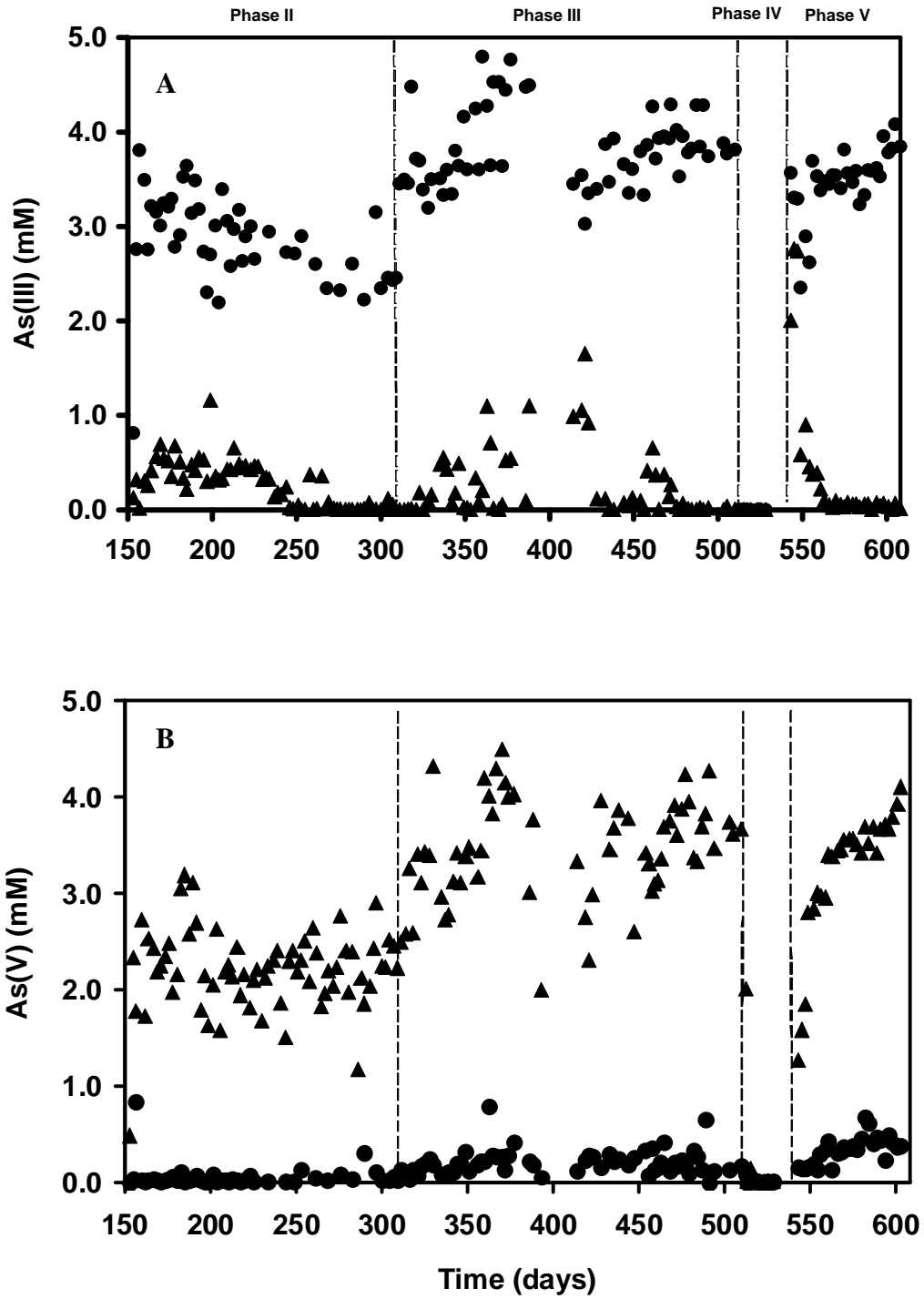
The microbial oxidation of soluble As(III) and the concomitant formation of soluble As(V) in R9 as a function of reactor operation time are illustrated in **Figures 1**. The conversion of As(III) to As(V) in column R9 was more than 87% throughout the length of the experiment. The results indicated that the microbial oxidation of As(III) was enhanced by the addition of nitrate as electron acceptor. In comparison, the removal of As(III) and the formation of As(V) were negligible in column R10 in the absence of nitrate (data not shown). This confirmed that nitrate was used as the electron acceptor for As(III) oxidation in R9. Likewise the absence of contaminating  $\text{O}_2$  in the influent was indicated by the lack of any As(III) oxidation in R10. **Figure 2** illustrates the oxidation efficiency of As(III) to As(V) in both columns during the period II. As(III) was

efficiently oxidized in the nitrate-amended column (91% removal) at volumetric loadings of up to 181 mg As/L<sub>r</sub> • d, compared with nearly no oxidation in the control column.

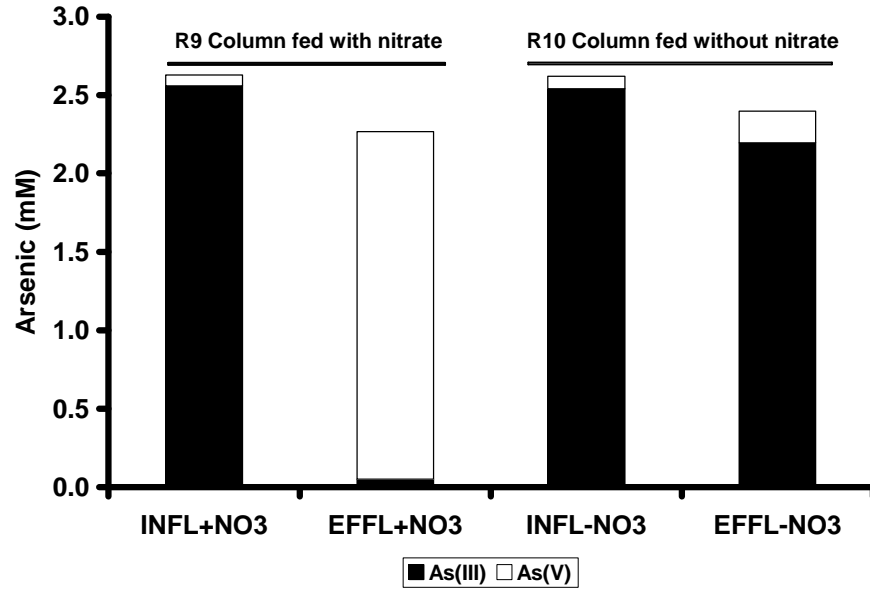
**Figure 3** shows the nitrate consumption in reactor R9 as a function of time. The nitrate concentration supplied (6.4 mM) was in excess of the concentration required for stoichiometric conversion of As(III) to As(V) (1.0 and 1.5 mM NO<sub>3</sub><sup>-</sup> for 2.5 and 3.75 mM As(III), respectively). In **period IV (Day 512-548)**, the endogenous consumption of nitrate was measured as 1.06 mM. For the periods II, III and V, the calculated molar ratios of ΔAs(V): ΔNO<sub>3</sub><sup>-</sup> were 2.38, 2.57 and 2.61, respectively. These ratios are very close to the theoretical stoichiometry ratio of 2.5 for As(III) oxidation linked to complete denitrification. Nitrite (NO<sub>2</sub><sup>-</sup>) and net production of ammonium (NH<sub>4</sub><sup>+</sup>), two possible products from the microbial degradation of nitrate, were not detected in the effluent of R9 and R10 throughout the experiment. These findings indicate that nitrate was completely denitrified to the benign end product dinitrogen gas (N<sub>2</sub>). **Table 3** presents a summary of performance data for the two reactors columns for the total duration of the study. The As(III) removal efficiencies for the R9 were very stable with around 90%, and the oxidation rates of As(III) to As(V) were also 90% with the increase of the As(III) volumetric load.

## Conclusions

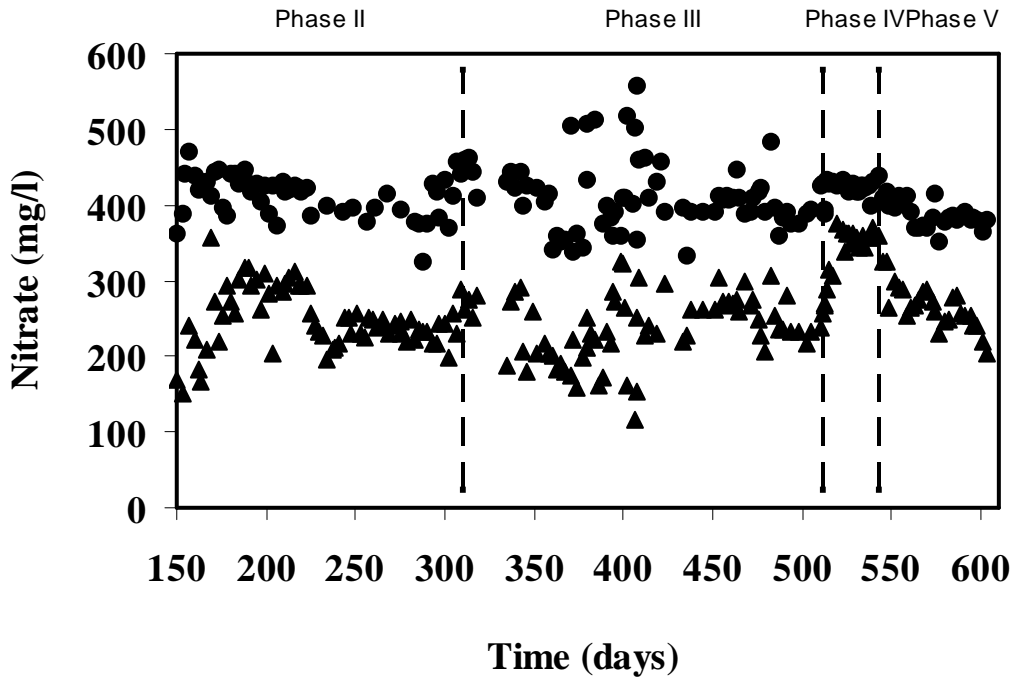
Due to the limitation of O<sub>2</sub> solubility and transport in some natural water system, anoxic oxidation of As(III) to As(V) by alternative oxidants became a very interesting research topic recently. Our study demonstrates for the first time that continuous columns can be operated to link As(III) oxidation to nitrate reduction under anoxic conditions. Based on the mass balance of nitrogen and the molar ratio of As(III) to NO<sub>3</sub><sup>-</sup>, the results from this study provide compelling evidence that complete chemolithotrophic denitrification process was responsible for the As(III) oxidation to As(V). Autotrophic As(III) oxidation is feasible and effective in a continuous denitrifying bioreactor with bacteria immobilized in bio-films. We have this proven that a bioreactor with capable of As(III) oxidation linked to complete denitrification is stable over extended periods of time. Above all, it is illustrated that microbiologically mediated As(III) oxidation under denitrifying conditions is an important component in the biogeochemical cycling of arsenic in the natural aqueous environment.



**Figure 1** Concentration of As(III) (Panel A) and As(V) (Panel B) in the continuous bioreactor R9 as a function of time: (●)- Influent, (▲)- Effluent



**Figure 2** Comparison of the As(III) and As(V) concentrations in the influent and effluent of reactors R9 and R10 during Period II (day 154-309).



**Figure 3** The influent and effluent concentrations of  $\text{NO}_3^-$  determined in the continuous column R9 as a function of time: (●)- Influent, (▲)- Effluent. Note: Phase IV is the endogenous period without feeding of As(III).

**Table 3** Summary of bioreactor R9 operation and performance data

Parameters	Units	Value of each phase				
		I	II	III	IV	V
As(III) removal efficiency	%	--	<b>91.0</b>	<b>93.0</b>	--	<b>86.6</b>
As(III) volumetric load	mg As/L <sub>r</sub> ·d	--	<b>181.0</b>	<b>254.0</b>	--	<b>206.0</b>
As(V) formed /As(III) removed	mol/mol	--	<b>0.83</b>	<b>0.90</b>	--	<b>0.91</b>
Net <sup>†</sup> As(III) removed/corrected* NO <sub>3</sub> <sup>-</sup> removed	mol/mol	--	<b>2.53</b>	<b>2.73</b>	--	<b>2.89</b>
Net <sup>†</sup> As(V) formed/corrected* NO <sub>3</sub> <sup>-</sup> removed	mol/mol	--	<b>2.38</b>	<b>2.57</b>	--	<b>2.61</b>

<sup>†</sup> Net means the positive difference between the effluent concentration and the influent concentration

\* Corrected for endogenous nitrate consumption measured in period IV