Report for 2002AZ3B: Microbial Mediated Mobilization of Arsenic from Drinking Water Treatment Residuals in Landfills

- unclassified:
  - Sierra, R., J. Field, W. Ela, I. Cortinas, C. de las Casas, G. Feijoo, and M. Moreira. Mobilization of arsenate from activated alumina under anaerobic landfill conditions?, 17th Annual Rocky Mountain Regional Meeting, American Chemical Society, October, 2002, Albuquerque, NM
  - Sierra, R., W. P. Ela, C. de las Casas, I. Cortinas, and J. Field. Microbially-mediated mobilization of arsenic from drinking water treatment residuals in landfills? 75th Annual Conference of Arizona Water & Pollution Control Association, May 1-3, 2002, Mesa, Arizona
  - Sierra-Alvarez, R,. J. A. Field, I. Cortinas, C. de las Casas, G. Feijoo, M. T. Moreira and W. Ela. Microbial reduction and mobilization of arsenate under anaerobic conditions. VII Latin America Workshop and Symposium on Anaerobic Digestion, Oct 22-25, 2002, Merida, Mexico
  - Sierra-Alvarez, R., I. Cortinas, J. A. Field. Microbial reduction and mobilization of arsenate under anaerobic conditions. Transition of Basic Science into Practical Applications to Meet Environmental and Public Health Challenges (National Institute of Environmental Health Sciences and Environmental Protection Agency Superfund Basic Research Program) November 3-6, 2002, Tucson, Arizona
  - Ela, WP, R Sierra-Alvarez, JA. Field, A. Ghosh, I. Cortinas, & C. de las Casas. 2003. Laboratory Tests on the Fate of Arsenic in Landfills. Presented at the Proceedings of the 2003 Residuals and Biosolids Symposium, Baltimore, MD, February, 2003.

Report Follows:

A. Problem and Research Objectives

Problem. The Environmental Protection Agency (EPA) has enacted a new drinking water legislation which will lower the standard for arsenic (As) in drinking water to 10 parts per billion (ppb). The new legislation will have the highest impact on small drinking water suppliers in the US Southwest (including Arizona), where the background levels of arsenate are often higher than 10 ppb. Arsenic in water exists as arsenate (As(V)) or arsenite (As(III)). The EPA recommended treatment alternative for small-scale drinking water suppliers is the oxidation of As(III) to As(V), followed by adsorption of arsenate onto activated alumina (AA, Al_2O_3) or ferrihydrite (Fhy, $Fe(OH)_3 \cdot nH_2O$). The EPA suggests these solid residuals may be disposed of in non-hazardous waste landfills . As a result of the newly enacted standard, approximately, 6 million pounds of As-laden drinking water residues, containing 40,000 pounds of As will be landfilled annually. This represents an unprecedented quantity of a known carcinogen to be deposited into non-hazardous landfills, justifying a closer look at the potential hazard of As mobilization.

The residuals will pass the current EPA protocol, *Toxicity Characteristic Leaching Procedure* (TCLP), regulating toxic waste disposal. However, the TCLP was designed for leaching cationic metals and thus is not very challenging for arsenate (an anion) and as such the protocol is very inadequate for regulating arsenate bearing wastes. The inadequacy is emphasized further by the fact that the TCLP does not take into account microbial mediated reduction processes expected in landfills, facilitating the mobilization of As from the disposed residuals.

Research Objectives. The primary objectives of the research are two-fold:

i) Test the hypothesis that microbial reduction processes will significantly contribute to the mobilization and thus the hazard of arsenate adsorbed onto landfilled drinking water treatment residuals.

ii) Evaluate whether combined microbial, physicochemical, and hydraulic conditions representative of landfills leads to significant leaching of arsenic from treatment residuals.

B. Methodology

Initially, batch bioassays were conducted to monitor the bioconversion of arsenate to arsenite in serum bottles inoculated with a mixed anaerobic microbial consortium. The batch assys were conducted in 135 ml flasks with 50 ml of medium. Granular methanogenic sludge from a full-scale up-flow anaerobic sludge bed (UASB) reactor was selected a stable methanogenic consortium for the use in these tests and the sludge was supplied at aproximately 1.5 g volatile suspended solids (VSS) per liter. The electron-donating substrate was typically a mixture of volatile fatty acids (acetate, propionate and butyrate) supplied at 2 g chemical oxygen demand per liter or otherwise 10 mM lactate unless alternative electron donors were studied as specified. Arsenate was typically supplied at 500 µM. The medium also contained basal mineral nutrients (macro- and micronutrients) and sodium bicarbonate (5 g/l) as a buffer. The medium was prepared with minimal sulfur content to avoid precipitation of arsenite. The headspace was filled with a flush gas composed of N_2:CO_2 80:20% (unless hydrogen was used as electron donor in which case H_2:CO_2 80:20% was used). In each experiment control were carried out in which arsenate was incubated with sterile medium or with the medium and autoclaved sludge in order to confirm minimal abiotic removal of arsenate.

In a second set of experiments, three continuous columns of 0.25 L each were operated and continuously fed with synthetic landfill leachate (Figure 1). All the reactors were loaded with 100 g dry weight of activated alumina containing 0.657 mg adsorbed arsenate (expressed as arsenic) per g dry weight activated alumina. The adsorbed concentration corresponds to an isotherm equilibrated with 20 ppb arsenic. Columns 1 and 2 were inoculated with 27 g VSS/L of granular anaerobic sludge to imitate the methanogenic conditions in a landfill; column 3 received no inoculum. All three columns received synthetic inorganic landfill leachate, with pH, bicarbonate and ammonia levels adjusted to average leachate values from mature landfills and additional nutrients of basal medium as indicated in Table 1. Only column 1 received an organic electron donating substrate representative of landfill leachate, which was a mixture of five volatile fatty acids (acetate, propionate, butyrate, valerate and caproate). Columns 1 and 2 represent the disposal conditions in a mature mixed landfill (receiving both organic and inorganic wastes). Column 1 represents the situation with continued release of leachates containing volatile fatty acid. Column 2 represents a landfill with stabilized organic matter (in the form of stable microbial biomass). Column 3 represents the situation in separated landfill cells (receiving only inorganic wastes) in which only physiochemical processes predominate.

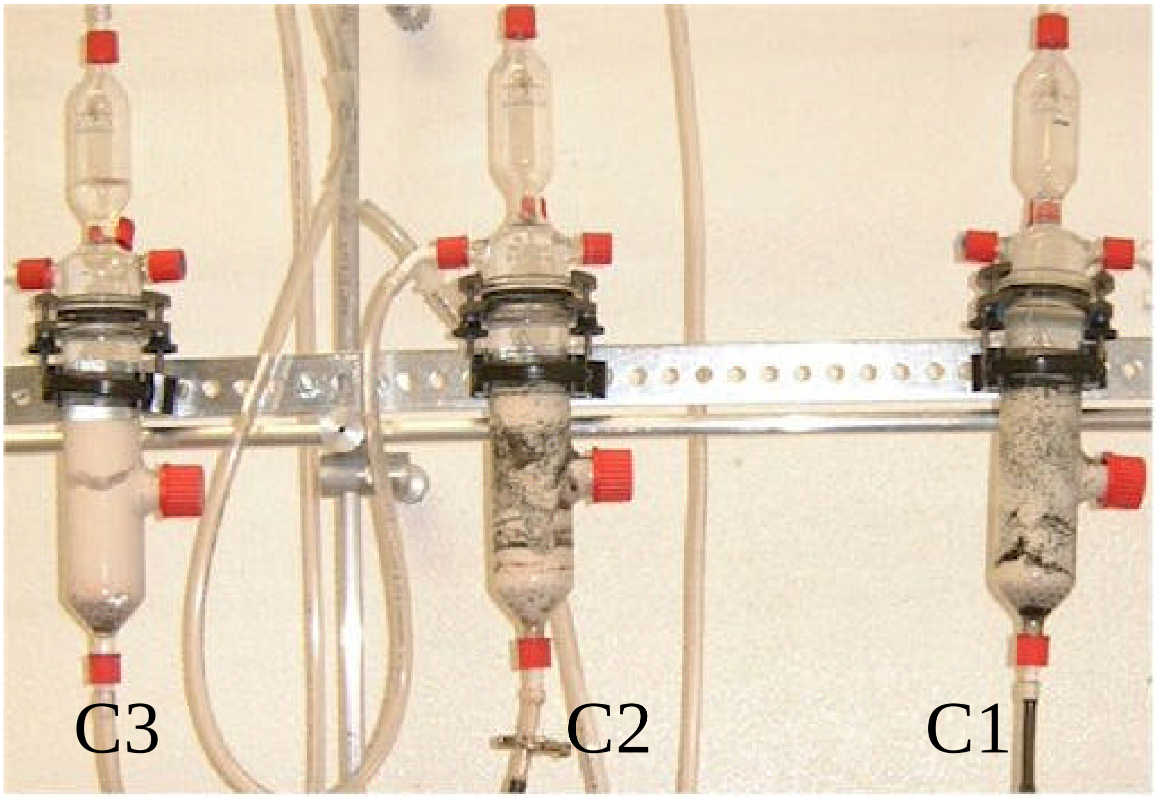

Figure 1. 0.5-L laboratory-scale anaerobic columns used to investigate the microbial mobilization and biotransformation of arsenate sorbed onto activated alumina under simulated landfill conditions. (**C1**) Biological column fed a synthetic landfill leachate containing both inorganic and organic components. (**C2**) Control column fed with an inorganic leachate (lacking organic substrates). (**C3**) Abiotic column fed with an inorganic leachate

The columns were operated initially 10 h empty bed hydraulic retention time for the first 24 days and later with a 20 h empty bed hydraulic retention time for the remainder of the experiment (lasting 6 months).

Arsenic speciation in liquid samples was analyzed by ion chromatography/inductively coupled plasma/ mass spectrometry (IC/ICP/MS) (LC Agilent 1100 series, ICP-MS Agilent 7500, Agilent Technologies), courtesy of the NIEHS Superfund Program based in the College of Pharmacy, using a Dionex IonPac AS7 analytical column. Aqueous As species determined included: arsenate; arsenite; as well as mono- and dimethylated trivalent and pentavalent arsenic derivatives (methylarsonic acid (MMA(V)), dimethylarsinic acid (DMA(V)), methylarsonous acid (MMA(III)), and dimethylarsinous acid (DMA(III)).

Table 1. Composition of Synthetic Landfill Leachate Utilized in the Continuous Study

Compounds	**Inorganic Leachate Components**	**Organic Leachate Components**
:	columns 1, 2 & 3	column 1 only
	(mg/L)	mg/L
KH_2PO_4	37	
$CaCl_2 \cdot 2H_2O$	10	
$MgSO_4 \cdot 7H_2O$	10	
$MgCl_2 \cdot 6H_2O$	78	
NH_4Cl	668	
$NaHCO_3$	2000	
Trace Element Solution†	1 (mL/L)	
Acetate		115
Propionate		47
Butyrate		115
Valerate		48
Caproate		72

†Trace Element Solution (ingredients in mg/L): $FeC1_3$.4 H_20, 2000; $CoCl_2$. 6 H_20, 2000; $MnCl_2$ 4 H_20, 50; $AlCl_3$ 6 H_20, 90; $CuCl_2.2H_20$, 30; $ZnCl_2$, 50; H_3BO_3, 50; $(NH_4)_6Mo_7O_2$.4 H_2O, 90; Na_2SeO_3.5 H_2O, 100; $NiCl_2$.6 H_20, 50; EDTA, 1000; HCl 36% (1 ml).

C. Principal Findings and Significance

Principal Findings. The research was divided into two tasks. The first task concerned batch assays evaluating the reductive biotransformation of arsenate to arsenite under various physiological conditions. The second tasks evaluated the mobilization of arsenate adsorbed onto activated alumina in simulated landfill columns.

Batch Assays. In the first set of experiments, the reductive biotransformation of arsenate to arsenite was evaluated in methanogenic sludge utilizing different electron donating substrates. These experiments were considered reloevant since the microbial ecology in a mature landfill is principally a methanogenic consortium. Figure 2 illustrates the relative ease by which 500 μM arsenate is transformed to arsenite under anaerobic conditions. In just a matter of several days the arsenate is stoichiometrically converted to arsenite in methanogenic sludge with no previous experience with arsenicals, suggesting that the biotransformation is a fortuitous capacity of methanogenic consortia. No conversion of arsenate occurred in control experiments with media containing autoclaved sludge, suggesting that transformation of arsenate is biologically catalyzed by microorganisms in the "living" sludge. Secondly, exogenous electron donating substrates, stimulated the transformation compared to assays with only slowly hydrolyzing endogenous substrates in the sludge. The stimulation was greatest with hydrogen, followed by glucose and lactate (not shown). The stimulation was least with acetate. A volatile fatty acid mixture representing the substrates available in landfill leachate was intermediate between H2 and acetate in stimulating arsenate reduction. The pattern follows that anticipated with respect to substrates providing the most interspecies H_2.

A second set of batch experiments evaluated the effect of arsenate concentration on arsenate biotransformation rates with lactate as the electron donating substrate. The results shown in Figure 3 indicate that the arsenate removal rates, which were similar to the arsenite formation rates, have a clear optimum at 2 mM arsenate. The lower rates at lower arsenate concentrations are most likely due to Monod kinetics. The decline in rates at concentrations in excess of 2 mM may reflect toxicity of arsenate or formed arsenite on arsenate reduction. Inhibition studies evaluating the toxicity of arsenate and arsenite to methanogenic activity revealed that arsenate was non-toxic; whereas, arsenite was highly toxic causing a 50% inhibition of methanogenesis as low as 20 μM.

Continuous Columns. Microbial reduction of As(V) sorbed onto activated alumina (AA) was also observed in the continuous-flow experiments operated under anaerobic conditions (Figure 4). The mobilization of arsenic from the AA was greatly stimulated in columns inoculated with anaerobic sludge. The mobilization was also the greatest in column 1, which received the electron donating volatile fatty acid substrate. However significant mobilization of arsenate was also observed in column 2, which did not receive any exogenous electron donor in the leachate. Reduction of arsenate was probably still feasible due to the slow decomposition of sludge. Initially the supply of electron donating substrate was limiting, accounting for a more rapid initial release of arsenic from column 1. During the initial period, effluent concentrations of arsenic reached 600 μg/l or greater. Approximately 80% of the leached arsenic was recovered as arsenite, clearly demonstrating that microbial reduction was the main mechanism of arsenic mobilization (Figure 5). Low amounts of the pentavalent organoarsenic metabolites, methylarsonic acid (MMA^V) and dimethylarsinic acid (DMA^V) were also detected.

After 40 days of operation, the rate of arsenic release from columns 1 and 2 were similar indicating that supply of electron donating substrate was no longer rate limiting. Instead limited bioavailability of sorbed arsenate probably became the rate-determining step. After 190 days, 16% of sorbed arsenate was leached from AA.

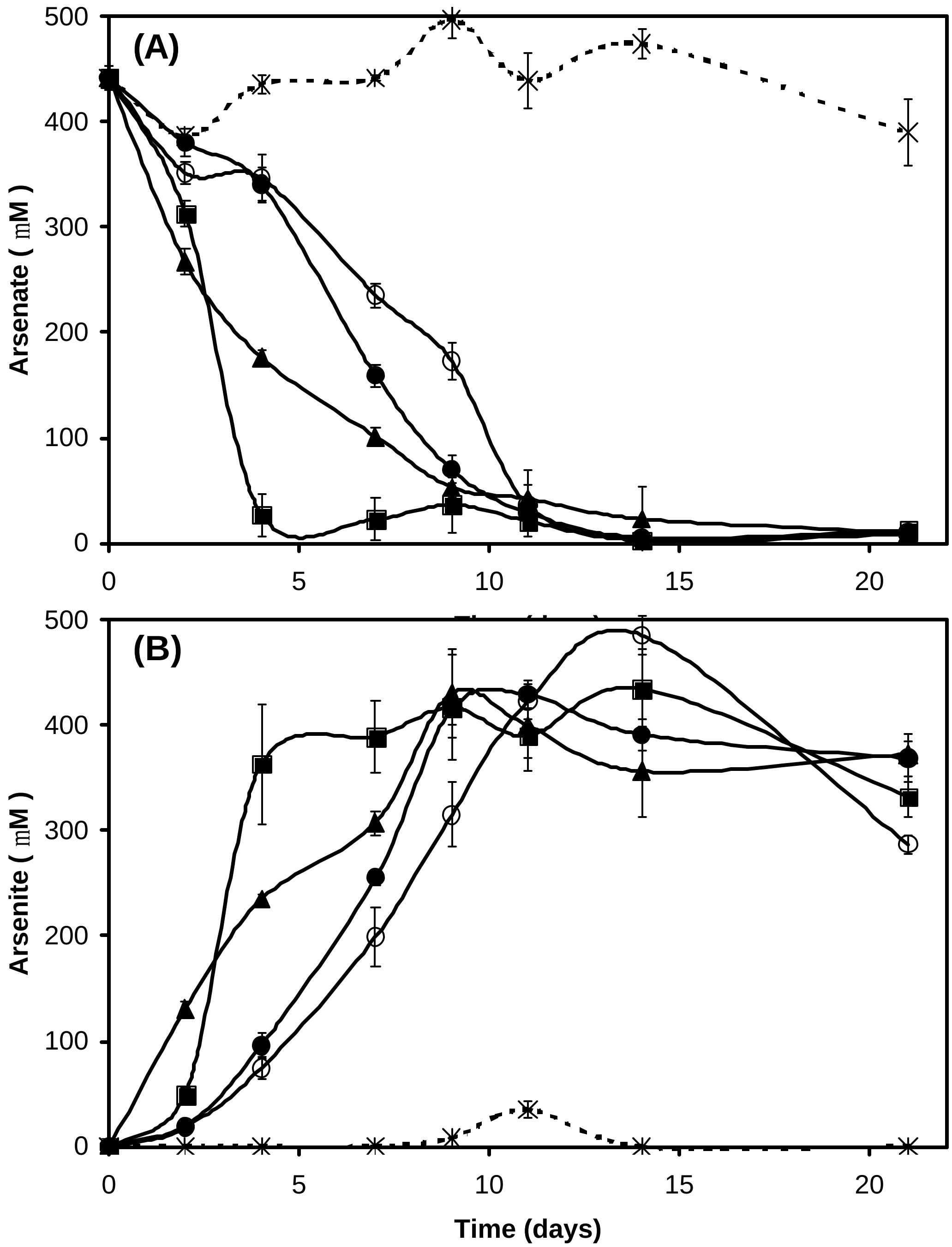

Figure 2. Effect of different electron donating substrates on the time course of arsenate reduction to arsenite in anaerobic granular sludge. **Panel A**. arsenate concentrations. **Panel B**. arsenite concentrations. Legend: ■, hydrogen 0.8 atm; ? , glucose 10 mM; ●, acetate 10 mM; ?, no added substrate, *, killed sludge (autoclaved).

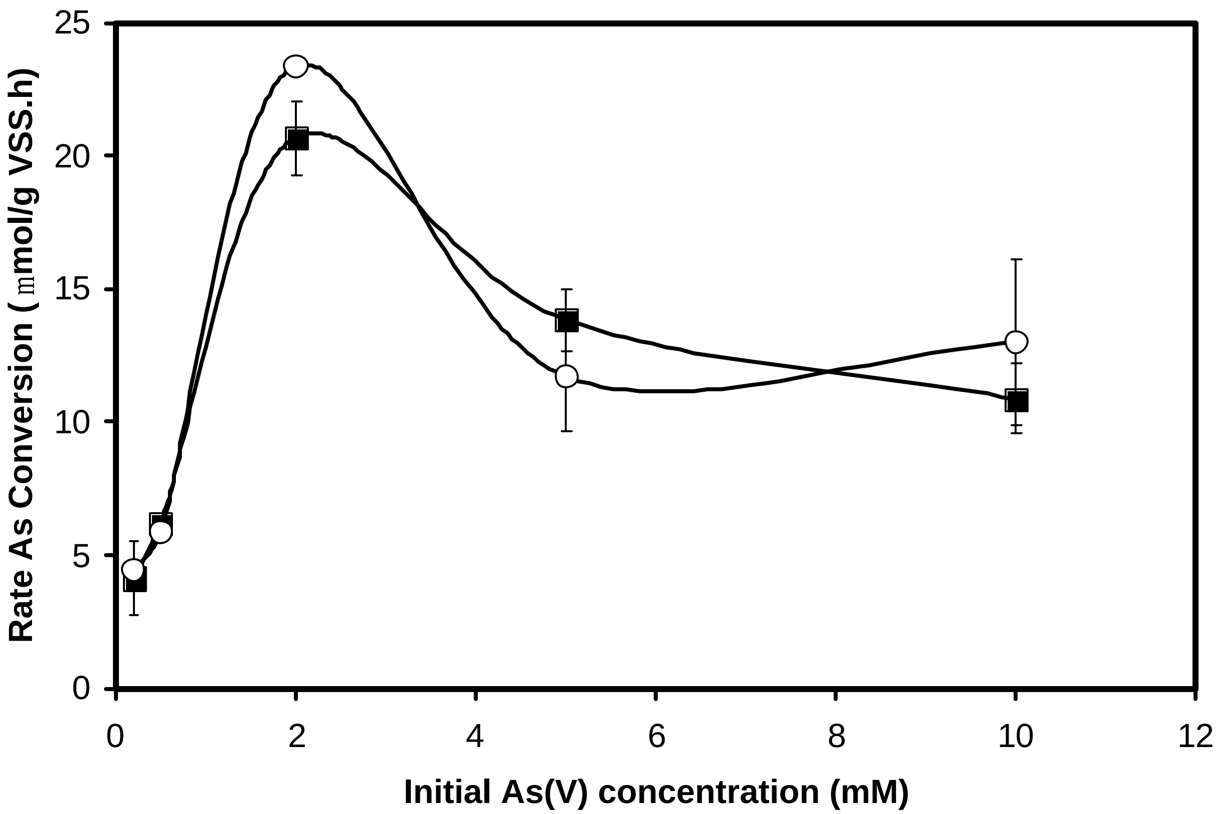

Figure 3. The rate of arsenate reduction to arsenite in anaerobic granular sludge incubated with at variable initial concentrations of arsenate (As(V)) with 10 mM of lactate as electron donor. Legend: ■, arsenate removal rate; O, arsenite formation rate.

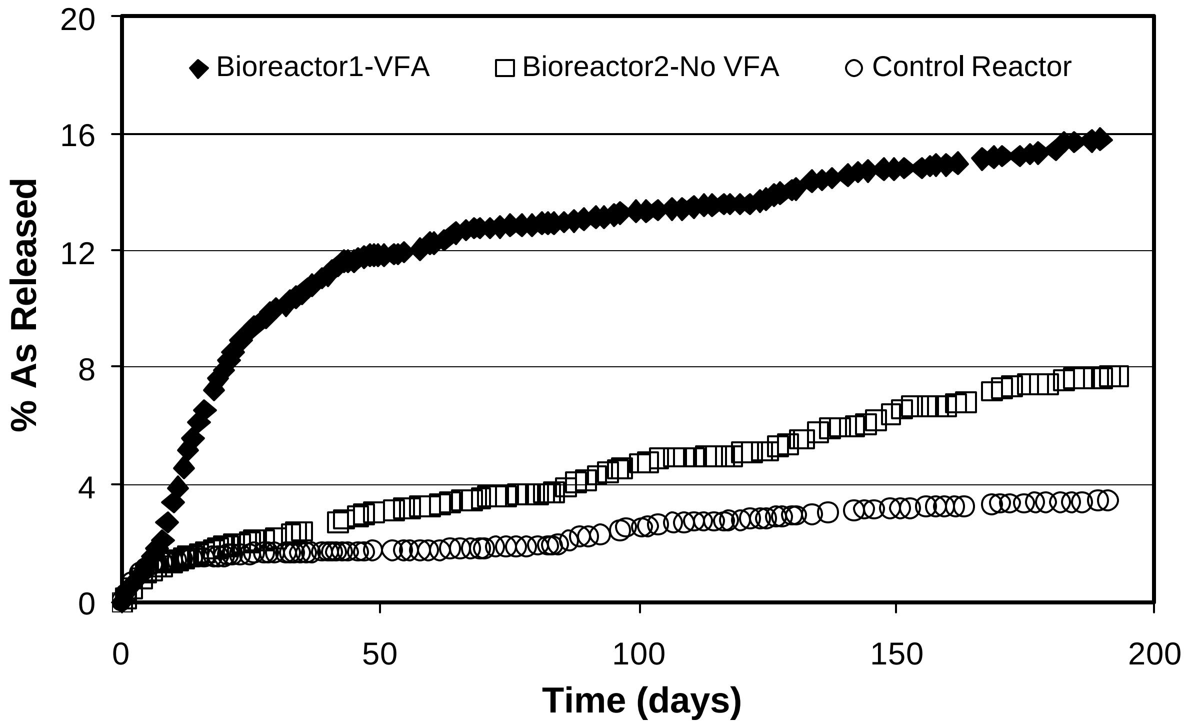

Figure 4. Release of arsenic (As) from activated alumina with sorbed arsenate in anaerobic columns percolated with model landfill leachate. Bioreactor 1 and 2 were inoculated with anaerobic sludge, but only bioreactor 1 was supplied with organic substrate, volatile fatty acid mixture (VFA). The control reactor was not inoculated.

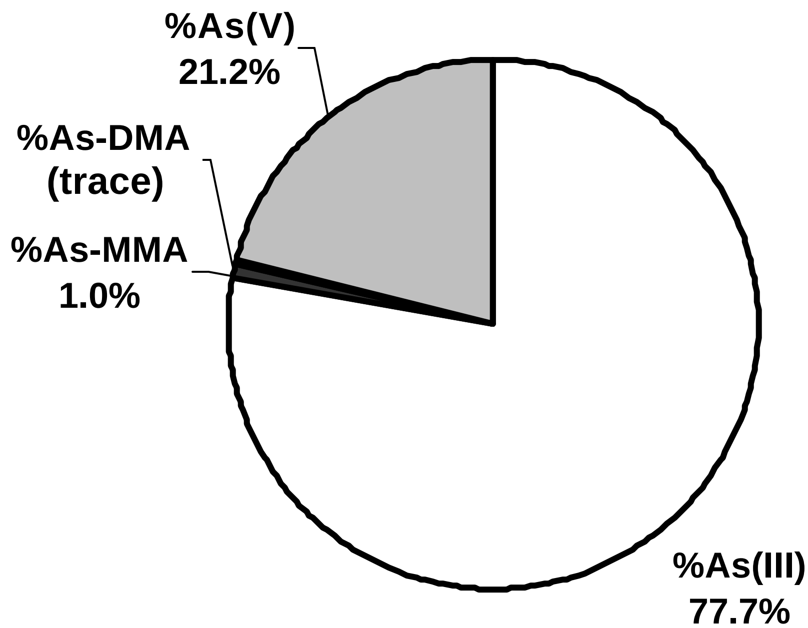

Figure 5. Arsenic speciation determined in the effluent of the anaerobic reactor (column 1) fed with a simulated landfill leachate containing organic substrates. Results shown are the average of the second month of reactor operation.

D. Conclusions

The results obtained indicate that extensive reduction and mobilization of As(V) sorbed onto AA should be expected if this spent sorbent is disposed of in municipal landfills. This finding provides strong evidence to support the importance of revising the current rule of the US-EPA that classifies As-bearing AA as a non-hazardous waste. Implied in this statement is a call to improve the protocol currently applied to determine the toxic characteristics of As-bearing waste materials such as spent AA, which neglects the impact of microbial processes.

The results also demonstrate that the mobilization of arsenate from spent sorbents can be minimized by preventing contact with microbial substrates. A practical outcome could be separate disposal of As-laden drinking water residuals in landfill cells lacking organic wastes.

Acknowledgements

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