Proceedings of the 9ICEG
9th International Congress on Environmental Geotechnics
25-28 June, 2023 | Chania, Greece
© Authors: All rights reserved, 2023
https://doi.org/10.53243/ICEG2023-301

Abiotic and microbial remediation of groundwater impacted by metalloids

H.M.I.P. Kulasekara[1], D.S. Rajapakshe[1], T. Quary[1], Y. Zhang[2], and C. Papelis[2,3]

[1]Graduate student, New Mexico State University, Las Cruces, United States of America, email: ishani@nmsu.edu

[2]Professor, New Mexico State University, Las Cruces, United States of America, email: lpapelis@nmsu.edu

[3]Director, Carlsbad Environmental Monitoring & Research Center, Carlsbad, United States of America

ABSTRACT

The release of metalloids such as selenium (Se), arsenic (As), and chromium (Cr) into the environment from both natural and anthropogenic sources threatens aquatic systems. These elements are redox active and their mobility and environmental impact depend strongly on their oxidation state. The removal of these oxyanions was investigated by a combination of abiotic and microbial processes. Abiotic processes focused on sorption on porous sorbents, zeolites and biochar. These sorbents were modified by iron coatings precipitated in situ. Microbial processes were carried out with either unmodified or iron-modified zeolite-filled columns with anaerobic sludge as microbial inoculum for the columns. Lactate served as an electron donor and the residence time was 100 minutes. In selenium experiments, regardless of selenium speciation, maximum selenium removal was 99% for Se concentration of 790 μg/L. Based on 16S rRNA sequencing, *Veillonella, Bacteroides*, and *Escherichia* were the most dominant selenium-reducers in biofilm communities. In batch experiments, for Cr concentration of 250 μg/L, 0.01 M $NaNO_3$ ionic strength, and sorbent concentration of 5 g/L, Cr removal by iron-coated biochar was 99.8%. The Cr removal using unmodified biochar was 95% after 5 days of equilibration time. Microbial removal of chromate in zeolite columns was approximately 60-70%. Arsenate was more efficiently removed compared to arsenite. In all cases, in addition to the effective removal of the metalloids of arsenic, chromium, and selenium, other oxyanions, such as nitrate and sulphate, were effectively removed in columns with microbial activity, although the presence of these anions dramatically affected the makeup of the microbial community.

Keywords: Metalloid oxyanions, porous sorbents, microbial reduction

1 INTRODUCTION

The toxic effect of selenium, chromium, and arsenic in water bodies has been identified as an environmental threat (Hamilton, 2004; Mohan & Pittman, 2007). It is a challenge to treat water contaminated with these metalloids because of their complex geochemistry. Selenium has six different oxidation states, including -II, 0, +IV, and +VI. Of these, +IV and +VI are common in aquatic environments as the selenite and selenate oxyanions, respectively (Lenz & Lens, 2009). Chromium can exist in nine oxidation states, with hexavalent chromium (Cr^{VI}) in the chromate oxyanion being the predominant form in water (McNeill et al., 2012). The most common forms of arsenic in water are the oxyanions arsenite (As^{III}) and arsenate (As^{V}) (Boddu et al., 2008).

Because of adverse environmental effects, the U.S. Environmental Protection Agency (EPA) has set maximum selenium, chromium, and arsenic concentrations in drinking water at 50, 100, and 10 μg/L, respectively. Anthropogenic selenium and arsenic contamination is generally caused by mining, coal combustion, oil refineries, and agriculture (Smedley & Kinniburgh, 2002; Zhang et al., 2019). Chromium contamination can be caused by leather tanning, wood treatment, and metal plating (McNeill et al., 2012).

Current treatment technologies can be classified as physical, chemical, or biological. Physicochemical processes such as chemical precipitation, adsorption, and ion exchange are oxidation-state specific.

For example, these treatment methods work best for selenite removal, while selenate removal is minimal. Moreover, they are not always economical (Kashiwa et al., 2000). However, adsorption methods could be more effective following surface modification.

Due to their abundance, cost-effectiveness, high porosity, thermal stability, and high surface area, zeolites have been used over the past decades as adsorbents for cations in water treatment. Different surface modifications, such as modification with Fe^{3+}, hexadecyltrimethylammonium bromide, and tetramethylammonium bromide have been employed to increase affinity for anions (Suhartana et al., 2017). Biochar is another environmentally friendly adsorbent used to remove micro-pollutants from water. Biochar production involves less energy and cost compared to activated carbon production (Choudhary and Paul., 2018). Modification of biochar shows promising ability to remove chromate. In this study, iron coating on zeolite and biochar surfaces was used to modify these sorbents. Iron oxides are remarkable adsorbents; however, they cannot be used directly in water treatment because they have low permeability and are difficult to separate from treated water. As an alternative, iron oxide materials can be used as coatings on solid supports (Siddiqui & Chaudhry, 2017). Reduction methods are more attractive as they can be used for the removal of oxyanions regardless of oxidation state (Larry et al., 2005). Biological removal methods are more attractive because of cost-effectiveness and eco-friendliness (Santos et al., 2015). For example, biological selenium removal is a viable alternative in industrial wastewater treatment because selenium recovery options are available, leading to partial recovery of treatment costs (Soda et al., 2011).

Oxyanion removal by biological reduction has been successfully demonstrated with different types of bioreactors and configurations, such as up-flow anaerobic sludge blanket (UASB) reactors, biofilm reactors, membrane biofilm reactors, suspended sludge growth reactors, or biofilters (Nancharaiah & Lens, 2015). A UASB type reactor seeded with granular sludge could reduce the Se level to less than 100 μg/L with acetate as electron donor (Soda et al., 2011). In another study, Cr^{VI} was reduced from 27 to 5 mg/L (Chen & Hao, 1997). In attached growth reactors, commonly used media are granular activated carbon, sand, rock, ceramic, and plastic. The media can be used for both filtration and as a point of attachment for microorganisms. The current study focuses on developing a simultaneous adsorption and biological reduction treatment process using iron-modified zeolites and biochar as sorbents.

2 MATERIALS AND METHODS

2.1 Adsorbent preparation and modification

The natural clinoptilolite zeolite, obtained from St. Cloud, New Mexico, was chemically modified by pre-treatment with sodium, followed by iron coating. The final product was classified as a sodium pre-treated, iron-modified zeolite (SPIMZ). Iron coating greatly increases the affinity of anions for the zeolite surface. The details of the treatment process are described elsewhere (Halalsheh, 2019). Biochar was coated with iron oxides using a process similar to the zeolite coating.

2.2 Adsorbent characterization

The characterization of zeolites and biochar included morphology and elemental composition using S-3400N II scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) spectroscopy, specific surface area and pore size distribution using nitrogen adsorption and an ASAP 2050 micropore analyzer (Micromeritrics USA) at 77 K and the Brunauer, Emmett, and Teller (BET) and Barrett-Joyner-Halenda (BJH) models, and mineralogy by x-ray diffraction (XRD) using Cu K_α radiation (λ = 1.540 nm) and a MiniFlex II, PANalytical Empyrean X-Ray Diffractometer.

2.3 Solution composition

Oxyanion concentrations used in these experiments were 790 μg/L for Se (selenite or selenate), 750 μg/L for As (arsenite or arsenate), and 250 μg/L for Cr (chromate). The ionic strength was adjusted using sodium nitrate ($NaNO_3$). The solution pH was adjusted using sodium hydroxide (NaOH) or nitric acid (HNO_3). For the microbial experiments, 2.24 g/L of lactate was used as the electron donor. Nitrogen, phosphorous, yeast, vitamins, and trace metals were also added to the medium. The pH was adjusted to 7.5 using sodium hydroxide.

2.4 Experimental Design

For the batch experiments, a 60 mL solution of 250 mg/L chromate in 0.01 M M $NaNO_3$ containing 0.30 g biochar (solid concentration 5 g/L) was mixed using a magnetic stirrer at room temperature. The pH was monitored during the experiments and was adjusted, as needed, using NaOH or HNO_3. Kinetic experiments were also conducted to determine appropriate equilibration times for the batch experiments.

Column experiments were run with 300 min empty bed contact time (EBCT). The columns were packed with either untreated or treated zeolites (SPIMZ). The column composition is shown in **Table 1**. Approximately 200 mL of anaerobic sludge from the Las Cruces, New Mexico, Wastewater Treatment Plant was added as microbial inoculum, layer-by-layer, during packing of the column. The fully packed columns were positioned vertically. The feeding solution was pumped upwards from the bottom of the column and effluent samples were collected from the top of the column.

Table 1. *Column configuration for microbial reduction experiments*

Column Notation	Bed Composition	Metalloid Speciation
A	80% Natural Zeolite + 20% Modified Zeolite + Anaerobic Microbes	Selenate
B	Natural Zeolite + Anaerobic Microbes	
C	80% Natural Zeolite + 20% Modified Zeolite + Anaerobic Microbes	Selenite
D	Natural Zeolite + Anaerobic Microbes	
X	Natural Zeolite + Anaerobic Microbes	Chromate

Samples from each biofilter were collected twice per week. The samples were filtered through 0.45 µm filters to exclude biomass and 10 mL of the filtrate were acidified by adding 100 µL of analytical grade nitric acid before analysis. Metalloid concentrations in the filtrate were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.5 DNA extraction method and microbial community analysis

Bacterial community analysis was carried out to identify the species of microorganisms responsible for the metalloid reduction. The DNA extraction process was performed using DNeasy PowerSoil Kit (Qiagen, USA). Zeolite samples were collected approximately one inch inside from each top and bottom end of the columns to determine the availability of microorganisms throughout each column. After DNA extraction, the quantity and quality of DNA were analysed using the microplate spectrophotometer with Take3™ multi-volume plate (Epoch, Bio Tek, USA) before 16S rRNA sequencing.

Bacterial community analysis was performed via next generation sequencing in MiSeq Illumina platform. Amplicon sequencing of the V4 region of the 16S rRNA gene was performed with the barcoded primer set 515f/806r designed by (Caporaso et al. 2011) and following the protocol by the Earth Microbiome Project (EMP) for the library preparation. PCR amplifications for each sample were performed in duplicate, then pooled and quantified using an accublue kit. A no template control sample was included during the library preparation as a control for extraneous nucleic acid contamination. 240 ng of DNA per sample were pooled and then cleaned using QIA quick PCR purification kit (QIAGEN). The pool was quantified using the qubit and the DNA pool was diluted to a final concentration of 4 nM then denatured and diluted to a final concentration of 4 pM with a 25% of PhiX. Finally, the DNA library was loaded in the MiSeq Illumina and run using the version 2 module, 2x250 paired end.

3 RESULTS AND DISCUSSION

3.1 Adsorbent characterization

The distinct physical appearance of unmodified and sodium pre-treated iron-modified zeolites can be seen in Figure 1. The brownish yellow colour of SPIMZ is consistent with the ferric hydroxide coating.



Figure 1. *Unmodified and modified zeolites*

The elemental composition, by mass, of the natural zeolite and SPIMZ is shown in **Table 2**. As expected, silicon (Si), aluminium (Al), and oxygen (O) are the main components of this aluminosilicate mineral framework, which is formed by interconnected aluminium and silicon tetrahedra coordinated through shared oxygen atoms.

Table 2. *Elemental composition of unmodified and modified sorbents*

Sorbent type	O	Mg	Al	Si	K	Fe	Na	Ca	C	Other
Zeolite	41.0	0.8	7.4	39.8	2.5	1.1	0.3	3.3	-	3.8
SPIMZ	40.9	0.9	7.6	40.7	2.5	4.0	0.8	2.7	-	-
Biochar	6.0	0.2	0.1	0.2	0.4	0.2	-	0.9	91.9	0.2
IMB	5.3	0.1	0.1	0.3	0.5	3.3	-	0.7	88.7	1.0

The sodium pre-treatment and iron coating processes are consistent with the SEM/EDX results shown in Table 2. The SPIMZ sample had lower percentages of Ca and higher percentages of Na and Fe, compared to the unmodified, natural zeolite sample. Similarly, the Fe percentage in the iron-modified biochar (IMB) was approximately 15 times higher compared to the unmodified biochar. In addition, elemental maps generated by EDX (not shown) were consistent with uniform distribution of the iron oxide coating on the sorbents.

The XRD spectra of natural zeolite and SPIMZ are shown in Figure 2. The presence of clinoptilolite is consistent with peaks at 2θ of 22° 23°, and 28° (Han et al., 2009). Compared to the natural zeolite, SPIMZ contains the peaks of ferric oxide at 2θ of 27°, 32.5° and 40° (Han et al., 2009; Popic et al., 2011).

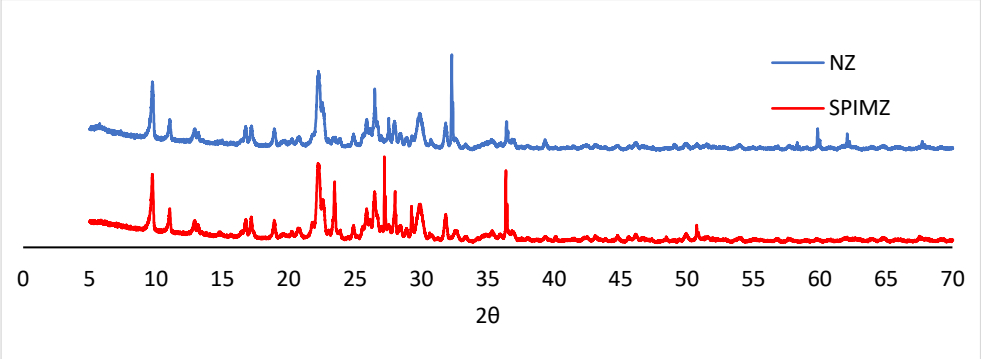


Figure 2. *XRD spectrum of natural zeolite (NZ) and SPIMZ*

The adsorption-desorption isotherms with N_2 gas on zeolites and biochar show type IV isotherms with type H4 hysteresis loops, consistent with narrow slit-like pores, particles with internal voids of irregular shape and broad size distribution, and hollow spheres with walls composed of ordered mesoporous silica (Figure 3). Compared to the natural form, modified adsorbents show a slightly smaller average pore width and higher BET surface area (natural 9.01 m^2g; modified 9.62 m^2g). Most of the surface area of both adsorbent types was contributed by mesopores (width of 2- 50 nm). The iron coating had an effect on both the specific surface area and pore size distribution of the sorbents.

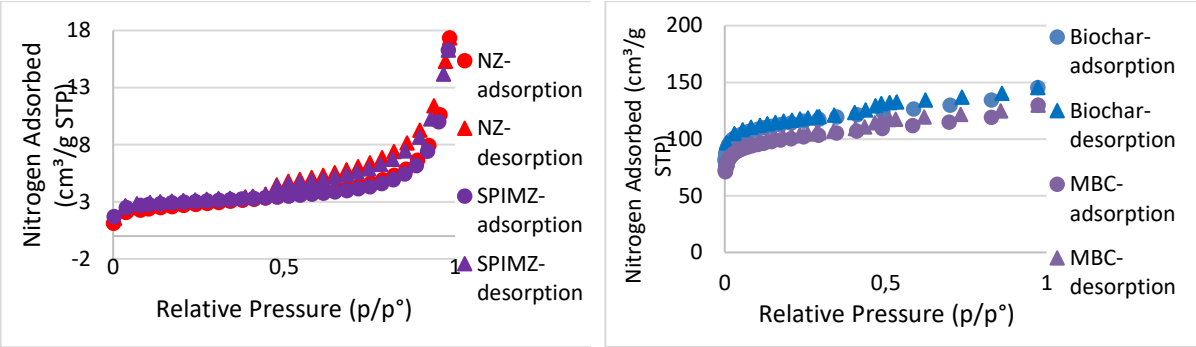


Figure 3. *Nitrogen gas adsorption/desorption isotherms of zeolite and biochar adsorbents*

3.2 Metalloid removal

3.2.1 Microbial reduction experiments

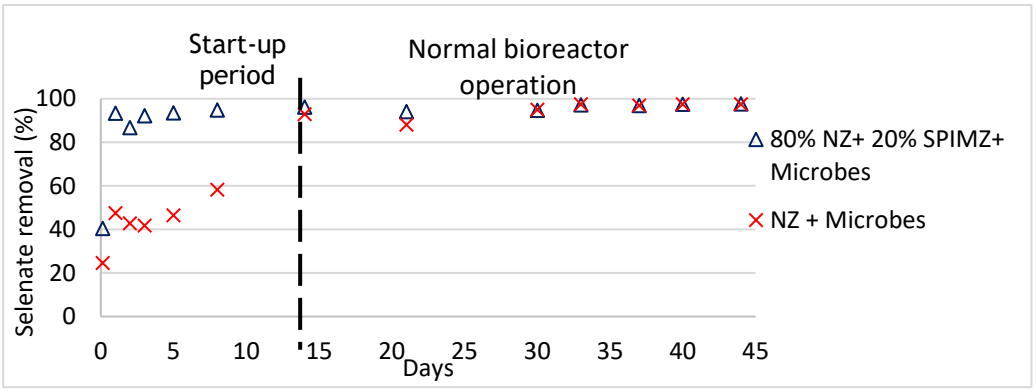


Figure 4. *Selenate removal efficiency vs. time in a bioreactor*

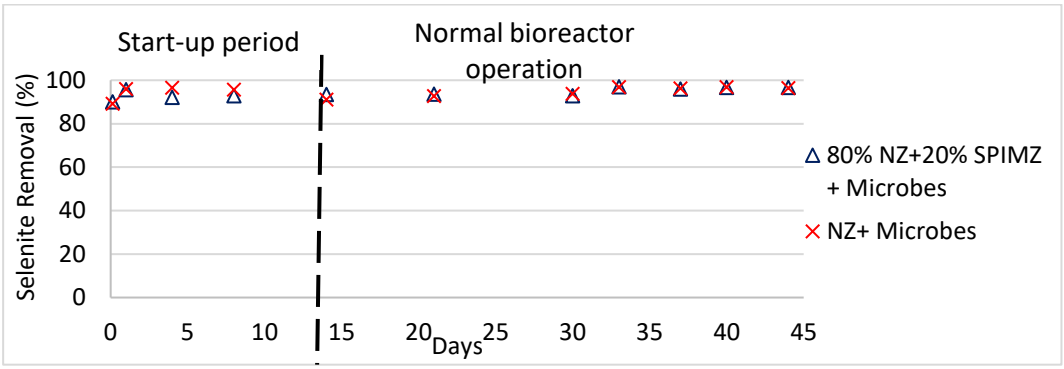


Figure 5. *Selenite removal efficiency vs. time in a bioreactor*

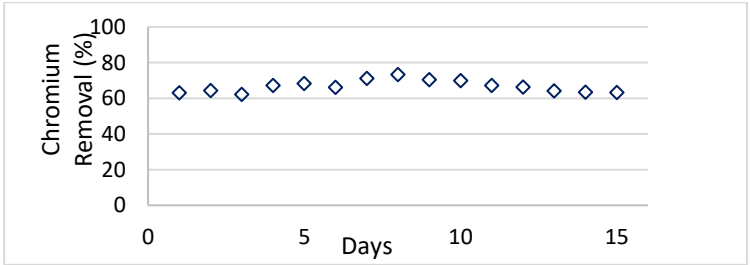


Figure 6. *Chromate removal in a bioreactor*

Figure 4 and Figure 5 show the selenium removal efficiencies for each column as a function of time. During the first 14 days, there was a higher removal of selenite compared to selenate, although the

differences in the columns that contained SPIMZ were minimal. This suggests that during the start-up phase the dominant removal mechanism is adsorption on the iron oxide coating. This trend is consistent with prior studies reporting much higher affinity of selenite for iron oxides compared to selenate (Hayes et al., 1988; Jevtic et al., 2014; Yigit & Tozum, 2012). Selenite is thought to form stronger, inner-sphere coordination complexes on iron oxide surfaces, rather than outer-sphere ion pair complexes, the presumed sorption mechanism for selenate (Hayes et al., 1988; Payne et al., 2013). In addition, size exclusion effects might contribute to the lower selenate uptake compared to selenite. The ionic radii for selenite and selenate are 2.39 Å and 2.49 Å, respectively (Cramer & Buscher, 1998; Vlaev et al., 2006). The smaller size selenite anions might be able to gain access to the internal micropores within the zeolites more readily than selenate (Yigit & Tozum, 2012).

During the start-up period, maximum selenate removal (34%) was observed with coated zeolite, twice as high compared to the results with natural zeolite, as expected. Maximum selenite removal was 89% in the column with modified zeolite. These results are consistent with previously reported results (Jevtic et al., 2014; Suhartana et al., 2017). It has been reported that Se^{VI} adsorption proceeds via the formation of Se–O–Fe bonds, whereas in the case of Se^{IV} it seems likely that not only Se–O–Fe bonds but also Se–O–Si bonds are formed during adsorption (Jevtic et al., 2014). Iron oxide coating has been previously identified as a factor in increasing total surface groups of different adsorbents, such as pumice and slag. Lower pH is known to favour anion sorption on amphoteric surfaces, given the increased attraction between the increasingly positively charged surface and the negatively charged anions (Yigit & Tozum, 2012). Note that the pH_{PZC} of clinoptilolite is around 4-5, whereas iron oxides and hydroxides have a pH_{PZC} between 7 and 8.5. However, strongly binding anions, such as selenite may overcome electrostatic repulsions through strong surface complexation-ligand exchange reactions, in which –OH groups on iron oxide surfaces are replaced by Se anions (Gu et al., 1994; Kitis et al., 2007; Masscheleyn & Patrick, 1993). After 14 days, regardless of the bed composition and Se speciation, Se removal reached approximately 99% (Figure 4 and Figure 5). This behaviour suggests that a specialized Se reducing microbial population developed in the columns. These results also suggest that the dominant removal mechanism in the early stages is sorption, but later microbial reduction becomes the dominant Se removal mechanism. Still, the chemical modification appears to enhance Se removal.

In the beginning, the microbial reduction is low due to aerobic conditions still persisting inside the columns during transition to anaerobic conditions. It should be noted that microbial selenium reduction can only occur under anaerobic conditions. Accumulation of red elemental selenium nanospheres could be observed inside the tubing and the red coloration in solids was assumed to be elemental selenium (Hageman et al., 2013; Nancharaiah & Lens, 2015). The rapid appearance of elemental selenium suggests that selenium reducing bacteria (SeRB) are ubiquitous and metabolically active in the anaerobic sludge and they were enriched in the zeolite column leading to the reduction of selenite and selenate.

The removal of Cr^{VI} (chromate) in a bioreactor as a function of time is shown in Figure 6. Chromate can be reduced to either elemental chromium or the much less mobile and less toxic chromium cation that precipitates or forms immobile, strong complexes on mineral surfaces. Chromium removal ranged between 60 and 80%. The initial chromate concentration was 250 μg/L (as chromium). Other competitive anions, including chloride, sulphate, and nitrate, were also present to simulate groundwater from a contaminated site. Even under the lowest removal of 60%, this effluent would be at or below the maximum contaminant limit for Cr, 100 μg/L. In addition, at least 85% of both nitrate and sulphate were removed in the bioreactor. Removal of these two anions is significant, not only because of their potentially adverse environmental effects, but also because they possibly interfere with Cr^{VI} reduction.

3.2.2 Abiotic experiments

The uptake of chromate as a function of time by unmodified and iron-coated biochar is shown in Figure 7. Although quantitative removal of chromate from the aqueous solution was eventually achieved with both sorbents, the reaction was approximately 5 times faster with the iron-coated biochar compared to the unmodified biochar, 20 and 100 hours, respectively. The iron coating of the biochar results in a more positively charged surface that favours sorption of the negatively charged chromate anion, compared to the unmodified biochar. Without modification, the carboxylic groups on the biochar would become

increasingly negatively charged with increasing pH as the carboxylic groups are being deprotonated (Sun Y et al., 2019).

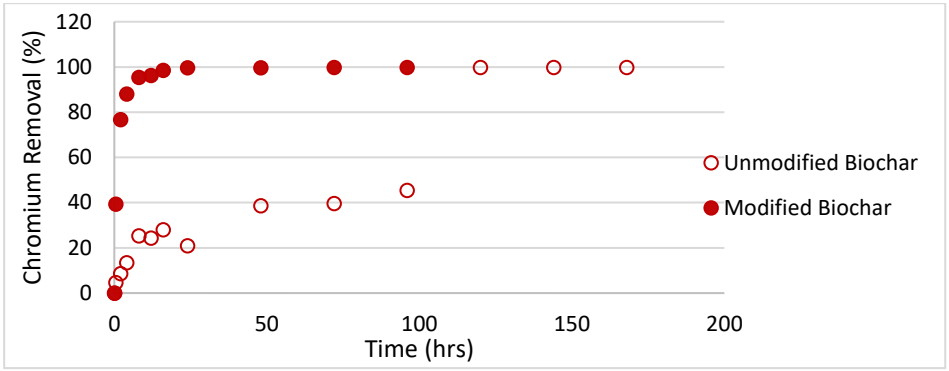


Figure 7. *Chromate uptake as a function of time in batch reactors*

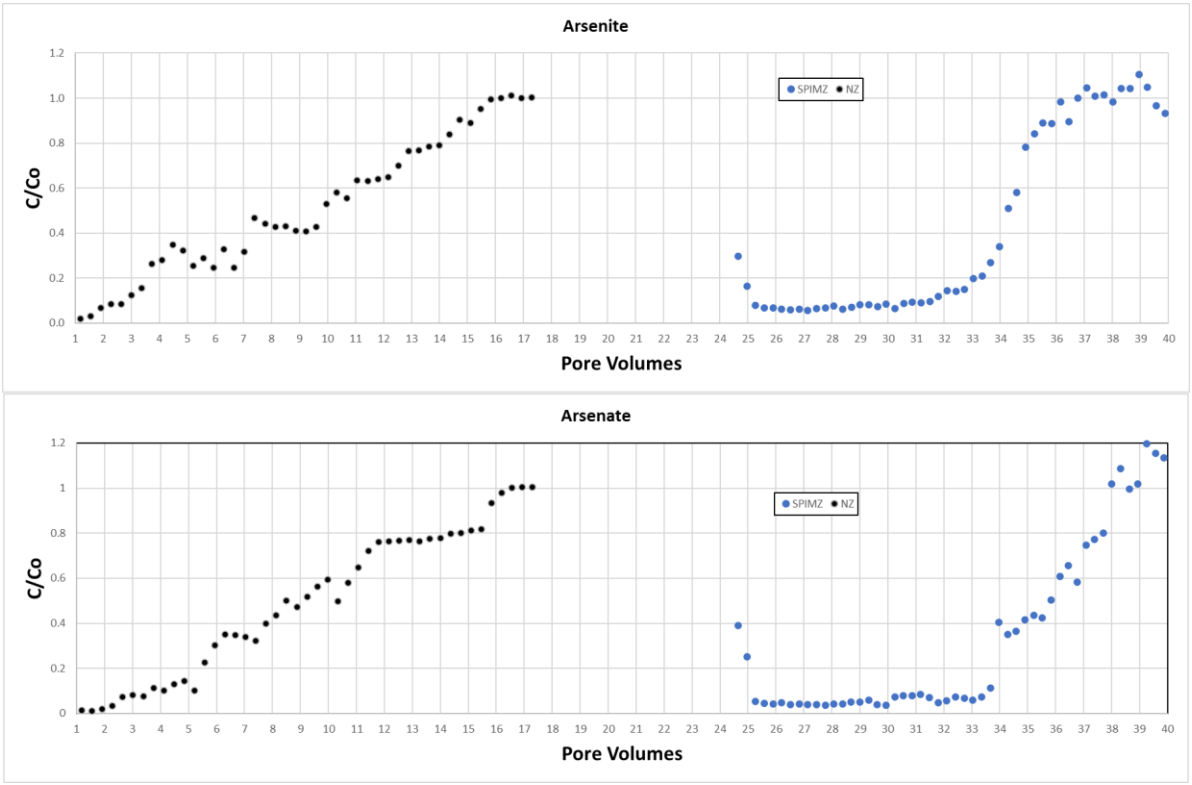


Figure 8. *Arsenic breakthrough in unmodified and modified zeolite columns*

The breakthrough curves for arsenite (top) and arsenate (bottom) are shown in Figure 8. Breakthrough curves are shown for both unmodified zeolites (black symbols) and modified zeolites, SPIMZ (blue symbols). The behaviour of the two arsenic oxyanions is similar, although the oxidized form, As^{V}, (arsenate), appears to be retarded slightly more compared to the reduced form, As^{III}, (arsenite), indicating a stronger affinity of arsenate for these surfaces compared to arsenite. In contrast to selenium, the oxidized As oxyanion is both less mobile and less toxic compared to the reduced form. The most important observation from Figure 8, however, is that the retardation of As increases by a factor of approximately 5 in the modified zeolite columns compared to the unmodified zeolite columns, even though modified zeolites accounted for only 20% of the total sorbent mass. The results clearly demonstrate the benefit of zeolite modification for anion retention.

3.3 Microbial community analysis

This study reveals that anaerobic sludge from the Las Cruces, New Mexico, wastewater treatment plant contains numerous types of bacteria that can play an active role in reducing oxyanion forming elements.

Bacterial communities in the bioreactors display phylogenetic diversity within three major phyla, Firmicutes, Bacteroidota, and Proteobacteria, of the bacterial domain.

Among the dominant genera *Veillonella* (8%-12%) and *Megasphaera* (13% - 22%), are the most abundant genera in selenium reducing bioreactors. However, the latter have not been previously reported as selenium reducing bacteria. These genera belong to the family Veillonellaceae, the order Selenomonadales class of negativicutes, and the phylum of Firmicutes. *Megasphaera* and *Veillonella* are the only species belonging to this family with the lactate fermentation capacity (Marchandin & JUmas-Bilal, 2014), which is consistent with the experimental conditions of this research, as lactate was used as the organic source. Followed by *Veillonella, bacteroid, Escherichia-shigella* and *desulfovibrio* are the most dominant genera among the previously identified selenium reducers (**Figure 9**). There is no significant difference among the microbial composition of the columns either based on selenium speciation or sorbent material composition.

Including these genera, most of the microorganisms present in the columns are gram-negative. Gram-negative microorganisms have a typical gram-negative cell wall structure with an outer membrane that suggests the importance of having an outer membrane that makes periplasm, the cellular compartment where selenium respiratory enzymes have been identified (C., 2021). Additionally, almost all microorganisms present among the dominant genera belong to gut microflora, something that should not be surprising as sludge from a secondary digester was used as anaerobic microbial inoculum. The gut microorganisms are capable to endure selenium as they are exposed to selenium because of the consumption of selenium, a micronutrient, by humans. Moreover, the relationship between selenium and gut microbiota has been studied in the past decade and about 25% of gut bacteria contain selenoproteins (Ferreira et al., 2021).

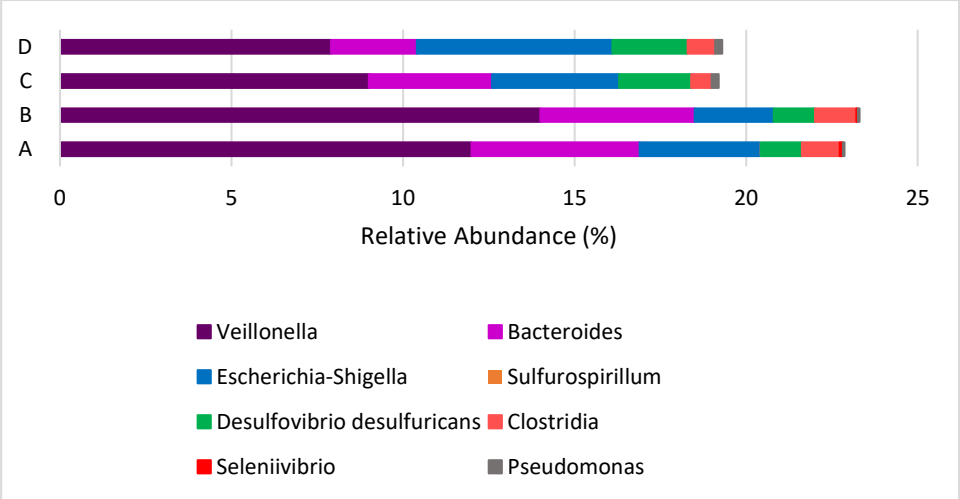


Figure 9. *Most dominant genera in selenium and arsenic reducing columns*

4 CONCLUSIONS

Adsorption combined with a microbial reduction system is a promising method for treating selenium and other oxyanions while generating high-quality effluent. The presence of an iron oxide coating increases the sorption capacity of zeolites and biochar for oxyanions. In microbial selenium reduction columns, after 14 days, as the biofilm developed, selenium reduction in all columns reached approximately 99%. Regardless of the initial selenium concentration, all four columns generated effluents that are well below the permissible level (40 μg/L, WHO). Within the biological reactors, zeolites not only act as adsorbents, but also provide a comparably higher surface area to grow microbes and act as a filter media for microbes and suspended solids. Based on 16S rRNA sequencing, *Veillonella, Bacteroides,* and *Escherichia* were the most dominant selenium-reducers in biofilm communities.

For initial chromate concentration of 250 μg/L, 0.01 M $NaNO_3$ ionic strength, and adsorbent concentration of 5 g/L, chromate removal by iron-coated biochar was 99.8%, reaching equilibrium in 24 hours. In comparison, unmodified biochar showed 95% removal within 5 days of equilibration time. Microbial removal of chromate in zeolite columns was approximately 60-70%. As expected, arsenate

was more efficiently removed compared to arsenite in modified-zeolite columns. In all cases, in addition to the effective removal of the metalloids of arsenic, chromium, and selenium, other oxyanions, such as nitrate and sulphate, were effectively removed in columns with microbial activity, although the presence of these competing anions dramatically affected the makeup of the microbial community present.

5 ACKNOWLEDGEMENTS

This material is based upon work primarily supported by the Engineering Research Center Program of the National Science Foundation under NSF Cooperative Agreement No. EEC-1449501. Any opinions, findings, and conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the National Science Foundation.

REFERENCES

Boddu, V. M., Abburi, K., Talbott, J. L., Smith, E. D., & Haasch, R. (2008). Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent. *Water Research*, *42*(3), 633-642. https://doi.org/10.1016/j.watres.2007.08.014

C., S. L. (2021). Selenium respiration in anaerobic bacteria: Does energy generation pay off? *Journal of Inorganic Biochemistry*, *222*.

Chen, J. M., & Hao, O. J. (1997). Biological removal of aqueous hexavalent chromium. *Journal of Chemical Technology and Biotechnology*, *69*(1), 70-76. https://doi.org/10.1002/(sici)1097-4660(199705)69:1<70::aid-jctb665>3.0.co;2-4

Cramer, C., & Buscher, M. (1998). Complete conductivity spectra of fast ion conducting silver iodide silver selenate glasses. *Solid State Ionics*, *105*(1-4), 109-120. https://doi.org/10.1016/s0167-2738(97)00456-6

Ferreira, R. L. U., Sena-Evangelista, K. C. M., De Azevedo, E. P., Pinheiro, F. I., Cobucci, R. N., & Pedrosa, L. F. C. (2021). Selenium in Human Health and Gut Microflora: Bioavailability of Selenocompounds and Relationship With Diseases. *Frontiers in Nutrition*, *8*, Article 685317. https://doi.org/10.3389/fnut.2021.685317

Gu, B. H., Schmitt, J., Chen, Z. H., Liang, L. Y., & McCarthy, J. F. (1994). ADSORPTION AND DESORPTION OF NATURAL ORGANIC-MATTER ON IRON-OXIDE - MECHANISMS AND MODELS. *Environmental Science & Technology*, *28*(1), 38-46. https://doi.org/10.1021/es00050a007

Hageman, S. P. W., van der Weijden, R. D., Weijma, J., & Buisman, C. J. N. (2013). Microbiological selenate to selenite conversion for selenium removal. *Water Research*, *47*(7), 2118-2128. https://doi.org/10.1016/j.watres.2013.01.012

Halalsheh, N. (2019). *Effect of Geochemical Conditions and Microbial Activity on Selenium Oxyanion Transport in Iron-Coated Porous Media* New Mexico State University].

Hamilton, S. J. (2004). Review of selenium toxicity in the aquatic food chain. *Science of the Total Environment*, *326*(1-3), 1-31. https://doi.org/10.1016/j.scitotenv.2004.01.019

Han, R. P., Zou, L. N., Zhao, X., Xu, Y. F., Xu, F., Li, Y. L., & Wang, Y. (2009). Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper(II) from solution in fixed bed column. *Chemical Engineering Journal*, *149*(1-3), 123-131. https://doi.org/10.1016/j.cej.2008.10.015

Hayes, K. F., Papelis, C., & Leckie, J. O. (1988). Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces [Article]. *Journal of Colloid and Interface Science*, *125*(2), 717-726. https://doi.org/10.1016/0021-9797(88)90039-2

Jevtic, S., Arcon, I., Recnik, A., Babic, B., Mazaj, M., Pavlovic, J., Matijasevic, D., Niksic, M., & Rajic, N. (2014). The iron(III)-modified natural zeolitic tuff as an adsorbent and carrier for selenium oxyanions. *Microporous and Mesoporous Materials*, *197*, 92-100. https://doi.org/10.1016/j.micromeso.2014.06.008

Kashiwa, M., Nishimoto, S., Takahashi, K., Ike, M., & Fujita, M. (2000). Factors affecting soluble selenium removal by a selenate-reducing bacterium Bacillus sp SF-1. *Journal of Bioscience and Bioengineering*, *89*(6), 528-533. https://doi.org/10.1016/s1389-1723(00)80051-1

Kitis, M., Kaplan, S. S., Karakaya, E., Yigit, N. O., & Civelekoglu, G. (2007). Adsorption of natural organic matter from waters by iron coated pumice. *Chemosphere*, *66*(1), 130-138. https://doi.org/10.1016/j.chemosphere.2006.05.002

Larry, T., Jay, M., Helen, J., Eric, D., & Andy, H. (2005). Removal of Selenium Oxyanions from Mine Waters Utilizing Elemental Iron and Galvanically Coupled Metals. In.

Lenz, M., & Lens, P. N. L. (2009). The essential toxin: The changing perception of selenium in environmental sciences. *Science of the Total Environment*, *407*(12), 3620-3633. https://doi.org/10.1016/j.scitotenv.2008.07.056

Marchandin, H., & JUmas-Bilal, E. (2014). The Family Veillonellaceae. In E. Rosenberg (Ed.), *The Prokaryotes-Firmicutes and Tenericutes* (pp. 21). Springer.

Masscheleyn, P. H., & Patrick, W. H. (1993). Biogeochemical Processes Affecting Selenium Cycling in Wetlands. *Environmental Toxicology and Chemistry*, *12*(12), 2235-2243. <Go to ISI>://A1993MG94100007

McNeill, L. S., McLean, J. E., Parks, J. L., & Edwards, M. (2012). Hexavalent chromium review, part 2: Chemistry, occurrence, and treatment. *Journal American Water Works Association*, *104*(7), 39-40. https://doi.org/10.5942/jawwa.2012.104.0092

Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents - A critical review. *Journal of Hazardous Materials*, *142*(1-2), 1-53. https://doi.org/10.1016/j.jhazmat.2007.01.006

Nancharaiah, Y. V., & Lens, P. N. L. (2015). Ecology and Biotechnology of Selenium-Respiring Bacteria. *Microbiology and Molecular Biology Reviews*, *79*(1), 61-80. https://doi.org/10.1128/mmbr.00037-14

Payne, T. E., Brendler, V., Ochs, M., Baeyens, B., Brown, P. L., Davis, J. A., Ekberg, C., Kulik, D. A., Lutzenkirchen, J., Missana, T., Tachi, Y., Van Loon, L. R., & Altmann, S. (2013). Guidelines for thermodynamic sorption modelling in the context of radioactive waste disposal. *Environmental Modelling & Software*, *42*, 143-156. https://doi.org/10.1016/j.envsoft.2013.01.002

Popic, J. P., Jegdic, B. V., Bajat, J. B., Veljovic, D., Stevanovic, S. I., & Miskovic-Stankovic, V. B. (2011). The effect of deposition temperature on the surface coverage and morphology of iron-phosphate coatings on low carbon steel. *Applied Surface Science*, *257*(24), 10855-10862. https://doi.org/10.1016/j.apsusc.2011.07.122

Santos, S., Ungureanu, G., Boaventura, R., & Botelho, C. (2015). Selenium contaminated waters: An overview of analytical methods, treatment options and recent advances in sorption methods. *Science of the Total Environment*, *521*, 246-260. https://doi.org/10.1016/j.scitotenv.2015.03.107

Siddiqui, S. I., & Chaudhry, S. A. (2017). Iron oxide and its modified forms as an adsorbent for arsenic removal: A comprehensive recent advancement. *Process Safety and Environmental Protection*, *111*, 592-626. https://doi.org/10.1016/j.psep.2017.08.009

Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, *17*(5), 517-568. https://doi.org/Pii S0883-2927(02)00018-5Doi 10.1016/S0883-2927(02)00018-5

Soda, S., Kashiwa, M., Kagami, T., Kuroda, M., Yamashita, M., & Ike, M. (2011). Laboratory-scale bioreactors for soluble selenium removal from selenium refinery wastewater using anaerobic sludge. *Desalination*, *279*(1-3), 433-438. https://doi.org/10.1016/j.desal.2011.06.031

Suhartana, Sukmasari, E., & Azmiyawati, C. (2017). *Modification of Natural Zeolite with Fe(III) and ItsApplication as Adsorbent Chloride and Carbonateions* IOP Conference Series: Materials Science and Engineering, Indonesia.

Vlaev, L. T., Georgieva, V. G., & Genieva, S. D. (2006). Use of the ion polarization theory to interpret certain regularities of changes in characteristics and properties of inorganic compounds. *Journal of Structural Chemistry*, *47*(5), 813-822. https://doi.org/10.1007/s10947-006-0396-3

Yigit, N. O., & Tozum, S. (2012). Removal of Selenium Species from Waters Using Various Surface-Modified Natural Particles and Waste Materials. *Clean-Soil Air Water*, *40*(7), 735-745. https://doi.org/10.1002/clen.201100740

Zhang, Y. Y., Kuroda, M., Arai, S., Kato, F., Inoue, D., & Ike, M. (2019). Biological removal of selenate in saline wastewater by activated sludge under alternating anoxic/oxic conditions. *Frontiers of Environmental Science & Engineering*, *13*(5), Article 68. https://doi.org/10.1007/s11783-019-1154-z