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New Electrobiochemical Reactor for Removal of Selenium, Arsenic, and Nitrate

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Abstract

Extraction and processing of minerals, metals, and fossil fuels can release various metals, including selenium and arsenic, and nitrates into wastewaters that can be costly and difficult to treat to levels meeting current drinking water and/or discharge criteria. A new electrobiochemical reactor (EBR) takes advantage of the Eh and pH behavior of contaminants using low voltage to lower oxidation reduction potentials (ORP), augment microbial transformations to achieve better contaminant removal, utilize fewer nutrients, and allow smaller, more robust treatment systems.

Key words: electrobiochemical, bioreactors, voltage, EBR selenium, arsenic, nitrate.

Introduction

Removal of metals, nitrates, and other inorganic contaminates represent a major US environmental problem that is common throughout the world. These contaminates come from many sources including petroleum refining, agricultural run-off, and mining and mineral processing. Many of these sources have characteristics of high volume and lower contamination levels, but still require treatment. Some contaminates like selenium and arsenic can be difficult to remove, and nitrates, often associated with these contaminants in wastewaters, can exacerbate their removal.

Various technologies exist for treatment of metals, nitrates, and other inorganics, including membrane filtration, ion exchange, chemical precipitation, ferrous hydroxide or iron, and biotreatment technologies, all of which have factors affecting their performance and cost. These methods can be somewhat selective for removing different contaminant forms, for example, selenite is removed more effectively than selenate and arsenite removal efficiencies are poor compared to arsenate [1,2,3]. Many methods also become prohibitively expensive for treating high volume, low-contaminant level waters and/or can produce large volumes of contaminated brine waters or precipitates.

Though conventional bioreactors have proved successful in an operational sense, several issues like robustness, capital cost, treatment residence times, and nutrient costs often cloud their acceptance over other treatment approaches. A combined electrochemical and biological system, a electrobiochemical reactor (EBR) technology, represents a new concept that increases transformation kinetics, removal efficiencies, and robustness of bioreactors by supplying electrons to the bioreactor system at low voltage (0.5-3 volts). The EBR system has been demonstrated to remove contaminates to low ppb levels using $\leq 1/2$ the retention time and nutrient costs [4].

The EBR is combined with other progressive technologies, such as a proprietary water gas mixing system (WGMS) that maximizes air-water interface at low pressure for rapid, energy efficient introduction of oxygen, for complete cutting edge treatment systems. The WGMS system has 70% to 90% gas transfer efficiency, a significant increase above existing air/gas entrainment technologies, at reduced costs while rapidly eliminating residual odors from the bioreactor discharge waters [4].

Materials/Methods

Microbes

Microbes employed to reduce selenium, arsenic, and nitrate in these tests were site indigenous microbes, isolated, screened for their respective contaminant reductive abilities, grown to high densities, and established within the EBR systems. Nucleic acid based individual microbe and microbial population used denaturing gradient gel electrophoresis (DGGE) and terminal restriction fragment (TRF) analysis to identify the bacteria present. Microbes present in the arsenic EBR were

Desulfobacterium sp., Desulfolobus sp.Desulfotomaculum sp., Desulfovibrio sp., Shewanella sp., Bacillus sp., and several uncultured (unidentified) bacteria. Bacteria present in the selenium EBR included *Pseudomonas sp., Desulfobacterium sp., Desulfolobus sp., Desulfotomaculum sp., Shewanella sp.,* and several uncultured (unidentified) bacteria. The microbial populations were examined after biofilm establishment using site waters containing indigenous microbes. Microbial density on the EBR support materials was assayed at an average concentration of ~$2E10^{11}$/g.

Site Test Waters
Selenium and nitrate were present in the site water at concentrations of ~350 ppb and ~70 mg/L, respectively and were adjusted to a pH of ~6.5. EBRs were operated at laboratory temperature of ~23° C and feed water was added to a clean feed water container on a daily. Arsenic and nitrate present in site waters fluctuate at concentrations between 90 -100 ppb and 10 - 20 mg/L, respectively. Water temperature averages ~19°C but is treading higher, influent pH averages ~7.4.

Nutrients
In both the selenium and arsenic tests, a balanced molasses, yeast extract, phosphate mixture was used at (2.5 to 0.75 g/L), yeast (1.0 to 0.25 g/L), and phosphate (1.0 to 0.05 g/L) (MYP). Higher nutrient levels, and a microbial culture media, trypticase soy broth (TSB), were used to establish the biofims to their desired density. Lower nutrient levels were used once the EBR and microbial populations reached more stabilized operating conditions. Nutrients were added on a daily basis by mixing the nutrient into 100 mL of pH adjusted test water and pumping them into each EBR separately over a five minute time period, then returning to normal flow rates.

EBR Configuration/Operation
The EBR tests presented in this document represent bench-scale selenium/nitrate tests and initial pilot-scale results from arsenic/nitrate waters. Typical EBR configuration is represented by the *Figure 1A* drawing. The bench-scale EBRs were tested as a two-stage, up-flow system in series. The EBRs were operated to simulate plug-flow conditions and contained modified pumice materials as the bulk of the microbial support surface and a pelletized activated carbon surface for electron distribution. Each EBR had a void volume of approximately 700 mL and retention time of 12 hours for a total retention time of ~24 hrs. Each reactor has three sampling ports used to monitor conditions within the system at the bottom, middle, and top. Voltage was applied to bench scale selenium EBRs at 1-3 volts as determined in prescreening tests.

The pilot-scale arsenic/nitrate EBRs are being operated as a two-stage, up-flow system in series using 3 volts, *Figure 1B*. The EBRs were operated to simulate plug-flow conditions and contained modified pumice materials as the bulk of the microbial support surface and an activated carbon surface for electron distribution. Each EBR has a void volume of approximately 500 gallons and retention time of 12 hours, for a total retention time of ~24 hrs.

Results and Discussion
The voltage required to increase contaminant transformation efficiencies varies with the bioreactor's microbial support materials, water chemistry, and microbes. Supplied voltage provides electrons at the bacterial surface and a readily available supply of elections to the bacterial-contaminant-surface environment that lowers the bacterial contaminant interaction and transformation energy requirements. Providing electrons at the bacterial support surface interface allows better development of controlled oxidation reduction potential (ORP) gradients for the effective removal of multiple contaminants in a single bioreactor.

Bacteria in the EBR system interact with the electrode through direct contact, mediating the transfer of electrons via conductive pilli and microbial surface interactions. Interaction also occurs through energy shuttle compounds that move energy to both electrode and non-electrode bound bacteria throughout the EBR system. The applied voltage reduces the system ORP in a controlled manner eliminating the need for excess nutrients to lower ORP; thus reducing nutrient costs. Readily available

electrons supply some of the energy (electrons) required for bacterial growth and contaminant transformation, again reducing nutrient costs.

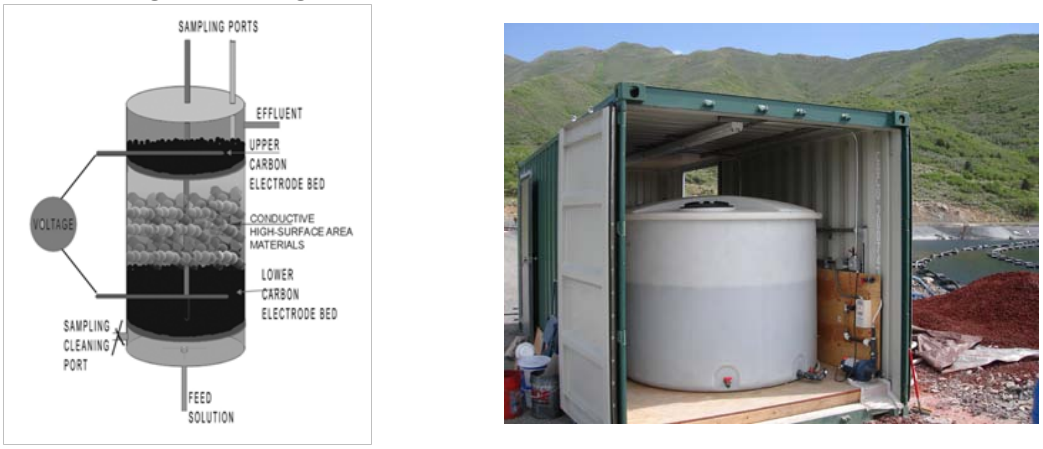

Figure 1. 1A shows a typical EBR configuration. 1B shows pilot-scale *EBR* Testing.

Many species of microorganisms can affect the reactivity and mobility of selenium, nitrates, and other inorganics and can be used to remove these contaminants from waters. The microorganisms used are endemic species, not genetically engineered, and the resulting products of the processes are elemental selenium and arsenic, and arseinc sulfides. Nitrates are converted to nitrogen gas, or ammonia that is readily utilized by microbes.

ORP in the environment, conventional bioreactors, and in the EBR system is influenced by a number of parameters, including pH, water chemistry, conductive surfaces, and added nutrients. *Figure 2* shows the results of addition of nutrients to site waters with and without applied voltage. Average ORP using 2.5 g/L nutrient without applied voltage was 98 mV. Average ORP in site waters with 1.5 g/L nutrient and 1 volt was 79 mV and average ORP with 1.5 g/L nutrients and 3 volts was -297 mV. Results were measured after a 24 hour period during the nutrient addition cycle.

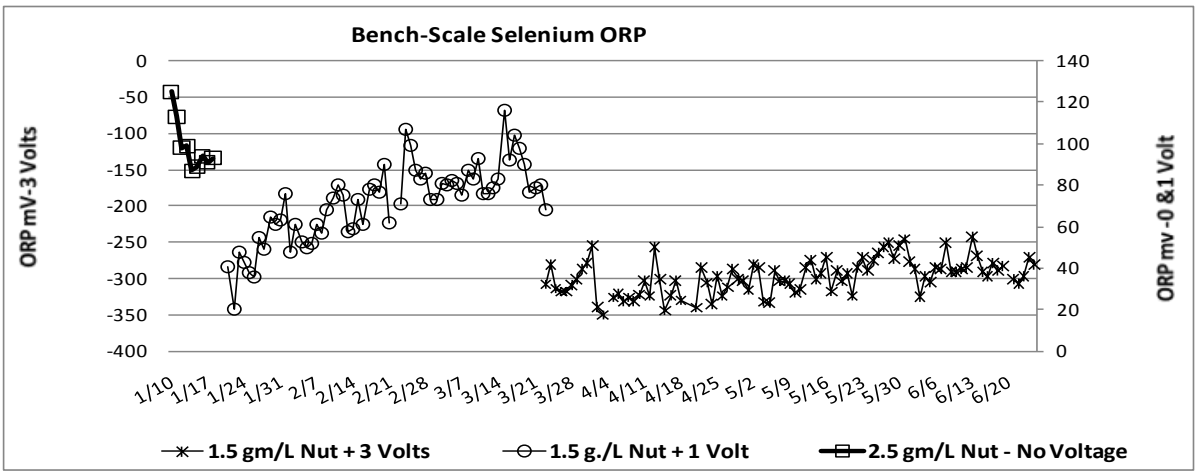

Figure 2. ORP as a function of added nutrient and voltage to site selenium waters.

Figure 3 shows the results of treatment of a selenium and nitrate containing site water using the EBR operated at 1 and 3 volts. Two identical EBR's were operated in series in an upward plug flow mode, initially without applied potential. After conditioning, voltage was applied at 1 and 3 volts. EBR's were operated at ~23° C with test waters adjusted to a pH ~6.5, using retention times of ~12 hrs each stage for a total retention time of ~24 hrs, Selenium and nitrate were present in the site water at concentrations of ~350 ppb and ~70 mg/L, respectively. Nitrate effluents was measured at the middle of the first EBR in series and were removed to below detection. Selenium is removed as elemental selenium to an average of ~0.125 mg/L using 1 volt and ~0.035 using 3 volts. A nutrient rebalance was made improved selenium removal to near detection, 0.002 mg/L.

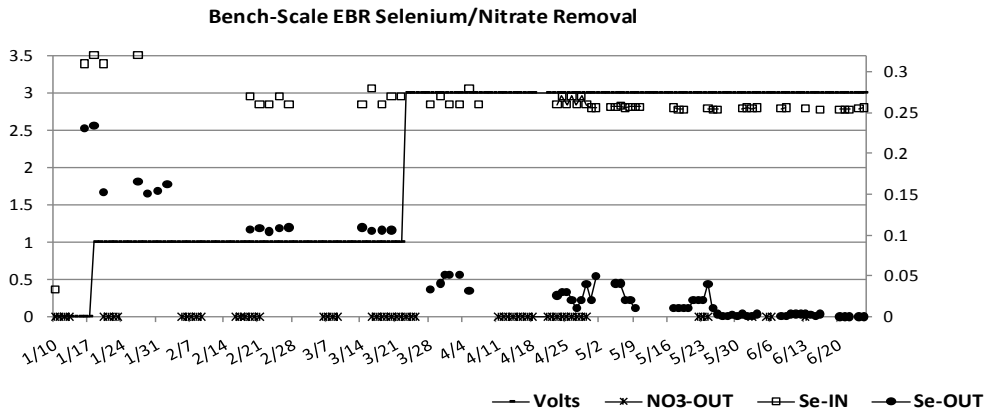

Figure 3. Selenium and nitrate removal as a function of applied voltage. The arrow indicates a nutrient adjustment to re-balance nitrogen and phosphate in the added nutrient.

Arsenic and other metals are precipitated in elemental and sulfide forms that are insoluble. *Figure 4* shows arsenic and nitrate removal in an on-site pilot-scale EBR system operated at 3 volts. Arsenic is being removed from ~100 µg/L to ~10 µg/L using a 24 hour retention time. Nitrates at ~10 to 20 mg/L are being removed in EBR-1. Site water temperatures average ~19°C, influent pH averages ~7.4. Nutrients are added on a daily basis as described in the *Materials/Methods* section.

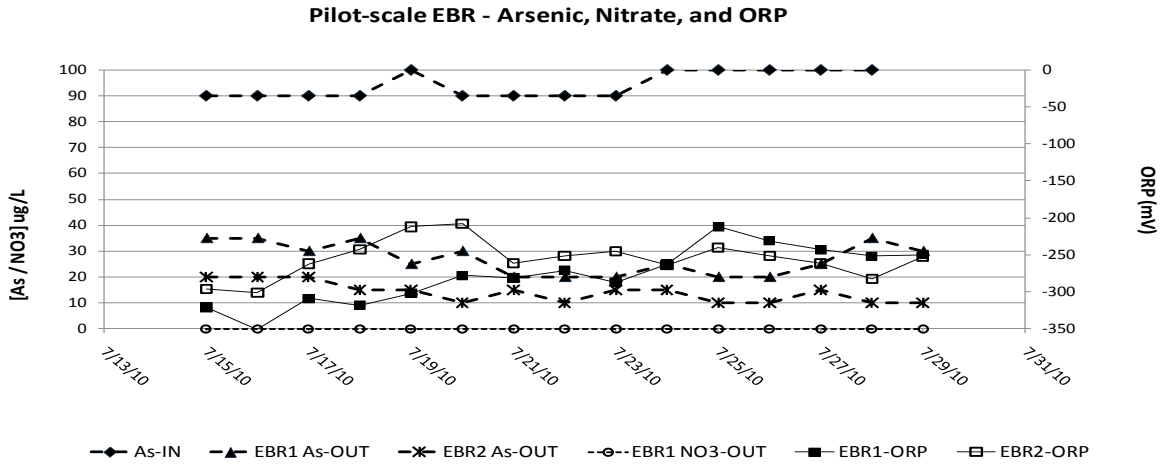

Figure 4. Arsenic and nitrate removal in a pilot-scale EBR system operated on-site at 3 volts using a total retention time of ~24 hours.

Conclusions

The EBR has been shown to be effective for removal of selenium, arsenic, and nitrate.

- The EBR system provides a more precise control over biotreatment system ORP, produces a more robust biofilm, and increases contaminant transformation kinetics and removal efficiency.
- EBRs remove target contaminants to low ppb levels.

References

1. Metcalf & Eddy, Inc., George Tchobanoglous, Franklin Burton, H. David Stensel *Metcalf & Eddy, Wastewater Engineering Treatment and Reuse*, Ed.4, (2002) Pages 616-700 ISBN10:0070418780

2. Ronald S. Oremland and John F. Stolz, (2005) *Arsenic, Microbes and Contaminated Aquifers, SHORT SURVEY Trends in Microbiology, Volume 13, Issue 2*, Pages 45- 49.

3. Twidwell, L.G., J. McCloskey, P. Miranda and M. Gale (2000) *Technologies and Potential Technologies for Removing Selenium From Process and Mine Wastewaters.* In Proceedings of Minor Elements. SME, Salt Lake City, UT, February, pp. 53.

4. Adams D. J., M. Peoples, N. Newton, and M. Nanduri (2010) *Electrobiochemical Reactor: Removal of Metals, Nitrate and BOD. INAP, Thatcher, AZ.*