ELECTRO-BIOCHEMICAL REACTOR (EBR) TECHNOLOGY FOR SELENIUM REMOVAL FROM BRITISH COLUMBIA'S COAL-MINING WASTEWATERS

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Abstract

The weathering of coal mine waste rock releases iron, calcium, sulfate and associated trace elements like selenium [Se], which are introduced to seepage waters. Nitrogen species, such as nitrate and ammonia, are also found in association with coal-mining drainages mainly due to leaching of residual blasting compounds. Elevated concentrations of Se are a ubiquitous occurrence in coal mining environments in British Columbia, with values ranging from below 50 to over 500 µg/L in site waters. Selenate is the most common form of selenium found in waste rock seepages, and is exceedingly mobile in aerobic freshwaters. A major concern with waterborne Se in British Columbia is the potential for its bioaccumulation in aquatic food chains.

Treatment to remove Se from coal-mining wastewaters has proven to be challenging for conventional water treatment technologies. Compounding this challenge, many streams are characterized by high flows and low selenium concentrations. Conventional membrane and ion exchange treatments produce concentrated brine streams that are difficult to treat or require disposal. Conventional biotreatment systems use excess nutrients to provide the required electrons to compensate for inefficient and variable electron availability, as well as to adjust reactor chemistry.

The Electro-Biochemical Reactor (EBR) technology provides electrons to the microbes directly at a low voltage potential (1-3 V), supplying a controllable and consistent supply of useable electrons to the system and microbes at low current. In this manner, the EBR technology overcomes the shortcomings found in conventional systems, as it reduces the required nutrient addition and provides a more controllable, efficient, economical, and robust biotreatment system than found in past generations of biological treatment systems. Additionally, the EBR process does not produce excess solids or biomass; therefore, solids management post-treatment is not required.

Laboratory EBR bench-scale and on-site pilot-scale systems were used to treat five British Columbia coal mine wastewaters; influent Se concentrations ranged from 35 µg/L to 531 µg/L. Se treatment targets for the tested waters ranged from 5 to 10 µg/L. Mean Se concentrations in EBR effluents ranged from 0.5 µg/L to 1.4 µg/L, while reducing sulfate concentrations. The test data demonstrate that the EBR technology is an effective Se removal option for British Columbia's coal-mining wastewaters.

Introduction

Selenium in Mining

Selenium (Se) is a naturally occurring trace element, which is an essential nutrient in small amounts (1, 2). However, it is also toxic to aquatic life, birds, and humans at very low concentrations. A major concern with waterborne Se is the potential for its bioaccumulation in aquatic food chains, resulting in acute and/or chronic toxicity to fish, water birds and amphibians (3, 4).

Selenium is chemically similar to sulfur and often substitutes it in mineral deposits and soils (5). Extensive mining of seleniforous coals in British Columbia (B.C.), Canada, has resulted in pronounced increases in Se in receiving waters in recent years, most notably in the Elk River valley. Elevated Se concentrations are a ubiquitous occurrence in coal mining environments in British Columbia, with values ranging from below 50 to over 500 µg/L in site waters. Selenate is the most common form of selenium found in waste rock seepages, and is exceedingly mobile in aerobic freshwaters. The weathering of coal mine waste rock releases selenium and other co-contaminants, such as sulfate and iron, into the seepage waters.

Treatment to remove Se from coal-mining wastewaters has proven to be challenging for conventional water treatment technologies (6, 7). In addition to elevated selenium concentrations, coal mining wastewaters contain other co-contaminants, e.g., nitrate, that requires removal prior to or simultaneously with Se (8). Nitrogen species, such as nitrate and ammonia, are found in these waters mainly due to the leaching of residual blasting compounds. Compounding this challenge, many streams are characterized by high flows and low selenium concentrations.

The Electro-Biochemical Reactor

Electromicrobiology is an emerging science discipline that studies microbial extracellular electron transfer mechanisms (9, 10). Synthesis of adenosine triphosphate (ATP), the molecule responsible for energy transfer in all living organisms, is dependent on electron flows and electrochemical gradients. In aerobic environments, microorganisms create energy by transferring the electrons derived from nutrients through a series of electron carriers to the terminal electron acceptor – oxygen. When oxygen is absent, microbes will utilize other electron acceptors in order of their free energy yield, including, nitrate, iron, and various oxidized metal species like selenate.

Even though the term electromicrobiology was coined in recent years, the microbial electron transfer has been studied since the early 20th century, with the invention of a microbial fuel cell (12). In the last decade, a process opposite to a microbial fuel cell has gained more interest. Specifically, it has been observed that certain microbes have the ability to utilize electrons provided directly from an electrode (13, 14). In recent years, numerous researchers have reported reductive biotransformations of oxyanions, such as nitrate, metal oxides, and other contaminants, such as tetrachloroethene, with electrodes being the sole electron donor in the system (15, 16, 17).

Our research has shown improved contaminant transformation kinetics throughout an Electro-Biochemical Reactor (EBR), at great distances from the electrodes. These directly supplied electrons impart energy to the microbes and system in a more controlled and stable oxidation-reduction environment, resulting in a reduced nutrient requirement, and better performance at lower temperatures (17, 18, 19). In conventional biological treatment systems, electrons are supplied from nutrients and chemicals added to the system. An excess of nutrients/chemicals is typically required to compensate for inefficient and variable electron availability needed to adjust the reactor chemistry for microbial growth and for contaminant removal.

The EBR overcomes these shortcomings by directly supplying electrons to the reactor and microbes, using a low applied voltage potential, supplying a controllable and consistent supply of useable electrons to the system and microbes at low voltage potential (1-3 V) and low milli amperage current across the reactor (1 mA provides 6.2 x 10^{15} electrons per second to the system and microbes). These directly supplied electrons are available to microbes without the added energy expense of metabolism; they provide 'free' useable energy to the microbes and bioreactor. Overall, the electron supply system afforded by EBR translates to reactors that are more controllable, economical, and robust than past generations of biological treatment systems.

Methods

Laboratory EBR treatment feasibility tests were performed on four different B.C. coal mining drainage waters. The goal of the bench-scale tests was to demonstrate and quantify selenium removal from coal mining waters to below discharge criteria. Bench tests are conducted in a manner that allows development of pilot test systems that have a high probability of successfully demonstrating treatment of site waters and developing the data required for design and operation of a full-scale facility. Wastewaters were collected on site and shipped to Inotec's laboratories, where they were tested using continuous plug flow type Electro-Biochemical Reactors.

The reactors were filled with activated carbon as microbial support media and a 1-3 V potential was applied across the reactor. Each bench-scale reactor was operated with a total hydraulic retention time (HRT) of 12 to 18 hours and were provided with a molasses-based nutrient. Monitoring points spaced throughout the process allow bench and pilot EBR performance assessment at shorter HRT's. Independent University of Utah water analysis laboratories performed Se measurements using ICP-MS.

In addition to the bench scale tests, one on-site pilot-scale test was performed with the goal to validate EBR technology, under site conditions, to develop engineering design and operational requirements for a full-scale EBR facility. In this system, waste rock seepage waters were treated in a pilot system designed to operate at a flow rate of 1 L/min. The EBR pilot system consisted of two EBR reactors in series. Total HRT of the system was 18 hours with sampling ports located at 6, 12, and 18 hours. Each EBR was connected to a power supply and provided with a 1-3V potential. During the pilot-scale test period, the EBR system was provided with $2.5x10^{17}$ to $4.9x10^{18}$ electrons per second. A molasses based nutrient source was used to provide required microbial components of C:N:P:etc. Testing was performed in September and October in British Columbia, with the starting average influent water temperatures of 14^{o}C; water temperatures dropped to

1°C by the end of the testing period. An accredited and independent laboratory (ALS Environmental) performed all analyses; metals were measured using ICP-MS, while inorganics (nitrate, sulfate, etc.) were measured using IC.

Results

Laboratory Feasibility Tests

Four wastewaters, obtained from four different B.C. coal mine drainages (Waters A through D), were treated using bench-scale EBRs. Total Se concentrations of the waters ranged from 35 to 531 µg/L (Table 1). Discharge targets for the mine operations range from 5-10 µg/L. In addition to Se, these waters contained elevated concentrations of nitrate-N, ranging from 11 to 170 mg/L (Table 1). Nitrate-N is a relevant co-contaminant that can interfere with selenium removal, as it is reduced under slightly higher ORP conditions (higher energy yield for microbes) and it competes with selenium oxyanions for electrons. In all four bench tests, nitrate-N was removed to levels below 1 mg/L (Table 1).

Se removal results for the EBR bench tests are shown in Figures 1 through 4. Every water tested produced effluent total Se concentrations well below the required discharge target, with average values of 1.2-1.4 µg/L. As a comparison to total Se, Figure 5 shows dissolved selenium concentrations during tests on Water D (average effluent concentration of 1.0 µg/L). Both total and dissolved Se (Figures 4 and 5) follow a similar trend, indicating that particulate selenium (elemental Se associated on/in the microbial cells or precipitated within the reactor microbial support matrix materials) is trapped within the bioreactor matrix. Total suspended solids (TSS) generated during both bench and pilot scale tests ranged between <3 to 18 mg/L. In this regard, the EBR system removes selenium without the need for extensive post-treatment for the removal and management of biosolids that contain precipitated or microbial cell-attached Se.

Table 1. Average influent and effluent selenium and nitrate-N concentrations for bench scale EBR tests.

	Parameter	Ave. Influent	Ave. Effluent
Water A	NO_3-N [mg/L]	170	<0.1
	Se [µg/L]	186	1.2
Water B	NO_3-N[mg/L]	16.4	<0.1
	Se [µg/L]	35.0	1.4
Water C	NO_3-N[mg/L]	37.0	1.0
	Se [µg/L]	531	1.4
Water D	NO_3-N[mg/L]	11.0	<0.1
	Se [µg/L]	355	1.2

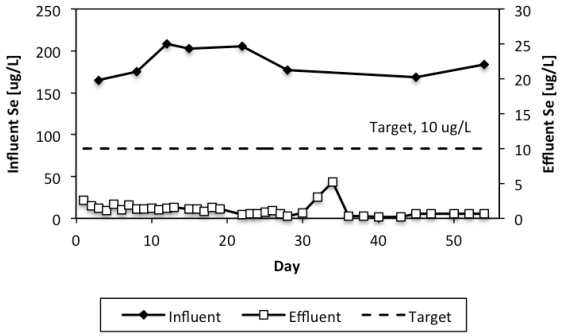

Figure 1. EBR bench scale total selenium removal from Water A. Effluent target concentration presented for comparison.

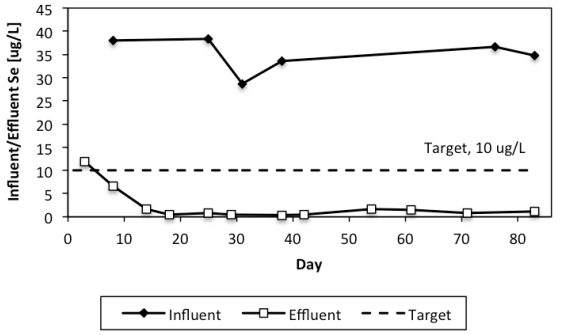

Figure 2. EBR bench scale total selenium removal from Water B. Effluent target concentration presented for comparison.

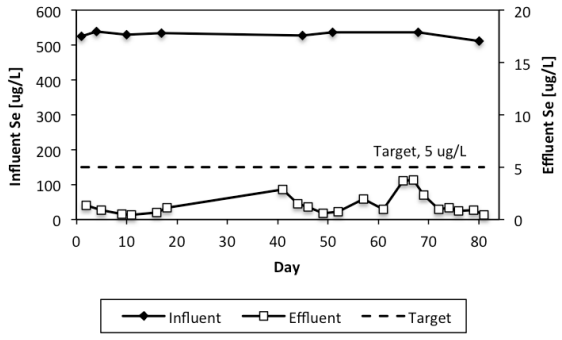

Figure 3. EBR bench scale total selenium removal from Water C. Effluent target concentration presented for comparison.

Pilot testing

For pilot scale testing, the tested coal mining seepage waters contained on average 105 µg/L total

selenium with site discharge target of 10 µg/L. Selenium was removed by the EBR system to an average effluent value of 0.5 µg/L for both total and dissolved species (Figure 6). Selenium concentration was monitored throughout the EBR system to establish the required HRT; the discharge target of 10 µg/L was consistently exceeded in the first sampling port equivalent to a 6-hr HRT (Figure 6). Data extrapolation indicates that a 3- to 4-hour EBR HRT would reliably meet the site Se discharge criteria for this effluent.

In the pilot-test waters, nitrate-N at 50 mg/L was the main co-contaminant of interest. Data extrapolation indicated that nitrate-N would be reduced to an average of 2 mg/L in the same 3- to 4-hour HRT required for Se removal. Other parameters that were not targeted for removal, but still removed by the EBR system included sulfate (475 mg/L), molybdenum (7.8 µg/L), nickel (113 µg/L), antimony (2.8 µg/L), uranium (18.2 µg/L), and zinc (64 µg/L) (Table 2).

Sulfate was removed to an average concentration of 235 mg/L, which is below the U.S. EPA drinking water standard. Most other metals were removed to below 1 µg/L. Nickel was reduced to an average of 2 µg/L while effluent zinc concentration was non-detectable. Worth noting is a low effluent TSS concentration, validating that the EBR process is capable of removing Se and other metals to low levels and not producing excess solids or biomass (i.e., the EBR process does not require a solids management post-treatment).

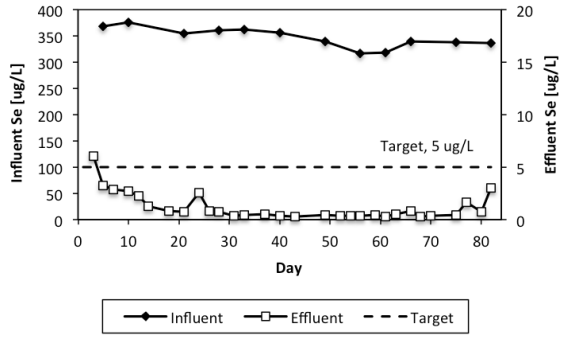

Figure 4. EBR bench scale total selenium removal from Water D. Effluent target concentration presented for comparison.

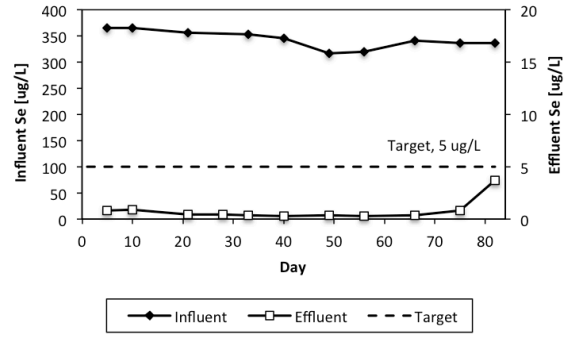

Figure 5. EBR bench scale dissolved selenium removal from Water D. Effluent target concentration presented for comparison.

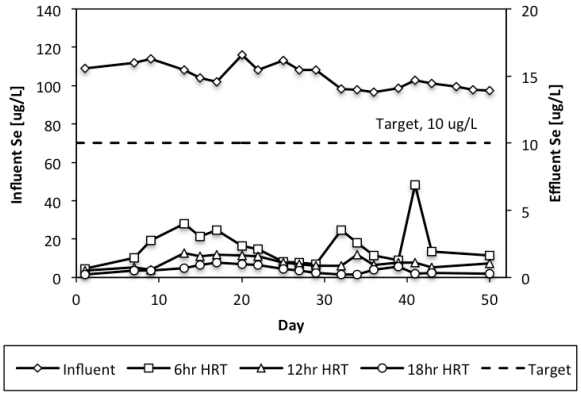

Figure 6. EBR pilot scale total selenium removal throughout the system at 6, 12, and 18 hour hydraulic retention time (HRT).

Table 2. Average influent and effluent water chemistry during pilot EBR tests.

	Ave. Influent	Ave. Effluent
Inorganics		
NO_3-N [mg/L]	50	2.0
NO_2-N [mg/L]	0.02	0.02
SO_4 [mg/L]	475	235
Physical parameters		
TSS [mg/L]	< 3.0	8.0
pH	7.6	6.4
Alkalinity - $CaCO_3$	460	860
Total metals		
Cd [µg/L]	0.61	0.04
Mo [µg/L]	7.8	0.3
Ni [µg/L]	113	2.0
Sb [µg/L]	2.8	0.3
Se [µg/L]	105	0.5
U [µg/L]	18.2	0.07

Zn [µg/L]	64.0	< 6.0

Conclusions

The EBR system was demonstrated during laboratory bench- and on-site pilot-scale to successfully remove selenium from coal mining wastewaters to effluent concentrations almost an order of magnitude below discharge targets (5 to 10 µg/L). Laboratory feasibility tests produced EBR effluents with average Se concentrations of 1.2 to 1.4 µg/L, while the on-site pilot test generated an average effluent Se concentration of 0.5 µg/L. The on-site test was performed with average influent water temperatures of 14ºC to a low of 1ºC, demonstrating the effectiveness of EBR at low temperatures. In addition to reducing selenium, the EBR system also demonstrated the effective removal of other inorganic co-contaminants, including nitrate, sulfate, and other metals (e.g., Cd, Mo, Ni, Sb, U, Zn).

The data generated to date for EBR technology shows that Se can be effectively removed from solution without producing excess biomass or solids that require expensive post-treatment. Overall, EBR has been demonstrated as a technology that can effectively and consistently treat coal mining wastewaters for Se and nitrate, even at the low temperatures experienced in British Columbia.

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