Biological Removal of Selenium from Mining Influenced Waters: A Critical Review of Challenges

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Abstract

Biological treatment of selenium (Se) contaminated mining-influenced water (MIW) has gained popularity in recent years. Some commonly used bioreactor configurations include; constructed wetlands, fluidized-bed bioreactors (FBR), packed-bed bioreactors (PBR), hydrogen-based membrane biofilm reactors (H_2-MBfR) and upflow anaerobic sludge blanket bioreactors (UASB). The successful operation of these bioreactors is dependent on seeding with mixed microbial consortium capable of removing selenium oxyanions without interference from competing co-contaminants. This review found that these bioreactors achieved widely varying selenium removal extents ranging from 59% – 99%. However, many of these technologies were studied under pilot and laboratory-scale conditions, with only a few implemented at full-scale operations.

Keywords: Selenium, mining-influenced water, biological treatment, bioreactor, microbial consortium

Introduction

Mining-influenced water (MIW) from some mining operations contains elevated concentrations of contaminants such as sulfate, nitrate, trace metals and metalloids such as selenium in some instances. Selenium, which typically occurs at concentrations lower than those of nitrate and sulfate in this complex MIW is a constituent of concern as it can have a disproportionate effect on receiving environments due to its extreme toxicity. When selenium is oxidized through exposure to air and water, it exists as oxyanions (SeOx); selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}) depending on the level of oxidation and these species constitute the bioavailable (and thereby the most toxic) forms of selenium. Selenium can bio-accumulate in aquatic organisms with the potential to bio-magnify up the food chain. For example, lethal and teratogenic effects of SeOx in waterfowl (Ohlendorf et al. 1986) were attributed to SeOx bioaccumulation in aquatic life in San Joaquin Valley, Western United States (Lemly 1985). In other parts of the world, selenium contamination resulting in serious negative effects to aquatic life have been reported in many countries, such as China, Australia, Japan, South Africa, Russia, Argentina, and France. This is as a result of activities conducted by a wide variety of industries such as mining (coal, hard rock, uranium, phosphate), power generation (coal-fired power plants, oil refineries) and also agriculture (CH2M Hill, 2010; Lemly 2004). In many of these places, biological treatment processes have been implemented to remove selenium from their wastewater. However, there is a wide range of methods for selenium removal reviewed in (CH2M Hill, 2010).

The removal of dissolved selenium compounds from MIW is particularly challenging when: 1) dissolved selenium occurs at relatively dilute concentrations (for example, less than 1 mg/L) and must be removed to much lower concentrations (≈1 µg/L in Canada, for instance) (Canadian Council of Ministers of the Environment, 2007) 2) it has a complex chemistry due to the possibility to exist in several oxidation states, 3) other contaminants in the MIW, such as nitrate and sulfate occur at concentrations much higher than those for dissolved selenium and thereby interfere with its removal. Dissimilatory reduction of soluble SeOx, the most common forms

of dissolved selenium found in MIW, to the less soluble elemental selenium Se^0 through microbial biochemical metabolic pathways constitutes a promising approach to removal of dissolved selenium from MIW (Tan et al., 2016; Nancharaiah and Lens, 2015; Lenz and Lens, 2009). This paper reviews some of the challenges associated with some of the common biological treatment technologies used for the removal of selenium from MIW.

Selenium Oxyanion Reduction Pathways by Bacteria

There is ample evidence in the literature that microorganisms can reduce selenium oxyanions (SeOx) for a variety of purposes. These include dissimilatory Se reduction, assimilatory Se reduction, and detoxification (Stolz and Oremland 1999). Certain heterotrophic bacteria are capable of dissimilatory Se reduction, in which they couple SeOx reduction as electron acceptors to oxidation of organic compounds as electron donors for respiration. These bacteria that can be used to effectively remove selenium from MIW. Oremland et al. (1990) first reported evidence for dissimilatory selenate reduction in experiments performed using sediment slurries sourced from a selenium-contaminated aquatic environment. The dissimilatory reduction of selenate that was measured was linked to the production of stoichiometric amounts of elemental selenium, meaning that this was the only product of selenate reduction. Following this, Oremland et al. (2004) reported that dissimilatory reduction of SeOx was performed by the bacterial species: *Sulfurospirillum barnesii, Bacillus selenitireducens* and *Selenihalanaerobacter shriftii*, all of which formed nano-sized elemental selenium particles that achieved removal of Se from soluble forms to an insoluble and immobilized form. *Thauera selenatis* was the first bacterium reported to carry out selenate respiration under anaerobic conditions (Macy et al. 1993). Schroder et al. (1997) purified and characterized a perisplasmic selenate reductase from *Thauera selenatis*. The enzyme has high affinity for selenate and can reduce selenate at high percentage (98%) without nitrate inhibition (Macy et al. 1993). In another study at pilot scale, Cantafio et al. (1996) reported that, a packed-bed reactor using *Thauera selenatis* as inoculum was able to achieve complete (100%) selenate removal and almost complete denitrification (98%).

Assimilatory SeO_x reduction occurs when Se is associated with cell biosynthesis of selenoproteins and this results in the accumulation of Se inside the cell biomass (Nancharaiah and Lens 2015). Microbial SeO_x reduction is also performed in order to reduce the toxicity of these chemical compounds. In this case, methylated forms of Se most prevalently, dimethylselenide and dimethyldiselenide, are produced to reduce the toxicity of SeOx and, in some cases, cause them to be volatilized (Nancharaiah and Lens 2015).

Biological Processes used for Removal of Dissolved Selenium Oxyanions

Biological reduction was identified as the preferred technology for removal of SeOx from industrial effluents versus other physical or chemical methods (CH2M HILL 2010; USEPA 2014). Biological treatment technologies are broadly classified as passive or active process. Passive or semi-passive treatments rely on natural biogeochemical processes on the site and require few if any chemical reagents, special equipment, energy, maintenance or operation. Active treatment processes are highly engineered, high capital cost installations needing special reagents, energy and personnel to operate and maintain. Active treatment systems include process control to maintain optimum conditions, while passive treatment systems are subject to seasonal and other types of variability. Some common biological treatment systems are described below (Table 1). These biological treatment systems described were successful in achieving selenium removal at extents ranging from 59 – 99% for incoming total dissolved selenium concentrations ranging from 15 to 41800 μg Se L^{-1}. However, many of them were pilot- or laboratory-scale studies, with only a couple of commercial full-scale operations. Most active treatment processes consist of several reactors in series

*Table1: **Operating** conditions and performance for some bioreactor configurations*

Bioreactor Type	Se influent (µg Se L^{-1})	Se effluent (µg Se L^{-1})	% Se Removal	Operating conditions	Reference
ABMet® (PBR)	1950	< 2	97	Gold MIW; Pilot-scale, Flow rate, 380 L/min and HRT 5.5 hours	CH2M HILL (2010)
	100	5	95	Gold MIW; Full-scale Flow rate, 380 L/min NO_3—N, 30 mg-N/L. HRT, not available. Temp., 8-16°C	Maniatis and Adams (2003)
Envirogen (FBR)	15 – 20	4.7 - 8.2	59-69	Coal MIW; Full-scale, Flow rate, 7,949 L/min, HRT, 25-30 mins, Temp., 16°C, NO_{3^-} - N, 3.5 mg-N/L	Sirinvasan et al. (2014)
	155 – 558 (as SeO_4^{2-})	2 - 4.6	98-99	Pilot-scale, Flow rate 11.4 – 5.7 L/min, Temp., 10°C, HRT, 60 – 120 mins, NO_{3^-} - N, 31 mg-N/l, SO_4^{2-}, 800 mg/L.	Gay et al. (2012)
Chemostat (*Bacillus sp.* SF-1)	41,800 (SeO_4^{2-})	50	99	Laboratory-scale, HRT, 95.2 hrs.	Fujita et al. (2002)
H_2-MBfR	260 -1000	12 – 50	95	Laboratory-scale, hollow-fiber membrane.	Chung et al. (2006)
Constructed wetlands	1,500	> 7	> 99	Pilot-scale, Microcosm water column, HRT, 72 hrs.	NSMP (2007)
Algal-bacterial	402 – 422	32 – 77	82 – 92	High rate aerobic-anoxic ponds for algae and anaerobic bacteria, HRT, 38 – 66 days.	Quinn et al. (2000)
UASB	790 (SeO_4^{2-})	8 – 24	97 – 99	Laboratory- scale, operated under methanogenic and sulfate-reducing conditions HRT, 6hrs	Lenz et al. (2008a)

so as to deal with interferences from co-contaminants, such as nitrate, and to remove metabolic byproducts, such as ammonia and colloidal Se^0.

To remove nitrate, a pretreatment bioreactor is used as the first stage followed by selenium removal in subsequent bioreactors(s), which are then followed by aerobic bioreactors to eliminate metabolic byproducts produced in the upstream bioreactors. The number of bioreactors required for treatment of selenium containing MIW could be reduced if the bioreactor supports a microbial community with enzymatic systems that are specific for SeOx reduction and not inhibited by the presence of nitrate.

Regarding the process conditions that are required for selenium removal down to regulated levels, most active treatment

bioreactors need HRTs ranging from 6 - 48 hours. The required HRT is dependent on the selenium loading rate into the bioreactor and the loading rate of co-contaminants that could interfere with the rate of selenium removal. Another important parameter to control is pH, which must be near neutral since this is optimal for microbial SeOx reduction. For instance, Lortie et al., (1992) reported that no selenate reduction occurred at pH below 6.5 or above 9.5. These bioreactors also use mesophilic bacteria, which operate within the temperature range of 15 - 35°C and any changes in temperature could affect bioreactor performance. For instance, it was found that a drop in temperature from 15 to 7°C reduced selenate removal from 88% to 35% in a UASB reactor (CH2M HILL 2010). However, the ABMet® system has been operated successfully over a wide temperature range (3-38°C) (Staicu et al., 2017). An important concern regarding bio-treatment of selenium containing MIW is the formation of colloidal Se that needs to be removed from the effluent before discharged into receiving environment. Different post-treatment steps for solid-liquid separation of colloidal Se^0 have been proposed including, media-filtration, coagulation and electrocoagulation(Staicu et al. 2017).

Challenges with using Bioreactors for Removal of Dissolved Selenium from MIW

Most of the bioreactors used for the removal of dissolved selenium have been tested at the laboratory- or pilot-scale, with the challenge of scaling-up most of these processes. Almost all of full-scale plants reported in the literature are located in Canada and US. However, most of these processes still experience performance deterioration and instability. As is typical for most biological processes, the success in reducing the contaminant of interest is dependent on creating the optimal conditions for the desired functional microorganisms to flourish, and maintaining these microbes throughout the treatment process. Briones and Raskin (2003) reported that, the stability of biological wastewater treatment systems is dependent on the functional redundancy of microbial communities in the bioreactor. Functional redundancy is having a diversity of functionally important groups of microorganisms that can perform desired treatment under a wide range of conditions. For mine water treatment, the challenge is the ability to maintain the functionally important microbial community members that can simultaneously remove selenate and nitrate in bioreactors. Selecting and maintaining the selenate-respiring specialists that can selectively remove selenium in the presence of other competing anions could reduce the amount of electron donor required for microbial respiration because the microbial reduction of the competing anions increases the electron donor proportionally. For instance, each mole of nitrate co-reduced with SeOx requires additional 5 electron equivalence to be reduced to N_2 gas. Organic carbon requirements are high for MIW treatment bioreactor operation, which increases the operating cost.

Constructed wetlands are useful when the wastewater is produced in large volumes but sensitive to temperature fluctuation and seasonal variation of vegetation, there is also the concern about gradual accumulation of selenium in vegetation and sediments in wetlands. Algae-bacterial process has the challenge of inability to consistently achieved selenate reduction to low levels unless nitrate is removed first (NSMP 2007, CH2M HILL 2010). The main operational limitation associated with ABMet® bioreactor process is its susceptibility to clogging (CH2M HILL 2010). When implementing FBR for full-scale mine water treatment, Sirivasan et al. (2014) reported that, the main operational challenges encountered was difficulty in controlling bed height in order to maintain bed expansion for selenium removal. For UASB bioreactor configuration, the challenges reported are; long acclimatization of the sludge, short-circuiting caused by accumulation of gas in the sludge, and variability in selenium removal efficiencies due to temperature sensitivity of the process (CH2M HILL 2010). When treating synthetic MIW under sulfate-reducing conditions in a UASB reactor, Lenz et al. (2008) observed that the removal of selenium is dependent of sulfate/selenate ratio with ratio greater than $8x10^{-4}$ being the most

effective for selenate removal. However, this sulfate/selenate ratio is impossible to achieve in actual MIW. The main challenge associated with the use of pure cultures e.g. *Thauera selenatis* and *Bacillus sp*. SF-1 as inoculum in bioreactors is out-competition by other microorganisms entering with the feedwater since a sterile environment is impossible to maintain. The challenges associated with H_2-MBfR bioreactor are the expensive electron donor (hydrogen) membrane fouling especially from colloidal Se (Nancharaiah and Lens 2015) and presence of nitrate has inhibitory effect on selenate reduction (Lai et al. 2014).

Conclusion

Biological treatment is one of the popular methods for removing Se from MIW. Previous research has shown that, the major mechanism for selenium removal for this process is reductive precipitation based on microbial reduction of selenium oxyanions under anoxic conditions to particulate Se^0. Several active bioreactors have been developed and operated at laboratory-scale, pilot-scale and few at full-scale. These include UASB, FBR, PBR, H_2-MBfR. Passive and semi-passive bio-treatment system have been developed and used in certain cases. The effectiveness of these bioreactor systems is challenged by the presence of other co-contaminants especially nitrate and sulfate which occur at much higher concentration. Perhaps, it's possible to overcome this challenge by using microbial community with enzymes that are specific for SeOx reduction. However, further research is needed to test this theory. Also, there is the need to optimize these bioreactor processes or develop new process to effectively treat actual mine water at full-scale. With further research, perhaps a combination of two different bioreactors could be a more effective strategy for removal of selenium from actual MIW at full-scale.

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