

Selenium removal from mining and process wastewater: a systematic review of available technologies

Jakub Stefaniak, Abhishek Dutta, Bram Verbinen, Manisha Shakya and Eldon R. Rene

ABSTRACT

Selenium is an important element that is required for humans, animals, plants and other life forms. Selenium is naturally present in the Earth's crust and its worldwide distribution has led to complex interactions between selenium and the natural environment (water, soil, sediments and air). The discharge of selenium contaminated water into the environment from industrial processes is a topic of regulatory (WHO – 40 µg/L, EU – 10 µg/L), environmental and health concern. The removal of selenium from water is complex, determined by its speciation and often expensive due to the characteristics of the wastewater and the stringent discharge limits for selenium and its oxyanions. In this review, selenium chemistry and its toxic effects on human health and the environment have been examined. An overview of the different physico-chemical and biological technologies used for the removal of selenium from contaminated water were discussed wherein adsorption capacities in the range of 0.22–120 mg/g and 0.135–127 mg/g, respectively, were reported in the literature. The challenges and future research directions in this progressive research field have also been stated.

Key words | biodegradation, bioreduction, membrane separation, mining operations, selenium, wastewater

Jakub Stefaniak
Abhishek Dutta
Bram Verbinen
Faculteit Industriële Ingenieurswetenschappen,
KU Leuven,
Campus Groep T Leuven, Andreas Vesaliusstraat
13, B-3000 Leuven,
Belgium

Jakub Stefaniak
Institute of Chemical Engineering and Technology,
Poznan University of Technology,
Pl. M. Skłodowskiej-Curie 2, 60-965 Poznan,
Poland

Manisha Shakya
Eldon R. Rene (corresponding author)
Institute for Water Education, Department of
Environmental Engineering and Water
Technology,
UNESCO-IHE,
P. O. Box 3015, 2601 DA Delft,
The Netherlands
E-mail: e.raj@un-ihe.org

INTRODUCTION

Selenium (Se) and its oxyanions are emerging contaminants of major health and environmental concern. The contamination of the environment by selenium compounds can originate from various sources that include agricultural drainage water, mine drainage, residues from fossil fuel, thermoelectric power plants, oil refineries and metal ores. In the last few decades, however, several studies have focused on the treatment of selenium-containing waters. The limited literature that can be found focuses on selenium removal by adsorption processes such as biosorption, chemisorption and physisorption, among others (Roberts *et al.* 2015; Mane *et al.* 2011; Moore & Mahmoudkhani 2011; Khamkhash *et al.* 2017). Selenium compounds are mainly used for the production of glass because they give glasses a

distinct red colour. As a semiconductor, it is used in solar cells and it is also used as an alloying element for the replacement of the more toxic lead. Part of the industrial emissions of selenium are therefore related to these industries by direct emissions to air, soil and water from the glass as well as solar cell-producing industries. Selenite (Se(IV)) and selenate (Se(VI)) are the predominant chemical forms of Se with most of their salts being soluble (Verbinen *et al.* 2013).

The removal of selenium from aqueous medium is complex and expensive, because of the high wastewater volumes generated, low discharge limits (even in µg/L) and the presence of Se(IV) and Se(VI) species (Santos *et al.* 2015). As regulatory limits are becoming stricter, selenium removal from wastewater has become more and more challenging.

Mushak (1985) points out that ca. 18% of 3000 tap water samples had selenium content exceeding the Environmental Protection Agency standards. Drinking water standards also require selenium removal from surface and groundwaters. The selenium concentration in contaminated wastewater must also be reduced to minimize its impact on natural water resources or to be reused (Santos *et al.* 2015). Due to its high toxicity, selenium is already classified as a harmful substance; however, nowadays it is also known as an essential micronutrient. Deficiency of selenium may cause liver, muscle and heart diseases such as the Kashin–Beck disease (Roberts *et al.* 2015). Selenium can be found in selenoproteins, substances that are needed to scavenge free radicals and prevent cancer and infections (Pilon-Smits & LeDuc 2009). It is bio-accumulative and therefore its concentration increases along the trophic chain (Santos *et al.* 2015).

Selenium is a trace element which occurs in ores containing other minerals like sulfides of heavy metals. However, there are no specific geologic deposits where selenium constitutes the main element. The main sources of selenium are black shale, phosphate rocks, coal and limestone. It may also be found in rare minerals like eucairite (CuAgSe), crooksite (CuThSe) and clausthalite (PbSe). It is produced as a by-product of other base metals and is also widely used in metallurgy, manufacturing of glass, chemicals, pigments, electronics, fertilizers, etc. (Khamkhash *et al.* 2017). Selenium can be emitted to the environment after mining activities. For example, selenides are commonly found in the ores of copper, lead and nickel, and can, therefore, be

refined from these ores. In parallel, selenium can also be discharged as a by-product after the extraction of these elements.

The concentrations of selenium that are found in industrial effluents range between 0.1 and 20 mg/L (Santos *et al.* 2015). Irrigation of agricultural land is only one of the pathways for selenium mobilization and transport. There are also other activities like coal combustion, silver, gold, coal and phosphate mining, metal smelting, municipal landfills and transport, refining and utilization of oil (Stillings & Amacher 2010). The main source of selenium in mining operations is waste rock. Selenium species leach or migrate to the environment from the rock when it is exposed to water. More frequently, selenium occurs in the soluble form in mine runoffs. Its concentration in mining wastewaters ranges from 3 to 12,000 µg/L (Sandy & DiSante 2010). At open mines, huge amounts of soil and rock are disturbed by blasting, excavation, trucking, dumping and reclamation activities. Such unit operations result in a landscape that is entirely different from the one before mining and it exposes the overburden to air and surface waters. Waste materials from mines are deposited on the surface of tailings piles, ponds, landfills and dumps. Surface waters drain from these deposits into the aquatic ecosystems and into streams that drain the local watershed (Wayland & Crosley 2006) as shown in Figure 1.

There are several challenges with the treatment/removal of selenium from mining wastewaters. Selenium is present in very low concentrations with variable and high flow rates. The concentration of selenium in wastewaters may vary

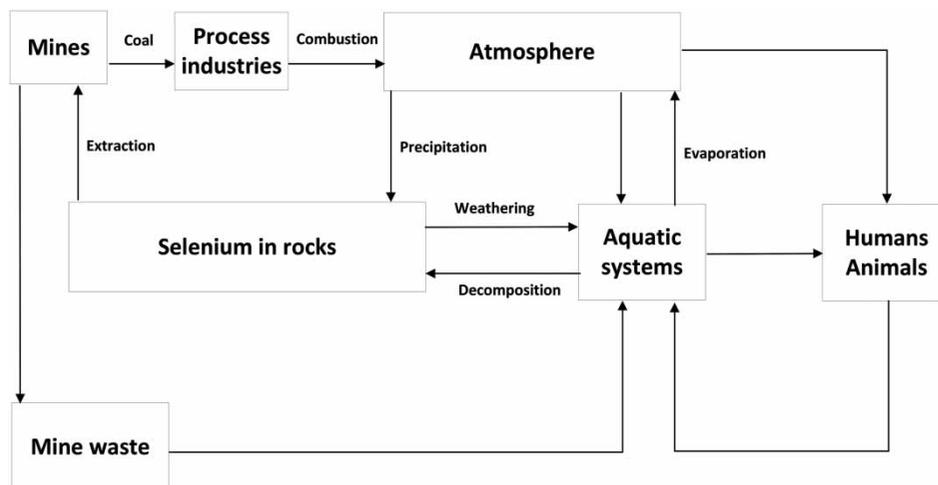


Figure 1 | Selenium cycle in the environment (Khamkhash *et al.* 2017).

widely depending on the temperature, pH, dissolved solids and the presence of other contaminants. These conditions affect the ability of selective and economical removal of selenium. One of the results of selenium treatment is generation of concentrated by-products which must be removed (Santos *et al.* 2015).

In the coal mining industry, every form of selenium is of a high level of interest. New regulations concerning selenium discharge are still being developed with selenium waste handling becoming more and more limited in the capacity of the mining industries. There are several physical and chemical approaches meant exclusively for selenium treatment; but in terms of optimal cost and efficiency, one of the most promising approaches to removing selenium is the biological treatment, especially fixed-film biological treatment (Sandy & DiSante 2010). One of the frequently obtained metalloids in effluents from mining and processing facilities is the oxyanion of selenium(VI). This cation is difficult to remove from industrial effluents like many metalloids (Johansson *et al.* 2015). Coal mining operations can mobilize trace elements like selenium into aquatic ecosystems in higher concentrations than they normally exist in the natural setting. In Luscar Creek, Canada, a significant increase in deformities in trout fry hatched from fertilized eggs of parent fish was reported (Wayland & Crosley 2006). After this report, the human consumption of fish and elk livers were regulated due to this incident. Higher concentration of selenium is a critical concern which is connected to the deaths and birth defects in waterfowl, wildlife and domestic stock (Stillings & Amacher 2004). Southeast Idaho, USA is one of the examples of places where selenium compounds influence the ecosystem. This review explores the most frequently used methods for selenium removal from mining and process wastewaters in order to give an extensive overview of the possibilities to reduce selenium concentrations and subsequently decrease the risks for humans, animals and the environment.

SELENIUM CHEMISTRY AND TOXICITY

Selenium was discovered in 1808 by Jons Jacob Berzelius. It obtained its name from the Greek word 'Selene' which means the moon. Selenium (Se) is a non-metal with

atomic number 34, falling on the fourth period of the periodic table in the Chalcogen group along with oxygen, sulfur and tellurium. A wide variety of physical and chemical forms of selenium found can be categorized into four different groups, namely, the inorganic selenium, the volatile and the methylated selenium, the protein and amino acid selenium, the non-protein amino acid and biochemical intermediate selenium. Selenium occurs in the environment in five oxidation states: Se(IV), Se(VI), Se(0), Se(-1) and Se(-II). In the oxidized system, selenium occurs as selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), as elemental selenium (Se(0)) and as selenides (HSe^-) in the anaerobic system (Koren *et al.* 1992; Lenz *et al.* 2006). The fully oxidized form of selenium is selenate. Speciation of selenium in water is governed by different factors such as pH, redox condition, the influence of biological processes, etc. Among the different species of selenium, the reduced forms of selenium (Se(0) and Se(-II)) are insoluble in water. Therefore, they occur in water bodies as colloidal suspension and as fine particles in the air. Selenate and selenite are generally soluble and stable oxyanions of selenium in natural water bodies but can also be found in the state of oxidation or reduction in mineral surfaces (Sandy & DiSante 2010; Seby *et al.* 2001).

The effect of selenium on human health can be both beneficial and damaging. At lower concentrations, it forms one of the constituents in the biological system, but at higher concentrations, it shows carcinogenic, genotoxic and cytotoxic effects. The range between toxicity and deficiency of selenium is very small (40 to 400 μg per day). Different regulatory agencies have set up different standard values for the safe level of selenium in diets, which makes the matter of selenium toxicity still confusing and somewhat controversial. For instance, the World Health Organization (WHO) and the European Commission (EC) have set the provisional guideline for Se at 40 $\mu\text{g}/\text{L}$ and 10 $\mu\text{g}/\text{L}$, respectively, in drinking water; while the United States has set the maximum contamination level to 50 $\mu\text{g}/\text{L}$ (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption 1998, USEPA; National Primary Drinking Water Regulations, List of Contaminants and their (MCLs) 2009; World Health Organization 2011). While many national authorities are seeking to reduce their limits in line with the WHO

guideline value, many countries and indeed all affected developing countries still operate at their own prescribed guidelines, in part because of the lack of adequate testing facilities for lower concentrations. This is also one of the reasons why the WHO cannot set binding standards.

The toxicity of selenium to the biological system depends upon its concentration and speciation. It also depends on several other factors, including the exposure time, physiological condition of the living organism exposed, bioaccumulation of selenium in some organisms (Fernández-Martínez & Charlet 2009) and reaction with metals. The inorganic forms (mainly selenite and selenate) have been reported to have higher toxicity (up to 40 times) than the organic forms (Latorre *et al.* 2013). In most of the organisms, selenite has been reported to be relatively more toxic than selenate (Sun *et al.* 2014). The effects of selenium on the human system have been frequently reviewed in the literature. For example, Vinceti *et al.* (2014) reviewed the neurotoxic effects of selenium. The effects of acute selenium exposure are long-lasting and irreversible and the authors suggested the need for further research on this topic.

OVERVIEW OF AVAILABLE TECHNOLOGIES FOR THE REMOVAL OF SELENIUM

Several technologies to remove selenium from wastewaters have been applied, and newer technologies have been developed in the past couple of years, or they are currently being developed. These technologies include, but are not limited to, adsorption and biosorption, membrane separation technologies, coagulation/flocculation, oxidation/reduction methods and phytoremediation. These technologies will be discussed here briefly. The direct precipitation of selenium compounds is of less importance, because selenium is mostly found as oxyanions in wastewaters and is therefore difficult to precipitate (Fu & Wang 2011).

Adsorption

From a cleaner production viewpoint, preventive measures to minimize selenium release should be considered and the treatment technologies should be evaluated following

the principles of green chemistry (Santos *et al.* 2015). Adsorption is useful for treating industrial and municipal wastewaters which have low pollutant concentrations. The main drawback of adsorption is the shift of the polluted medium, i.e., the contaminant, from the water phase to a solid phase on which the pollutant is concentrated, and in most cases, this adsorbent should be regenerated before reuse, or treated prior to ultimate disposal (Verbinnen *et al.* 2015; Ali *et al.* 2016). The adsorption capacity (Q_m) depends primarily on the type and characteristics of the adsorbent being used. However, environmental parameters such as temperature, pH, competitive metals, etc. also play an important role in determining the adsorption capacity (Ayangbenro & Babalola 2017).

The adsorption capacity of a material can show how much of the adsorbate can be adsorbed on the adsorbent. The ultimate adsorbent would be a chemical or material by means of which the low discharge limits that apply to selenium can be achieved with as little of the adsorbent material as possible. In an ideal situation, a desorption process can be applied which regenerates the adsorbent. In some cases, this is not feasible or only partial regeneration of the adsorbent is possible from the column (Santos *et al.* 2015). After some time, the adsorbent will be saturated and will no longer have the capacity to remove selenium and its oxyanions from wastewaters. The adsorbent then needs to be removed from the column and replaced with the new material. This process might lead to long shut-down times and be far less cost-effective than simply rinsing and regenerating the adsorbent.

As illustrated in Figure 2, the maximum adsorption capacities reported in the literature (Santos *et al.* 2015) for selenium compounds on oxides, minerals and carbon-based adsorbents range between 0.22 and 120 mg/g. The adsorption of Se(IV) is effective in a wide range of pH; on the other hand, the removal of Se(VI) is more difficult. Adsorption is ineffective at pH values greater than 10.0 (Suzuki *et al.* 2000). The dominant selenium form in acidic pH is selenious acid (H_2SeO_3). Between pH 3.5 and 9.0 mostly biselenite (HSeO_3^-) anion occurs, while at pH >9.0 selenite (SeO_3^{2-}) occurs (El-Shafey 2007a, 2007b). The main critical factor affecting the sorption rate is the sorbent surface. Film resistance also plays an important role in the solute's transport (Zhang *et al.* 2009).

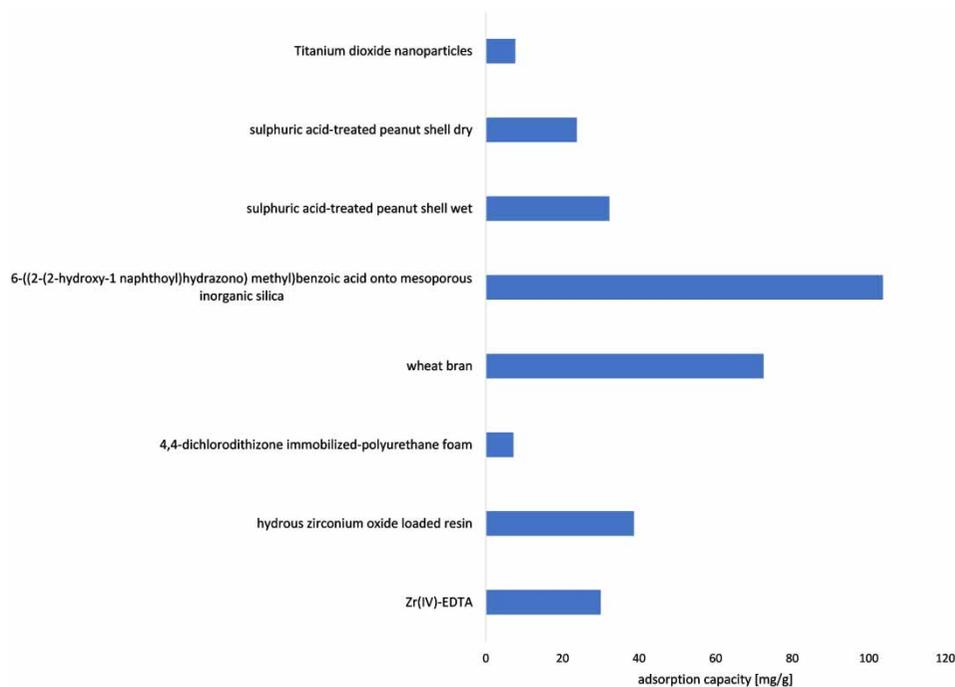


Figure 2 | Comparison of the adsorption capacities of different adsorbents.

One of the most popular sorbents used for adsorption is activated carbon. To prepare activated carbon, first the carbon precursor material should be cut into small pieces and washed with distilled water to remove the impurities and air dried. An example of a carbon precursor material is peanut shell (El-Shafey 2007a, 2007b) and in these studies, the carbonization of the peanut shell was carried out by sulphuric acid, at 170 °C. It might also be conducted by pyrolysis and microwave treatment. Se(IV) sorption on this kind of sorbent increases at higher activation temperatures. This might be caused by increasing the swelling properties of the sorbent which makes more active sites available for the removal of selenium ions (El-Shafey 2007a, 2007b).

Minerals and nanoparticles can also adsorb selenium. Hydrous oxides of high valence metals have a high affinity to selenium oxo-anions which are able to form weak conjugate acids. It is interpreted by an ion exchange mechanism based on electrostatic interactions. Ligand exchange of anions with coordinated water might also be a good choice for selenium removal. Suzuki et al. (2000) investigated Se(IV) adsorption on Zr(IV)-EDTA complex and reported that the retention of Se(IV) complex occurs mostly on the unsaturated site of Zr(IV) in the polymer. Polymer-Zr complex is very stable, thus, no leaking of

zirconium occurs. Even trace amounts of selenium were removed by the adsorbent containing Zr(IV). For the case of Zr(IV)-EDTA complex, the pH does not have an influence on the adsorption rate constant because diffusion into the resin particles is the rate determining step. Thus, the reaction rate might be enhanced by increasing the surface area of the polymer (Suzuki et al. 2000). In another study, the sorption capacity of TiO₂ nanoparticles was investigated (Zhang et al. 2009). The mechanism of selenium adsorption was predominantly diffusion in the boundary layer and between the nanoparticles. Nano-TiO₂ has high adsorption capacity. It effectively removes Se(IV) (>95%) from aqueous solution in a pH range of 2.0–6.0 (Zhang et al. 2009). Hematite and goethite are examples of minerals that also have shown good potential to adsorb selenium. For each case, the sorption of selenium decreases at high pH because of predominant selenium species. For Se(VI), at alkaline pH, there are a lower amount of aqueous species, i.e., HSeO₄⁻. For Se(IV), the maximum sorption occurs with the predominance of HSeO₃⁻. However, in some instances, the maximum sorption capacities can be miscalculated and misinterpreted because of the surface complexation model, and it was reported that even at high selenium concentrations, not all of the active sites were occupied (Rovira et al. 2008).

Biosorption

Biosorption uses inactive, non-living biomass as adsorbents to remove compounds from a system by accumulating these compounds in and around the cell wall of the organism involved. When natural materials or waste streams are used as the adsorbents, the more specific term ‘biosorption’ is commonly used in the literature (Dutta et al. 2016). When living biomass is used to sequester metals inside the organism’s cells, the term ‘bioaccumulation’ is used. In this process, the metal ion has to pass the cellular walls of the organism involved, which is only possible in living cells. Bioaccumulation is a much slower process than biosorption because of the independence of metabolic energy in biosorption (Joutey et al. 2015). Use of dead biomass is more beneficial in industrial applications than living cells. The biosorptive capacity is greater and the dead biomass can be obtained from industrial sources as a waste product (Abbas et al. 2014). For this reason, dead cells are used more often in biosorption studies, and bioaccumulation is not discussed further here.

The dead cell walls can also be broken, providing additional binding sites and slow sorption rate of bioaccumulation. The materials used as the biosorbent should be relatively less expensive, and they should be available in large quantities locally. The biosorbents can even come from biomass that is otherwise considered as a waste product (Chuah et al. 2005). Some typical materials that are used as biosorbents (either in original or in modified form) for the removal of heavy metals and mining water containing selenium are cells of bacteria, fungi and microalgae, seaweeds, plant tissues, processing waste from plants and animals such as fruit rinds and crab and shrimp shells (Kikuchi & Tanaka 2012). Most of the biosorption studies employ batch tests where a closed system with a known concentration of a particular pollutant is introduced to a biomass. The closed system is agitated in order to maintain the biomass under suspension conditions and to ensure good contact between the pollutant and the sorbent.

In batch tests, parameters such as pH, temperature, contact time, etc. are usually varied from low to high levels to examine their effect on the removal potential of the studied biomass. In most studies, ideal operating conditions are determined, which in return yield the highest sorption

potential (Dutta et al. 2016). Working with a continuous setup is more complex and, in this case, mostly breakthrough curves are determined (Gadd 2009). Samples of effluent are taken at pre-determined time intervals and their concentration is measured. The results are compared to the initial concentration. When the effluent concentration equals the initial metal/selenium concentration of the wastewater, the biomass is considered to be saturated and no more pollutant can be retained. In Table 1, a brief summary of the Q_{max} values obtained from different batch biosorption studies from recent literature are summarized.

The removal of contaminants by biosorption process relies on several complex mechanisms that are governed and easily affected by mass transfer and heat transfer properties. The main mechanisms involved in biosorption are adsorption, ion exchange, surface complexation, ion entrapment in intra- and interfibrillar capillaries, chelation and precipitation (Volesky & Holan 1995; Garg et al. 2012). In general, there are many functional groups present on the cellular wall sites of the organisms that could attract and sequester the target pollutants. The composition differs for every type of biomass, but the most important structures

Table 1 | Maximum biosorption capacity (Q_{max}) reported in the literature for the biosorption of selenium-containing compounds by biomass

Biosorbent	Species biosorbed	Q_{max} (mg/g)	References
<i>Gracilaria</i> seaweed	Se(VI)	2.72	Roberts et al. (2015)
<i>Ganoderma Lucidum</i> red mushroom	Se(IV)	127	Nettem & Almusallam (2013)
<i>Aspergillus</i> sp. J2	Se(IV)	5.67	Li et al. (2013)
<i>Eichhornia crassipes</i> aquatic weed	Not defined	0.135 ^a	González-Acevedo et al. (2012)
Lemna minor aquatic weed	Not defined	0.743 ^a	González-Acevedo et al. (2012)
Wheat bran	Se(IV)	73.05 ^a	Hasan et al. (2010)
Wheat bran	Se(VI)	58.29 ^a	Hasan et al. (2010)
<i>Cladophora Hutchinsiae</i> green algae	Se(IV)	74.9	Tuzen & Sarı (2010)
Sulfuric acid-treated peanut shell	Se(IV)	23.76	El-Shafey (2007a, 2007b)
Rice husk	Se(IV)	28.25	El-Shafey (2007a, 2007b)

^aThe results from continuous studies were originally expressed in units of $\mu\text{g/g}$.

for metal biosorption are carboxyl, carbonyl, hydroxyl, thiol, sulfonate, thioether, amine, secondary amine, amide, imidazole, phosphonate and the phosphodiester group (Volesky 2007; Naja & Volesky 2011). For some types of biomass, one or more typical functional groups can be identified that are responsible for carrying out the biosorption process. For example, the acetamido groups are the functional groups that promote biosorption in chitin, carboxyls and sulfates. This functional group is present in the polysaccharides of marine algae, structural polysaccharides in fungi, and hydroxyl groups present on lignin and hemicellulose in straw (Volesky & Holan 1995). Besides the presence of functional groups, other factors will also influence the biosorption behaviour. Temperature, pH, specific surface area of the biosorbent, the presence of competing metal ions, pre-treatment of the biosorbent, initial biomass and metal ion concentration are important factors that can influence the efficiency of the biomass as a sorbent (Garg et al. 2012).

Application of microbial biomass as biosorbents for the removal of selenium

Selenium treatment from any industrial wastewater is a big challenge for engineers and plant operators. First, in some wastewater, selenium concentration is very low and it is technically and economically difficult to treat using conventional treatment technologies. Second, the permissible discharge limit for selenium in treated water is very low (5 µg/L or even less). Conventional technologies fail to treat the effluent to meet this limit in many cases. Third, because of its complex chemical nature and interfering chemicals present in wastewater that contains selenium, change in chemical speciation may often cause the treatment process to be ineffective. Similarly, changing pollutant concentration is also a hindrance for a conventional treatment system to treat selenium. Finally, there is difficulty in the management of disposal of residues and by-products that are generated from the conventional treatment technologies to treat selenium (Sandy & DiSante 2010). All these factors have directed the research of selenium removal to biosorption-based technologies.

Different microbial biomass has attracted great attention in the field of metal and metalloids remediation from

wastewater. The biologically active molecules have an affinity to bind certain ions or molecules from the aqueous medium (Tan & Cheng 2003; Gautam et al. 2014). The adsorption of matter occurs on the biological material due to the biological activities in live/living cells or metal binding functional groups of cells in both living and dead cells (Bakircioglu et al. 2010). Generally, the use of microorganisms as adsorbents has proven to be an efficient, cost-effective and safe technique for the removal of different metals and metalloids. In addition to this, biosorption techniques lead to the minimization of chemicals in the wastewater treatment sector. This biocatalyst-based technology can also reduce chalcogen oxyanions under room temperature, standard atmospheric pressure and neutral pH. The technology is also able to meet the regulatory limit of selenium in wastewater. Special types of microorganisms are resistant to selenium oxyanions and are able to reduce them to their elemental forms.

In order to avoid toxicity and the requirement of growth medium that would increase the operational costs, dead biomass is preferred. Application of dead biomass for biosorption also allows desorption of the adsorbed selenium for the purpose of resource recovery. The use of dried, non-living or chemically pre-treated microorganisms appears to be promising for selenium removal. Living cells, after physical and chemical treatment, have also shown good performance in the biosorption process. Several studies have reported the bioremediation of selenium using microorganisms such as fungi, yeast, bacteria and algae. Application of each type of biomass for the removal of selenium has been discussed and a comparison of the different types of biomass is shown in Table 2.

Bacteria

Application of bacteria as a biosorbent offers the following advantages: it takes less time, provides better genetic handling and is easy to manage. Different types of heterotrophic aerobic and anaerobic and chemotropic bacteria have been used for the reduction of selenium oxyanions and to treat wastewater contaminated with selenium. Bacteria can reduce selenate to selenite and further to elemental selenium, selenide and organic selenium. Different species of bacteria such as *Wolinella succinigenes*, *Pseudomonas stutzeri*,

Table 2 | Comparison of different types of adsorbents for selenium removal

Biomass type	Selenium species	Temperature (°C)	pH	Model	Q _{max} (mg/g)	References
<i>Cladophora hutchinsiae</i>	Se(IV)	20	5.0	Langmuir	74.9	Tuzen & Sarı (2010)
<i>G. lucidum</i>	Se(IV)	20	5.0	Langmuir and Freundlich	126.99	Nettem & Almusallam (2013)
<i>Gracilaria</i> modified biochar	Se(IV) and Se(VI)	20	4.0		2.72	Roberts et al. (2015)
<i>Gracilaria</i> modified biochar	Se(VI)	–	–	–	3.80	Johansson et al. (2015)
<i>S. cerevisiae</i>	Se(IV)	45	5.0–6.0	Sip isotherm	39.02	Khakpour et al. (2014)
Wheat bran	Se(IV) and Se(VI)	30	2.0	Thomas, BDST, Yoon-Nelson	72.54 and 62.51, respectively (μg/g)	Hasan et al. (2010)
<i>Pseudomonas stutzeri</i>	Se(IV) and Se(VI)	25–35	7.0–9.0	–	–	Lortie et al. (1992)
<i>Enterobacter taylorae</i>	Se(VI)	21	8.2	–	–	Zhang & Frankenberger (2005)
Bacterial inoculum	Se(VI)	25	8.5	–	–	Twidwell et al. (1999)
<i>Clostridium</i> and <i>Desulfovibrio</i>	Se(VI)	–	–	–	–	Twidwell et al. (1999)
<i>Saccharomyces cerevisiae</i>	Se(IV)	0–125	7.0	–	–	Pérez-Corona et al. (1997)
<i>Lactobacillus plantarum</i>	Se(IV) and Se(VI)	20–50	3.0–9.0	–	700 (μg/g)	Tyburska & Jankowski (2011)

Bacillus sp. SF-1, *Bacillus selenitireducens*, *Pseudomonas* sp. strain CA5, *Bacillus* sp. strain STG-83 have been tested successfully for the reduction of Se(IV). Similarly, *Citerobacter freundii*, *Citerobacter braakii*, *Enterobacter taylorae*, *Bacillus* sp. strain STG-83 have been used to reduce Se(VI) (Lortie et al. 1992; Tomei et al. 1992; Blum et al. 1998; Kashiwa et al. 2000; Zhang et al. 2004; Zhang & Frankenberger 2006; Hunter & Manter 2009).

Twidwell et al. (1999) demonstrated the application of *Pseudomonas stutzeri*, which is able to reduce both Se(IV) and Se(VI). The bacteria were grown on carbon surfaces pre-treated with biopolymers and the biofilm was created. Thereafter, the enzymes from the bacteria were extracted. The biofilm and enzymes were treated with 620 μg Se(IV)/L in aerobic bioreactors. The biofilm-based reactor produced effluent containing <10 g Se/L for nearly nine months of operation without achieving breakthrough. On the other hand, the enzyme-based reactor produced effluents containing the same amount of selenium with breakthrough after four months of continuous operation. Tan et al. (2018) compared the performance of a biotrickling filter and an upflow anaerobic sludge blanket (UASB)

reactor for the treatment of a model mining wastewater contaminated with SeO₄²⁻ and SO₄²⁻. Although the Se removal performance of the UASB reactor was not affected by the presence of SO₄²⁻, the results from that study showed that the performance improved by >70% using the biotrickling filter biofilm. According to Kuroda et al. (2011), *Pseudomonas stutzeri* NT-I can reduce the selenium up to a concentration of 10 mM in the form of Se(VI) and 9 mM in the form of Se(IV), respectively. In that study, the experimental conditions were as follows: pH range of 7.0–9.0 and temperature 20–50 °C for selenite reduction and pH 6.0–9.0 in the temperature range of 20–50 °C for selenite reduction. Altringer et al. (1989) treated three different types of mine wastewater with selenium concentrations ranging from 1.7 to 30 mg/L, pH of the wastewater between 8.4 and 8.9, using two types of bacteria, namely, *Pseudomonadaceas* and *Enterobacteriaceae*. The effluent after bacterial biosorption had selenium concentration within the range of 160–1,000 μg Se/L.

Pieniz et al. (2011) has reported the Se(IV) bioadsorption capacity of *Enterococcus* species. A total of 36 *Enterococcus* species were isolated from dairy product

among which two species, namely, *Enterococcus faecalis* and *Enterococcus faecium*, grew optimally and were able to remove selenium at an initial pH of 7.0 and at a temperature of 25 °C. After 24 hours, these species were able to remove 9.9 mg/L and 59.7 mg/L of selenite, respectively. Similarly, in a related study (Fujita et al. 2002), the reduction of selenate into elemental selenium using *Bacillus* sp. SF 1 in an anaerobic continuous flow reactor was observed. Within a short retention time, selenate was reduced; however, the authors reported an accumulation of selenite. At longer retention times, both oxyanions were converted into elemental selenium which is non-toxic in nature. According to the first order kinetics constant, selenate and selenite reduction rate were calculated to be 2.9×10^{-11} L/cells/h and 5.5×10^{-13} L/cells/h, respectively.

Fungi

In the field of environmental biotechnology, fungi and yeast have a special place. The rapid proliferation of their cells, genetic variation and easy morphological and genetic manipulation capabilities, survival in a wide range of environmental conditions like temperature and pH have captured the interest of researchers for their use as potential biosorbents. Besides these, the waste biomass is also available free of cost if obtained as a by-product from the industries. If the biomass has to be grown, it can be easily grown without the application of expensive technology and growth medium (Kuyucak 1990). Even though the application of fungal and yeast biomass has been explored for the adsorption of different types of heavy metals, very limited studies are available in the field of selenium biosorption using fungal biomass (Kapoor et al. 1995). Species such as *Saccharomyces cerevisiae* (Lazard et al. 2010, 2011; Pérez-Corona et al. 2011; Khakpour et al. 2014), *Candida utilis* (Zhil'tsova et al. 1996), *Phanerochaete chrysosporium* (Espinosa-Ortiz et al. 2015), *Aspergillus* sp. (Li et al. 2013), *Rhodotorula mucilaginosa*-13B (Ruocco et al. 2014), and *Lactobacillus plantarum* (Calomme et al. 1995) have been used for the biosorption of selenium. Fungi and yeast are able to bind selenium in its organic and inorganic forms. They can bioaccumulate selenium intracellularly as well as extracellularly. During the extracellular binding of selenium proteins, phospholipids or polysaccharides play an active

role to form an ionic bond or complexation of selenium. In the case of intracellular accumulation, active transportation of selenium occurs in the interiors of the cells (Kieliszek et al. 2015).

Application of *Saccharomycn cerevisiae* to sequester selenium in different oxidation states was studied by Pérez-Corona et al. (1997). The authors reported that the dependency of Se(IV) bioaccumulation depended on factors such as temperature and the amount of biomass used, but Se(VI) showed low affinity to the biomass. The solution pH did not affect the accumulation of Se(IV). In a recent study (Espinosa-Ortiz et al. 2015), the capacity of *Phanerochaete chrysosporium* – a white rot fungus – was tested for the successful removal of selenite from synthetic wastewater in a continuously flowing bioreactor. During the 41 days of reactor operation, the authors reported ~70% total soluble Se removal at a continuous Se loading rate of 10 mg Se/L/day. In addition, morphological changes in the fungi was also observed due to the intracellular production of elemental selenium nanoparticles.

According to Gharieb et al. (1995), among the different fungi tested, *Fusarium* sp., *Trichoderma reesei*, *Aspergillus niger*, *Mucor* SK and *Rhizopus arrhizus* were the species that were able to reduce selenite to its elemental form. In the case of *Fusarium* sp. and *Trichoderma reesei*, the fungal cells could reduce selenite in Czapek-Dox agar medium, while the other three species were able to reduce selenite when grown on malt extract agar. Similarly, Marinescu et al. (2011) demonstrated the selenium adsorption capacity of *Saccharomyces uvarum* when it was treated with sodium selenite at different temperatures, pH, selenium concentrations, and biomass proportions, using two types of agar (malt wort and sparge water). In that study, at initial concentrations in the range of 30–180 µg/mL sodium selenite, accumulation of selenium was observed in the range of 0.6–2.2 mg/g for malt wort and 0.3–0.9 mg/g for sparge water, respectively. Nettem & Almu-sallam (2013) studied the effect of different parameters such as pH of the solution, adsorbent dose, initial metal ion concentration, contact time and temperature on the biosorption of selenium using *Ganoderma lucidum* biomass. The adsorption capacity was found to be 127 mg/g. Fourier transform infrared spectroscopy (FT-IR) analysis of the fungal cells suggests that amino, carboxyl, hydroxyl and carbonyl groups were responsible for facilitating the biosorption process.

Algae

Marine algae or seaweeds are also frequently studied microorganisms for the biosorption of selenium from contaminated water. They are attractive biosorbents because of the high metal binding capacity due to the presence of polysaccharides, proteins or lipid on their cell wall. They contain functional groups such as amino, hydroxyl, sulfate and carboxyl groups which act as binding sites for metal and metalloid removal (Shelef 2018). In addition, algae are naturally abundant species, renewable and thus a cost-effective biosorbent (Tuzen & Sari 2010). Mane *et al.* (2011) investigated the effect of pre-treatment of *Spirogyra* sp. on the selenium biosorption capacity. For this purpose, the biomass was subjected to heat, autoclaving and chemical treatment with sodium hydroxide and acetic acid. This physical and chemical treatment had a positive effect on the adsorption capacity of selenium, wherein maximum metal removal was achieved using autoclaved biomass.

In another study, the waste biomass of *Gracilaria* generated after the commercial production of agar showed an affinity to adsorb Se(IV) and Se(VI) after the biomass was treated with a ferric solution and converted into biochar through slow pyrolysis (Roberts *et al.* 2015). Even though the biosorption capacity of this biochar was lower (2.7 mg/g), this was the first attempt to show the adsorption ability of *Gracilaria* modified biochar. Another study by Johansson *et al.* (2015) demonstrated the application of *Gracilaria* modified biochar to remove 98% of Se(VI) from mock solution.

Membrane separation technologies

The typical pressure-driven membrane separation technologies consist of microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Among these, only nanofiltration and reverse osmosis are capable of separating selenium compounds from a contaminated wastewater stream. Kharaka *et al.* (1996) showed that the use of nanofiltration was capable of selectively removing 95% of selenium from highly contaminated water. Solar powered ultrafiltration-nanofiltration/reverse osmosis systems described by Richards *et al.* (2008) were capable of removing 74–94% of the initially present selenium concentrations in Australian groundwaters. Further evidence of selenium removal by

nanofiltration or reverse osmosis is, to say the least, very scarce in the scientific literature. Twidwell *et al.* (1999) stated that reverse osmosis is listed as one of the best available technologies (BATs) by the USEPA, but that further industrial implementation of this technology is probably hindered by the fact that the solutions to be treated contain very dilute concentrations of solids, which is most often not the case for industrial wastewaters like acid mining wastewaters. Therefore, pre-treatment is required and reverse osmosis for selenium removal from polluted waste streams can only be used as a final polishing step, often described in the literature as a post-treatment step.

Coagulation or flocculation

Coagulation or flocculation is a commonly used technique in wastewater and drinking water treatment. The colloidal and suspended particles that cannot be settled gravitationally can be precipitated by destabilization of the charged particles. The coagulants that are used commonly are Fe^{3+} and Al^{3+} salts that hydrolyze spontaneously when added to water, to form a series of metastable hydrolysis products. When positively charged, these hydrolysis products can neutralize negatively charged particles and can thus counteract the repulsive forces. When neutrally charged (i.e., $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$), the coagulants can form large aggregates that can enclose the contaminants in their densely enmeshed network when precipitating (Staicu *et al.* 2015).

Coagulation/flocculation has proven to be effective for the removal of several toxic metals and metalloids (Fu & Wang 2011). However, for the removal of selenium, literature information is rather scarce. Staicu *et al.* (2015) compared the removal of colloidal Se(0) from wastewater by centrifugation, filtration and coagulation/flocculation with aluminum sulfate or ferric chloride. According to the authors, coagulation/flocculation achieved the highest removal (92%) compared to centrifugation (91% at 4,500 rpm, 73% at 3,000 rpm and 22% at 1,500 rpm), filtration over a 0.45 μm filter (87%) and coagulation/flocculation with ferric chloride (43%). In addition, Se(0), Se(IV) and Se(VI) were also removed by coagulation/flocculation. Hu *et al.* (2015) observed that the removal of Se(IV) was much more pronounced than the removal of

Se(VI), but also that the Fe-based coagulants were much more effective than the Al-based coagulants.

(Biological) Oxidation/reduction

Oxidation/reduction processes are only seldom used for the remediation of selenium-containing waters and soils. Contrary to the Cr(VI)/Cr(III) systems where only the very mobile compound (Cr(VI)) can be converted to a less soluble one and the precipitated form (Cr(III)), the naturally prevalent forms of selenium (i.e., Se(IV) and Se(VI)) are highly soluble. Therefore, reduction to metallic selenium and subsequent precipitation can decrease the selenium levels. This method has already been applied before and it can be used to remove other unwanted components (Plotnikov 1960). On the other hand, for the reduction of Se(IV) or Se(VI) to their metallic state, a strong reducing agent is required which makes the whole process unfavourable. Instead of using strong reducing agents, Se-reducing bacteria can also be used. Cantafio et al. (1996) performed tests with the selenate-respiring bacterium *Thauera selenatis* in a pilot scale biological reactor and were able to reduce the selenium content in the tested agricultural drainage water by 98%. Selenate was reduced to elemental Se and could be recovered using a precipitant-coagulant. Successful attempts to reduce selenite to elemental Se using bacteria were performed with *Geobacter sulfurreducens*, *Shewanella oneidensis* and *Veillonella atypica* (Pearce et al. 2009) and *Rhodospirillum rubrum* (Kessi et al. 1999), respectively.

Phytoremediation

Phytoremediation is defined as the removal of pollutants from contaminated soils, water or air by plants (Lee 2013). The plants can either accumulate and/or detoxify the toxic elements. It can be used for metals and metalloids, explosives, solvents, pesticides, etc. It is a relatively inexpensive technique compared to excavation and *ex situ* remediation of a contaminated soil. The cleanup can be performed *in situ* and no external supply of energy is required to grow the plants; however, some energy may be required for harvesting the biomass. Processing the biomass to yield energy (e.g., by incineration with energy recovery, pyrolysis or anaerobic digestion) can, in its turn, generate some profit,

while the pollutants concentrated in the ashes can be extracted and sold (phytomining) (Ali et al. 2013; Li et al. 2017). One disadvantage of phytoremediation is that it is a very slow process and it can take several years to clean up a contaminated site.

The effective removal of selenium from contaminated soils and waters by phytoremediation has been demonstrated recently. Tests with constructed wetlands vegetated with sturdy bulrush, Baltic rush, smooth cordgrass, rabbit-foot grass, salt grass, cattails, tulle, widgeon grass, or a combination thereof showed a removal of 59% selenium from the water phase (Gao et al. 2003). Other successful selenium phytoremediation studies were performed with broccoli plants (Zayed & Terry 1994), wheat (Li et al. 2008), cattails (Huang et al. 2012) and water hyacinths (Pal & Rai 2010). Another promising approach is the identification of unique genes from natural selenium hyper accumulators and their subsequent transfer to fast-growing species (LeDuc & Terry 2005; Zhu et al. 2009).

CHALLENGES IN SELENIUM ADSORPTION AND FUTURE DIRECTIONS IN SELENIUM REMOVAL TECHNOLOGIES

Based on the literature review, most of the current research focuses on Se(IV) and Se(VI) removal, but the main problem is the removal of the organic form of selenium. It has higher bioavailability and bioaccumulates more rapidly than other selenium compounds. It is produced during the reduction of selenium compounds by bacteria and probably related to the amounts of soluble organic materials used by the bacteria for this process (Zhang & Frankenberger 2005). Further research should also focus on understanding the mechanism of biosorption in flow through systems that simulate natural aquifers. For example, when the pH is higher than the pKa of a functional group, that group is negatively charged and has affinity to metal cations. On the contrary, when the pH drops below the pKa value, it is saturated by protons and has positive charge and can adsorb oxyanionic contaminants more efficiently (Roberts et al. 2015). Thus, it is evident that the availability of functional groups for metal adsorption and metal speciation depends on the prevailing pH of the water. Cationic biosorption is influenced

by pH and the mechanism of uptake differs from cation biosorption to unmanipulated biosorbents (Roberts *et al.* 2015). Another issue about which not enough is known is the degree of selenium associations with organic matter. The cycling of selenium has an impact on the biotic process. Nevertheless, in the literature, there is a lack of mechanistic description of these processes and their mechanisms (Fernández-Martínez & Charlet 2009).

As discussed previously, it is still difficult to assess the problems of selenium deficiency/toxicity in living organisms. A deep understanding of the different types of antagonistic or synergistic interactions between selenium/soil/water/plants may be helpful. Determination of selenium forms which should be taken in case of selenium deficiency and identifying the best remediation procedures for contaminated sites still pose a problem because at present they are done on a case-to-case basis. The application of spectroscopic tools would allow the selenium adsorption process to be studied at the nanoscale. The use of such tools will increase our knowledge about selenium retention at the mineral/water interface and it would be helpful to suggest an appropriate treatment system for selenium removal from contaminated sites. As seen from the literature, the complex geochemistry of selenium causes complex interactions between the mineral phases and organic matter. Although, in some instances, the mechanisms involved in the formation of organic matter–metal–selenium complexes are known, information on their stability constants and chemical structure under different environmental conditions are scarce (Fernández-Martínez & Charlet 2009).

One of the promising substances used for selenium adsorption is a complex of zirconium with polymer resin. It adsorbs trace amounts of selenium and arsenic (Suzuki *et al.* 2000). *Gracilaria*-modified biochar has proven to be effective for the adsorption of Se(IV) and Se(VI) from aqueous solutions, in contrast to existing selenium treatment technologies (Roberts *et al.* 2015). This would also improve the stability of *Gracilaria* cultivation by redirecting the unused waste for the treatment of selenium containing wastewaters. From a practical viewpoint, in places like the Kesterson reservoir (USA), which is a natural selenium contaminated site, researchers are still investigating suitable options for treatment (Fernández-Martínez & Charlet 2009). In such environments, selenium nano-precipitates are

inherently produced due to biotic reactions with the local environment although the reactivity and surface chemistry of the nano-precipitates are still not known. Further research in this direction would be practically helpful to widen the knowledge about the reactivity of selenium nanoparticles as well as their fate in the environment.

CONCLUSIONS

The different physico-chemical and biological treatment technologies available for the removal of selenium oxyanions, namely, selenite and selenate, were reviewed. It is noteworthy to mention that some of these technologies are often expensive because the removal of selenium from a polluted water/soil environment is a complex process and the discharge limits are rather stringent. Also, the presence of organic matter, competing ions, dissolved solids and other metals or metalloids in the water interferes with the degree of treatment achieved. In such situations, it is advisable to implement a hybrid or two-step process, i.e., in the first stage, the selenium oxyanions can be selectively adsorbed onto the active sites of a sorbent material (first stage adsorption) or biologically oxidized/reduced (first stage bioreactor) and, subsequently, in the second stage, the remaining non-treated competing compounds can be removed. The application of a hybrid process, such as combination of electrocoagulation and membrane filtration or adsorption and precipitation, is expected to yield promising results for the removal of selenium present in mining water. The review ends with the suggestion of two promising substances (both chemical and biological) for selenium adsorption – a complex of zirconium with polymer resin and *Gracilaria*-modified biochar. The fate of selenium nano-precipitates in the environment still remains unknown. Further research in this direction would be practically helpful to deepen the knowledge about the reactivity of selenium nanoparticles as well as their fate in the natural environment.

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