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REVIEW

Production, recovery and reuse of biogenic elemental selenium

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Abstract Selenium (Se) has caused several ecological disasters due to its toxicity and bioaccumulation along trophic networks. Industrial activities that process fossil fuels and mineral ores, such as electricity generation, metal extraction and oil refining, produce wastewaters containing selenium. Currently, these wastewaters are insufficiently treated before being discharged into the environment. Several environmental biotechnological processes are used to convert soluble selenium oxyanions, selenite and selenate, to solid elemental selenium, Se(0), because elemental selenium is less toxic. Applying a post-treatment solid–liquid separation step to these biological processes removes and separates Se(0) from the treated effluent. Here, we review the sources of selenium-rich waste streams, and we propose several techniques for the removal and reuse of selenium. The major points are as follows: (1) Biogenic Se(0) has colloidal properties that can be offset by the addition of coagulants, either by dissolving multivalent salts or by electrogenerating the coagulant in situ; (2) recovered biogenic Se(0) is a secondary raw material and (3) biogenic Se(0) can be used for niche applications such as fertilizers and adsorbent for metals. The biological treatment of industrial wastewater containing selenium can be linked with resource recovery as a sound and economic approach to alleviate the demand for this critical element.

Keywords Selenium · Biogenic · Resource · Recovery · Reuse

Introduction

Selenium (Se) is a chalcogen element with complex biogeochemistry (Fernandez-Martinez and Charlet 2009). Se oxyanions, selenite (Se[IV], SeO_3^{2-}) and selenate (Se[VI], SeO_4^{2-}), have been documented to exhibit toxicity toward various aquatic groups (Simmons and Wallschlaeger 2005). During the mid-1970s, chronic Se poisoning occurred as a result of Se oxyanions leached from ash deposited in the vicinity of Lake Belews (North Carolina) by a coal-fired power plant. The impact was devastating for the resident fish populations: 19 out of 20 species were eliminated (Lemly 2002). Another major event occurred in the 1980s when agricultural drain water enriched in Se severely affected the migratory bird populations in Kesterson Reservoir, California (Ohlendorf 1989).

Among its valence numbers, elemental selenium, Se(0), has long been considered as the least toxic due to its solid state and low bioavailability (Chapman et al. 2010). Se(0) has nevertheless been shown to be bioavailable to filter feeders and fish (Li et al. 2008; Luoma et al. 1992; Schlekat et al. 2000). Extensive research on the impact of colloidal Se(0) on filter-feeding mollusks and the trophic networks has been conducted in San Francisco Bay area (Presser and Luoma 2006; Purkerson et al. 2003; Schlekat et al. 2000; USEPA 2010). Furthermore, micro- and nanosize Se(0) particles have increased reactivity caused by their high surface–volume ratio, leading to concerns about the short-term toxicity of Se(0) nanoparticles (SeNP) (Zhang et al. 2005). Moreover, Se(0) is reoxidized to SeO_3^{2-} and SeO_4^{2-} when Se(0) reaches an environment with an

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elevated redox potential, e.g., surface waters compared to anaerobic bioreactors or sediments (Zhang et al. 2004).

Biogenic Se(0): metabolism

Se(0) can be produced by chemical (i.e., chemogenic) or biological (i.e., biogenic) synthesis (see Glossary). Even if pure cultures have been shown to withstand high concentrations of toxic Se oxyanions (Hunter and Manter 2011; Staicu et al. 2015b), mixed microbial cultures, e.g., those present in anaerobic granular sludge, are used in full-scale bioreactors that treat large volumes of selenium-laden wastewaters (Opara et al. 2014; Pickett et al. 2008). Mixed cultures are preferred over pure cultures as wastewaters are not sterile, and thus have a contamination potential by microorganisms present in the wastewater. Besides, mixed cultures often grow in flocs, biofilm or granular sludges, which have an increased capacity to withstand toxicants (Schmidt and Ahring 1996; van Hullebusch et al. 2003).

To date, only a limited number of bacteria (Kuroda et al. 2011a; Lortie et al. 1992; Tomei et al. 1992, 1995) were shown to reduce SeO_4^{2-} to Se(0) (Fig. 1a), whereas the reduction of SeO_3^{2-} appears to be a more common feature of many phylogenetically diverse bacterial species (Sura-de Jong et al. 2015). Certain fungal species can also reduce SeO_3 (Espinosa-Ortiz et al. 2015). The end product of Se oxyanions reduction can be Se(0) (Fig. 1b). Sometimes, the complete reduction to Se^{2-} occurs, but this most reduced Se species is rapidly reoxidized to Se(0) under oxic conditions (Kagami et al. 2013).

The reduction of selenate is mediated by *SerA* reductase in *Thauera selenatis* (Krafft et al. 2000; Schröder et al. 1997) and by *SrdA* reductase in *Bacillus selenatarsenatis* (Kuroda et al. 2011b). A distinct selenate reductase, YnfE, was reported in *Citrobacter freundii* (Theisen and Yee 2014). However, the exact biochemical mechanism of selenite reduction is still unclear. A vast amount of data suggest the presence of a common metabolic pathway used by bacteria for the reduction of other compounds (nitrate, nitrite and sulfate) as well (Fig. 1a). In the β-proteobacterium *T. selenatis*, a nitrite (NO_2^-) reductase has been reported to be involved in selenite reduction (DeMoll-Decker and Macy 1993). In *Clostridium pasteurianum*, an inducible sulfite (SO_3^{2-}) reductase has been reported to reduce selenite pointing toward another putatively shared metabolic pathway (Harrison et al. 1980; Harrison et al. 1984).

Also, thiols have also been proposed to play a role in Se(0) formation. When amended with selenite, cultures of *Escherichia coli* (Bebien et al. 2002) and *Rhodospirillum rubrum* (Kessi and Hanselmann 2004) showed overexpressed glutathione reductase activity, indicative of a detoxification process. Staicu et al. 2015b (unpublished results) reported a subspecies of *Pseudomonas moraviensis* able to withstand high levels of SeO_3^{2-} (up to 120 mM) and SeO_4^{2-} (over 150 mM). The strain was isolated from the roots of the Se hyperaccumulator plant *Stanleya pinnata* growing on seleniferous soils in Colorado (USA). In addition, the strain can aerobically reduce 10 mM of SeO_3^{2-} below the detection limit within 48 h, to red Se(0) as the end product. Because of its fast Se metabolism, the new isolate holds promise for the development of a more efficient aerobic treatment system of selenite-laden wastewaters.

Selenium-laden wastewater

Even if selenium is a trace element in the earth's crust, it can be enriched in certain rocks and soils. As it can substitute for sulfur in biolites and minerals, Se is often found associated with fossil fuels and sulfide minerals, e.g., pyrite and chalcopyrite (Fernandez-Martinez and Charlet 2009). Fossil fuels (e.g., crude oil and coal) can contain high levels of Se: High-sulfur coals have been reported to contain up to 43 mg Kg^{-1} Se (Yudovich and Ketris 2006) and crude oil can also be highly enriched in Se with concentrations in the range 5–22 mg L^{-1} (Lemly 2004).

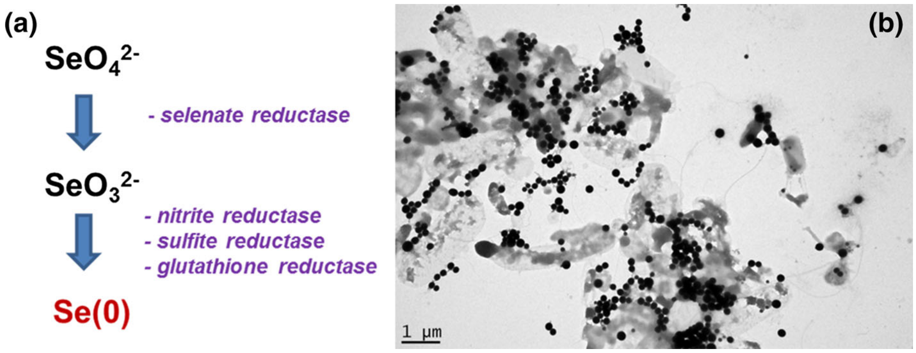

Fig. 1 **a** Biological reduction of Se oxyanions to Se(0) and **b** Biogenic Se(0) produced by anaerobic granular sludge (Staicu et al. 2015c)

Human activities such as fossil fuel burning, non-metal smelting industry and agriculture practiced on Se-rich soils have resulted in the introduction of important quantities of selenium in the environment, thus modifying its natural cycle (Chapman et al. 2010). Wen and Carignan (2007) connected the increasing Se anthropogenic emissions to the onset of the Industrial Revolution (eighteenth century). A positive correlation between the high coal combustion activity observed in 1940 and 1970, and the Se accumulation in archived herbage and soil samples from the Rothamsted Experimental Station (UK) has been documented (Haygarth 1994). Considering the future trends in energy production based on fossil fuel combustion, it is expected that Se will increase its presence and toxicity in the environment (IEA 2014).

By burning or processing Se-containing raw materials, wastewaters contaminated with high concentrations of this element are generated. Major sources of wastewaters containing selenium oxyanions are those of the oil refining industry, coal combustion and metal processing (Lemly 2004; USEPA 2010). Se-laden wastewaters can be treated by a number of physical–chemical and biological treatment technologies (NAMC 2010). Biological treatment processes using bioreactors produce different concentration levels of colloidal Se(0) as a function of the initial Se content and the Se conversion rate (NAMC 2010). Several reactor types are currently employed on a full-scale configuration, notably fluidized bed reactors and the *Advanced Biological Metals Removal* (ABMet®) system. ABMet® employs anaerobic bacteria fixed to a granular activated carbon bed or a biomatrix (Pickett et al. 2008).

Se(0): separation

Biogenic Se(0) has been shown to exhibit colloidal properties, making it stable in suspension and difficult to sediment by gravitational settling (Buchs et al. 2013; Staicu et al. 2015c). The colloidal stability of biogenic Se(0) particles (Fig. 2) is related to the coating biopolymer layer that imparts an overall negative charge preventing the particles from aggregation (Buchs et al. 2013; Dobias et al. 2011). The chemogenic Se(0) undergoes allotropic transition shortly after synthesis unless not stabilized with a capping agent, e.g., protein and polyvinylpyrrolidone (Gates et al. 2002). This implies that the stability of chemogenic Se(0) is not intrinsic, but can be modified by adding stabilizing agents such as organic polymers (Jain et al. 2015b). Removal of colloidal Se(0) from a bioreactor effluent is necessary to reduce its environmental load and the potential negative impact of Se(0) exerted on aquatic ecosystems (See section "Introduction"). Several approaches have been investigated for the removal of colloidal Se(0), such as chemical dosing (Staicu et al. 2015c) and electrocoagulation (Staicu et al. 2015a).

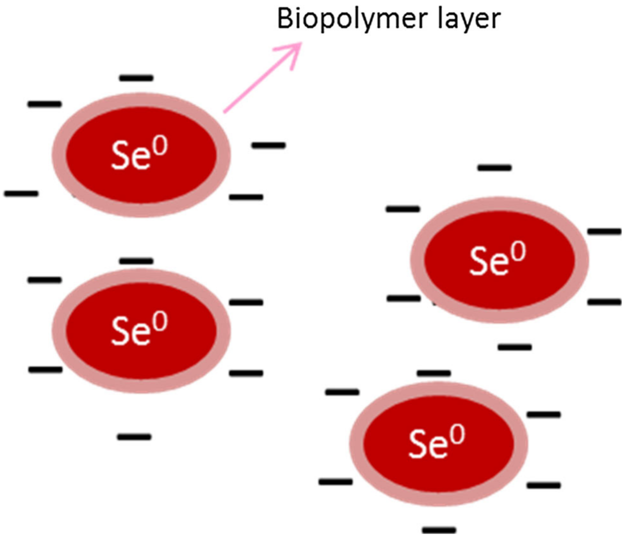

Fig. 2 Biopolymer coating that confers colloidal stability to biologically produced SeNP

Chemical dosing (coagulation–flocculation)

Coagulation–flocculation relies on the destabilization and settling of colloids and suspended particles that cannot sediment by gravity within practical time frames. When coagulants are added to water, the metal ions (e.g., Al^{3+} and Fe^{3+}) hydrolyze spontaneously and form a series of metastable metal hydrolysis products that alter the physical state of the suspended particles. The coagulants act by repressing the charge of the colloids and by forming large aggregates of $Al(OH)_3$/$Fe(OH)_3$ which ultimately leads to particle sedimentation (Gregory and Duan 2001). Staicu et al. (2015c) investigated the effect of aluminum sulfate and ferric chloride on the solid–liquid separation of highly turbid (850 NTU) colloidal Se(0) solutions produced by anaerobic granular sludge under anaerobic conditions. Aluminum sulfate achieved the highest turbidity removal efficiency (92 %) at a dose of 10^{-3} M, whereas ferric chloride achieved a maximum turbidity removal efficiency of only 43 %. Charge repression appeared to play a minor role in particle neutralization.

Electrocoagulation

In electrocoagulation, an electrical current is applied between two electrodes (including a sacrificial anode) immersed in wastewater (Fig. 3a). Applying current across the electrodes creates an electrical field and causes the dissolution of the sacrificial anode to form a coagulant and the electrolysis of water. The coagulants are thus

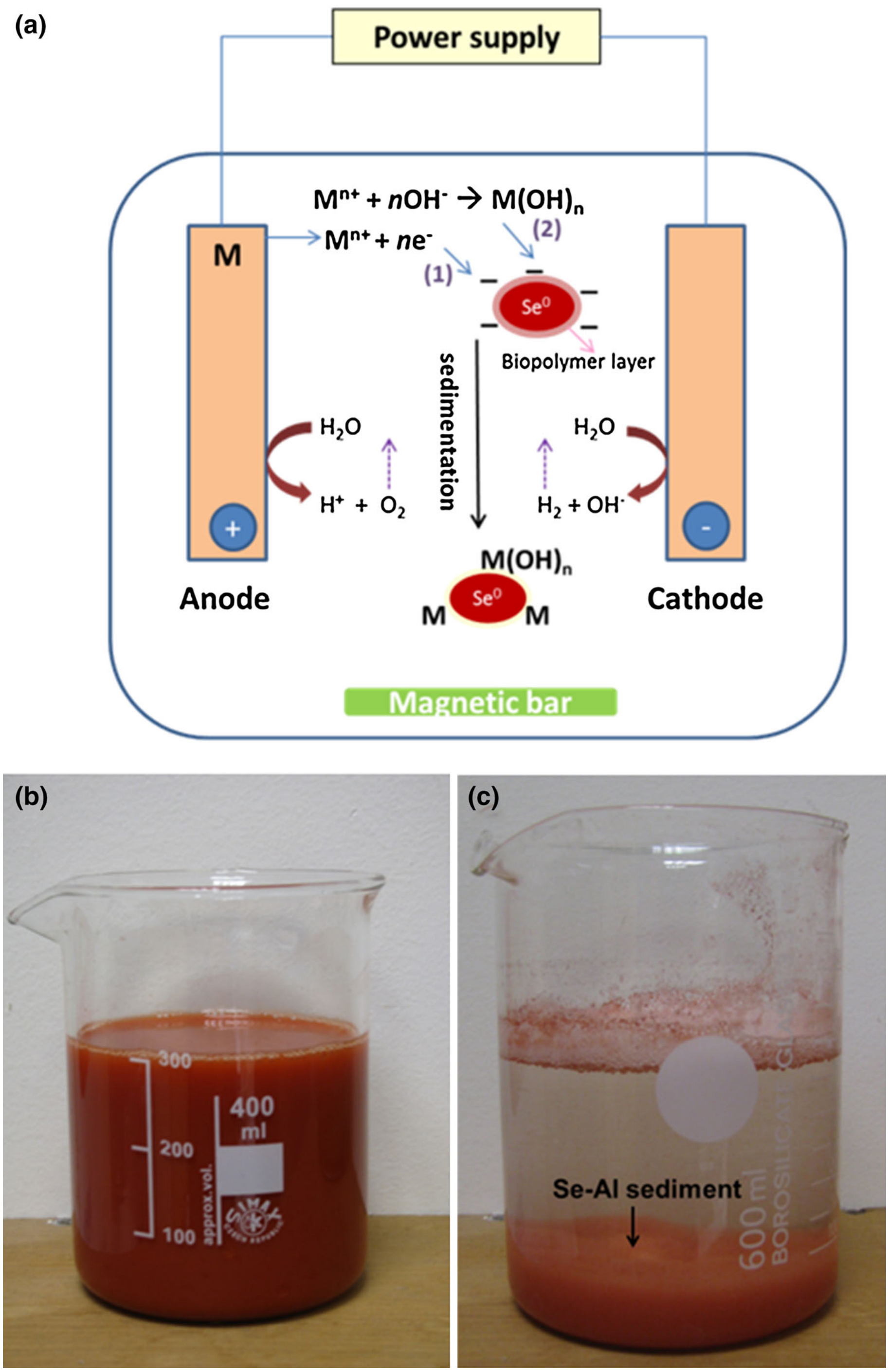

Fig. 3 **a** Electrocoagulation setup and treatment effectiveness using Al sacrificial electrodes. Notes: M = metal (e.g., Al and Fe), **b** colloidal biogenic Se(0) produced by *P. moraviensis* stanleyae and **c** colloidal Se(0) treated by electrocoagulation with aluminum electrodes (Staicu et al. 2015a)

electrogenerated in situ and in a continuous manner during the coagulation–sedimentation process. Another advantage of using an electrochemical approach for the treatment of wastewaters stems from the electrical field that exerts an electrophoretic action on the charged particles, inducing their migration toward the oppositely charged electrode.

Staicu et al. (2015a) reported the removal of colloidal Se(0) produced aerobically by *P. moraviensis* stanleyae by electrocoagulation (Fig. 3b). Iron and aluminum sacrificial anodes were employed under galvanostatic (i.e., constant current) conditions. The best Se(0) turbidity removal efficiency (97 %) was achieved using iron electrodes at 200 mA. Aluminum electrodes removed 96 % of the colloidal Se(0) at a slightly higher current intensity (300 mA). Due to the less compact nature of the Al flocs (Fig. 3c), the Se–Al sediment was three times more voluminous than the

Se–Fe sediment. The toxicity characteristic leaching procedure test showed that the Fe–Se sediment released Se below the regulatory level (1 mg L^{-1}), whereas the Se concentration leached from the Al–Se sediment exceeded the limit by about 20 times. This entails that the Se–Fe sediment might be landfilled, although recovery of Se is a more preferred alternative.

Recovery and reuse

Figure 4 presents a possible scheme of recovering and reusing Se oxyanions present in wastewaters. Biological treatment is a promising alternative that can reduce the load of Se that reaches the environment. In contrast to sulfur (S), Se can be converted from its oxidized forms directly to the Se(0) and, thus, Se removal can be achieved in a single reactor unit. The direct reduction of sulfur oxyanions to S(0) occurs in nature only in minor quantities. Therefore, high-rate sulfur removal from wastewater needs to be achieved by a two-step process: first the complete reduction to sulfide (S^{2-}) and the subsequent oxidation to elemental sulfur (Muyzer and Stams 2008). Furthermore, to avoid the complete reoxidation back to sulfate, the S^{2-} oxidation must proceed under strict micro-aerophilic conditions that are difficult to control (Janssen et al. 2001). If recycling is adopted, biogenic Se(0) particles, formed as a by-product of the biological treatment of selenium-laden wastewater, can link bioremediation with the generation of new materials. Several potential applications of the removed biogenic Se(0) are given below.

Fertilizer

The recovered biogenic Se(0) can be applied on soils that are low in bioavailable Se. Various regions of the world suffer from low Se (e.g., Finland, China and Ireland), and in some countries (e.g., Finland), national programs have been successfully implemented to overcome this deficit (Alfthan et al. 2014). A slower degradation and, therefore, a longer lifetime in the soil can be an argument in favor of using Se(0) instead of fertilizers containing selenate. Staicu et al. (2015a) have reported the precipitation of biogenic Se(0) with iron hydroxides using an electrocoagulation strategy. The Fe–Se sediment generated at the end of the treatment was shown to have a strong binding capacity, and Se was slowly released from the iron matrix. However, a detailed study is needed to investigate the behavior of Se(0) or Fe–Se sediment in agricultural soils. Other limitations, such as social acceptance and the potential contamination of Se(0) with toxic metals co-present in wastewaters, should also be addressed.

Semiconductors

Having *photoconductive* properties (i.e., decreased electrical resistance with increased illumination) as well as *photovoltaic* properties (i.e., the direct conversion of light into electricity), metal selenides are routinely exploited in a variety of industrial applications including solar and photo cells, exposure meters and xerography (Johnson et al. 1999). The use of Se(0) as a starting material for the production of the II–VI semiconductors ZnSe and CdSe could

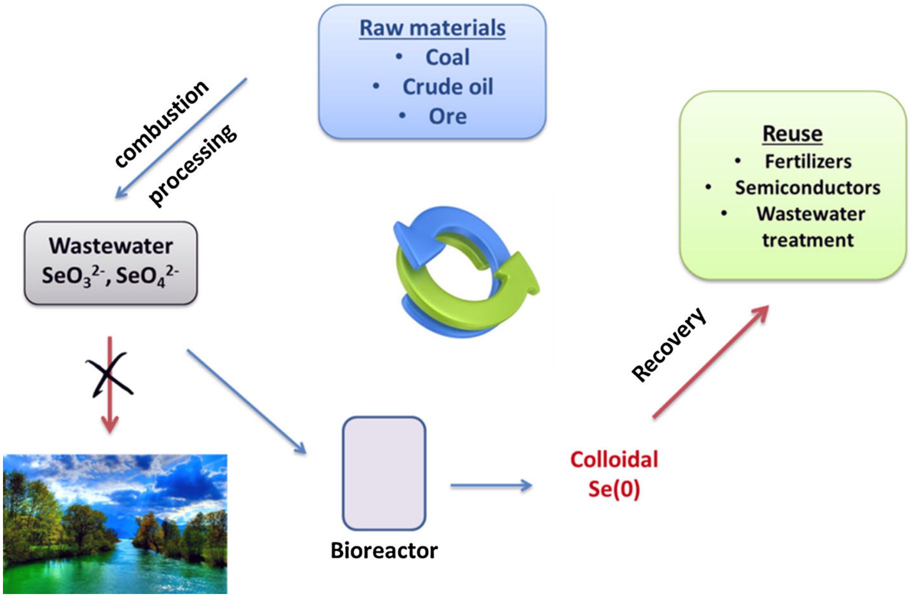

Fig. 4 Proposed Se recovery and reuse scheme using Se-rich wastewaters as a secondary Se resource

be an alternative process for the production of metal selenides. ZnSe nanoparticles were generated when selenite was reduced sequentially to Se(0) and then to selenide under anaerobic conditions by *Veillonella atypica* in the presence of $ZnCl_2$ (Pearce et al. 2008). The formation of metal selenides through a disproportionation reaction between Se(0) and Ag^+ and Hg^{2+} has also been proposed (Nuttall 1987).

Adsorbent for toxic metals

Another potential application for biogenic Se(0) is its use as adsorbent in the treatment of wastewaters and waste gases containing heavy metals (Jain et al. 2015a). Because biogenic Se(0) is covered by a biopolymer layer with an overall negative charge (Jain et al. 2015b), it will bind positively charged ions from the bulk solution. Several studies were focused on the interaction of Se(0) with mercury (Hg^{2+}) (Fellowes et al. 2011; Jiang et al. 2012; Johnson et al. 2008) and zinc (Zn^{2+}) (Jain et al. 2015a). Se(0) was shown to form HgSe on the surface of Se(0) particles (Johnson et al. 2008). The retention of Hg in a solid phase is desirable from an ecotoxicological standpoint as the formation of toxic methyl mercury and volatile liquid Hg(0) is thus prevented. The Se(0) particles were shown to be around 20 times more efficient than commonly used adsorbents such as nanosilver (188 vs 8.5 mg g^{-1}) and around 70 times than sulfur-impregnated activated carbon nanotubes (188 vs 2.6 mg g^{-1}) (Johnson et al. 2008). It is interesting to note that the other nanoparticles tested (Cu, Ni and Zn), even if their size was in the nanorange domain, exhibited a limited adsorption capacity for Hg, pointing toward the influence induced by the biopolymer layer (Johnson et al. 2008).

The Zn^{2+} (added as $ZnCl_2$) adsorption capacity of biogenic Se(0) produced anaerobically by anaerobic granular sludge of onto was recently quantified (Jain et al. 2015a). The maximum adsorption capacity amounted to 60 mg Zn g^{-1} biogenic Se(0). The effect of competing cations showed that the Zn^{2+} ion adsorption onto Se(0) was impacted by the presence of Ca^{2+} and Fe^{2+}, whereas the presence of Na^+ and Mg^{2+} had only a marginal impact. This is particularly relevant when treating industrial wastewaters, which usually have a complex matrix. As a comparison, zero valent iron (ZVI) has a much higher Zn adsorption capacity, 393 mg Zn g^{-1} ZVI (Yan et al. 2010). In order to gain more acceptance, the removal of soluble metals using Se(0) should be further investigated, particularly, with respect to the absorbance capacity of biogenic elemental Se and the stability of the metal Se(0) matrices.

Perspectives

Considering the depletion of raw materials at an accelerated pace, the change of perception relative to the waste-resource dichotomy is an important pillar of sustainable development (Macaskie et al. 2010). Instead of discharging Se-laden wastewaters into the environment, Se can be converted into Se(0) through a bioremediation approach and recovered for further use. As there is limited incentive for such a strategy to become popular, legislation should be the major driving factor. Similarly to the removal of sulfur from flue gas streams under the pressure of the Clean Air Acts, selenium can become an element of great concern and increased interest. The biological treatment of Se wastewaters is likely to gain popularity in the coming years and so the amount of biogenic Se(0) produced and reused.

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Glossary

Anaerobic granular sludge	Biomass in granular form produced by the auto-immobilization of mixed microbial populations and employed for the treatment of wastewater in up flow anaerobic granular sludge reactors
Biogenic	Resulting from the action of a living organism; in the current context, Se nanoparticles produced by the metabolic activity of microorganisms.
Chalcogen	Chemical element in group 16 of the periodic table; i.e., Oxygen (O), Sulfur (S), Selenium (Se), Tellurium (Te) and Polonium (Po). These elements are strongly associated with metal-bearing minerals.
Chemogenic	Resulting from chemical action; in the current context, Se nanoparticles produced through the reduction of Se oxyanions using a chemical reducing agent.
Colloidal system	System containing fine particles dispersed within a continuous medium that cannot be settled easily by gravitation.

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