Industrial Selenium Pollution: *Sources and Biological Treatment Technologies*

Lucian C. Staicu, Eric D. van Hullebusch, Bruce E. Rittmann and Piet N.L. Lens

Abstract Selenium (Se) discharge into the environment is becoming a matter of increasing concern because it induces toxic effects to biota at low concentrations (several micrograms per liter). Industrial activities that include energy generation, metal and oil refining, mining, and agriculture irrigation generate effluents contaminated with selenium. Biological treatment of these effluents is gaining in popularity in recent years. Microbial reduction of selenium oxyanions to particulate elemental Se^0 can be achieved in a number of bioreactor systems that are emerging as a viable bioremediation option because of their favorable cost, footprint, and treatment efficiency. Traditionally, granular sludge bioreactors (e.g., upflow anaerobic sludge blanket, UASB) have been tested for the treatment of selenium-laden wastewaters. Fluidized-bed bioreactors (FBBR) and packed-bed bioreactor systems were later adapted for Se treatment. The hydrogen-based hollow-fiber membrane biofilm reactor (MBfR) is a technology that delivers H_2 gas as the electron donor by diffusion to the biofilm formed on non-porous hollow-fiber membranes. A hybrid electro-biochemical reactor (EBR) which uses electrons that are delivered from an external power source through electrodes to selenium-reducing bacteria growing on electrodes has been developed. Constructed wetlands may be useful when the wastewater is produced in large volumes, but they are sensitive to temperature fluctuations and seasonal variation of the vegetation,

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and they have a large footprint. If Se^0 colloids are not captured efficiently within the bioreactor, a challenge is removing colloidal Se^0 from the effluent. When properly recovered, Se^0 can be a valuable product due to its photo-optical, semiconductive, and adsorptive properties.

Keywords Selenium · Wastewater · Biotreatment · Bioremediation · Toxicity

List of abbreviations

ABMet®	Advanced biological metals removal
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DIET	Direct interspecies electron transfer
DO	Dissolved oxygen
EBCT	Empty bed contact time
EBR	Electro-biochemical reactor
FGD	Flue gas desulfurization
FBBR	Fluidized-bed biofilm reactor
GAC	Granular activated carbon
HRT	Hydraulic residence time
MBfR	Membrane biofilm reactor
NAMC	North American Metal Council
ORP	Oxido-reduction potential
Se	Selenium
Se^0	Elemental (zero-valent) selenium
SeO_x	Selenium oxyanions (selenite and selenate)
TDS	Total dissolved solids
TOC	Total organic carbon
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

1   Introduction

Environmental pollution by selenium started to be recognized as a major problem following a number of incidents that affected aquatic ecosystems in the USA. The first incident occurred in North Carolina during the mid-1970s, when Lake Belews was contaminated by Se waste deposited by a coal-fired electric generating facility in the vicinity of the lake, resulting in a massive die-off of the local fish populations: 19 out of 20 species were eliminated! (Lemly 2002). In the early 1980s, selenium-bearing agricultural drainage water released in the Kesterson Reservoir,

Fig. 1 Black-necked stilt (*Himantopus mexicanus*) embryos from nests at Kesterson Reservoir: **S-313**—Normal; **S-9**—Eyes missing, severe exencephaly (protrusion of brain) through orbits, lower beak curled, upper parts of legs shortened and twisted, and only one toe on each foot. Photographs courtesy of U.S. Fish and Wildlife Service

San Joaquin Valley (California), severely affected migratory bird populations (an example is shown in Fig. 1) and triggered environmental-protection actions (Ohlendorf 1989). Other environmental problems posed by Se pollution followed in the next decades, culminating with the contemporary pollution event occurring in Elk Valley, British Columbia (Canada), due to coal-mining activities (Wellen et al. 2015).

One of the greatest concerns related to Se pollution is that it bioaccumulates. As a consequence, even low levels of Se build up through the trophic levels (i.e., *biomagnification*), leading to deleterious effects on aquatic ecosystems (Chapman et al. 2010). Industrial activities contribute significant amounts of Se that ultimately end up in the environment. Wen and Carignan (2007) connected the increasing anthropogenic emissions of Se to the onset of the Industrial Revolution (eighteenth century). They found a positive correlation between the high coal combustion activity observed between 1940 and 1970 and the Se accumulation in archived herbage and soil samples from Rothamsted Experimental Station (UK). Other intensive anthropogenic activities, such as crude oil processing, metal refining, mining, and crop irrigation, lead to the mobilization of large amounts of Se into aquatic and terrestrial ecosystems.

Chronic Se poisoning recorded in the fish populations of Lake Belews was associated with swelling of gill lamellae, anemia, corneal cataracts, popeye, reproductive failure, teratogenic deformities of the spine, head, mouth, and fins, and alterations in liver, kidney, heart, and ovary (Lemly 2002). A survey of the residual impact on Lake Belews, performed 10 years after the Se inputs had stopped, revealed a slow recovery at the ecosystem level and that sediment-associated Se still posed a hazard to fish and aquatic birds through selenium remobilization (Lemly 1996). Oil processing by refineries and agricultural activities on seleniferous soils surrounding San Francisco Bay have severely undermined vulnerable mollusks (e.g., bivalves), fish (e.g., white sturgeon), and birds (e.g., black-necked stilt) through trophic-level transfer (Presser and Luoma 2006).

This chapter begins by summarizing the characteristics and sources of Se pollution. It then provides an overview of the biological treatment systems employed for Se-containing wastewaters. Physical and chemical methods also can be used for SeO_x removal and are reviewed in chapter "Industrial Selenium Pollution: *Wastewaters and Physical–Chemical Treatment Technologies*" from this volume. We discuss the mechanistic bases and advantages and disadvantages of each biological treatment technology. We orient our examples and discussion as much as possible toward technologies that have been evaluated with real Se-bearing wastewaters.

2 Selenium Chemistry and Toxicity

2.1 Selenium Speciation

Selenium is a group-16 element that shares common properties with sulfur (S) and tellurium (Te). The element can exist in the environment in several valence states, namely +6, +4, 0, −1, and −2, and it can cycle through these states due to abiotic and biotic processes, as illustrated in Fig. 2 [based on Winkel et al. (2011)].

The two oxidized forms—the oxyanions (i.e., SeO_x), selenite (Se[+ IV], SeO_3^{2-}), and selenate (Se[+ VI], SeO_4^{2-})—are water-soluble, bioavailable, and toxic (Simmons and Wallschlaeger 2005). In natural aquatic environments, SeO_x have limited interactions with major cations (e.g., Ca^{2+} and Mg^{2+}), and, therefore, only a small fraction can be removed from the solution by precipitation (Séby et al. 2001).
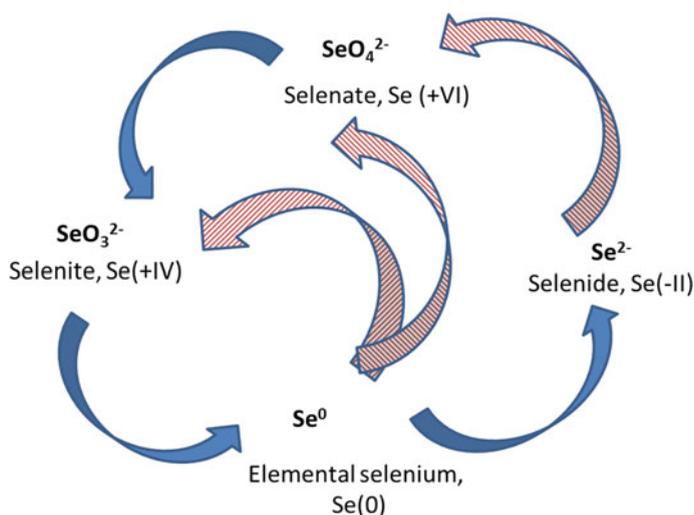

Fig. 2 Biogeochemical cycle of Se. *Blue-filled arrows* indicate reduction reactions, whereas *red-pattern filled arrows* show oxidation reactions. Winkel et al. (2011) provide an extensive presentation of the biogeochemical transformations of Se

Moreover, unlike metals that form solid phase hydroxides with increasing pH, SeO_x are stable over the entire pH scale (Chapman et al. 2010). All these characteristics make selenate and selenite persistent in aquatic ecosystems. The toxicity of SeO_x results from the incorporation of Se into S-related proteins and protein structures, leading to dysfunctional biomolecules (Stadtman 1974). In addition, SeO_x poisoning has been linked to oxidative stress through the generation of reactive oxygen species (ROS) (Hoffman 2002).

In contrast, elemental selenium (Se^0) is solid and less toxic (Lenz and Lens 2009), although recent reports cast doubt on the previously assumed innocuous nature of Se^0. Concerns have been raised in relation to the negative effects on certain ecological receptors such as filter-feeding mollusks (e.g., bivalves) and fish (Luoma et al. 1992; Schlekat et al. 2000; Li et al. 2008). Furthermore, when Se^0 is a product of microbial metabolism (i.e., *biogenic*), it has a size in the nanometer range (50–300 nm) and shows high colloidal stability. The **Box** explains the colloidal properties of biogenic Se^0 colloids and their biotechnological implications. In addition, the nanometer size adds to its potential toxicological impact, since size and reactivity are inversely related. Moreover, biogenic Se^0 can be re-oxidized to SeO_3^{2-} and SeO_4^{2-} when exposed to surface water with higher redox conditions (Zhang et al. 2004).

The most reduced valence state, selenide, Se[-II], is present only under strongly reducing conditions, and it forms metal selenides (H_2Se) and organic Se-compounds. The latter include volatile methylated forms (e.g., dimethylselenide and dimethyldiselenide), metabolic by-products (e.g., trimethylselenonium), and two seleno amino-acids (i.e., selenomethionine and selenocysteine) (Fernandez-Martinez and Charlet 2009). Due to their high reactivity, selenides combine readily with other elements. Some notable selenides having toxic potential include H_2Se and the selenocyanate ion ($SeCN^-$) (see **Box** from chapter "Industrial Selenium Pollution: *Wastewaters and Physical–Chemical Treatment Technologies*"), both of which are found in wastewaters generated by energy industries (NAMC 2010).

Box. Biogenic Se^0. *Natural colloids*

Although zero-valent Se bears no surface charge, biologically produced Se^0 particles have a negative surface charge in the range from -20 to -30 mV (Buchs et al. 2013). This negative charge is caused by a biopolymer coating composed mainly of proteins in extracellular polymeric substances (EPS) (Lenz et al. 2011; Jain et al. 2015b; Staicu et al. 2015b) surrounding the Se^0 particles. It is not yet clear if the coating attaches to Se^0 during particle nucleation inside the cell, during transport to the extracellular environment, or in the spent (extracellular) medium. A recent report identified bare Se^0 particles inside a novel strain of *Pseudomonas moraviensis*, indicative of the acquisition of the biopolymers during transport outside the cell or at a later stage once the particles are excreted (Ni et al. 2015). Having particle sizes of 50–300 nm, biogenic Se^0 clearly are colloids, which are fine particles dispersed within a fluid medium and not settling out by gravity. The negatively charged biopolymers that attach tightly onto the Se^0 particles impart their surface properties that impair aggregation. Because Se^0 particles are stable in

the water column, they can be subjected to long-range transport. Furthermore, this extended lifetime increases the probability of exposure to ecological receptors such as fish and filter-feeding mollusks. Thus, a solid-separation stage is often needed downstream of anaerobic bioreactors that convert SeO_x to biogenic Se^0. Several solid–liquid separation solutions have been employed, including media filtration, chemical precipitation, centrifugation (Staicu et al. 2015b), and electrocoagulation (Staicu et al. 2015a). From a solid-separation standpoint, colloidal Se^0 poses problems, such as membrane fouling, and this aspect has particular implications in bioreactor design (Nancharaiah and Lens 2015b). Re-oxidation of Se^0 must be avoided. Anaerobic bioreactors that treat Se-charged wastewaters have a negative ORP that allows selenate or selenite to be reduced to Se^0, but the biogenic Se^0 particles can be re-oxidized to SeO_3^{2-} and SeO_4^{2-} when discharged into aerobic aquatic environments, therefore reverting Se to its toxic valence states (Zhang et al. 2004). Biogenic Se^0 should not be regarded merely as a by-product of the bioremediation process, but rather as a potentially valuable resource (Staicu et al. 2015c). Se^0 particles possess unique photo-optical and semiconducting physical properties (Oremland et al. 2004) and can be used as a selective adsorbent for divalent cations (Jain et al. 2015a, 2016).

2.2 Sources of Selenium

Table 1 lists the Se content of important natural and processed materials. Selenium is a naturally occurring element in the Earth's crust, although at relatively low abundance (0.05–0.5 mg kg^{-1}) that is unevenly distributed (Kabata-Pendias 2000). Selenium is cycled through different environmental compartments by natural and anthropogenic actions.

Table 1 Concentration of selenium in raw and processed materials

Material	Se concentration (mg kg^{-1})
Earth's crust	0.05–0.5
Volcanic rocks	0.35
Soil (adequate)	0.4
Seleniferous soils	1–5000
Carbon-shale China	206–280
USA coal	0.46–10.7
Coal (fly ash)	73–440
Ash-settling ponds	0.087–27 mg L^{-1}
Fly ash leachate	0.04–0.61 mg L^{-1}
Crude oil	0.01–1.4
Refined oils	0.005–0.26 mg L^{-1}
Copper ore	20–82
Phosphate	1–300

Compiled from Lemly (2004) and Plant et al. (2014)

Natural processes include terrestrial weathering of rocks and soils, volcanic activity, wildfires, and volatilization from soils, vegetation, and water bodies (Haygarth 1994). Although natural processes are important, human activities have greatly modified the natural Se cycle since the beginning of the Industrial Revolution (1750–1850) (Wen and Carignan 2007).

In nature, selenium occurs rarely as pure element (Se^0). Because selenium can substitute for sulfur, metal-sulfide minerals (e.g., pyrite and chalcopyrite) and coal are prone to enrich this element. Typical selenide minerals include berzelianite (CuSe), klockmannite (CuSe), tiemannite (HgSe), penroseite (NiSe), clausthalite (PbSe), and stilleite (ZnSe). These typically occur together with copper, zinc, lead, gold, and nickel ores (Kyle et al. 2011). Smelting of various sulfide ores releases trace amounts of Se. Currently, the main source of industrial production of Se is linked to copper and lead refining. The slimes generated by the electrolytic refining of primary copper contain 5–25% Se (Hoffmann 1989). Even though lead is used much less today (due to its toxicity), copper production continues to soar due to its intensive utilization by the power sector. Thus, Se release will parallel the mining and the refining of copper ores, increasing its potential to reach the environment.

Selenium is an element that typically accumulates in coal at 1–1.6 mg kg^{-1}, but can reach 43 mg kg^{-1} (Yudovich and Ketris 2005). An interesting feature pointed out in Table 1 is that the processing of parent materials containing relatively low concentrations of Se results in by-products enriched in Se. Selenium enrichment in crude oils occurred in the same way as with coal. The refining of crude oil is an important source of Se emission to the environment.

During the Cretaceous period, the Earth's rocks became significantly enriched in Se (up to 100 mg kg^{-1}) as a result of volcanic gases and dust deposited in marine sediments (Kabata-Pendias 2000). Consequently, soils that developed on such Cretaceous parent rocks are naturally rich in Se (i.e., *seleniferous* soils). Notable examples are found in parts of China, India, Ireland, the US Central Valley, and other areas in the Western and Central United States (Kunli et al. 2004; Pilon-Smits et al. 2010).

When irrigation is practiced on seleniferous soils underlain by an impervious clay layer ("hardpan"), drains must be constructed to prevent water from building up and waterlogging the top soil (Ohlendorf 1989). A classic example is in the California Central Valley, where the drained agricultural runoff was diverted to wildlife marshes and artificial wetlands. In 1968, the Bureau of Reclamation created the San Luis Drain and the Kesterson Reservoir. The Kesterson reservoir was completed in 1971 and consisted of 12 evaporation ponds that developed into a wetland supporting a wide variety of wildlife. Selenium leached from the irrigated soils into the drain water built up in the water and bioaccumulated in the aquatic ecosystems. The outcome was a severe environmental pollution event that affected the fish and migratory bird populations of Kesterson Reservoir, or the "Kesterson effect" (Presser 1994). The enriched levels of Se were linked to increases in mortality, congenital deformities, and reproductive failures in the aquatic bird populations, along with the collapse of the reservoir's fishery (Ohlendorf 1989).

Phosphate mining and processing are also significant sources of selenium pollution, especially by leaching of surface waste rock dumps (Hamilton 2004; Myers 2013). For instance, the Phosphoria Formation (centered in Idaho, USA) contains phosphate ores with an average of 125 mg kg^{-1} Se and a maximum of 1500 mg kg^{-1} (Knotek-Smith et al. 2006). Another source of environmental Se is the use of phosphate fertilizer containing traces of Se (Chapman et al. 2010).

A number of anthropogenic activities result in the release of Se into the environment. The energy sector based on coal combustion contributes high amounts of Se in the form of volatile species, combustion ash, and liquid effluents [e.g., Flue Gas Desulfurization (FGD) wastewater]. The mining sector releases Se when the extracted overburden rock is exposed to environmental factors (e.g., rain, snow melt, and temperature variations), and the element is weathered and transferred to ground and surface water systems. The extractive industry (e.g., copper, zinc, lead, and noble metals) separates Se from the ore during the purification process of the target metal. Se resulting from this activity is often considered an impurity, eventually being discharged to the environment. Other anthropogenic activities, such as oil refining and agriculture practiced on seleniferous soils, liberate Se to aquatic and terrestrial ecosystems. Selenium concentrations in typical industrial effluents range from several hundred µg L^{-1} to 5–10 mg L^{-1} (NAMC 2010). Apart from selenium, other potentially toxic elements, such as aluminum, boron, cadmium, mercury, and uranium, exist in certain types of industrial effluents (e.g., FGD wastewater) (Cordoba et al. 2011).

2.3 Regulatory Limits

The discharge limits for selenium are based on toxicity tests that differ widely among regulatory agencies. This creates disparities among regulations and legal thresholds (Luoma and Presser 2009). Selenium is a freshwater priority pollutant for the existing US National Recommended Water Quality Criteria, with a criterion continuous concentration or chronic level of 5 µg L^{-1} total Se (dissolved and particulate) (USEPA 2013). This particularly low Se discharge limit is currently a big challenge for most treatment technologies. The USEPA's latest effluent guidelines for Se discharge for the steam-generated power industry (i.e., coal power plants) allow for 12 µg L^{-1} (monthly average), with a daily maximum limitation of 23 µg L^{-1} (USEPA 2015). In Canada, the target guideline for total selenium content in surface waters is 1 µg L^{-1} (Canadian Council of Ministers of the Environment 2007). In addition, British Columbia developed a water quality guideline for saline water of 2 µg L^{-1} (Nagpal and Howell 2001). Selenium is not listed in the European Commission's Dangerous Substances Directive or the Environmental Quality Standards Directive (Environmental Quality Standard Directive 2008/105/EC). In Japan, irrespective of the industrial source, the discharge limit for Se is 100 µg L^{-1} (Nishimura et al. 2007).

The presence of selenium in drinking water is also regulated, but the permissible limits vary by as much as 10-fold among issuing agencies. Lower values, e.g., 10 μg L^{-1}, are required by the European Union, China, and Canada (European Drinking Water Directive 1998; Canadian Drinking Water 2012), whereas the USA imposes a higher criterion, 50 μg L^{-1} (USEPA 2013). For countries lacking a legislative framework for drinking water pollutants, the World Health Organization (WHO) provides guidelines on the standards to be achieved. In the case of Se, the WHO proposes a 40 μg L^{-1} value (WHO 2011).

3 Biological Treatment

Biological treatment of Se-laden wastewaters has gained in popularity in the last two decades and constitutes the most technically and economically feasible approach to Se removal. We begin by reviewing the metabolic basis for all biological processes used for Se removal. We then summarize information on biological approaches that have been applied for Se removal from water and wastewaters of various origins.

3.1 Microbial Metabolism of Se

Microbial processes transform selenium among its different oxidation states and between inorganic and organic forms. Bacteria employ different strategies to deal with SeO_x, by far the most common form of Se in wastewater. The strategies are *dissimilatory* Se reduction (energy generating), *assimilatory* Se reduction (used for the synthetic cellular machinery), and *detoxification* (Stolz and Oremland 1999). Treatment technologies for Se removal are based on the dissimilatory mechanisms, which we review in detail. Assimilation of selenium is a prerequisite for microbial metabolism, since Se is an essential cofactor for a number of enzymes such as glutathione peroxidase (GPx), thioredoxin reductase, and selenophosphate synthetase (Labunskyy et al. 2014). However, the Se content of biomass is too small (<1%) to make assimilation into biomass a realistic treatment mechanism. Detoxification is often reported in the case of aerobic transformations of selenite, but is too minor to support a treatment technology. Chapter "Bacterial Metabolism of Selenium—For Survival or Profit" in this volume and Nancharaiah and Lens (2015a) provide more thorough reviews on the bacterial transformations of selenium.

In the dissimilatory metabolism, selenate or selenite serves as the terminal electron acceptor in respiration, which allows the cells to conserve energy in ATP via the electron-motive force (Stolz and Oremland 1999). The reduction half reactions for selenate (Eq. 1) and selenite (Eq. 2) are:
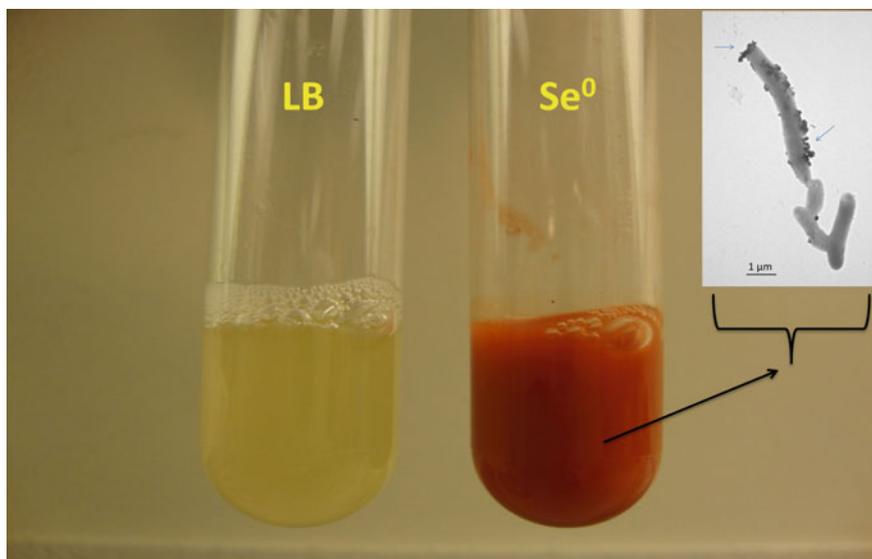
Fig. 3 Colloidal *red-colored* Se^0 produced by *Pseudomonas moraviensis* stanleyae under aerobic conditions. *Note* LB stands for Luria-Bertani growth medium and represents the medium containing 10 mM Na_2SeO_3, but no bacterial inoculum; Se^0 represents *red-colored* elemental Se produced through microbial metabolism of 10 mM Na_2SeO_3 after 24 h of incubation in LB (28 °C, 200 rpm, aerobic). *Inset* Transmission electron micrograph (scale: 1 μm) of Se^0 particles produced by *Pseudomonas moraviensis* stanleyae under the above-mentioned growth conditions (Staicu et al. 2015d)
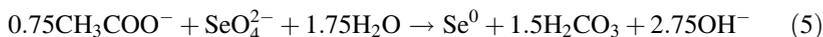
$$SeO_4^{2-} + 6H^+ + 6e^- \rightarrow Se^0 + 2H_2O + 2OH^- \tag{1}$$

$$SeO_3^{2-} + 4H^+ + 4e^- \rightarrow Se^0 + H_2O + 2OH^- \tag{2}$$
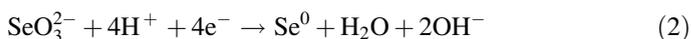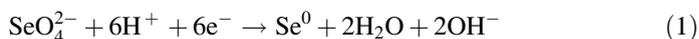
The microbial reduction of SeO_x leads to nanoparticulate Se^0 that displays interesting colloidal properties (see Fig. 3 and the **Box**).

In most environments, selenate respiration requires oxidation of an electron donor. Many organic electron donors, such as acetate, lactate, and ethanol, are possible. H_2 can also be used as an inorganic electron donor. The provision of an electron load using an external electric current has also been accomplished [e.g., Electro-biochemical reactor (EBR)]. The following two reactions show the donor half reactions for acetate (Eq. 3) and H_2 (Eq. 4):

$$CH_3COO^- + 5H_2O \rightarrow 2H_2CO_3 + 8H^+ + 8e^- + OH^- \tag{3}$$

$$H_2 \rightarrow 2H^+ + 2e^- \tag{4}$$
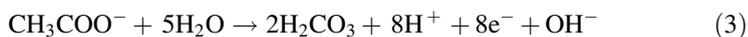
Combining the two donor half reactions with the selenate half reaction shows the overall respiration reactions (Eqs. 5 and 6):

$$0.75CH_3COO^- + SeO_4^{2-} + 1.75H_2O \rightarrow Se^0 + 1.5H_2CO_3 + 2.75OH^- \quad (5)$$

$$3H_2 + SeO_4^{2-} \rightarrow Se^0 + 2H_2O + 2OH^- \quad (6)$$

The overall reactions show that full reduction of one mole of selenate requires at least 0.75 mol of acetate and 3 mol of H_2. The actual amount can be considerably higher due to net biomass synthesis and reduction of more favorable electron acceptors, like oxygen, sulfate, and nitrate often present in the wastewater. The biological process has to be designed to provide at least this amount of electron donor from external sources. Electron donor delivery is the most essential aspect of dissimilatory SeO_x reduction processes.

The overall reactions also demonstrate that SeO_x reduction produces a substantial amount of strong base (OH^-), which increases the alkalinity and can increase the pH if the wastewater's alkalinity is insufficient to balance the pH increase. Thus, pH control is often required for selenate treatment.

Wastewaters containing SeO_x often contain nitrate and sulfate in concentrations several orders of magnitude higher (NAMC 2010; Staicu et al. 2017). Nitrate and sulfate are microbial electron acceptors that can compete with SeO_x for available electrons. It is desirable (even mandatory if nitrate levels potentially exceed the discharge value) to reduce nitrate prior to SeO_x reduction, although sulfate reduction is usually undesirable due to the formation of sulfides which can be toxic. When nitrate is co-reduced with SeO_x, its reduction increases the donor demand proportionally, since each mole of nitrate requires 5 electron equivalents to be reduced to N_2 gas. Likewise, nitrate reduction to N_2 generates one base equivalent that also augments the alkalinity and can increase the pH. Wastewaters are described in terms of organic compounds present in the form of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC), but also by more general parameters like total dissolved solids (TDS) and total suspended solids (TSS). In general, industrial effluents containing Se are low in organic content, and this leads to the need of adding exogenous electron donors.

Even though the energy yield of the dissimilatory metabolism of Se is not as high as for respiration of O_2, it still generates enough energy to sustain microbial growth (Stolz et al. 2003). It is possible that reduction can proceed all the way to Se (-II), which can be volatilized or reacted with metals to form insoluble metal selenides. However, practical SeO_x-treatment processes produce particulate Se^0.

Thauera selenatis was the first bacterium reported to carry out selenate respiration under anaerobic conditions (Macy et al. 1993a). Following the initial report, a periplasmic reductase with high affinity for selenate was purified and characterized (Schröder et al. 1997). Several studies attempted to use a *Thauera selenatis* inoculum for bioremediation purposes on drainage water. Macy et al. (1993b) showed that the reduction of selenate (350–450 µg L^{-1}) was not inhibited by nitrate, which is significant since nitrate is thermodynamically more favorable for

bacterial anaerobic respiration and its environmental concentration normally exceeds that of selenate. When acetate was provided as an organic electron donor, high Se-removal yields (~98%) were recorded. In a follow-up study (Cantafio et al. 1996) at the pilot-scale, packed-bed biological reactor using the same bacterium had similar high Se-removal yields, an almost total conversion of selenate to Se^0, and almost complete (~98%) denitrification.

Aerobic reduction of selenite appears to be ubiquitous among phylogenetically diverse bacterial groups, as they probably share metabolic pathways used for the reduction of other compounds such as nitrate or sulfate (Sura-de Jong et al. 2015). Regarding selenite reduction under aerobic conditions, it is well established to be a detoxification strategy employed by bacteria (Kessi et al. 1999; Staicu et al. 2015d). In contrast, only a handful of reports (reviewed by Kuroda et al. 2011) describe bacteria capable to aerobically reduce selenate to red Se^0, and none identified the strategy used by such bacteria to accomplish this conversion.

In spite of a significant number of studies focused on the metabolism of pure (axenic) Se-reducing bacterial isolates, mixed microbial cultures (flocs, biofilms, and granular sludge) are the option of choice for bioremediation purposes. Two of the arguments in favor of this approach include the non-sterile nature of wastewater, making it impossible to avoid input of diverse microorganisms, and the value of having a metabolically diverse community to thrive in the chemically complex wastewater matrix. A number of mixed-culture inocula coming from full-scale reactors treating brewery (Staicu et al. 2015b) and paper mill (Hageman et al. 2013; Jain et al. 2015a) wastewater or environmental samples (e.g., sediment inoculum collected from an end-pit lake) (Luek et al. 2014) have been used as seeds in various bioreactor systems for the bioremediation of Se-laden wastewater.

3.2 Granular Sludge Bioreactors

Upflow anaerobic sludge bed (UASB) reactors use a granular sludge developed by the self-aggregation of microbial cells (McHugh et al. 2004). The influent is pumped to the bottom of the reactor and flows upward through the sludge bed, where Se oxyanions are reduced to Se^0 by the suspended biomass. The upper section of the reactor includes a gas–solid–liquid separator that retains the biomass while collecting the biogas and the treated effluent. Panels a and b of Fig. 4 present a schematic of an UASB reactor and a picture of a sludge granule that originated from an UASB reactor treating SeO_4^{2-} effluents (Astratinei et al. 2006). McHugh et al. (2004) provide a more comprehensive discussion on the granulation process and the types of granular reactors used for wastewater treatment.

UASB reactors were pilot-tested for selenium remediation at the Adams Avenue Agricultural Drainage Research Center in San Joaquin Valley (California). The influent had a total Se content of 500 μg L^{-1}, and the removal efficiency ranged from 58 to 90% (NAMC 2010). Among the limitations encountered were the long
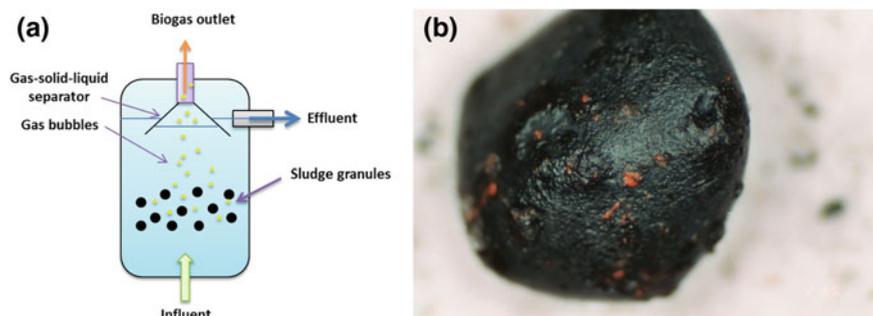
Fig. 4 Granular sludge bioreactor for the treatment of Se-rich wastewaters. **a** Schematic of the upflow anaerobic sludge bed (UASB) reactor configuration; **b** Sludge granule showing *red* Se^0 on its surface (photograph courtesy of Dr. Violeta Astratinei). *Note* The bioreactor schematic is not drawn to scale

acclimation period of the granular sludge (about 6 months), short-circuiting of the bioreactor caused by the accumulation of gas in the sludge, and variability in Se-removal efficiencies due to the temperature sensitivity of the process. When the temperature dropped from 15 to 7 °C, the removal efficiency decreased from 88% to 35% (NAMC 2010).

The removal of SeO_x from an oil refinery wastewater—characterized by extremely low pH (<1.0), high salinity (6–7%), and Se mainly present as selenite (13–74 mg L^{-1})—was investigated using an UASB bioreactor (Soda et al. 2011). In order to precondition for optimal microbial growth, the wastewater pH and salinity were adjusted to about 7.5 and 1.1%, respectively. The bioreactor was operated at 30 °C, pH 6.0–9.0, and a HRT of 24 h using ethanol as electron donor. The Se level in the effluent was ≤ 100 µg L^{-1} by day 15 of operation, and the removed selenium was accumulated in granular sludge as red Se^0.

3.3 Fluidized-Bed Biofilm Reactor

A fluidized-bed biofilm reactor (FBBR) operates on the same principle as an UASB reactor, but growth of the microbial community and the biofilm formation occur on added solid particles. The particles are fluidized by the upward movement of the liquid, which minimizes substrate-transport limitations observed in stationary-bed processes (Chan et al. 2009). A schematic of an FBBR system is depicted in Fig. 5.

The FBBR technology from Envirogen Technologies Inc. uses fine sand and/or activated carbon that are colonized by heterotrophic facultative bacteria for the anoxic reduction of SeO_x to red Se^0. Selenium-containing wastewater is pumped into the FBR in an upflow direction to suspend the biofilm-supporting media. A recirculation line provides for continual fluidization, even if no feed water is
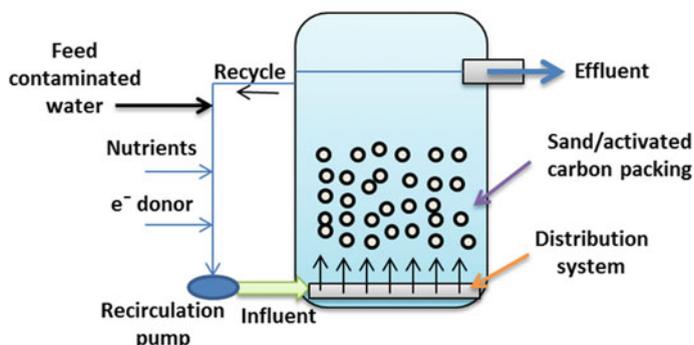
Fig. 5 Schematic of the fluidized-bed biofilm reactor (FBBR) configuration. *Note* The bioreactor schematic is not drawn to scale

supplied to the FBBR. A variety of organic electron donors are used, including acetate, ethanol, methanol, and molasses. Typically, a solid–liquid separation stage that could also include a BOD/COD polishing step is required downstream to remove washed-out biomass and colloidal Se^0. The continuous operation of the reactor requires no cyclic backwash operations. The FBR technology has been demonstrated to effectively perform at influent water temperatures down to 4 °C (Webster Todd, personal communication).

Selenium removal from mining water was pilot-tested using the Envirogen FBBR system. The influent contained Se, mainly as selenate, was in the 155–588 µg L^{-1} range (average 360 µg L^{-1}), along with 31 mg L^{-1} nitrate nitrogen (N–NO_3^-) and around 800 mg L^{-1} sulfate (Gay et al. 2012). Molasses and MicroCg (proprietary engineered carbon source) were used as electron donors during the operation of the reactor (Gay et al. 2012). Based on the expanded-bed volume, the HRT ranged between 60 min at the 11.4-Lpm flow condition and 120 min at the 5.7-Lpm flow condition. Although the influent had an average positive oxidation-reduction potential (ORP) of 130 mV, the reactor average ORP ranged between −70 and −170 mV as a function of the test conditions, indicative of the anoxic conditions that characterized the microbial conversions of selenate. The temperature of the reactor fluctuated around 10 °C, depending on the test conditions, which is an important aspect for using the system in colder climate conditions. Se concentrations in the treated effluent ranged between 2.0 and 4.6 µg L^{-1}, below the target filtered Se concentration of 10 µg L^{-1} (Gay et al. 2012).

In order to remove residual degradable organic material from the FBR effluent, a moving bed bioreactor (MBBR) was deployed as post-treatment. The MBBR is a hybrid of an activated sludge and a fixed film biological treatment system used to aerobically degrade organics. The MBBR achieved ∼80% BOD removal to a final BOD concentration of ∼15 mg L^{-1}. Currently, 5 full-scale FBBR reactors treating selenium-laden wastewater from applications in the mining sector are in operation in the USA (Webster Todd, personal communication).

3.4 Packed-Bed Reactors

Packed-bed reactors, also known as fixed-bed reactors, employ a packing support (e.g., polymer, ceramic, glass, or gravel) for cell immobilization and biofilm formation. In contrast to the FBBR configuration, no hydrodynamic requirements have to be fulfilled, and the wastewater can flow, depending on the reactor design, in an upward or downward direction through the bed (Warnock et al. 2005).

The attached-growth downflow filter ABMet® System produced by General Electric is a packed-bed reactor that employs attached-growth bacteria to remove selenium, nitrate, and other constituents (Pickett et al. 2008). A schematic of the ABMet® system is illustrated in Fig. 6. In contrast to the UASB reactor technology, the wastewater flows downwards through a granular activated carbon (GAC) biofilter. ABMet® uses facultative anaerobic bacteria that are active across a temperature range of 3–38 °C and consists of one or two biofilters in series in multiple trains, depending on the application, with a typical empty bed contact time (EBCT) of 2–4 h in mining water treatment applications and 4–8 h in power plant FGD wastewater treatment (Citulski Joel, personal communication). The wastewater entering the system typically has a positive ORP of +200 to +300 mV and is blended with a molasses-based carbon source injected upstream of each biofilter. The molasses is used to promote bacterial growth, since the wastewaters being treated are typically deficient in organic substrate.

Molasses is a cost-effective source of electrons and micronutrients required for bacterial metabolism (NAMC 2010). The amount of molasses dosed into the system is controlled to achieve an optimal ORP for selenate and selenite reduction within the biofilter. According to the vendor's technical reports (Pickett et al. 2008), a sequential cleaning up of the wastewater takes place (Fig. 7), starting with denitrification and followed by selenite and selenate removal. Below −200 mV, sulfate-reducing bacteria form sulfides (S^{2-}), which result in the precipitation of divalent metals (e.g., Zn, Cu, Ni, or Pb) as metal sulfides.

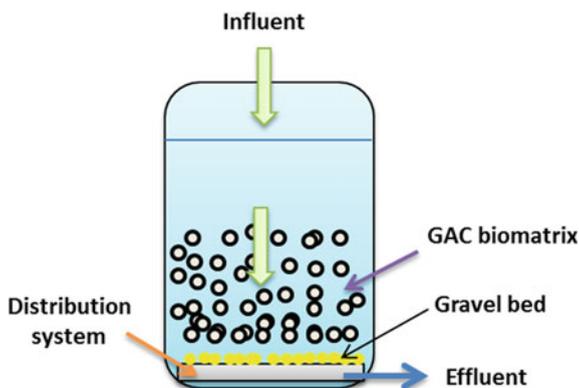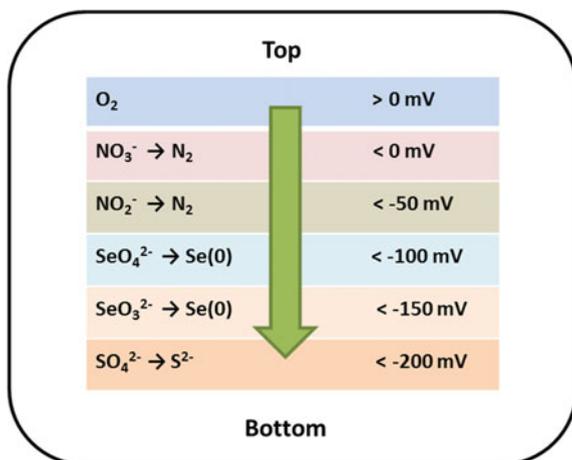Fig. 6 Schematic of the ABMet® system. *Note* The bioreactor schematic is not drawn to scale

Fig. 7 ABMet® reactor gradational ORP zones (adapted from Pickett et al. 2008). *Note* The ORP is expressed in millivolts (mV). The *arrow* indicates the direction of wastewater flow from *top* to the *bottom* of the bioreactor

The EBCT is mainly determined by the concentration of nitrate and selenium in the influent, as these are the main constituents targeted for removal (Citulski Joel, personal communication). Due to the packed-bed design, ABMet biofilters are periodically degassed and backwashed (Citulski Joel, personal communication). Degassing releases built-up gas resulting from denitrification and is typically done between once per day to once per week, depending on the nitrate concentration in the feed water. The biofilter retains the elemental selenium within the biofilm, preventing its wash out with the effluent stream. Backwashing removes solids, such as excess biomass, precipitates (including Se^0), and suspended solids, from the feed stream retained by the GAC bed. Backwashing is typically done between once every two weeks to once every six weeks depending on the application. The effluent water may be aerated to increase the dissolved oxygen (DO) level and reduce the concentration of excess soluble organics. In applications with soluble organic effluent targets down to 20 mg L^{-1} as BOD, a polishing step downstream of the ABMet system is required.

Pilot and full-scale ABMet® systems have been tested for a variety of selenium-containing wastewaters, e.g., from the power generation, oil and gas, mining, and agricultural sectors. A pilot demonstration was performed at the Kennecott Utah Copper Corporation. The process reduced 1950 µg L^{-1} Se to below 2 µg L^{-1} (MSE 2001). Currently, 9 full-scale ABMet® systems are in operation in North America (USA and Canada) and Europe (Belgium): 5 treating coal-fired power plant FGD wastewater, and one treating coal-fired power plant ash landfill leachate, coal-mining effluents, precious metal refinery wastewater, and agricultural runoff (Citulski Joel, personal communication).

3.5 Hydrogen-Based Membrane Biofilm Reactor

The H_2-based membrane biofilm reactor (MBfR) is a new technology designed to reduce oxidized dissolved pollutants with H_2 gas as the electron donor. Figure 8a provides a schematic of H_2-based MBfR. H_2 or a mixture of H_2 and CO_2 (4:1) is delivered by diffusion through the walls of non-porous hollow-fiber membranes. A biofilm of H_2-oxidizing bacteria (Fig. 8b) develops naturally on the outer wall of the membranes and uses the electrons from H_2 to reduce one or more of a range of electron acceptors that are water contaminants: nitrate, perchlorate (ClO_4^-), chromate (CrO_4^{2-}), selenate, uranium (VI), and chlorinated solvents (Nerenberg and Rittmann 2004; Rittmann 2007; Martin and Nerenberg 2012). Since H_2 is an inorganic electron donor, the H_2-oxidizing bacteria are autotrophs that use bicarbonate as their carbon source. The MBfR has been commercialized by APTwater (Sacramento, CA) and tested at large scale for reduction of nitrate and perchlorate. Commercial units are fully automated for pH control, biofilm management, and generation of H_2 on demand. Figure 9 depicts APTwater ARoNite® Autotrophic Bioreactor based on spiral-wound hollow-fiber membrane modules.

The MBfR has been tested for the removal of selenate using synthetic wastewaters (Nerenberg and Rittmann 2004; Chung et al. 2006a, b; Lai et al. 2014). The Se-removal efficiencies were high, e.g., $\sim 95\%$ (from 260 to 12 μg L^{-1}) by Chung et al. (2006a). Studies with actual FGD wastewater gave high selenate reduction with a maximum selenate removal flux of 360 mg Se m^{-2} d^{-1} (Van Ginkel et al. 2011a). Nitrate and nitrite did not compete with the removal of selenate; in fact, selenate reduction was faster than nitrate reduction in FGD wastewater (Van Ginkel et al. 2011b). A study of the microbial community in an MBfR treating synthetic medium showed that a nitrate surface loading exceeding 1.14 g of N m^{-2} d^{-1} had an inhibitory effect on SeO_4^{2-} reduction. *Hydrogenophaga sp.*, an autotrophic denitrified
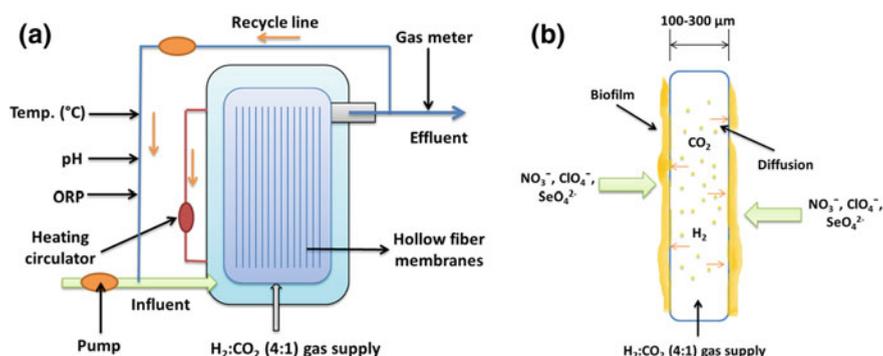

Fig. 8 Hydrogen-based membrane biofilm reactor: **a** Schematic of the MBfR configuration. The reactor includes a temperature control device, as well as probes for temperature, pH, and ORP (modified from Shin et al. 2015); **b** Hollow-fiber membrane supporting biofilm (modified from Nerenberg and Rittmann 2004). *Note* The bioreactor and hollow-fiber schematics are not drawn to scale
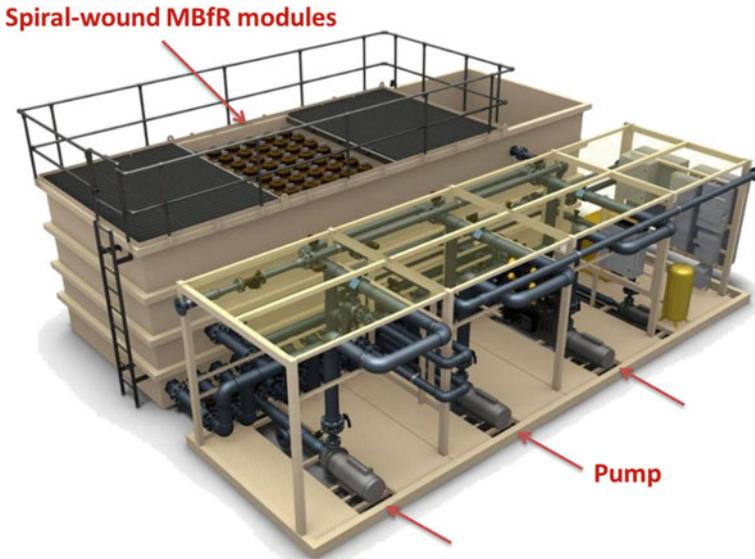
Fig. 9 APTwater ARoNite® Autotrophic Bioreactor using hollow-fiber membranes (photograph courtesy of APTwater, LLC). *Note* The bioreactor schematic is not drawn to scale

β-proteobacterium, was positively correlated with the NO_3^- flux (Lai et al. 2014). These findings indicate that it is necessary to manage electron-acceptor fluxes in the MBfR.

3.6 Electro-Biochemical Reactor

The EBR produced by INOTEC Inc. provides electrons to the microbial community using electrodes and a low voltage potential (1–3 V) (Opara et al. 2014a). The direct provision of electrons to the Se-reducing microbes using a low voltage potential without the need for microbial metabolism to generate electron donors is in contrast to conventional biological treatment systems where the electrons are supplied by an electron donor added to the bioreactor. A schematic of the EBR system is depicted in Fig. 10.

Various bacterial consortia transfer electrons from one species to another within the biofilm (Direct Interspecies Electron Transfer, DIET) or accept electrons provided by an anode. These electrons are subsequently used to reduce organic/inorganic compounds both when associated with the electrode and at a distance from the electrode (Gregory et al. 2004; Shrestha and Rotaru 2014). In addition to minimizing the supply of electron donor, the electrodes also ensure a way to control the ORP needed to sequentially remove nitrate, selenium oxyanions, and sulfate (Opara et al. 2014a).
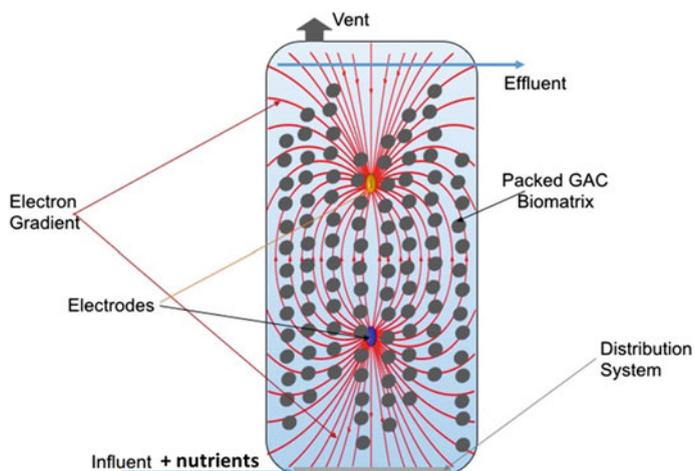
Fig. 10 Schematic of the electro-biochemical reactor configuration. *Note* The bioreactor schematic is not drawn to scale

Laboratory bench- and on-site pilot-scale studies have been completed that demonstrate the decrease of Se concentrations (35–4500 µg L^{-1}) from mining wastewaters below discharge targets (1–10 µg L^{-1}). Furthermore, nitrate-N (11–340 mg L^{-1}) was reduced to below 0.1 mg L^{-1} at bench, pilot, and full scale (Opara et al. 2014a). Another field test was deployed at the Landusky Montana gold mine site primarily for the removal of nitrate at 100–350 mg L^{-1}, selenium (majority present as selenate) at 0.8–1.5 mg L^{-1} [site discharge criterion is 0.05 mg L^{-1}], and total cyanide at 0.1–3.0 mg L^{-1}. The Landusky Mine is a closed gold mine located in the Little Rocky Mountains (Montana, USA). Ore was mined from open pits, placed on valley fill leach pads, and cyanide leaching was used to extract the precious metals (Opara et al. 2014b). During operation (July to October), the influent water temperatures ranged from 17 to 1 °C. The total HRT of the system was 16 h, with 8 h per EBR reactor. Each tank was connected to a power supply and provided with a 3 V potential. Molasses was used to provide microbial nutritional prerequisites such as nitrogen and phosphate. Nitrate-N was reduced from 300 mg L^{-1} to below 0.03 mg L^{-1}, while the Se-removal efficiency achieved 95% with an average effluent concentration of 0.04 mg L^{-1} (Opara et al. 2014b).

3.7 Passive Treatment Systems

3.7.1 Biobed Percolator Systems

The Biopass system was initially developed for passively treating cyanide-bearing heap leachates from gold extraction (Cellan et al. 1997). The system was built in an

excavated area isolated with a geomembrane, and a substrate layer (gravel, composted manure, wood chips, alfalfa, or peat) was filled in. The wastewater is seeped gravitationally through the decaying organic matter and treated under anaerobic conditions by the microbial activity, and the effluent is collected at the bottom using an underdrain device (NAMC 2010).

A full-scale system at a gold mine in Montana reduced influent Se concentrations from 20 $\mu g\,L^{-1}$ to less than 1 $\mu g\,L^{-1}$ (Golder 2009). An 18-month pilot study conducted at the Brewer Mine (South Carolina) of mine-influenced water derived from an acidic pit lake reported 97% Se removal (from 1500 to 50 $\mu g\,L^{-1}$) (Golder 2009).

The treatment potential of percolator systems is limited because the organic substrate is depleted by the microbial communities over time and thus requiring periodic replacement. Another potential issue is the resolubilization of the immobilised Se (Knotek-Smith et al. 2006).

3.7.2 Enhanced in Situ Microbial Reduction

Enhanced in situ microbial reduction adds microbial inocula, nutrients, and organic donors to Se-contaminated water, e.g., in pit lakes and groundwater contaminated from mining. Organic electron donor must be added in a sufficient amount to deplete the DO and reduce selenate and other oxidized pollutant, e.g., nitrate (Nelson et al. 2003).

Implemented at full scale at a New Mexico Reclamation Project, this approach brought the Se concentration down to less than 5 $\mu g\,L^{-1}$ (from initial 50–100 $\mu g\,L^{-1}$) (Alberta Environment 2013). At Sweetwater Pit Lake (Wyoming), sugar, alcohols, fats, proteins, phosphate, and nitrate were added over a 2-month period to an open-pit uranium mine, which resulted in the depletion of 460 $\mu g\,L^{-1}$ Se to less than 10 $\mu g\,L^{-1}$ (Nelson et al. 2003). The addition of phosphate induced algal blooms that provided an in situ organic donor for Se reduction. Pit-lake treatment also was performed at Beal Mountain Mine (Montana) using addition of organic substrates. Se levels were decreased from 45 $\mu g\,L^{-1}$ to 2–3 $\mu g\,L^{-1}$ (Nelson et al. 2003).

Because electron donor addition creates anoxic conditions, this approach is not suitable for environments containing fish or other aquatic life. Water treatment by enhanced in situ microbial reduction requires post-treatment prior to discharge in surface waters to increase the dissolved oxygen level, filtration of particulate metals and Se^0, and removal of hydrogen sulfide (Nelson et al. 2003). A challenge is related to the suitability of the microbial inoculum, since some pit-lake waters are saline, cold and contain high DO levels.

3.7.3 Constructed Wetlands

Constructed wetlands are designed and constructed for the treatment of large volumes of wastewater (Table 2). Various configurations of constructed wetlands have

Table 2 Selenium removal from wastewaters in full-scale surface flow wetlands

Site	Wastewater	Influent Se$_{tot}$ (µg L^{-1})	Effluent Se$_{tot}$ (µg L^{-1})	Removal efficiency (%)
Great Falls (Montana)	Drainage	26	1	96
Richmond (California)	Refinery	25	5	80
Albright (Pennsylvania)	Coal ash leachate	4	2	50
Corcoran (California)	Agricultural drainage	16	9	44
Imperial (California)	Agricultural drainage	7.1	5.9	17
PG-4 (Confidential)	FGD wastewater	170	150	12

Adapted from Kadlec and Wallace (2009) and NAMC (2010)

been proposed, the main designs being surface flow and subsurface flow systems. They use vegetation, soil, and their associated microbial activity to convert Se oxyanions into Se^0. The anoxic environment created by the decomposition of wastewater and biological detritus favors the anaerobic reduction of Se oxyanions. Se^0 generated through microbial activity is bound to the wetland sediments (Oremland 1993; Johnson et al. 2009). Unlike natural wetlands, constructed wetlands contain monocultures of macrophyte species such as cattails (*Typha* spp.) or bulrushes (*Schoenplectus* spp.), and they have regulated inflow rates and water depths (NAMC 2010).

The microbiota involved in the transformation of Se are bacteria, fungi, and algae (NAMC 2010). Microbial and plant volatilization of Se can be an important Se sink, in some cases up to 61% according to Johnson et al. (2009). Hansen et al. (1998) investigated the role of biological Se removal in a 36-ha constructed wetland located adjacent to San Francisco Bay. The constructed wetland (rabbit's foot grass, cattail, and salt marsh bulrush) removed 89% of Se (20–30 µg L^{-1} decreased to <5 µg L^{-1} in the outflow) from selenite-contaminated oil refinery wastewater. Most of the Se was removed by immobilization into the sediments and plant tissues, while biological volatilization contributed to 10–30% of the Se removed.

Gao et al. (2003) found that sediments were an important sink (56%) of Se that entered in their system. The other fractions were 3% assimilated by vegetation, 2% volatilized, 4% infiltrated into the groundwater, and 35% lost in the effluent. Selenium was reduced from 20 to 3–6 µg L^{-1} (up to 85% removal) at a residence time of 7 days, but temperature was a rate-limiting factor below 10–15 °C (Gao et al. 2003).

A microcosm study using *Thalia*, cattails, and rabbit's foot (*Polypogon monspeliensis*) grasses attempted to treat wastewaters containing selenocyanate (Ye et al. 2003). The system achieved a 64% removal efficiency by decreasing Se from

1440 to 510 µg L^{-1}. Furthermore, the primary sink of Se was within the sediments (63%), with 18% in the effluent and 11% in the surface water. Only small fractions were assimilated by the plants (4%) or volatilized (3%).

Some major limitations of using wetlands to treat Se-bearing wastewaters are related to the large footprints (determined by the low HRT of several days to weeks) and susceptibility to temperature fluctuations and seasonal variation of the vegetation. Other considerations are the potential for exposures to ecological receptors, clogging of the system over time that will affect the hydraulic conductivity of the media, and the potential of contaminated water percolating through the degraded liner (geomembrane) and subsequently seeping into groundwater.

4 Conclusions

This chapter provides an overview of the main sources of selenium, its effects, and the biological treatment technologies to remove selenium. Biological treatment is based on the microbial reduction of Se oxyanions into particulate elemental Se^0. It has been employed at bench and full scales using granular sludge bioreactors, fluidized-bed and packed-bed reactor systems, hydrogen-based MBfRs, and hybrid EBRs. Passive systems may be applicable in certain cases. While the bioreduction of Se oxyanions can be reliable and cost-efficient, further fundamental and applied research is required to produce bioreactor systems capable of treating real Se-laden wastewater at large scale. Se-laden wastewaters contain several types of electron acceptors (e.g., nitrate, sulfate) that may significantly affect the Se biological removal efficiency. Among the technical needs is to separate colloidal elemental selenium from the effluent, particularly since recovered Se^0 could be a valuable resource due to its photo-optical, semiconductive, and adsorptive properties.

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