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Methods for selenium removal from contaminated waters: a review

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Abstract

Worldwide contamination of waters by metals, metalloids, and organometallic pollutants is a major health issue. In par-ticular, the occurrence of the selenium metalloid at rather high concentrations in the environment, especially in the water compartment, is of increasing concern, notably in developing countries. Selenium is difficult to remove from groundwater and industrial effluents because selenium is often present in complex polycontaminated mixtures, thus inducing competi-tion issues with other anions. Moreover, the efficiency of remediation methods depends on selenium speciation and water parameters, e.g. pH and concentration of competing anions. Here, we review methods for selenium removal from water, wastewater, and industrial effluents. Technologies are based on zero-valent iron, iron-oxy-hydroxides, supported materials, nanofiltration, reverse osmosis, chitosan-enhanced ultrafiltration, electrodialysis, and activated granular sludge.

Keywords Selenium · Pollutant · Wastewater treatment · Selenium removal · Technologies available

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Introduction

Selenium is an intermediate chemical element with properties between metals and nonmetals, and is described as a metalloid in environmental chemistry and biology. Selenium is both an essential trace element for nutrition and human health, useful, for example, in cancer prevention or pharmacology, and a toxic substance at high concentration (INERIS 2011; INRS 2011; OMS 2011; ANSES 2012).

From a toxicological point of view, the natural presence and contamination of selenium induce major health risks in some parts of the world. The accumulation of selenium resulting from geological and geothermal activities, further aggravated by human activities, has become a serious environmental problem and public health concern. Selenium is known as the 'double-edged sword element' for its dual beneficial and toxic characters to health (Fernández-Martínez and Charlet 2009). Indeed, despite nutritional benefits, this metalloid is one of the most toxic natural elements. Selenium is ubiquitous in the environment and the two main sources of human exposure are food and water. In Canada, food is recognized as the main source of selenium, while in France there is some debate (Crini 2017). At normal dietary doses, selenium is a natural element that has nutritional and biological properties and is necessary to maintain good health in humans and animals. Humans need to absorb certain amounts of selenium daily to maintain good health, and food usually contains enough selenium. Selenium deficiency is a major problem worldwide, with several cases of deficiency reported. However, exposure to high concentrations of selenium is harmful to living beings. This is the paradox of many chemical substances (ANSES 2012; Fordyce 2013; Health Canada 2014; Santos et al. 2015; Crini 2017; Dinh et al. 2018; Donner et al. 2018; Tabelin et al. 2018; Di Marzio et al. 2019; Paul and Saha 2019).

In terms of contamination, especially in soil, aquifer sediments, and groundwater, selenium receives particular attention, especially in North America and in Europe. In France, the presence of selenium in some groundwater in several regions does not represent a health emergency. Nonetheless, the situation is worrying because the selenium concentrations observed in several drinking water catchments are high (Crini 2017; Lichtfouse et al. 2021). For drinking water, although the World Health Organization has set a regulation limit of 40 µg/L, most European countries, including France, have set the regulation limit at 10 µg/L, while the upper limit set by the United States Environmental Protection Agency is 50 µg/L. For drinking water, according to Canadian water quality guidelines, the selenium threshold not to be exceeded is 10 µg/L. However, this value of 10 µg/L is often exceeded in groundwater, especially in France. Standards are also different in other countries: 50 µg/L (class 2) or 20 µg/L (class 1) for South Africa, and 10 µg/L for Australia and New Zealand. Regulatory wastewater discharge standards for selenium also vary from country to country. Selenium is mainly of natural origin, e.g., alteration and leaching of the earth's crust and volcanism. Anthropogenic sources include mining, petroleum refining and metallurgical activities, oil refining, discharges from industries, agricultural irrigation, and fossil fuel combustion. Selenium is found in the environment in both inorganic and organic forms, and is generally present as selenide, selenite or selenate forms, and more rarely in the elemental state (Chapman et al. 2010; INERIS 2011; INRS 2011; OMS 2011; ANSES 2012; DeForest et al. 2012; Fordyce 2013; Bañuelos et al. 2014; Health Canada 2014; Pettine et al. 2015; Santos et al. 2015; Sharma et al. 2015; Wu and Sun 2016; Crini 2017; Donner et al. 2018; Kumkrong et al. 2018; LeBlanc et al. 2018; Di Marzio et al. 2019; Paul and Saha 2019; Etteieb et al. 2020).

Over the past two decades, selenium has become a new substance of concern, which has been the subject of numerous studies in the literature and debates, not only in the fields of nutrition and medicine, but also in the field of water pollution (Fernández-Martínez and Charlet 2009; Santos et al. 2015; Vinceti et al. 2017, 2018a, 2018b; Hejna et al. 2018; Ullah et al. 2018, 2019). Indeed, research on selenium is rising in environmental science to study selenium presence, behavior, transfer and bioaccumulation; in toxicology to study toxicity, impact and risk; and in water engineering to design removal methods. Today, we have entered the Pollutant Removal Age (Crini and Lichtfouse 2019; Crini et al. 2019), characterized by the development of technologies to reduce contaminant emissions and clean contaminated media. This issue is challenging because it is difficult to remove trace selenium from complex mixtures of substances. In its natural form as an element, selenium cannot be degraded. From a chemical point of view, selenium forms, due to their structure and stability, are difficult to treat, and often competes with other substances (BRGM 2011; Crini 2017). The removal of selenium from water and wastewater is indeed complex, determined by its speciation and the chemical composition of the water from the supply source.

Selenium treatment is also often costly due to the characteristics of the aqueous solution to be treated and the strict discharge limits on the release of selenium and its oxyanions such as Se(IV) and Se(VI) (Crini 2017; Stefaniak et al. 2018; Rene et al. 2019). Speciation of selenium in groundwater or in a raw effluent plays an essential role in the effectiveness of treatment methods used for its elimination, especially when selenium is present at low concentrations, below 1 mg/L, which is often the case (Fernández-Martínez and Charlet 2009; BRGM 2011; Santos et al. 2015). Most of the current research focuses on Se(IV) and Se(VI) removal, and an interesting challenge is the removal of the organic forms

of selenium. Like other metalloids, selenium is difficult to remove, especially the oxyanion of Se(VI), which is present, for example, in mining effluents (Rene et al. 2019). In addition, it is important to distinguish whether the raw water is intended for consumption, in this case the initial selenium concentrations are usually below 0.1 mg/L; or whether this is Se in industrial effluents with concentrations above 1 mg/L. Noteworthy, in both cases, effluents containing selenium are often associated with the presence of other substances and high salinity (Koren et al. 1992; Kapoor et al. 1995). The choice and effectiveness of a treatment process is influenced not only by the oxidation state of selenium, its concentration and the presence of other contaminants, but also by several other factors such as pre-existing treatment facilities and processes, treatment objectives, as well as waste treatment concerns, and costs.

Actually, there is no single method to ensure adequate treatment, and, in practice, a combination of different methods is used to achieve the desired water quality. Achieving residual concentrations below the European Union regulation limit of 10 µg/L for drinking water in the most economical way. Selenium removal methods are classified into three treatment categories (Fig. 1): chemical, biological, and physical technologies. Technologies can also be classified in 1) conventional methods, e.g., coprecipitation, reduction-adsorption and oxidation–reduction, 2) established processes, e.g., adsorption, ion exchange and membrane filtration, and 3) emerging methods such as fluidized bed reactors, algal–bacterial removal, and catalyzed cementation (Crini 2017) (Koren et al. 1992; Kapoor et al. 1995; Twidwell et al. 1999; Shamas et al. 2009; Sandy and DiSante 2010; Moore and Mahmoudkhani 2011; Santos et al. 2015; Crini 2017; Stefaniak et al. 2018; Mohapatra and Kirpalani 2019; Rene et al. 2019).

For drinking water, there are some local remediation solutions to keep Se levels below the threshold without increasing residents' bills. For instance, groundwater can be treated by sand filtration coupled with ion exchange resins and membrane treatments, e.g., microfiltration and nanofiltration, reaching 95% removal (Crini 2017). However, these solutions are often poorly adapted, not very selective and costly. Innovations are therefore needed to find water treatment methods that are efficient, inexpensive, technologically feasible, and also environmentally friendly. Generally, in France, the solution consists either in asking the competent authorities for operating exemptions or, more often than not, in seeking another water resource (Lichtfouse et al. 2021). For industrial scale selenium removal, the first possible method is iron coprecipitation and adsorption, further coupled, if necessary, with coagulation-flocculation.

Fig. 2 An iron coprecipitation unit at the industrial scale. This technology is a well-known and well-accepted chemical process for the removal of metals and metalloids, including the removal of selenium and arsenic, and has been widely implemented in various industries; briefly, a ferric salt is added to the effluent, forming an amorphous iron oxyhydroxide precipitate; the trace elements are then adsorbed and trapped in the precipitate; the settled precipitate is then separated from the clarified effluent; with the technology of iron coprecipitation, metal concentration can be reduced to ppb levels

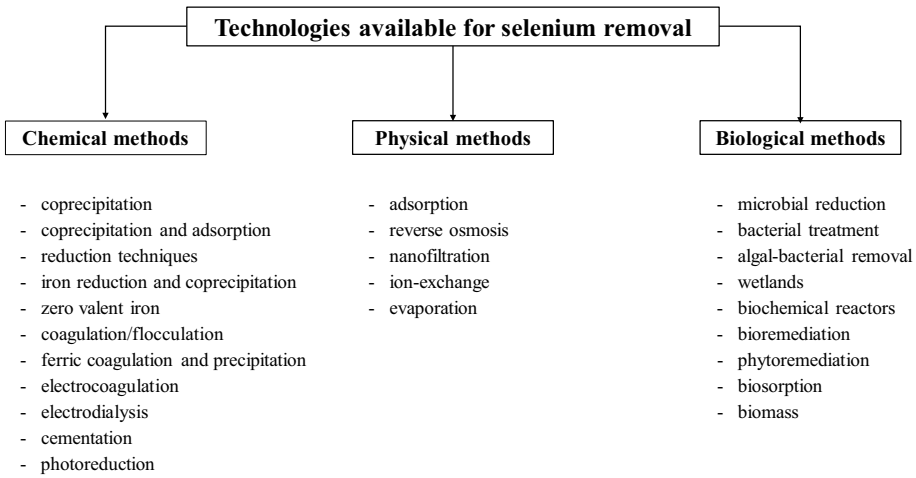

Fig. 1 Technologies available for selenium removal

Fig. 3 An electrocoagulation unit at the industrial scale. Electrocoagulation is a well-known technique for the treatment of several metals and metalloids present in water and wastewater, in particular for selenium and arsenic, for example in the mining industry. Briefly, the process uses a metallic cation as a coagulant in an electrochemical reaction involving iron or aluminum electrodes as anodes; when a current is applied to electrodes in wastewater, the metal anode is oxidized and cations are released to the effluent, which then forms hydroxide precipitates

Other treatments include reduction, adsorption, e.g., using metal oxides, activated alumina and activated carbon, ion exchange, reverse osmosis, and nanofiltration, reaching 75–99% removal depending on selenium form. In general, a combination of physicochemical processes such as chemical reduction, coprecipitation, coagulation, adsorption, and filtration, is used (Rene et al. 2019). Figures 2 and 3 show two examples of physicochemical technologies, namely an iron coprecipitation unit and an electrocoagulation unit, used on an industrial scale to treat pollutants including selenium. Biological techniques such as microbial reduction, aerobic wetlands and biochemical reactors can also be used to treat industrial effluents. Adsorption on non-conventional materials and innovative biological techniques such as microalgal-bacterial treatment, bioremediation, and phytoremediation, are currently explored (Crini 2017; He et al. 2018b).

This article reviews the removal of selenium from wastewater using technologies based on zero-valent iron, iron-oxy-hydroxides, supported materials, nanofiltration, reverse osmosis, chitosan-enhanced ultrafiltration, electrodialysis, and activated granular sludge. It is an abridged version of the chapter published in the series Environmental Chemistry for a Sustainable World (Lichtfouse et al. 2021).

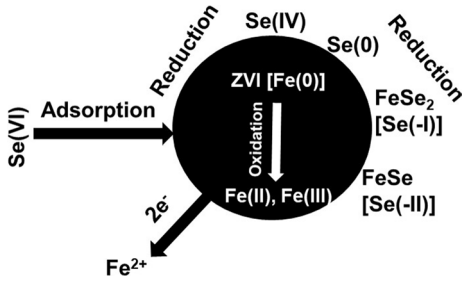

Fig. 4 Se(VI) adsorption and subsequent reduction to Se(IV), Se(0), Se(-I), and Se(-II) by zero-valent iron. This diagram shows the fractionation of selenium during the reduction of selenate by zero-valent iron, Se(VI) being reduced into various other species. The zero-valent iron technology involves complex redox and adsorption interactions between metallic iron and selenium oxyanions in the effluent, iron acting as a strong oxidant being the electron donor and as a catalyst for oxyanion reduction. Adapted from Shrimpton et al. (2015)

Selenate removal by zero-valent iron

Zero-valent iron has been used to treat wastewater and groundwater contaminated by selenium (Zhang et al. 2005; McCloskey et al. 2008; Olegario et al. 2010; Yoon et al. 2011; Gibson et al. 2012; Liang et al. 2013; Das et al. 2017, 2019). This strong reducing agent is an attractive treatment option because it is non-toxic, has a high reactivity, is readily availability, and is cost effective (Zhang et al. 2005; Ezzatahmadi et al. 2017; Liu and Wang 2019). Zero-valent iron has a concentric structure with a rim of iron oxide surrounding a metallic iron (Fe^0) core (Li and Zhang 2006; Liu et al. 2019; Ezzatahmadi et al. 2017; Das et al. 2019). Contaminants adsorb to the iron oxide rim via surface complexation reactions (Li and Zhang 2006; Liu et al. 2019) while the metallic core acts as an electron donor (reductant) (Eq. 1) (Li and Zhang 2006; Liu et al. 2019). The reduction process in Eq. (1) can be enhanced by ferrous iron (Fe^{2+}), which can also donate an electron to the zero-valent iron surface and oxidize to Fe(III) oxides or hydroxides (Li and Zhang 2006). As such, zero-valent iron can oxidize under both oxic (fast process) (Eq. 2) and anoxic (slow process) (Eq. 3) conditions (Zhang et al. 2005). As a result, corrosion and oxidation of zero-valent iron is more pronounced in oxic than anoxic conditions (Zhang et al. 2005; Das et al. 2019).

The removal of selenate [Se(VI)] and selenite [Se(IV)] from solution with zero-valent iron and nano-scale zero-valent iron has been evaluated under oxic (Zhang et al. 2005; Olegario et al. 2010; Yoon et al. 2011; Liang et al. 2013;

Das et al. 2017) and anoxic (Gibson et al. 2012; Tang et al. 2014a, 2014b; Das et al. 2019) conditions. The formation of OH^- and H_2 (as in Eqs. 2 and 3, respectively) increases the solution pH and decreases the redox potential during Se(VI) removal by zero-valent iron (Shrimpton et al. 2015; Das et al. 2017, 2019). In summary, Se(VI) removal by zero-valent iron can be described as the adsorption of soluble Se(VI) onto the iron oxide layer followed by reduction to less soluble selenium species such as Se(IV) and subsequent reduction to insoluble selenium species such as elemental selenium [Se(0)] and or selenide [Se(-II)] (Genin et al. 1998; Murphy 1988; Yoon et al. 2011, 2016; Gibson et al. 2012; Liang et al. 2013) (Eqs. 4 and 5). Figure 4 shows a schematic diagram of Se(VI) adsorption and subsequent reduction to Se(IV), Se(0), Se(-I) and Se(-II) by zero-valent iron.

$$Fe^0 = Fe^{2+} + 2e^- \quad (1)$$

$$2Fe^0 + 2H_2O + O_2 = 2Fe^{2+} + 4OH^- \quad (2)$$

$$Fe^0 + 2H_2O = Fe^{2+} + 2OH^- + H_2 \quad (3)$$

$$HSeO_4^- + 3H^+ + 2e^- = H_2SeO_3(aq) + H_2O \quad (4)$$

$$H_2SeO_3(aq) + 4H^+ + 4e^- = Se(s) + 3H_2O \quad (5)$$

Spectroscopic studies including X-ray absorption near edge spectroscopy, extended X-ray absorption fine structure spectroscopy, and X-ray photoelectron spectroscopy, show that Se(VI) adsorbs onto zero-valent iron surfaces early, and with increasing reaction time, is reduced to Se(IV), Se(0), $FeSe_2$ [Se(-I)] (ferroselite), and eventually selenide (FeSe) [Se(-II)] (Achavalite), suggesting a step-wise reduction mechanism of Se(VI) by zero-valent iron during the removal process (Zingaro et al. 1997; Roberson 1999; Olegario et al. 2010; Yoon et al. 2011; Gibson et al. 2012; Tang et al. 2014a; Shrimpton et al. 2015). Spectroscopic analyses also demonstrate that Se(VI) adsorption and subsequent reduction to other selenium species is not only dependent on reaction time, but also on the initial Se(VI) concentration (Yoon et al. 2011). For example, selenium speciation on the surface is dominated by Se(-II) or Se(0) at dissolved Se(VI) concentrations below 25 mg/L, and by both Se(VI) and Se(IV) at dissolved concentrations above 50 mg/L, which implies partial reduction of adsorbed Se(VI) by zero-valent iron during the removal process (Yoon et al. 2011).

Se(VI) removal via reduction by zero-valent iron is a fast process under pristine conditions (Das et al. 2017, 2019). However, competing ions such as sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chloride (Cl^-) can reduce the rate of Se(VI) removal in both oxic and anoxic environments (Zhang et al. 2005; Das et al. 2017, 2019). The rate-limiting effect of SO_4^{2-} is attributed to similarities in the chemical properties of SO_4^{2-} and selenate (SeO_4^{2-}), resulting in competition for surface sites on zero-valent iron (Zhang et al. 2005). Similarly, PO_4^{3-} also lowers the rate of Se(VI) removal by zero-valent iron, which is attributed to the reaction of aqueous PO_4^{3-} with ferrous iron (Fe^{2+}) generated via oxidation of Fe^0 during Se(VI) removal (Zhang et al. 2005). This reaction leads to the formation of iron-phosphate minerals such as vivianite [$Fe_3(PO_4)_2(H_2O)_8$] and, as such, depletes the Fe^{2+} available for further Se(VI) reduction (Zhang et al. 2005). PO_4^{3-} also has a higher affinity for iron oxide/hydroxide surfaces compared to Se(VI) and, as such, might reduce Se(VI) adsorption to zero-valent iron surfaces and in turn decrease Se removal rate (Goldberg, 1985; Balistrieri and Chao 1987). Dissolved HCO_3^- can also decrease the rate of Se(VI) removal (Zhang et al., 2005) via precipitation of iron minerals (similar to PO_4^{3-}) such as siderite ($FeCO_3$), and thus depletes the Fe^{2+} available for Se(VI) reduction (Phillips et al. 2003; Zhang et al. 2005). Although NO_3^- also limits the rate of Se(VI) removal by zero-valent iron (Zhang et al. 2005; Das et al. 2017, 2019), the effect is not as intense as for SO_4^{2-}, PO_4^{3-}, or HCO_3^-. NO_3^- does not limit the rate of Se(VI) removal when aqueous NO_3^- concentrations increase from 1 to 10 mM (Zhang et al. 2005). The rate-limiting effect of NO_3^- is due to the oxidation of zero-valent iron by NO_3^-, resulting in the formation of an oxidative layer that inactivates the zero-valent iron surface for Se(VI) removal (Reinsch et al. 2010). The presence of dissolved Cl^- displays little or no effect on Se(VI) removal by zero-valent iron. The rate of Se(VI) removal by zero-valent iron varies widely depending upon the solution chemistry. Nonetheless, the kinetics of Se(VI) removal can be best described by either first or pseudo-first-order reactions, irrespective of oxic and or anoxic test conditions (Zhang et al. 2005; Olegario et al. 2010; Yoon et al. 2011; Liang et al. 2015; Shrimpton et al. 2015; Das et al. 2017, 2019).

The presence of dissolved SO_4^{2-} also plays a major role in controlling selenium speciation during Se(VI) removal by zero-valent iron under oxic conditions (Das et al. 2017). Concentrations of Se(0) decrease by more than 50% on zero-valent iron surfaces in the presence of SO_4^{2-}, irrespective of the type of zero-valent iron used during Se(VI) removal (Das et al. 2017). Testing conditions such as oxic *versus* anoxic also play a crucial role in Se speciation during Se(VI) removal by zero-valent iron. For example, Se(0) is the dominant reduction product (70–80%) followed by Se(-II) (2–13%) during Se(VI) removal by zero-valent iron under anoxic conditions regardless of the solution chemistry, e.g., the presence of dissolved SO_4^{2-}, NO_3^-, or both (Das et al. 2019). By contrast, reduction products are dominated by Se(IV) or an even mixture of Se(IV) and Se(0), depending

on the solution chemistry under oxic conditions (Das et al. 2017).

Se(VI) reduction by zero-valent iron and subsequent selenium speciation on zero-valent iron surfaces also depend on the type of zero-valent iron (Das et al. 2017, 2019). For example, X-ray absorption near edge spectroscopy results demonstrate that Se(VI) reduction products are dominated by both Se(IV) and Se(0) under oxic test conditions. However, metallurgical granular Fe from Rio Tinto Metal Powders (Montreal, Canada) produced more Se(0) compared to ground cast Fe aggregate from Connelly GPM Inc. (Chicago, USA) or Peerless Metal Powder and Abrasives (Detroit, USA) (Das et al. 2017).

Although zero-valent iron and nano-scale zero-valent iron have been used widely to remove dissolved Se(VI) from aqueous solutions, the precipitation of iron oxides and hydroxides onto zero-valent iron, e.g., magnetite, hematite, lepidocrocite, wüstite, ferrihydrite, schwertmannite, vivianite, and mikasaite, can decrease the Se(VI) removal efficiency of zero-valent iron due to passivation effects caused by coatin of these oxide/ hydroxides onto zero-valent iron surfaces (Olegario et al. 2010; Reinsch et al. 2010; Yoon et al. 2011; Gunawardana et al. 2012; Petr et al. 2012; Liu et al. 2019; Das et al. 2017, 2019). In addition, particle agglomeration of nano-scale zero-valent iron results in a decrease of reactive surface areas and in a lowering of the reactivity for contaminant removal (Ezzatahmadi et al. 2017). Additional testing has been conducted using organic matter (Gibson et al. 2012), divalent cations such as Fe^{2+}, Mn^{2+} and Co^{2+} (Tang et al. 2014a, 2014b), clay minerals such as bentonite (Li et al. 2015; Dong et al. 2016), and a weak magnetic field (Liang et al. 2014a, 2014b) to augment both Se(VI) and Se(IV) removal by zero-valent iron.

Despite having a low surface area of 0.36–2.3 m^2/g (Zhang et al. 2005; Yoon et al. 2011; Das et al. 2017, 2019) and concerns with respect to its longevity (Henderson and Demond 2007), zero-valent iron can remain active for many years depending on controlling factors (Henderson and Demond 2007). Under appropriate conditions, permeable reactive barriers using zero-valent iron could represent a valuable approach for selenium remediation and an alternative to other approaches such as adsorption onto iron oxide and hydroxides, coprecipitation with ferrihydrite, and membrane separation.

Adsorption of selenium species by iron-oxy-hydroxides

Iron oxides and hydroxides have drawn attention from the scientific community with respect to their potential to sequester selenium from aqueous solutions via adsorption due to their natural abundance, moderate-to-high specific surface areas, and surface affinity for selenium (Balistrieri and Chao 1990; Cornell and Schwertmann 2000). Many recent studies have investigated the adsorption behavior and mechanism of two major selenium species, Se(IV) and Se(VI), onto iron oxides/oxy-hydroxides, including ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), goethite [α-FeO(OH], hematite (α-Fe_2O_3), magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and lepidocrocite [γ-FeO(OH] (Hingston et al. 1971; Davis and Leckie 1980; Leckie et al. 1980; Benjamin and Bloom 1981; Balistrieri and Chao 1987, 1990; Hayes et al. 1987, 1988; Dzombak and Morel 1990; Zhang and Sparks 1990; Manceau and Charlet 1994; Hiemstra and Van Riemsdijk 1999; Su and Suarez 2000; Wijnja and Schulthess 2000; Rietra et al. 2001; Kang et al. 2002; Peak and Sparks 2002; Duc et al. 2006; Catalano et al. 2006; Martinez et al. 2006; Fukushi and Sverjensky 2007; Rovira et al. 2008; Chan et al. 2009; Gonzalez et al. 2012; Das et al. 2013; Jordan et al. 2014).

Adsorption of both Se(IV) and Se(VI) species onto iron oxides and hydroxides depends on many factors such as solution pH, selenium species, strength of electrolytes, concentrations of selenium species, types of adsorbate, concentrations of adsorbate, and the presence of competing ions. Laboratory results indicate the adsorption of both Se(IV) and Se(VI) onto iron oxides and hydroxides is a fast process that reaches equilibrium within 25 min (Su and Suarez 2000). Adsorption of Se(IV) and Se(VI) is strongly dependent on solution pH, with greater sequestration occurring at lower *versus* higher pH (Balistrieri and Chao 1987; Dzombak and Morel 1990; Su and Suarez 2000; Duc et al. 2006). This occurs because iron oxide and hydroxide surfaces are negatively charged above their point of zero charge value. As a consequence, lesser electrostatic attraction for negatively charged ions such as Se(IV) and Se(VI) onto iron oxide and hydroxide surfaces leads to a lower adsorption efficiency (Benjamin et al. 1982; Cristiano et al. 2011). However, the free energy of adsorption is also dependent on both chemical (specific) and electrostatic effects (Stumm et al. 1970). Therefore, the adsorption of anions such as Se(IV) can occur above the point of zero charge of iron hydroxide, such as goethite, when a specific constituent is dominant over a non-specific or electrostatic counterpart (Balistrieri and Chao 1987). Laboratory results also indicate that Se(VI) adsorbs to a lesser extent than Se(IV) at a given pH, and desorbs more rapidly with increasing solution pH compared to Se(IV) from iron hydroxide surfaces (Balistrieri and Chao 1987; Goldberg 2014). However, the percentage of adsorption also depends on the adsorbing solids. For example, amorphous iron hydroxide (ferrihydrite) has a greater affinity for both Se(IV) and Se(VI) compared to goethite, hematite, and lepidocrocite under similar experimental conditions, e.g., pH, strength of electrolytes, and total selenium

concentrations (Su and Suarez 2000; Kang et al. 2002; Peak and Sparks 2002; Das et al. 2013).

Ionic strength also plays a crucial role in selenium sequestration by iron oxides and hydroxides. For instance, a remarkable decrease in Se(VI) adsorption occurred when the ionic strength increased from 0.01 to 0.1 M (Su and Suarez 2000). Adsorption of selenium also depends on the concentration of the sorbate, with higher sorbate concentrations resulting in greater adsorption. The adsorption of Se(IV) also increases with increasing goethite concentration, reflected by an increase in distribution coefficient value (K_D) for a given solution pH (Balistrieri and Chao 1987). Anion competition can also affect selenium adsorption onto iron hydroxide surfaces, depending on the affinity of anions on the surface of adsorbing solids (Balistrieri and Chao 1987). Selenium adsorption decreases when phosphate, silicate, and arsenate are present in the system, followed by bicarbonate/carbonate, citrate, molybdate, oxalate, fluoride and sulfate (Balistrieri and Chao 1987).

Experimental results on selenium adsorption behavior onto iron oxides and hydroxides have been successfully simulated by a number of modeling approaches, such as those considering the distribution coefficient (Balistreri and Chao 1987) or Langmuir isotherms (Das et al. 2013; Kang et al. 2002; Peak and Sparks 2002; Rovira et al. 2008), as well as surface complexation models including CD-MUSIC (charge distribution multisite ion complexation), double-layer, and triple-layer models (Davis and Leckie 1980; Balistreri and Chao 1990; Dzombak and Morel 1990; Zhang and Sparks 1990; Hiemstra and Van Riemsdijk 1999; Rietra et al. 2001; Fukushi and Sverjensky 2007; Rovira et al. 2008; Goldberg 2014). Outputs from all of these adsorption models describing Se adsorption mechanisms and the nature of surface complexes onto iron oxides and hydroxides have been corroborated by spectroscopic studies based on extended X-ray absorption fine structure spectroscopy, attenuated total reflectance-Fourier transform infrared spectroscopy, and Raman spectroscopy (Hayes et al. 1987; Manceau and Charlet 1994; Su and Suarez 2000; Wijnja and Schulthess 2000; Peak and Sparks 2002; Das et al. 2013).

Surface complexation models and spectroscopic studies on the mechanism and nature of surface complexes of Se(IV) on all iron oxides and hydroxides studied, e.g., ferrihydrite, goethite, hematite, maghemite, and magnetite, demonstrated strong inner-sphere surface complexation, irrespective of solution pH (Balistrieri and Chao 1987; Hayes et al. 1987; Su and Suarez 2000; Catalano et al. 2006; Duc et al. 2006; Martinez et al. 2006; Jordan et al. 2014). On the contrary, spectroscopic studies indicate that Se(VI) forms a weakly bound outer-sphere complex on goethite in acidic conditions, e.g., pH 4, as reflected by the absence of a second shell (Se–Fe) in the absorption spectra (Hayes et al. 1987). Reports also demonstrate that the nature of Se(VI) complexation onto goethite is pH-dependent, with outer-sphere surface complexes dominating at pH values above 6 and inner-sphere surface complexes at pH values below 5 (Manceau and Charlet 1994; Wijnja and Schulthess 2000; Rietra et al. 2001; Peak and Sparks 2002). The formation of outer-sphere surface complexes of Se(VI) on goethite has also been reported at pH lower than 5 (Hayes et al. 1987). However, results are contradictory with respect to the type and nature of surface complexes of Se(VI) on goethite surfaces. Spectroscopic and adsorption data obtained from a number of studies demonstrate that Se(VI), similarly to Se(IV), forms strong inner-sphere surface complexes on ferrihydrite, goethite, and lepidocrocite over a range of pH values and Se(VI) surface coverage (Manceau and Charlet 1994; Su and Suarez 2000; Peak and Sparks 2002; Fukushi and Sverjensky 2007; Das et al. 2013). Spectroscopic studies indicate that the absorption spectra of Se(VI) on ferrihydrite, goethite, and lepidocrocite display a second shell (Se-Fe), suggesting inner-sphere complexation, either bidentate mononuclear or bidentate binuclear, on the iron hydroxide surfaces (Manceau and Charlet 1994; Peak and Sparks 2002; Das et al. 2013).

Adsorption data indicate that Se(VI) adsorption on goethite is dependent on the electrolyte strength, with lower adsorption observed at greater ionic strengths, implying the formation of an ion-pair type complex (outer-sphere) on goethite surfaces; the shell of hydration of Se(VI) being retained during the adsorption process (Hayes et al. 1987). Although ionic strength-dependent adsorption of Se(VI) onto iron hydroxide has been demonstrated (Hayes et al. 1987; Su and Suarez 2000), an electrophoretic study indicates that Se(VI), similarly to Se(IV), has lowered electrophoretic mobility and point of zero charge on the goethite surface (Su and Suarez 2000). The shift in both electrophoretic mobility and extended X-ray absorption fine structure spectroscopy towards lower values indicates that the inner-sphere complexation of Se(VI) on the goethite surface as chemically or specifically bound ions rises at the mineral–water interface, thus contributing additional negative charges on the surface and shifting the point of zero charge towards lower pH values (Sposito 1984; Su and Suarez 2000; Jordan et al. 2014). Thus, electrolyte strength-dependent adsorption of Se(VI) cannot alone be used to differentiate between outer- versus inner-sphere complexation onto iron hydroxide surfaces (Su and Suarez 2000).

In adsorption experiments, ferrihydrite has been found to sequestrate greater amounts of both selenium species compared to any other iron oxide or hydroxide tested, including hematite, goethite, and lepidocrocite (Kang et al. 2002; Peak and Sparks 2002; Das et al. 2013). Irrespective of the contradictory nature of surface complexation of Se(IV) and Se(VI) onto iron oxide and hydroxide surfaces, published studies generally agree that iron oxide and hydroxide surfaces have a

higher affinity for Se(IV) compared to Se(VI) under a range of solution pH values, ionic strengths and surface loadings. For instance, Se(IV) adsorbs more strongly onto iron oxide/hydroxide surfaces compared to Se(VI) under given geochemical conditions (Balistrieri and Chao 1987; Su and Suarez 2000).

Supported materials for selenium removal

Adsorbents include inorganic materials, e.g., metal oxides/oxy-hydroxides and zero-valent iron, organic materials, e.g., activated carbons and synthetic resins, and biosorbents. The adsorption-based removal of selenium species from aqueous media can be either physisorption or chemisorption, depending on the nature of the adsorbent. Various inorganic and organic adsorbents have a wide range of efficiency, according to the external conditions such as ionic strength, adsorbate concentration, adsorbent dosage, pE, and pH.

The use of nanomaterial adsorbents and their different morphological forms provide an opportunity to improve the adsorption efficiency of various materials. In the case of nanomaterials, there are challenges with their relative stability and practical utility in terms of recovery for multiple cycles of adsorption–desorption, due to their high reactivity and high surface-to-volume (S/V) ratio. To address the shortcomings of chemical oxidation and agglomeration effects of nanomaterials in their dispersed form, the preparation of supported materials provides an opportunity to extend the field of application by improving the chemical stability and the recoverability through immobilization onto a suitable substrate. There are examples of adsorbent preparation illustrating the use of conventional and unconventional substrates. For unconventional substrates, Kong and Wilson (2017) report the preparation of goethite and its supported forms onto cellulose supports and evaluate their utility as adsorbents for the uptake of 4-hydroxy-3-nitrobenzene arsenic acid (roxarsone) from aqueous media. Results show that, while iron oxide materials such as goethite are considered as efficient adsorbents for inorganic/organic oxyanions of arsenic, the supported nanomaterials reduce iron leaching while maintaining comparable uptake of arsenic species at fractional iron oxide content (30%). The cellulose-goethite supported materials displayed favorable adsorption properties that rival those of the pure mineral phase of goethite. Similarly, Kwon et al. (2014) reported the use of iron oxide supported onto activated carbon for the adsorption of roxarsone, and revealed that activated carbon-supported magnetite may serve as multi-purpose adsorbents; they propose that co-removal of inorganic and organic arsenicals can be achieved due to the presence of graphene and iron oxide adsorption sites. The removal of inorganic oxyanions was later supported in a kinetic adsorption study of selenite anions using magnetite and its supported materials onto activated carbon (Kwon et al. 2015).

The benefits of supported materials is further illustrated by a comparison of the uptake of hexavalent chromium by iron oxide (Fe_3O_4) particles in its decorated nanoparticle form with MoS_2 (MoS_2@Fe_3O_4 nanoparticles) and supported forms. An approximate 18-fold increase was observed for the uptake of Cr(VI) by MoS_2@Fe_3O_4 nanoparticles versus unmodified Fe_3O_4. Similar trends were shown for these iron oxide materials with various oxyanions, as shown for selenite and arsenate species (Kumar et al. 2017). Ramola et al. (2014) compared several feedstocks and the resulting biochar with and without ferric hydroxide impregnation of the biochar. In the case of orthophosphate adsorption, a five-fold increase was noted for ferric ion-impregnated biochar versus pristine biochar for this oxyanion system. Chubar (2014) reported a Mg–Al-carbonate layered double hydroxide for the adsorption of selenite and selenate species. In the case of selenite, the following removal capacities were obtained: 80, 120 and 160 mg Se per gram (dry wt. basis of layered double hydroxide), whereas removal of selenate occurred at 30, 45 and 90 mg Se per gram (dry wt. basis of layered double hydroxide) at pH 8.5, 7 and 5, respectively. The interlayer carbonate ion of the layered double hydroxide played an important role in the removal of selenite, and it was a major mechanism for selenate adsorption by the layered double hydroxide. In this case, chemisorption was the key mechanism for selenite removal, whereas inner-sphere complexation was not detected for selenate adsorption for this adsorbent. The layered double hydroxide materials reported herein also reveal notably higher uptake for selenite and selenate, as compared against activated carbon and various metal oxides reported in the literature (Jeqadeesan et al. 2003; Chan et al. 2009; Mandal et al. 2009; Yamani et al. 2014; Bleiman and Mishael 2010; Das et al. 2013; Gaini et al. 2009). Recently, a series of hierarchical and porous monolithic layered double hydroxide composites with tunable microcages were prepared by modifying the set of cationic species in the layered double hydroxide crystal (Tarutani et al. 2015).

Verbinnen et al. (2013) reported that a zeolite-supported magnetite is a suitable adsorbent for the simultaneous adsorption of oxyanions from wastewater. In this study, it was shown that at the ideal pH of 3–3.5, the adsorption capacities for Mo, Sb and Se oxyanions are high, of 18–23 mg/g. Anions such as sulfate and chloride, which often occur in large amounts in wastewaters, do not really compete for adsorption places on magnetite, but other typical oxyanions largely interfere with each other. The reason for this competition is a similar adsorption mechanism, e.g. inner-sphere complex formation, for all studied oxyanions, except for selenate, which forms outer-sphere complexes, as supported by modeling results. Li et al. (2015) reported the

preparation of a positively charged pillared bentonite (Al-bent) that was used as a support for nano-zero-valent iron particles for the reductive removal of anionic Se(VI) from water. A synergistic removal effect for Se(VI) removal was observed for the supported Al-bent composite, inducing a removal efficiency of 95.7%. By comparison, this removal exceed that for the sum, of 72%, of either a single component (nano-zero-valent iron, 62.1%) and non-supported Al-bent adsorption (9.86%).

Tan et al. (2019) carried out a study where biochar and activated carbon were both produced from corn straw. Biochar and activated carbon were used as supports for zero-valent iron, denoted as biochar-zero-valent iron and activated carbon-zero-valent iron, which were then studied as adsorbents for Se(IV)/Se(VI) removal. The adsorption capacity of biochar-zero-valent iron for Se(IV) and Se(VI) was 62.52 and 35.39 mg/g respectively. By comparison, a lower adsorption capacity was observed for activated carbon-zero-valent iron, 56.02 and 33.24 mg/g for Se(IV) and Se(VI), respectively. This is explained by the higher iron content and more positive charges of biochar-zero-valent iron, in spite of the much lower BET surface area and pore volume of biochar-zero-valent iron. The mechanism of removal of Se(IV) and Se(VI) from wastewater in the case of zero-valent iron involves coprecipitation, reduction, and sorption. Moreover, the use of supported zero-valent iron overcomes drawbacks associated with the long-term performance such as oxidization and agglomeration.

Huang et al. (2019) reported the preparation of activated carbon-supported Fe(II) and nano-zero-valent iron as the permeable reactive barrier media for use in an electrolyzer. In aqueous media at equilibrium conditions, the adsorption results for the activated carbon-supported nano-zero-valent iron medium had a higher adsorption capacity over the other adsorbents. The Langmuir adsorption capacity for selenite was reported, as follows: activated carbon, 26.8 mg/g; activated carbon/Fe(II) 33.7 mg/g; and activated carbon/nano-zero-valent iron, 46.5 mg/g. Mandal et al. (2020) have reported the use of biochar as a support for zero-valent iron and polysulfide to immobilize selenium in soil. The soil immobilization results show that the polysulfide-nano-zero-valent@biochar (PS-nZVI@BC) is more effective for the control of selenium (selenite) versus biochar and nZVI@BC. The available selenium content decreased by 77.3% in PS-nZVI@BC amended soil after 30 days. The ternary material promoted the conversion of the more accessible selenium, in water-soluble and exchangeable fractions, into the less accessible forms via a range of surface process, e.g. precipitation, reduction, complexation and surface adsorption, the latter three being dominant mechanisms for selenium immobilization. Hence, PS-nZVI@BC is a promising and effective material for immobilizing selenium in contaminated soils by lowering its water exchangeable mobile fraction.

The selected examples described above reveal how the use of supports for conventional and unconventional adsorbents can contribute to a wider field of application by improvement in the overall adsorption properties, materials stabilization toward leaching, and oxidation.

Selenium rejection by nanofiltration and reverse osmosis membranes

Among all pressure-driven membrane separation technologies including microfiltration, ultrafiltration, nanofiltration and reverse osmosis, only nanofiltration and osmosis membranes were found to be effective for the treatment of selenium contaminated water (Santos et al. 2015; Stefaniak et al. 2018). Nanofiltration and osmosis membrane offer many advantages such as minimal impact of water quality variations, no addition of chemicals is required, and a smaller footprint required for the process equipment (Mondal and Wickramasinghe 2008).

Nanofiltration and osmosis membrane are membrane separation processes in which the driving force is the pressure applied on a liquid to force this liquid to pass through a so-called semi-permeable membrane. The target contaminant size in nanofiltration is in the nanometer range, e.g., for multivalent ions and micropollutants which corresponds to the approximate pore size of the membrane. Osmosis membrane, a typical process for seawater desalination, is used for the rejection of monovalent ions. The separation process for inorganics in nanofiltration and reverse osmosis is generally dominated by two principle factors including steric hindrance and electrostatic interaction (Owusu-Agyeman et al. 2017). The high rejection of selenium species, i.e., selenite Se(IV) and selenate Se(VI), by nanofiltration/reverse osmosis membranes is explained by size exclusion, given the high molecular weight and hydrated radius of both selenium species (Chung et al. 2010). Se(IV) has a molecular weight of 126.96 g/mol and a hydrated radius of 0.276 nm as SeO_3^{2-} (Vlaev and Genieva 2004), while Se(VI) has a molecular weight of 142.96 g/mol and a hydrated radius 0.384 nm as SeO_4^{2-} (Nightingale 1959). In nanofiltration, the Donnan exclusion mechanism, based upon electrostatic interactions between the charged membrane surface and ions present in solution, contributes to the rejection of selenium species (He et al. 2016). The main retention mechanisms in nanofiltration/osmosis membrane is shown in Fig. 5.

Various nanofiltration/reverse osmosis membranes were investigated for selenium rejection, from laboratory to full pilot scale and for different water types (Kharaka et al. 1996; He et al. 2016, 2018c; Chung et al. 2010; Richards et al. 2011; Chehayeb and Lienhard 2017; Cingolani et al. 2018; Malhotra et al. 2020). Table 1 summarizes the work reported to date on selenium rejection with nanofiltration/

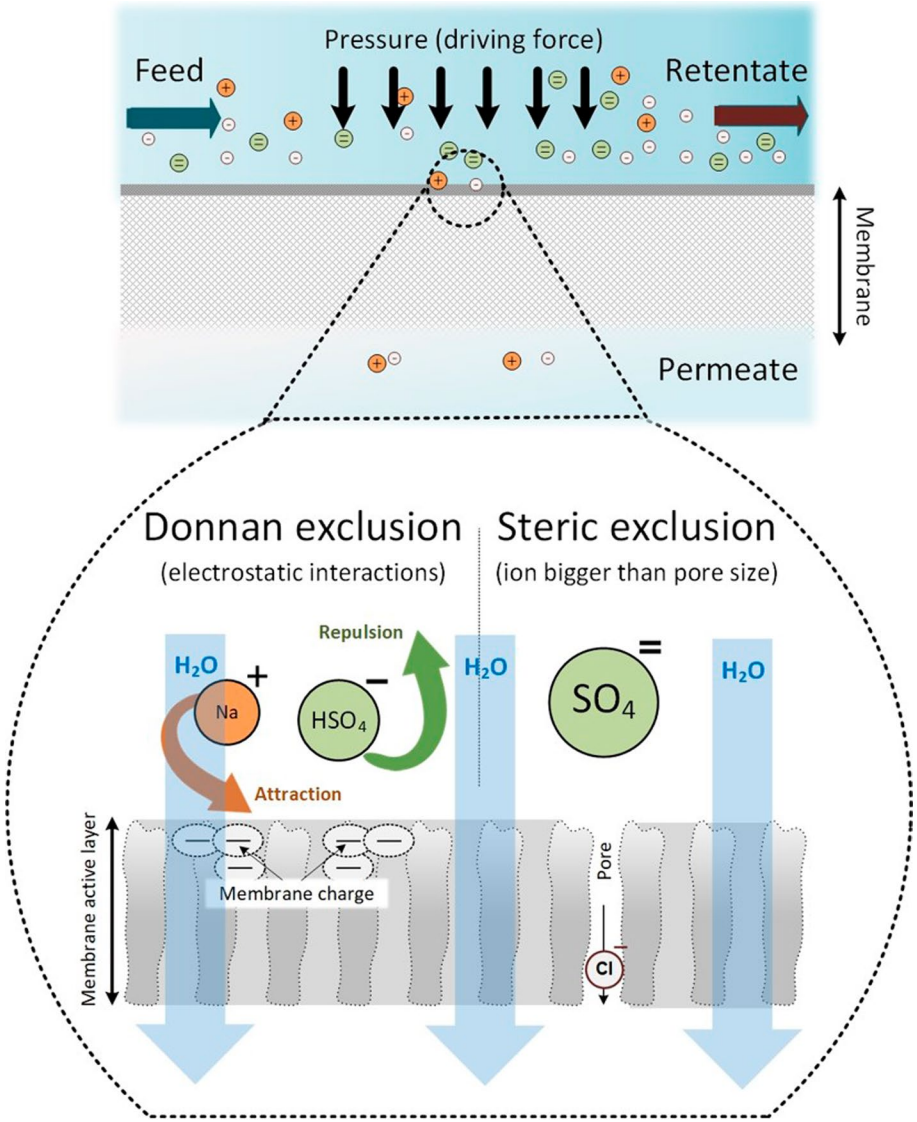

Fig. 5 Mechanisms of ions rejection in nanofiltration/reverse osmosis. Rejection mechanisms are processes that cause the ions to be rejected by the membrane. Donnan exclusion is a separation method based on the electrostatic attraction/repulsion between the ions and fixed ionic groups of the membrane, while steric exclusion is a size-base exclusion at the pore opening. Source: Youssef-Amine Boussouga, Eggenstein-Leopoldshafen, Germany

reverse osmosis. The rejection of selenium is generally higher with tight membranes, e.g., nanofiltration with NF1 and NF90, and reverse osmosis (BW30), than with the loose membranes, e.g., NF2 and NF20. This is due to the different molecular weight cut-off and hence the interplay between size exclusion and charge repulsion during the separation (Krieg et al. 2005). Water type at neutral pH does not appear to influence the efficiency of the membranes. To further understand the effect of water chemistry on the rejection of selenium with nanofiltration/reverse osmosis, the impact of pH is discussed in the next section. pH determines what type of species selenium occurs in water, and, given the importance of size exclusion and charge repulsion, pH may be an important contributing factor in retention.

In water, selenium can occur in different oxidation forms (-II, IV, VI), which depends on the redox potential, pH, dissolved organic matter, and microbial activities (Kumar and Riyazuddin 2011). Se(IV) and Se(VI) species are the predominant selenium forms in water (Chand and Prasad 2009). Se(IV) species are found in moderately oxidizing environment, e.g. with moderate concentration of dissolved O_2 as electron acceptor, while Se(VI) species are mostly present in oxidizing environment with high dissolved O_2 concentration (Sharma et al. 2019). For instance, in environment conditions of pH 8.1 and with electron activity (pE) of 12.5, the concentration of Se(VI) is estimated to be 10 times higher than Se(IV) concentration (Sharma et al. 2019). In nanofiltration/reverse osmosis, the speciation chemistry of a contaminant affects the rejection mechanisms in both size and charge mechanisms (Richards et al. 2009).

The influence of the pH on the speciation of selenium has been studied by He et al. (2016). The authors have investigated the effect of the speciation on Se(IV) and Se(VI) rejection by varying pH

Table 1 Selenium rejection with different nanofiltration/reverse osmosis membranes

Membrane	Water type	Pressure	Flux	Selenium rejection	References
NF-1[a]	groundwater; 1600 µg/L, pH 8	15	130.0	95 for Se(VI) species	Malhotra et al. (2020)
NF-2[a]	groundwater; 1600 µg/L, pH 8	15	280.0	76 for Se(VI) species	Malhotra et al. (2020)
NF20[a]	groundwater; 1600 µg/L, pH 8	15	170.0	61 for Se(VI) species	Malhotra et al. (2020)
BW30[a]	brackish groundwater; 15 µg/L, pH 8	9	13.5	≥ 93.8[d]	Richards et al. (2011)
NF90[a]	brackish groundwater; 15 µg/L, pH 8	15	23.1	≥ 92.9[d]	Richards et al. (2011)
TFC-S[a]	brackish groundwater; 15 µg/L, pH 8	15	24.3	90.2[d]	Richards et al. (2011)
ESPA4[a]	brackish groundwater; 15 µg/L, pH 8	15	23.1	92.6[d]	Richards et al. (2011)
FILMTEC NF[a]	agricultural drainage water; < 1000 µg/L	–	–	> 95[d]	Kharaka et al. (1996)
ESPA[a]	wastewater; 326 µg/L, pH 7.2	8	–	99–94 for Se(IV) species	Chung et al. (2010)
ESNA[a]	wastewater; 326 µg/L, pH 7.2	8	–	93–72 for Se(IV) species	Chung et al. (2010)
POSS-PA TFN[b]	synthetic solutions; 1000 mg/L, pH 7.5	10	54.0	93.9 for Se(VI) species	He et al. (2016)
POSS-PA TFN[b]	synthetic solutions; 1000 mg/L, pH 7.5	10	54.0	96.5 for Se(IV) species	He et al. (2016)
TFN-30[b]		10	115.0	96.5 for Se(VI) species	Chehayeb and Lienhard (2017)
TFN-30[b]		10	115.0	97.4 for Se(IV) species	Chehayeb and Lienhard (2017)
TFC-50[b]		10	85.0	98.2 for Se(VI) species	He et al. (2018a)
TFC-50[b]		10	85.0	99.1 for Se(IV) species	He et al. (2018a)
DT-RO (Gel GPT-BW 30)[c]	landfill leachate; 63 µg/L, pH 7.2	60[c]	32.5	> 94[d]	Cingolani et al. (2018)

Pressure in bar; flux in L/m^2 h; selenium rejection in %

[a]commercial membrane

[b]laboratory made membrane

[c]data from the third stage of a multistage disc tube reverse osmosis (DT-RO) system

[d]no information about the rejected Se species

during filtration experiments with a laboratory made nanofiltration membrane. Higher rejection, above 90%, of Se(IV) was observed at pH above 9, where the divalent SeO_3^{2-} becomes the dominant species. On the other hand, the rejection of Se(VI) was higher than the rejection of Se(IV) at all pH values due to the presence of the divalent SeO_4^{2-} species in water at pH higher than 4. A similar behavior was observed with commercial nanofiltration membranes used to remove Se(VI) (Malhotra et al. 2020). Further, the increase in Se(VI) rejection with pH is influenced by the membrane surface charge, which becomes more negative with increasing pH: this is observed for most polymeric nanofiltration/reverse osmosis membranes. To sum-up, pH variation in water and wastewater affect the efficiency of nanofiltration/reverse osmosis process, especially when using loose nanofiltration membranes where the dominant separation mechanism is charge exclusion. In addition to water chemistry, the separation efficiency of nanofiltration/reverse osmosis processes further depend on the operating conditions, such as pressure and recovery, reviewed below.

Nanofiltration/reverse osmosis performance is also influenced by operating conditions such as the applied (transmembrane) pressure and recovery (Ballet et al. 2007; Lee et al. 2015). Transmembrane pressure variations affect the water transport and hence the diluting effect (Verliefde et al. 2013), and determines flux and recovery. The recovery, which is the ratio of permeate production by feed volume, is influencing permeate quality and membrane fouling/scaling (Lee et al. 2015). Malhotra et al. (2020) have investigated the effect of the transmembrane pressure on the Se(VI) rejection with loose (NF2) and tight (NF2) nanofiltration

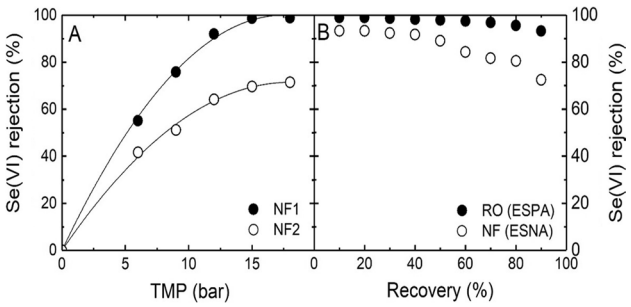

Fig. 6 Rejection of Se(VI) with nanofiltration/reverse osmosis membranes versus **A** transmembrane pressure (TMP) and **B** recovery. Sources: A) is adapted from Malhotra et al. (2020): Se(VI) 1600 µg/L and pH 8; B) is adapted from Chung et al. (2010): S(VI) 326 µg/L, pH 7.2 and pressure 8 bar

membranes, whereas, Chung et al. (2010) have studied the effect of the recovery and Se(VI) rejection with nanofiltration/reverse osmosis membranes. Results from both studies are shown in Fig. 6. Results shows that, the rejection of Se(VI) increased with transmembrane pressure, and, from 15 bar, the rejection remained constant for both nanofiltration membranes (Fig. 6A). This behavior is explained by the solution-diffusion mechanism where the solvent flux increases with the transmembrane pressure, resulting in high rejection (Verliefde et al. 2013). On the other hand, the observed decrease in rejection with recovery (Fig. 6B) has been attributed to the increase of the Se(VI) concentration at the membrane surface, named 'concentration polarization', which enhances the solute transport through the membrane Chung et al. (2010). In addition, at higher recovery, the rejection of Se(VI) by nanofiltration was more affected than by the reverse osmosis membrane where ion transfer is less convective and more diffusive (Pontié et al. 2008). In summary, the rejection of selenium with nanofiltration/reverse osmosis membranes increases with transmembrane pressure whereas rejection decreases with recovery. However, further in-depth investigations are needed to work at high recovery and thus to decrease the retentate quantity without affecting the efficiency of the nanofiltration/reverse osmosis process.

Besides studies on the effect of pH and speciation on the rejection of selenium with nanofiltration/reverse osmosis, future studies should investigate the impact of solute–solute interactions. The presence of other compounds and how these interact with selenium, such as phosphates in case of wastewater, hardness, and organic matter in case of natural water has to date not been investigated. In this context, further research is needed to fully understand, for instance, the solute–solute interactions that can impact the rejection of selenium and the complex transport mechanism through the nanofiltration/reverse osmosis membrane. Regarding the impact of the operating conditions on selenium rejection with nanofiltration/reverse osmosis, futures studies need to focus on the velocity variations that modify mass transfer, in the case of cross flow systems. Concerning the process itself, work should focus on system design and optimization of the operating parameters to achieve zero liquid discharge and eventually lower specific energy consumption.

Selenium removal by electrodialysis

Electrodialysis is an electro-membrane process, in which the driving force is the electrical potential over the membrane stack that generates a direct electric current. Anions move from the cathode to anode, while cations move in the other direction. While counter-ions can easily pass through the ion exchange membranes, co-ions are repulsed from the surface of the membranes and cannot be transported across. Electrodialysis only removes charged ions, therefore electrodialysis is generally incapable of removing non-charged elements from water streams. Electrodialysis is more energy efficient compared to reverse osmosis for desalinating brackish water. Electrodialysis has been used for desalinating brackish water containing salinity of 4 g/L total dissolved solids or less (Karimi et al. 2015). Both selenium species, selenite (Se(IV)) and selenate (Se(VI)) are anions in the neutral pH range. As a consequence, electrodialysis can in principle remove common selenium species from water. Electrodialysis can indeed remove different trace inorganic contaminants including fluoride, nitrate and arsenic(V) from brackish water to some extent (Onorato et al. 2017). However, reports on selenium removal by electrodialysis are to date very sparse.

In the absence of data on selenium removal by electrodialysis, one can consider the removal of similar ions. Kim et al. (2012) have investigated the competitive separation of single- versus double-charged ions by electrodialysis at different flow rates. The results suggest that at higher flow rates, double-charged ions show a somewhat increased transport compared to single charged ions. The higher transport of double-charged ions at higher flow rates is attributed to the thinner boundary layer, which is the limiting factor for ion transport in electrodialysis, during which ion diffusivity and mobility play an important role in transport. Selenate is analogous to sulfate and has similar chemistry and diffusivity in water (see Table 2), therefore a similar removal by electrodialysis can be expected.

Sosa-Fernandez et al. (2019) have shown that an increase in current intensity has little impact on the final sulfate removal. By contrast, Onorato et al. (2017) have investigated the effect of applied electrical potential on selenium removal, and have found that an increase in electrical

Table 2 Diffusion coefficient of different anions in water at 25 °C and 1 atm

Diffusion coefficient	Se (IV)[a]	Se (VI)[b]	Sulfate[c]	Chloride[c]	Nitratec[b]	Fluoride[c]
Ionic mobility ($\times 10^{12}$ mol s/kg)	0.36	0.38	0.43	0.82	0.77	0.59
Diffusivity ($\times 10^{9}$ m^2/s)	0.89	0.94	1.06	2.03	1.90	1.47

[a]Iida et al. (2011)

[b]Yuan-Hui and Gregory (1974)

[c]HDR (2002)

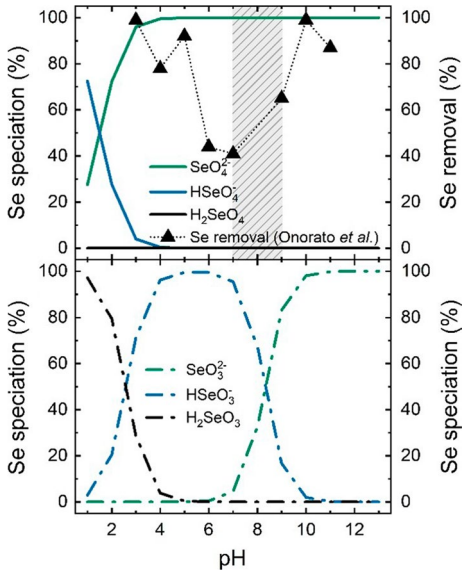

Fig. 7 Speciation of selenium VI (top) and IV (bottom), and removal of selenium VI, versus pH. Conditions: electric potential 12 V; feed salinity 5.3 g/L; membranes Neosepta CMX-SB & AMX-SB, Tokuyama Soda Ltd., Japan. The highlighted pH range shows the real pH of sample water used, which was then modified by adding HCl and NaOH. Adapted from Onorato et al. (2017)

potential from 12 to 18 V improves selenium removal from 33 to 48%. Karimi and Ghassemi (2015) have shown that electric potential has a higher impact on divalent ions compared to monovalent ions. Figure 7 shows the speciation of selenium compounds over a pH range of 1 to 13. As the pH of the sample water tested by Onorato et al. (2017) is 7 to 9, selenium is divalent. In a general study with brackish water that contained some selenium, Onorato et al. (2017) have also investigated selenium removal as a function of pH. The brackish water had an electric conductivity of 8290 µS/cm (≈5.3 g/L NaCl). Here, selenate (Se(VI)) was the dominant selenium species at a relatively low concentration of 20 µg/L, considering theWHO guideline of 40 µg/L (WHO 2017), and the European Union directive maximum contaminant level of 10 µg/L (EU 1998), while no data for selenite Se(IV) was reported.

Removal of Se(VI) is shown in Fig. 10, along with speciation simulation for both Se(VI) and Se(IV) at pH 1 to 13 by Minteq (v3.1, KTH, Sweden). Removal of selenate (Se(VI)) at neutral pH was about 40%, and indeed relatively low. Unfortunately, no removal data for selenite (Se(IV)) is available. Nonetheless, based on the speciation of Se(IV) in Fig. 7, it is expected that Se(IV) removal would be maximum at pH 4 to 7, where selenium is dominantly monovalent. This is expected due to the higher diffusivity and lower hydration number of monovalent species compared to divalent ions (Marcus 1997; Tanaka et al. 2013). The increased removal of Se(VI) at pH 8 to 11 (Fig. 7) was attributed to the presence of calcium, which may have caused a coprecipitation of various ions, i.e., $CaSeO_4$ (Onorato et al. 2017). The complexity of the real water used in these experiments makes it difficult to draw meaningful conclusions about selenium removal by electrodialysis. In the case of specific wastewaters that require pretreatment steps before the electrodialysis process, the pH of the feed must be considered because selenium removal is pH-dependent and hence will be affected strongly by pH variation. For example, Gingerich et al. (2018) investigated selenium removal from wastewater of coal-fired power plants. After a pretreatment process necessary for removing other contaminants, the pH of the wastewater is high and therefore the solution pH may have an impact on selenium removal by electrodialysis based on the very limited observations from Onorato et al. (2017).

While electrodialysis can in principle remove trace selenium concentrations, presence of other anions in water may hinder selenium removal by competition. While there is no data available for selenium, this process is likely from observations with other ions. For example, in experiments removing sulfate from saline water, Sosa-Fernandez et al. (2019) showed that the removal of sulfate was always lower than that of chloride. It is therefore expected that oxoselenium anions removal follows the same trend as sulfate, because selenium and sulphur are both in the 15th group of the periodic table and have chemical similarities, e.g., ionic mobility and diffusion coefficient (Table 2). Ionic mobility and diffusion coefficient of selenium species and different anions are presented in Table 2. Lower mobility and diffusivity of both Se(IV) and Se(VI) suggest that an increase in the salinity of the feed water may result in a lower removal of selenium due to the competition of other present anions in water to be transported.

Very few studies on selenium removal by electrodialysis have been reported to date. Several handbooks (HDR 2002) and patents (Wallace 2013a, 2013b) mention electrodialysis as a process to remove selenium from water, yet in the reviewed documents no references or experimental results other than reports of the charged state of selenium species in water was observed. Moreover, in the mentioned patents (Wallace 2013a, 2013b), it is suggested to add a selenium removal process after electrodialysis to ensure complete selenium removal from product water. This implies that no complete removal was expected. Additionally, the complex chemistry of real brackish groundwater in the only published study of Onorato et al. (2017) makes it difficult to conclude on the effectiveness of electrodialysis for selenium removal. Presence of other compounds, e.g., hardness, organic matter, multivalent ions, and salinity, in water may affect selenium removal by electrodialysis. More systematic experiments are needed to understand the mechanisms and the ability of various electrodialysis membranes and operating parameters to achieve effective removal.

Remediation by chitosan-enhanced ultrafiltration

Pressure-driven membrane processes such as reverse osmosis and nanofiltration are able to reject species with very low molecular weight such as metal ions. In reverse osmosis, the separation of various species of a mixture is related directly to their relative transport rates within the membrane, and these rates are controlled by diffusivity and solubility in the membrane material. In nanofiltration, the separation of solutes is due to a complex mechanism involving steric hindrance, which depends on 1) the relative sizes of the pores and solutes (Ferry 1936), 2) Donnan exclusion resulting from the Coulomb interaction between charged solutes and the membrane fixed charge (Donnan 1995), and 3) dielectric exclusion in terms of both the Born dielectric effect resulting from the solvation energy barrier due to the decrease of the dielectric constant of the solution inside the membrane pores (Bowen et al. 1997; Déon et al. 2012) and image charge effects due to the interaction between the ions and the polarization charges, induced by the ions, at the interface between the membrane matrix and the solution inside the pores (Yaroshchuk 2000; Szymczyk et al. 2005). Reverse osmosis is generally used when a total retention of ions is desired, whereas nanofiltration is rather dedicated to partial demineralization of waters. However, even if reverse osmosis and nanofiltration processes are capable of rejecting ions, unfortunately, they produce relatively low permeation fluxes and requires high transmembrane pressures to obtain significant flux, which result in a high energy cost. Oppositely, ultrafiltration requires lower applied pressures while providing higher permeation fluxes, but the solute removal performances are much lower due to larger pores.

The range of use of ultrafiltration can be enlarged towards solutes smaller than membrane pores by pretreatments such as micellization (Witek and Koltuniewicz 2005; Chhatre and Marathe 2008) or complexation (Rumeau et al. 1992; Kryvoruchko et al. 2002; Mimoune et al. 2007). These preliminary treatments increase the effective size of ions for improving their rejection due to steric effects. This step can be implemented by complexation of metal ions with either synthetic polymers, such as polyethylenimine (Molinari et al. 2004) poly(acrylic acid) (Cojocaru and Zakrzewska-Trznadel 2007) and macrocycle and macromolecular compounds (Walkowiak and Kozlowski 2009) or natural polymers such as alginate (Fatin-Rouge et al. 2006) and chitosan (Crini et al. 2017) as chelating agent. Due to their many potential donor sites, these polymers have shown very interesting trends for complexation of various metal cations such as copper, lead, nickel, and cobalt by coordinate bonds with lone pairs of ligand. This mechanism of metal complexation is well-known (Rivas et al. 2003) and has been investigated many times (Lam et al. 2018). Polymers can also be used for the removal of anionic pollutants. In this case, physicochemical mechanisms leading to links between ions and polymers are different, and attractive electrostatic interactions can be used. In the case of selenium removal, a polymer with positively charged groups such as protonated amine groups ($–NH_3^+$) must be chosen to induce attractive electrostatic interaction with oxyanions of selenium.

The rejection of oxyanions forms of Se(IV) and (VI) by chitosan-enhanced ultrafiltration was investigated under various experimental conditions by Déon et al. (2017). Chitosan was chosen because the chitosan structure contains amino ($–NH_2$) groups as well as numerous hydroxyl groups conferring a strong hydrophilic character. In this study, polymer-enhanced ultrafiltration of oxyanions was implemented under acid conditions ($pH < pK_{a\ chitosan} = 6.3$) for which amine groups ($–NH_2$) of the deacetylated part are protonated. The polymer thus behaves as a positively charged polyelectrolyte. In order to better understand the rejection of Se(IV) and Se(VI), it is also worthwhile to keep in mind that Se species can be present in different forms depending on pH value. As shown by Fig. 8, for acid pH, Se(IV) can

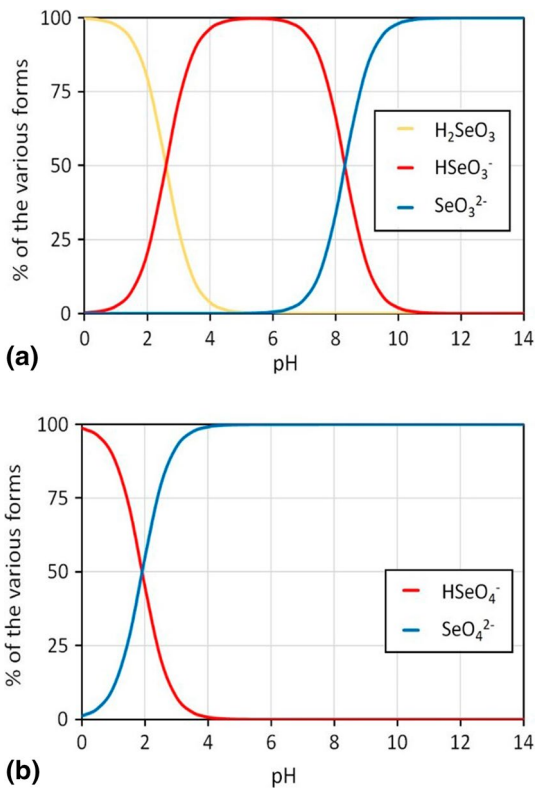

Fig. 8 Speciation distribution of selenium forms versus pH. **a** Se(IV) and **b** Se(VI). At acidic pH, Se(IV) is either neutral selenious acid and/or monovalent anion (hydrogen selenite). At basic pH Se(IV) is either monovalent anion (hydrogen selenite) and/or in divalent anion (selenite ions). Se(VI) is mainly in the form of divalent anion (selenite ion) with a pH above 3.5

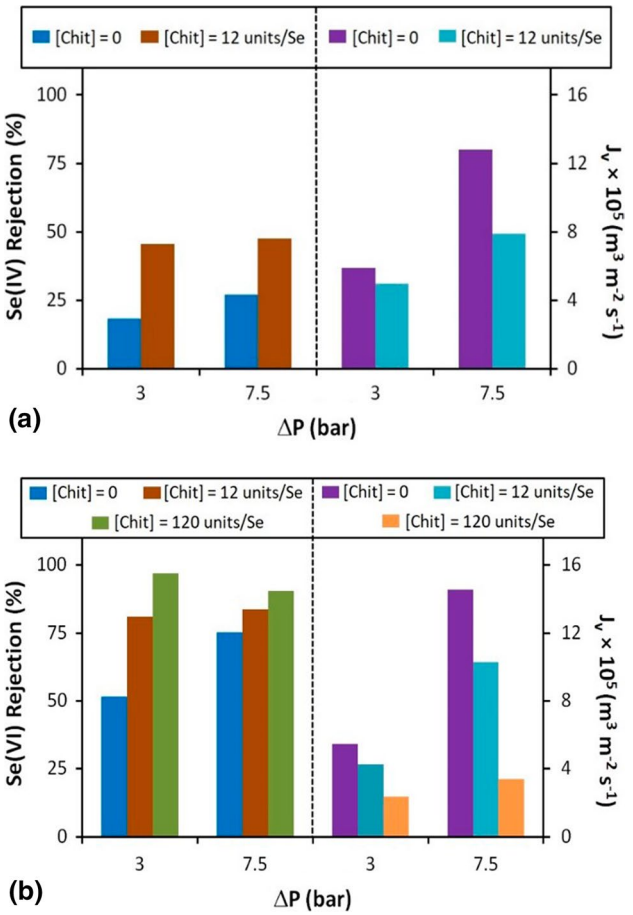

Fig. 9 Rejection and permeation flux obtained by ultrafiltration of solutions containing 1.7 mmol/L of **a** Se(IV) and **b** Se(VI) with and without chitosan at pH 4. CERAM 60 membrane, molecular weight cut off: 8 kDa

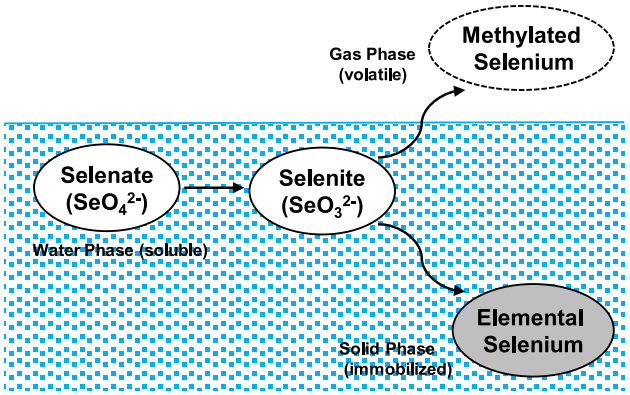

Fig. 10 Microbial selenium metabolism enabling the removal of soluble selenium, e.g. selenate and selenite, from the water phase. Selenate reduction into selenite proceeds mainly under anoxic conditions; selenite volatilization occurs mostly under aerobic conditions, while selenite reduction into elemental selenium proceeds under both aerobic and anoxic conditions

be in neutral form (selenious acid) and/or monovalent anion form (hydrogen selenite) whereas it can be in monovalent anion form (hydrogen selenite) and/or in divalent anion form (selenite ions) at basic pH values. As to Se(VI), it is mainly in divalent anion form (selenite ion) for pH above 3.5.

The impact of chitosan addition on rejection of Se(IV) and (VI) by a ultrafiltration membrane can be observed in Fig. 9a and b, respectively. Results show that chitosan addition before filtration contributes substantially to increasing rejection of selenium, the form of which is monovalent ($HSeO_3^-$) or divalent (SeO_4^{2-}) at the pH of the solution (4). At this pH condition, electrostatic attraction between the positive $-NH_3^+$ groups of chitosan and the negative charge of oxyanions induces a notable increase of selenium rejection, although complexation does not occur. The addition of 120 mol of monomer units per mol of Se(VI) even makes it possible to obtain rejection rate close to 95% (Fig. 9b). In the absence of polymer, it should be noted that Se(VI) is more rejected than Se(IV) in the same conditions, due to stronger repulsive interactions between the negatively charged membrane and divalent anions (SeO_4^{2-}) as compared with monovalent anion ($HSeO_3^-$). Figure 9a and b also show that the permeation flux decreases notably when the concentration of chitosan increases due to the increase in viscosity of solutions and accumulation of polymer/ion at the membrane surface. However, these flux values are still much higher than those produced by nanofiltration (and reverse osmosis) membranes at the same applied pressures.

These results have, therefore, shown that polymer addition in selenium solutions before ultrafiltration, can have a positive effect on selenium rejection, providing that polymer and selenium species have opposite charges and that the ionic strength is sufficiently low in order not to shield the electrostatic interactions between oxyanions and polymer. Polymer-enhanced ultrafiltration appears as a potential option to remove anionic pollutants from wastewaters.

Biological removal of selenate by activated sludge

Microbial metabolism can reduce selenate into solid selenium (elemental Se) via selenite, and selenite can be reductively transformed into volatile selenium, e.g., dimethyl selenide. These processes enable the removal of soluble selenium from the water phase to the solid or gas phase and can be utilized to develop cost-effective and eco-friendly technologies for the treatment of Se-containing water and wastewater (Fig. 10). Such microbial selenium metabolisms are mediated by different types of microbes and are known to proceed under both aerobic and anaerobic conditions. Since

various kinds of aerobic and anaerobic microbes exist in activated sludge, activated sludge has a considerable potential for the biological treatment of selenium-containing wastewater under alternating anoxic/oxic conditions. This section describes a trial to utilize activated sludge for the treatment of selenate.

The activated sludge taken from a coke-oven wastewater treatment facility in a steel plant was used to remove selenate from artificial wastewater in a model sequencing batch reactor under alternating anoxic/oxic conditions (Zhang et al. 2019). The synthetic wastewater was composed of 1 or 5 mM selenate, 44 mM sodium lactate as the carbon source, 30 g/L NaCl, and other minerals, simulating high salinity selenium refinery industrial wastewater. The model sequencing batch reactor was constructed in a 200-mL Erlenmeyer flask with a working volume of 160 mL, and operated at a constant temperature of 28 °C. At the beginning, the sequencing batch reactor was operated under anoxic conditions with a 7-day cycle duration to specifically enrich bacteria that reduce selenate as a terminal electron acceptor of anaerobic respiration because these bacteria are considered the main contributors to selenate reduction (startup period; phases I and II). After almost complete removal of soluble selenium was achieved, treatment with the 3-day cycle duration was started (phases III to VI). In phase III, the sequencing batch reactor was operated under the same anoxic conditions, and an aeration step was added in the following phases. In those alternating anoxic/oxic conditions, the aeration period was prolonged stepwise from 3 to 7 h, from phases IV to VI to evaluate the influence of aeration on the selenium removal.

The selenium treatment performance of the sequencing batch reactor is shown in Fig. 11. In all treatment phases, selenate concentration in the effluent was maintained below the detection limit, and soluble selenium was almost completely removed (> 97%) without significant accumulation of selenite, independent of the length of the aeration step. However, a considerable amount of solid selenium was found in the effluent as suspended solid-Se, and consequently removal

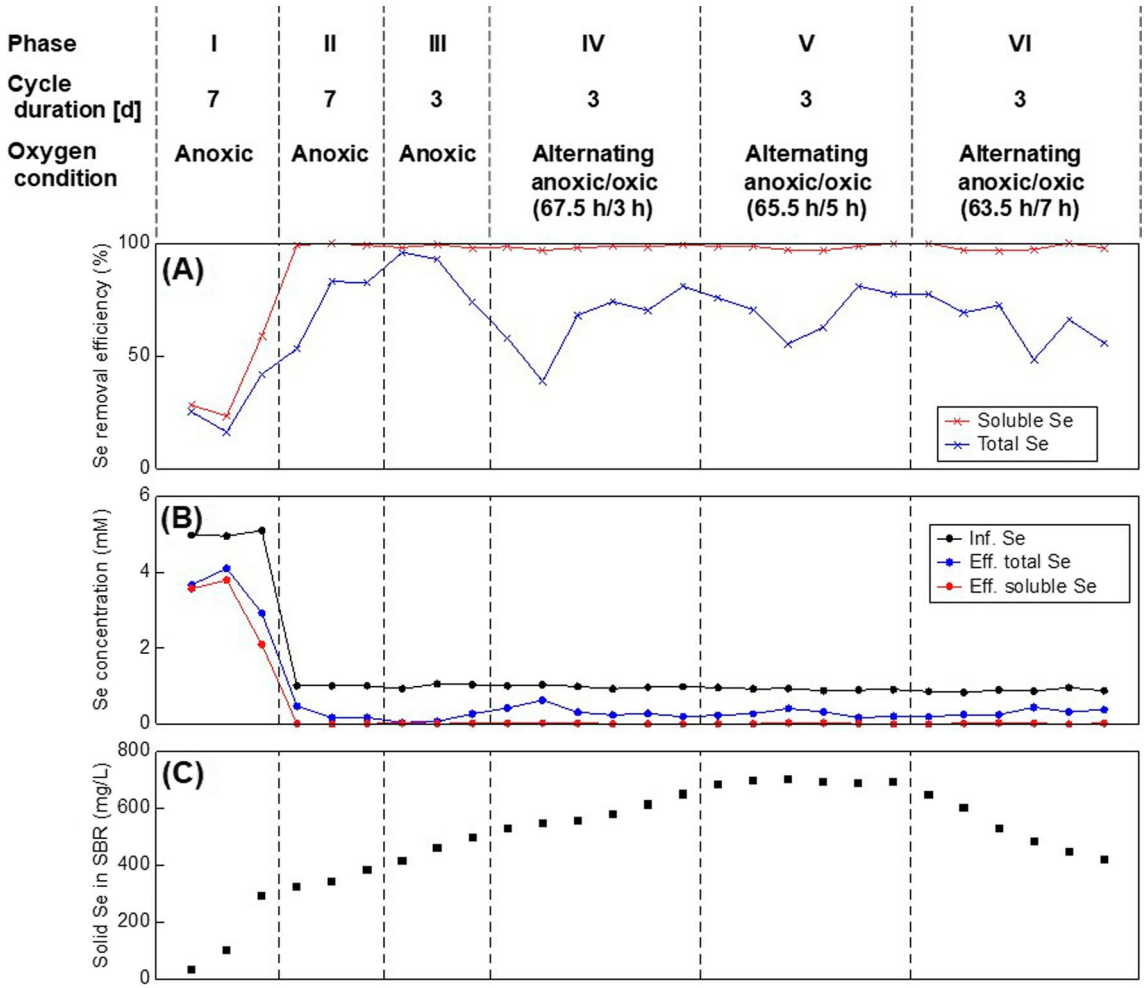

Fig. 11 Selenium removal performance of the sequencing batch reactor: **A** Se removal efficiencies, **B** Se concentrations in the influent and effluent, and **C** solid Se in the reactor. Adapted from Zhang et al. 2019

of total selenium was much lower than that of soluble selenium. The suspended solid-Se concentration was maintained at relatively low levels, and the average total selenium removal during the anoxic operation (phase III) was 88%. On the other hand, during alternating anoxic/oxic conditions (phases IV to VI), total selenium removal was not stable, varying from 39 to 81%, and the suspended solid-Se concentration in the effluent tended to be higher than that observed during the anoxic operation. The shear force generated by aeration seemed to disperse the solid selenium particles in the sequencing batch reactor and make them remain in the effluent. During the series of treatments, the amount of solid Se in the sequencing batch reactor gradually increased from the startup to phase IV, indicating that selenium removed from the water phase accumulated in the sequencing batch reactor as solid selenium, most likely elemental selenium, by bioimmobilization and bioprecipitation. The extension of the aeration period in phases V and VI clearly changed the fate of selenium in the sequencing batch reactor; specifically, the amount of selenium in the sequencing batch reactor was kept constant during phase V, and the amount of selenium decreased during phase VI. Based on the selenium mass balance calculation, the disappearance of selenium from the sequencing batch reactor in phase VI was found to be due to the generation of volatile selenium, such as dimethyl selenide, dimethyl diselenide, and dimethyl selenyl sulfide, by biovolatilization.

Through the above-mentioned trial, it was confirmed that activated sludge has a promising potential to treat wastewater containing selenate, which is difficult to efficiently remove by typical physicochemical technologies. Soluble selenium could be completely removed by activated sludge; however, a considerable amount of suspended solid-Se remained in the effluent, especially in alternating anoxic/oxic conditions. Therefore, post-treatment, such as high-speed centrifugation, filtration, chemical coagulation (Staicu et al. 2015a, 2015b, 2017), and electrocoagulation (Staicu et al. 2015c), which are described in detail in other sections, is necessary to remove suspended solid-Se in the effluent to improve the removal efficiency of total selenium. Further, activated sludge can convert selenate to both solid selenium and volatile selenium, depending on the duration of the aeration period. Under anoxic conditions, selenate was reduced into elemental selenium, which should be removed and disposed of as waste sludge, while biovolatilization of selenium became efficient under prolonged oxic conditions and selenium was removed into the gas phase. The use of activated sludge under anoxic conditions enables the establishment of energy-saving treatment processes. On the other hand, alternating anoxic/oxic conditions with longer aeration periods allow the feasibility of recovering selenium with few impurities with the treatment process by trapping volatile selenium using an off-gas trap (Kagami et al. 2013).

Conclusion

Removing selenium from raw water and wastewater is challenging because this metalloid is often trapped in a mixture of complex and more abundant substances. This metalloid is also difficult to remove from groundwater and industrial effluents because Se chemical forms determine the effectiveness of a treatment method, as well as water parameters such as pH and concentration of competing anions. Technologies based on zero-valent iron, iron-oxy-hydroxides, supported materials, nanofiltration, reverse osmosis, chitosan-enhanced ultrafiltration, electrodialysis, and activated granular sludge can be used for the removal of selenium from drinking water or wastewater and industrial discharges. Each technology has its advantages and disadvantages. Zero-valent iron is an effective agent for the treatment and removal of selenium, especially when Se is present in groundwater. Zero-valent iron has also been extensively applied also for the treatment of industrial wastewaters. Although there are only a few studies on the use of activated sludge for the treatment of selenium-rich wastewater, this microbial technology is promising, mainly due to the low cost, efficiency and robustness of the bioprocess. Remediation of selenium-containing solutions by chitosan-enhanced ultrafiltration seems also appears to be a promising avenue, as this coproduct of the food industry is cheap and effective in removing traces of pollutants including selenium.

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Declarations

Conflict of interest The authors declares no conflict of interest.

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