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Abstract After major pollution by nitrates and pesticides, soils and groundwater in some parts of the world are now facing the emergence of a third major issue of selenium (Se) contamination. Selenium occurrence in ecosystems results naturally from weathering of Se-containing rocks, and is further aggravated by human activities. Selenium is ubiquitous in the environment, and the two main sources of human exposure by Se are food and water. Se, a metalloid, is an important micronutrient due to Se antioxidant, anti-inflammatory and chemo-preventative properties. At normal dietary doses, selenium is an essential diet element that has nutritional proper-

E. Lichtfouse (✉)
Aix Marseille University, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France

N. Morin-Crini · G. Crini (✉)
Laboratoire Chrono-environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France
e-mail: nadia.crini@univ-fcomte.fr; gregorio.crini@univ-fcomte.fr

C. Bradu
Department of Systems Ecology and Sustainability, PROTMED Research Centre, University of Bucharest, Bucharest, Romania
e-mail: corina.bradu@g.unibuc.ro

Y.-A. Boussouga · M. Aliaskari · A. I. Schäfer
Institute for Advanced Membrane Technologies (IAMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Eggenstein-Leopoldshafen, Germany
e-mail: youssef-amine.boussouga@kit.edu; aliaskari.mehran@kit.edu; andrea.iris.schaefer@kit.edu

S. Das
Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada
e-mail: soumya.das@usask.ca

L. D. Wilson
Department of Chemistry, University of Saskatchewan, Saskatoon, SK, Canada
e-mail: lee.wilson@usask.ca

ties and is necessary to maintain good health in humans and animals. Nonetheless, exposure to high concentrations of selenium is harmful to living beings. In terms of contamination, selenium as an emerging hazardous substance is receiving particular attention in developing countries, where research is focussing on water treatment. Actual remediation techniques are limited because removing Se from complex mixtures of substances is very challenging. Yet, techniques of water decontamination are developing rapidly. Here, we review selenium occurrence, pollution, properties and remediation. Advanced remediation include technologies based on zero-valent iron, iron-oxy-hydroxides, supported materials, nanofiltration, reverse osmosis, enhanced ultrafiltration, electrodialysis, and activated granular sludge.

Keywords Selenium · Water · Wastewater · Removal technologies · Coprecipitation · Reduction techniques · Zero-valent iron · Metal oxides · Activated alumina · Activated carbon · Ion-exchange · Supported materials · Membrane filtration · Electrodialysis · Activated granular sludge

3.1 Introduction

> *Sola dosis facit venenum – All things are poison, and nothing is without poison; only the dose determines what is not a poison*. Paracelsus (1493–1541)

Metals and metalloids, and their organometallic derivatives are among the substances that present a recognized danger to humans and the environment. Metals and metalloids are part of our daily lives because they are used in a wide variety of products and applications. Due to their particular physical, chemical and biological properties, they have many industrial applications, e.g. in anti-corrosion coatings, stainless steel composition, electrical industry, pigment manufacturing, fruit fungicide manufacturing, construction, catalytic converters, alloy and semiconductor manufacturing, wood processing, glass manufacturing, catalysis, and cosmetology.

In the field of nutrition, certain metals and metalloids are also useful or even essential at trace levels for our health, contributing to the proper functioning of living organisms (Amiard 2011; Crini 2017; Hejna et al. 2018). However, these

M. Ike · D. Inoue
Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan
e-mail: ike@see.eng.osaka-u.ac.jp; d.inoue@see.eng.osaka-u.ac.jp

M. Kuroda
Graduate School of Environmental and Disaster Research, Tokoha University, Suruga-ku, Shizuoka, Japan
e-mail: kuroda@sz.tokoha-u.ac.jp

S. Déon · P. Fievet
Institut UTINAM, UMR CNRS 6213, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France
e-mail: sebastien.deon@univ-fcomte.fr; patrick.fievet@univ-fcomte.fr

substances can also have negative impacts at individuals, population and ecosystem levels, resulting from their transport, transfer, bioaccumulation and biomagnification along the food chain. For example, metals such as iron, cobalt and zinc, are either essential for human health because they have a physiological role, or toxic in larger amounts or certain forms. Other substances have no biological function and can become toxic if they are absorbed in excess. Other substances such as cadmium, mercury, lead and arsenic are poisonous in their ionic form. This is the paradox of these contaminants, they are both useful and potentially dangerous. For these reasons, many metals and their derivatives are among the most monitored hazardous substances. Toxicity depends not only on concentration but also on speciation. For instance, many elements such as arsenic, chromium, nickel, manganese and vanadium, exist under several different oxidation states. Other elements such as mercury, tin, manganese and arsenic occur under different chemical forms. From a chemical and toxicological point of view, these substances are now well-known (Amiard 2011).

The intensive use of metals and metalloids by humans began with the Industrial Revolution more than 250 years ago (Crini and Lichtfouse 2018). From the beginning, this use began to affect the environment, and therefore our ecosystems. Their presence in different environmental compartments, e.g. water, soil and air, is mainly due to contamination generated by human activities, e.g. soil degradation. Yet there are also natural sources such as earth's crust elements, volcanic activities and natural biological activity. Anthropogenic sources of Se are numerous and varied, for instance: agricultural activities, e.g. fertilizing; industrial activities, e.g. mining and metallurgy; industrial discharges in water, soil and air; combustion by incineration for energy production, and transport activities (Rosenfeld and Beath 1964).

In Europe, in order to improve the quality of the environment and guarantee the health of populations, regulations have been gradually set up since the 1970s, particularly in the field of industrial waste (Crini and Badot 2007, 2010; Fordyce 2013; Crini 2017; Hejna et al. 2018). The objective was to reduce or eliminate emissions of targeted substances according to criteria of toxicity, persistence and bioaccumulation. Metals are now one of the most closely controlled classes of chemicals, classified as hazardous or priority hazardous substances. In Europe, currently, out of forty or so metals in the periodic table, the following twelve metals are subject to special monitoring, particularly for discharges and industrial wastes: aluminum, arsenic, cadmium, chromium, chromium, nickel, copper, tin, iron, manganese, mercury, lead and zinc. Considerable environmental efforts have been made by the industry over the past 30 years, yet metals and metalloids continue to be the subject of constant debate and concern.

Selenium is a subject of particular attention. Se is known as the "double-edged sword element" for its dual beneficial and toxic character to health (Fernández-Martínez and Charlet 2009). Indeed, despite Se nutritional benefits, it 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. This metalloid is an important micronutrient for living beings and an essential trace element of fundamental importance to health due to its nutritional and biological properties. At normal dietary doses, selenium is necessary to maintain good health in humans and animals.

Indeed, Se deficiency is a major problem worldwide, with several cases of deficiency reported. However, exposure to high concentrations of selenium is harmful to living beings.

Overexposure and selenium deficiency have been associated with adverse health effects. In 1999, Peter M. Chapman, a world-renowned environmental toxicologist, asked the following question: is selenium a potential time bomb or just another contaminant? This issue highlights "the valuable but risky nature of this chemical element" (Chapman 1999). Over the past two decades, selenium has become a new substance of concern, not only for nutrition and medicine but also for water pollution (Hatfield 2001; Wu 2004; Fernández-Martínez and Charlet 2009; Santos et al. 2015; Vinceti et al. 2017, 2018a, b; Hejna et al. 2018; Ullah et al. 2018, 2019). As a consequence, research on selenium is developing in environmental science to study its presence, behavior, transfer, and bioaccumulation; in toxicology to assess toxicity and impact; and in water engineering to clean waters.

Selenium is naturally present and widespread in the environment. It is released by natural processes, including geological and geothermal activities, and human activities, e.g. mining, industry, and agriculture. Various parts of the world, especially in North America and in Europe, are experiencing issues of selenium contamination, especially in soils, aquifer sediments and groundwater (Wu 2004; Conley et al. 2009; DeForest et al. 2012; Fordyce 2013; Santos et al. 2015; Crini 2017; Di Marzio et al. 2019; Paul and Saha 2019). Living organisms can be exposed to selenium through Se presence in food and drinking water. Exposure to selenium also occurs when living beings come into contact with soil or air that contains selenium. The two main sources of selenium exposure are food, e.g. bread, cereals, nuts, fish, eggs and milk, and tap water (Rosenfeld and Beath 1964; Combs and Combs 1986; Combs 1988; Mayland 1994; Hatfield 2001; Reilly 2002; Fernández-Martínez and Charlet 2009; ANSES 2012; Bañuelos et al. 2014; Health Canada 2014; Santos et al. 2015; Crini 2017; Kieliszek 2019).

After pollution by nitrates and pesticides in some parts of the world like France face the issue of selenium pollution. Unlike most pesticides, selenium is mainly of natural origin (INERIS 2011; INRS 2011; OMS 2011; ANSES 2012; Health Canada 2014; Paul and Saha 2019). There are also anthropogenic sources of selenium in many industries including mining, petroleum refining and metallurgical activities. Other human activities such as the release of sedimentary construction waste rocks, irrigation and fossil fuel combustion also contribute to selenium contamination (Crini 2017). For drinking water, the World Health Organization has set a regulation limit of 40 µg Se/L, most European countries have set the regulation limit at 10 µg/L, and the upper limit set by the United States Environmental Protection Agency is 50 µg/L. However, the value of 10 µg/L is often exceeded in groundwater (Fordyce 2013; Santos et al. 2015; Crini 2017).

Today, we have reached the *Pollutant Removal Age* of the anthropocene, and there has been considerable efforts to develop technologies to reduce contaminant emissions (Crini and Lichtfouse 2018). The removal of selenium from water and wastewaters is of great interest in the field of water pollution. However, the problem is not simple because it is difficult to remove trace selenium from complex mixtures

of substances. In its natural form as an element, selenium cannot be destroyed but it does have the ability to change of form. From a chemical point of view, due to their structure and stability, selenium forms are difficult to treat and often compete with other substances (BRGM 2011; Crini 2017). The removal of selenium from water and wastewater is controlled by Se speciation and the chemical composition of the water from the supply source. Treatment is also costly due to the characteristics of the aqueous solution and due to the strict discharge limits of selenium and its oxyanions such as Se(IV) and Se(VI) (Koren et al. 1992; Kapoor et al. 1995; Crini 2017; Stefaniak et al. 2018; Rene et al. 2019). Speciation of selenium in groundwater or in a raw effluents plays an essential role in the effectiveness of treatment methods used for Se removal, especially because selenium is often present at low concentrations, less than 1 mg/L (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 form of selenium. Like other many metalloids, selenium is difficult to remove, especially the oxyanion of Se(VI) present, for example, in mining effluents (Rene et al. 2019).

Two types of contaminated waters should be distinguished: waters to be treated for drinking, which usually contain less than 0.1 mg Se/L, and industrial waters that contain more than 1 mg/L. In both cases effluents containing selenium are often associated with other substances and high salinity (Koren et al. 1992; Kapoor et al. 1995). As a consequence, 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.

Technologies available for the removal of selenium can be classified in chemical methods, e.g. coprecipitation, reduction-adsorption, oxidation-reduction, electrocoagulation, catalyzed cementation; physical treatments, e.g. adsorption, membrane filtration, ion-exchange; and biological methods such as microbial reduction, bacterial treatment, enzymatic reduction, fluidized bed reactor, algal assimilation and constructed wetlands (Koren et al. 1992; Kapoor et al. 1995; Sandy and DiSante 2010; Santos et al. 2015; Crini 2017; Rene et al. 2019).

For drinking water, local disposal solutions such as sand filtration coupled with ion exchange resins and membrane treatments, e.g. microfiltration and nanofiltration, show removal performances above 95% (Crini 2017). However, such solutions are often poorly adapted, poorly selective and costly. Innovations are therefore needed to find treatment methods that are efficient, inexpensive, technologically feasible and environmentally friendly. Generally, in France, the solution consists either in asking the competent authorities for operating exemptions or, more often, in seeking another water resource.

For industrial-scale selenium removal, the first possible method is iron coprecipitation and adsorption, coupled, if necessary, with a coagulation-flocculation. Other treatments include reduction techniques, adsorption, e.g. using metal oxides, activated alumina or activated carbon; ion exchange; reverse osmosis and nanofiltration; showing 75–99% removal efficiencies depending on selenium form. For

drinking water production, lime softening (decarbonation) and reverse electrodialysis show lower removal, below 70%. For the treatment of industrial effluents, a combination of physicochemical processes such as chemical reduction, coprecipitation, coagulation, adsorption, filtration is generally used (Rene et al. 2019). Biological techniques such as microbial reduction, aerobic wetlands and biochemical reactors can also be used. Adsorption on non-conventional materials, e.g. biosorbents, and innovative biological techniques such as microalgal-bacterial treatment, bioremediation, and phytoremediation are being explored (Crini 2017; He et al. 2018b). Among innovative treatments to removing selenium, one of the most promising approaches is fixed-bed biological treatment in terms of efficiency and cost. The next section present selenium chemistry, occurrence and decontamination methods from water and wastewater.

3.2 Selenium Chemistry and Applications

For more general information on selenium, the reader can consult a very interesting technical document, published in March 2014 by Health Canada of the Canadian Federal Department (Health Canada 2014; www.santecanada.gc.ca). Other comprehensive reports are given in OEHHA (2010), BRGM (2011) and ANSES (2012). Book references include Rosenfeld and Beath (1964), Combs and Combs (1986), Frankenberger and Benson (1994), Frankenberger and Engberg (1998), Hatfield (2001), Lemly (2002), Surai and Taylor-Pickard (2008), Reilly (2006), Woollins and Laitinen (2011), Preedy (2015), Crini et al. (2017), and van Hullebusch (2017).

3.2.1 Selenium, a Metalloid

Selenium (Se) belongs to the non-metallic family but is considered as a metalloid because selenium has properties of both metals and non-metals. This chemical element was identified as a new substance in 1817 by the Swedish chemist Berzelius in leaden chamber mud during sulfuric acid production. It was given the name selenium in resemblance after the Greek goddess of the moon “Selene”, in homology to the chemically similar tellurium.

Selenium belongs to the elements of group 16 (chalcogens) of the periodic table, together with oxygen, sulphur, tellurium and polonium. Se has thus similar chemical and physical properties with these elements. Particularly, selenium displays a chemical behavior similar to sulfur, and as a result, Se is found associated with naturel sulfides, e.g. pyrite and chalcopyrite, mainly in trace concentrations. Selenium can conduct electricity or act as an insulator and display unipolar conductance of electricity. The most outstanding physical property of crystalline selenium is its photoconductivity. The gray, metallic form of Se is the most stable under ordinary conditions. This form has the unusual property of greatly increasing in

electrical conductivity when exposed to light (Combs and Combs 1986; Simonoff and Simonoff 1991; White and Dubrovsky 1994; Frankenberger and Engberg 1998; Plant et al. 2003; Fernández-Martínez and Charlet 2009; Lide 2009; INERIS 2011; INRS 2011; Eklund and Persson 2014; Health Canada 2014).

Selenium has five redox states: -II, -I, 0, +IV and +VI (Table 3.1). There are also six stable selenium isotopes. Selenium speciation is complex because it exists in different oxidation states in nature, in both inorganic and organic forms, in solid, liquid and gas phase (Haygarth 1994). Biological transformations of selenium are manifold. In selenium-contaminated environments, a cocktail of different Se species may be present due to the variety of transformations, which poses a major challenge for the analysis of selenium speciation, and therefore the difficulty of choosing an appropriate method for selenium removal.

Elemental selenium Se(0) is present in nature as a non-soluble form. Se(0) occurs in different allotropic forms and may be amorphous or crystalline; seven different crystalline forms have been described. Se chemistry is complex, e.g. selenium can be mixed with sulfur in any ratio. Elemental selenium is precipitated after microbial reduction processes and also by inorganic processes. The oxidation states Se(-II) and Se(-I) are stable under strongly reducing conditions in metallic selenides and organic compounds (Table 3.1). The -II state is also present in nature as a product of microbial processes, e.g. H_2Se, and in metastable anions such as selenosulfate SO_3Se^{2-}, which is involved in the formation of metallic selenides. Volatile H_2Se is an analogue to H_2S under strongly reducing conditions. Organic species include: volatile compounds formed upon bacterial methylation, e.g. dimethylselenide and dimethyldiselenide; products of microbial methylation processes, e.g. dimethylseleniumsufilde and dimethyseleniumdisulfide; selenocysteine present in organic tissues; selenomethionine in

Table 3.1 The different forms of selenium compounds

Compound	Oxidation state	Form	Solubility (g/L)	pKa_1 and pKa_2	Example(s)
Selenides	-II, -I	Inorganic	Insoluble	3.8 and 14[a]	H_2Se, $SO_3Se_2^-$
Elemental selenium	0	Inorganic	Insoluble		crystalline trigonal Se
Selenite[b]	+IV	Inorganic	>850 (20°C)	2.7 and 8.54	SeO_3^{2-}, $HSeO_3^-$, H_2SeO_3
Selenate[c]	+VI	Inorganic	>840 (20°C)	−2.01 and 1.8	SeO_4^{2-}, $HSeO_4^-$
Selenium dioxide	+IV	Gas			SeO_2
Methylated species	-II	Organic			$(CH_3)_2Se$
Selenomethionine	-II	Organic		1.56 and 9.5	$C_5H_{11}NO_2Se$
Selenocysteine	-II	Organic		2, 5.2 and 10	$C_3H_7NO_2Se$

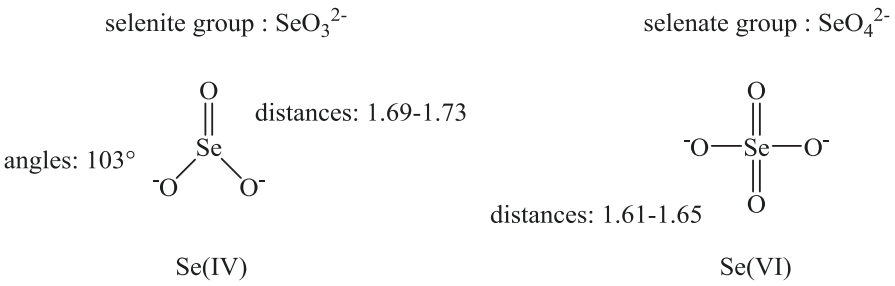
[a] H_2Se
[b] Na_2SeO_3
[c] Na_2SeO_4

plants; trimethylselenonium, an urinary metabolite; selenoproteins such as proteins and enzymes; and selenocyanate present in industrial wastewaters.

Table 3.2 compares the different forms of selenium from a chemical and geochemical point of view. Inorganic species of selenium +IV and +VI are soluble

Table 3.2 Main differences between the different forms of selenium from a chemical and geochemical point of view

Elemental selenium
– insoluble
– garlic smell in water
– mildly reducing
– colloidal: 1 nm to 1 μm
– red-color
– associated with natural organic matter
Selenate
– soluble
– not odiferous in water
– weakly adsorbed (outer-sphere)
– adsorption: surface hydroxyl group, oxyhydroxide charge
– net positive at lower pH: for anion adsorption
– net negative at higher pH: for cation adsorption
– two adsorption types: outer-sphere (weak ionic charge attraction - ionic strength, pH), inner-sphere (strong covalent bonds - pH)
– low precipitation and adsorption capacities
– aqueous chemistry similar to that of sulfates
– low reduction kinetics
– microbial reduction to selenite and elemental selenium
Selenides
– soluble unless metals are present
– garlic smell in water
– precipitation
– strongly reducing
– may adsorb weakly
– H_2Se toxicity
Selenite
– soluble
– not odiferous in water
– more strongly adsorbed (inner-sphere)
– reduction kinetics faster than selenate
– microbial reduction to elemental selenium and selenide
– reduced by organic acids
– more toxic than selenate
Organic selenium
– formed from biological activity, e.g. in plants, microorganisms
– some compounds are volatile



Scheme 3.1 Structures of selenite and selenate oxyanions, showing distances between Se and O atoms

oxyanions known as selenite and selenate, respectively (Scheme 3.1). Oxyanion selenite SeO_3^{2-} has a C_{3v} symmetry with pyramidal shape which is reduced to C_1 upon protonation. The oxidation state +IV also exists as gaseous selenium dioxide SeO_2, which is present in volcanic eruptions and combustions processes. Selenite is a weak acid occurring as H_2SeO_3, $HSeO_3^-$ and SeO_3^{2-}, depending upon pH. Selenite is present in oil refinery wastewaters, for example. In the moderate redox potential range, selenite is the major species, and selenite mobility is governed by adsorption/desorption processes on various solid surfaces including organic matter. Oxyanion selenate SeO_4^{2-} has a T_d tetrahedral symmetry, reduced to C_{3v} upon single protonation and to C_s upon double protonation. This fully oxidized form exists in solution as biselenate $HSeO_4^-$ or selenate SeO_4^{2-} with a pKa_2 of 1.8. The doubly protonated species with pKa_1 of −2.01 do not exist under natural conditions. Selenate species are predominant in waters, sediments and soils. Noteworthy, selenate has high solubility, low precipitation and adsorption capacities, and the aqueous chemistry of selenate and sulfate are quite similar (Fordyce 2007).

The inorganic forms selenate and selenite are the two most common oxyanions in water, due in particular to their high solubility (White and Dubrovsky 1994). For example, these two most oxidized species are frequently encountered in surface waters and are transported mostly in particulate-associated form. Both oxyanions display a high bioavailability and bioaccumulation potential (Sharma et al. 2015).

3.2.2 Industrial Applications of Selenium

In the industry, selenium is considered as a rare metal with many and varied applications. The most important applications are electronics, optoelectronics, glass, metallurgy, chemistry, pigments and nutrition (Surai and Taylor-Pickard 2008; Bañuelos et al. 2014; Gu et al. 2019; Zhu et al. 2019). These industries require only small quantities of Se. In addition, despite numerous applications, selenium currently competes in industry with other elements such as silicon, germanium, sulfur and tellurium. For example, many photocell applications using selenium are replaced by

other devices using elements that are more sensitive and more readily available than selenium.

Due to its photovoltaic, photoconductive and photosensitive properties and its ability to transform light into electricity, selenium is used extensively in electronic and electrical industries, mainly in rectifiers for electroplating, and in photoelectric cells (Zhu et al. 2019). Below its melting point, Se is a semiconductor, a property highly sought-after in the electronics sector. Other uses include metal alloys such as lead plates used in storage batteries, light meters, solar cells, detectors, colorimeters, photographic photosensitizers, photocopiers, and semiconductors (Gu et al. 2019; Zhu et al. 2019). Rechargeable metal batteries using selenium or selenide as cathodes have attracted considerable attention during the past few years because selenium/selenide possess a high volumetric energy density that is comparable to that of sulfur, and a moderate output voltage (Gu et al. 2019). Various other devices such as alarm devices, mechanical opening and closing devices, safety systems, and television rely on properties of selenium. Selenium is widely used in photocopying, xerography to copy documents, e.g. photographic toner, toning of photographs, and in sound films. For example, Se is used artistically to intensify and extend the tonal range of black and white photographic images.

The second major application of selenium is in the glass industry. Here, Se is used to decolorize glass by neutralizing the glass greenish tinge caused by ferrous impurities. Selenium is also added to glass to reduce the transmission of solar heat. As a red pigment, Se is used to make ruby-red colored glasses and enamels for ceramics and steel ware. For example, selenium imparts to glass a clear red color that is useful in signal lights. Se is used in the paint, plastic and ceramic industries to produce stains and dyes. Selenium is also used as an additive to stainless steel, e.g. to control porosity in stainless-steel castings. The third main use is sodium selenite for animal feeds and food supplements.

Selenium and derivatives are also used in the manufacture of many chemicals such as pigments, reducing agents, parasiticides, bactericides, insecticides, fertilizers, fungicides, herbicides, lubricating oils and solvents; they are also used in metallurgical applications, and in the military field. Selenium pigments are used to color many products such as plastics, paints, inks, glass, enamels and rubber. Selenious acid is used in the steel industry as an etchant. Selenium find applications as lubricants for metal polishing and is replacing lead in brass alloy plumbing fittings. Selenium serves for the vulcanization of rubber to increase resistance to abrasion; here selenium diethyldithiocarbonate acts as an accelerator and vulcanizing agent. In the rubber industry, Se also promotes resistance to heat and oxidation, and increases the resilience of rubber. Selenium is used as a paint and varnish remover, and as a solvent for rubber resins and other organic substances. Selenium catalysts, due to their high efficiency, moderate reaction conditions, good functional compatibility and excellent selectivity, have attracted a lot of interest over the past two decades as recently discussed by Shao et al. (2019).

Finally, selenium find applications in pharmaceuticals where selenium sulphide is used as a catalyst, and in cosmetology and agriculture. Selenium has been applied in producing cortisone, and radioactive selenium has been utilized in radiography.

Nanoparticles containing selenium were proposed for the diagnosis and therapy of Alzheimer's disease (Gupta et al. 2019), and as biosensors for detection of biological targets (Gandin et al. 2018). Selenium sulfide and other selenium-based compounds are added to anti-dandruff shampoos. As fungicide, Se is used in the manufacture of deodorant. Selenium is also used as a protective agent against pests. Mechora (2019) recently summarized pest control by selenium. Selenium can repel pests, reduce their growth, or cause toxic effects while having a positive effect on plant growth. Accumulated selenium in plants protects plants against aphids, weevils, cabbage loopers, cabbage root flies, beetles, caterpillars, and crickets due to both deterrence and toxicity. Mechora (2019) concluded that the use of selenium can be an alternative pest management method to conventional plant protection products that pose environmental and health problems.

Further developments are expected in the near future in the following domains: cancer prevention and therapy (Gandin et al. 2018; Sayehmiri et al. 2018; Tan et al. 2019b), biomedical, imaging and detection (Gandin et al. 2018; Gupta et al. 2019), designing selenium functional foods and beverages (Adadi et al. 2019), and agrochemistry (Garduño-Zepeda and Márquez-Quiroz 2018; Mechora 2019). Selenium has most probably a protective role against the development of prostate cancer, and therefore selenium supplementation is suggested for prevention of prostate cancer (Sayehmiri et al. 2018). Selenium supplementation also yielded promising results concerning radioprotection in tumor patients and should be considered as a promising adjuvant treatment option in subjects with a relative selenium deficit (Muecke et al. 2018). The agronomic and genetic biofortification of crops with selenium are novel strategies to improve the nutraceutical quality of staple crops. Biofortification with selenium in agricultural crops is increasingly becoming a solution to solve trace element deficiency in the human population, as well as to increase the content of bioactive compounds (Garduño-Zepeda and Márquez-Quiroz 2018).

3.2.3 Selenium in the Environment

Selenium has been found in all environmental compartments of the Earth, including the atmosphere, geosphere, hydrosphere and biosphere, due to the presence of both natural, e.g. alteration and leaching of the earth's crust, volcanism, and anthropogenic processes such as fossil fuel combustion and mining (Sharma et al. 2015). Se is found in the environment in both inorganic and organic forms, it is generally present in selenide, selenite or selenate forms, and more rarely in the elemental state (Shrift 1964; Rosenfeld and Beath 1964; Combs and Combs 1986; Combs 1988; Ihnat 1989; Frankenberger and Benson 1994; Frankenberger and Engberg 1998; Lemly 2002, 2004; Plant et al. 2003; Fernández-Martínez and Charlet 2009; Chapman et al. 2010; Bañuelos et al. 2014; Pettine et al. 2015; Sharma et al. 2015; Wu and Sun 2016; Donner et al. 2018; Kumkrong et al. 2018; LeBlanc et al. 2018; Etteieb et al. 2020).

Selenium concentrations in natural waters is a subject of intense interest (Sharma et al. 2015). Selenium in groundwater is of both natural, e.g. from inputs such as soil

leaching, or anthropogenic origin, e.g. industrial emissions, metal refining and coal combustion. Inorganic forms of selenate and selenite and organic species such as mono- and dimethylated derivatives have been reported in aquatic systems, the two common forms being oxyanions (White and Dubrovsky 1994; Lemly 2002; Fernández-Martínez and Charlet 2009; Chapman et al. 2010; Sharma et al. 2015). However, the valence states of the selenium in water are still poorly known and few studies have been published on transformations of selenium species in aqueous systems (Sharma et al. 2015; Pettine et al. 2015; Wu and Sun 2016; Donner et al. 2018). This depends on Se origin, e.g. natural leaching of soils or industrial discharges.

Due to their high solubility, oxyanions are mobile in soils, which explains their presence in some catchment areas. Due to rock erosion, selenium also enters inland waters and oceans. Selenate and selenite can be found in fresh and salt waters. Therefore, not only drinking water play an important role in human exposure to selenium but also the oceans *via* seafood (Fernández-Martínez and Charlet 2009; Santos et al. 2015). The global average concentration of selenium in freshwater is 0.02 µg/L and less than 0.08 µg/L in seawater. Groundwater generally contains higher selenium levels, from a few µg/L to more than 50 µg/L, than surface water due to contact with rocks (Fernández-Martínez and Charlet 2009; Santos et al. 2015). In industrial wastewater, concentrations are much higher (Crini 2017).

The bioavailability, mobility and reactivity of selenium in waters are also determined by Se speciation. Selenium speciation is controlled by physical processes, e.g. adsorption effects of soil and sediments; chemical processes, e.g. pH, redox conditions, organic matter, and presence of competitive ions; and biological processes, e.g. bacterial transformations. In natural waters of pH 6–9, under oxidizing conditions, Se(VI) is predominant in a divalent ionic form, i.e. the selenate anion SeO_4^{2-}. Se(IV) is the most frequent form encountered under reducing conditions; the hydrogenoselenite ion $HSeO_3^-$ being the dominant form below pH 8.15. At a pH above 8.15, the divalent selenite anion SeO_3^{2-} is the dominant form. Insoluble reduced species such as elemental selenium and selenides are generally released as colloidal suspensions into surface waters. The organic forms of selenium found in natural waters are produced by microbiological assimilation and degradation (Ivanenko et al. 2018). A comprehensive discussion on the chemistry and biogeochemistry of selenium in terms of variation of pH and redox conditions can be found in the reviews by Fernández-Martínez and Charlet (2009) and by Sharma et al. (2015).

3.2.4 Selenium and Industrial Emissions

Selenium in water also come from anthropogenic sources such as mining, oil refining, agricultural irrigation and discharges from industries producing and using selenium compounds (Crini 2017; Dinh et al. 2018; Donner et al. 2018; Tabelin et al. 2018). Mining and metal refining (copper), coal mining and fossil fuel combustion in coal-fired power plants are industrial sectors particularly affected by selenium releases (Plant et al. 2003; Wen and Carignan 2007; Fernández-Martínez and Charlet 2009; BRGM 2011; Health Canada 2014; Santos et al. 2015). These Se

releases are mainly responsible for the migration of selenium to different compartments of the environment. In mining wastewaters, selenium is found at concentrations from 3 µg/L to more than 12 mg/L. Wastewater resulting from flue-gas-desulfurization contains selenium at a typical concentrations of 1–10 mg/L (Santos et al. 2015). Other contaminated wastewaters such as coal mining pond water, uranium mine discharges, gold mine effluent, petroleum industry wastewater and lead smelter wash water also contain significant levels of selenium. Other human activities such as agricultural irrigation can also promote corrosion of selenium-bearing iron rocks, thus leaching selenium into aquifers as soluble oxyanions of Se(IV) and Se(VI). Selenium is also present in sewage treatment plants, mainly in sludge (Crini 2017).

3.3 Selenium and Water: A Substance of Concern?

Selenium is ubiquitous in the environment. Life is exposed to selenium through Se presence in soil, air, water and food, the two latter being the major sources of human exposure (Rosenfeld and Beath 1964; Combs and Combs 1986; Combs 1988; Reilly 2002; Fernández-Martínez and Charlet 2009; ANSES 2012; Fordyce 2013; Health Canada 2014; Santos et al. 2015; Donner et al. 2018). In Canada, food is recognized as the main source of selenium, while in France this is debated (Crini 2017).

Nowadays, it is widely recognized that selenium is both essential to human health and toxic in high quantities or in certain forms (Mayland 1994; Amiard 2011; Chauhan et al. 2019; Ibrahim et al. 2019; Kieliszek 2019; Varlamova and Maltseva 2019). Humans need to absorb small amounts of selenium daily in order to maintain good health and to prevent diseases, and food usually contains enough selenium because Se is naturally present in cereals, breads, nuts, fish, eggs, milk, meat, crab and tuna (Combs 1988; Mayland 1994; Hatfield 2001; Surai and Taylor-Pickard 2008; Amiard 2011). Selenium is essential to human health and should be present in the diet of all age groups to provide an adequate intake because Se is a key component of amino acids, e.g. selenocysteine and selenomethionine in selenoproteins found in all forms of life (Cai et al. 2019; Ibrahim et al. 2019; Varlamova and Maltseva 2019). In adults and teenagers, Se daily needs are estimated at 50–200 µg/day while in children they range from 30 to 120 µg/day. The water consumed also provides selenium (Reilly 2002; Crini 2017; Kieliszek 2019). However, despite Se nutritional benefits, it is one of the most toxic natural elements, and therefore particularly followed from a regulatory point of view.

In the field of water pollution, a worldwide problem is the presence of selenium in drinking water, groundwater and wastewater. Although benefits and toxicity of selenium are known, the levels considered to represent a threat to humans and environment are not yet well established (Fordyce 2013; Santos et al. 2015). For drinking water, according to European standards (Directive 98/83, European Commission, EU 1998) and Canadian water quality guidelines (Kwon et al. 2015), the selenium threshold should not exceed 10 µg/L, while the upper limit set by the United State Environmental Protection Agency USEPA (2004, 2016) is 50 µg/L. The EU has

revised the drinking water directive on 16 December 2020 for total selenium which is now 20 µg/L (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020L2184&from=EN). 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. There is a lack of clarity in national, European and international regulations concerning selenium (Fordyce 2013; Santos et al. 2015; Crini 2017; Kumkrong et al. 2018; LeBlanc et al. 2018).

In France, various departments such as Seine-et-Marne, Essonne, Loiret, Vienne and Marne have selenium issues because rocks and soils are naturally rich in selenium are concerned. The quality limit for selenium in tap water intended for human consumption is 10 µg/L according to the *Code de la Santé Publique* (Public Health Code, Order of 11 January 2007). However, this value is exceeded in several regions for certain drilling waters (AFSSA 2007; Vilaginès 2010). In some seleniferous areas, natural water concentrations can reach values of 50–300 µg/L (Vilaginès 2010). Over the past ten years, French public authorities have thus taken on the dimension of the selenium phenomenon (Crini 2017). A French Mayor must request an operating derogation if the selenium content is 10–40 µ/L, with a restriction on use, particularly for children under 4 years of age if the content exceeds 20 µ/L. This three-year derogation must allow time to provide a technical solution to this excess of selenium. Many cities are waiting for the standard to be raised because treatment would be very expensive. *L'Agence Nationale de Sécurité*, The National Health Security Agency, has set the value at 30 µg/L in October 2012 without any consumption restrictions. For several years, the World Health Organization has also recommended changing the threshold from 10 to 40 µg/L, it has provisionally set the value at 40 µg/L in 2011. To solve the problem of selenium in drinking water, some American regions have chosen to mix water to reduce material requirements and costs, others have chosen low selenium supply sources or to remove excess selenium using treatment processes in public distribution systems or at home (Crini 2017).

For industry, selenium is also considered as an emerging hazardous substance. In Europe, the release of selenium-contaminated water into the environment through industrial processes is currently a regulatory, environmental and health concern (Crini 2017).

3.4 Methods to Remove Selenium from Water

3.4.1 Main Treatment Methods

There is actually no single method to ensure adequate treatment, and, in practice, a combination of different methods is used to achieve the targeted water quality in the most economical way; for example, achieving residual concentrations below the European Union regulation limit of 10 µg/L for drinking water. Selenium removal methods are classified into three categories: chemical, biological and physical

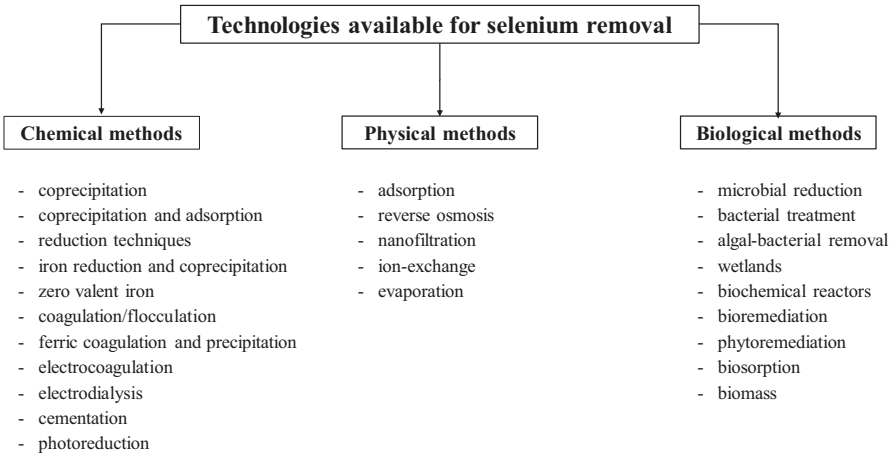


Fig. 3.1 Classification of the technologies for selenium removal

technologies (Fig. 3.1, Koren et al. 1992; Twidwell et al. 1999; Shamas et al. 2009; Sandy and DiSante 2010; Moore and Mahmoudkhani 2011). Technologies can also be classified into conventional methods, e.g. coprecipitation, reduction-adsorption and oxidation-reduction; established removal processes, e.g. adsorption, ion-exchange, membrane filtration, and emerging removal methods such as fluidized bed reactors, algal-bacterial removal and catalyzed cementation (Crini 2017). Nonetheless, only few methods are commonly used by the industry, mainly for economic reasons. In general, the removal of contaminants from effluents is done by chemical and biological means, with research focusing on effective and less costly combinations. Table 3.3 summarizes advantages and disadvantages of the main technologies for the treatment of selenium-contaminated water and industrial wastewater.

3.4.2 Coprecipitation

The main technology used at the industrial scale to remove metals and metalloids from wastewaters is direct precipitation. However, selenium is difficult to precipitate because it is mainly found in the form of oxyanions in wastewaters, which are highly soluble and perfectly stable (Plotnikov 1960). In addition, similar to selenocyanate, selenite and selenate may also form a variety of stable complexes with several transition metals.

One solution is to use iron coprecipitation coupled, if necessary, with a coagulation-flocculation step (Fig. 3.2). This technology is also known as ferrihydrite adsorption and some authors mention a double technology: coprecipitation and adsorption (Merrill et al. 1986, 1987; MSE 2001; Twidwell et al. 2005; Gingerich

Table 3.3 Comparison of chemical, biological, physical and physicochemical technologies for the treatment of selenium-contaminated water and industrial wastewater

Chemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Coprecipitation				
Iron coprecipitation ferrihydrite adsorption precipitation-adsorption chemical precipitation cupric coprecipitation	Uptake of selenium and separation of the products formed A two-step process: precipitation with simultaneous adsorption of selenium on ferrihydrite and ferric hydroxide surfaces	Technologically simple: the contaminants are sequestered in the mineral during crystal growth Both economically advantageous and efficient (to treat wastewater): short treatment time Integrated physicochemical process Established by US EPA as best demonstrated available technology for selenite removal Widely implemented in industry Very efficient for selenite Significant reduction of other contaminants	Chemical consumption ($FeCl_2$, $FeSO_4$) Physicochemical monitoring of the effluent: pH-dependent (optimal conditions in the range of pH 4 to 6) Requires primary treatments: coagulation and flocculation Ineffective in removal of selenium at low concentration (less than 5 µg/L) Not able to remove selenate Competition from phosphate, silica and other elements (vanadium present in flue gas desulfurization effluents) High sludge production, handling (thickening and dewatering) and disposal problems (management, treatment, cost) Toxicity of sludge considered as hazardous waste Requires tertiary treatment in some cases: media filtration, pH adjustment Requires a step of oxidation of the selenocyanate to selenite before removal Potential release of selenium from ferrihydrite residuals	Merrill et al. (1986, 1987); Koren et al. (1992); Kapoor et al. (1995); Kashiwagi and Kokufuta (2000); MSE (2001; Fujita et al. (2002); Twidwell et al. (2005); Gingerich et al. (2018); He et al. (2018b)

Coagulation/Flocculation				
Coagulation-precipitation Coagulation-adsorption	A two-step process: formation of flocs and separation of the products formed	Process simplicity Widely implemented in industry with coprecipitation technology Good sludge settling and dewatering characteristics Significant reduction of suspended solids Well-known mechanism: coagulation, formation of hydroxide flocs, adsorption, and precipitation	Chemical consumption: high coagulant dosage Physicochemical monitoring of the effluent: pH-dependent Fe-based coagulants are much more efficient that Al-based coagulants in selenium removal Large volume of sludge generated	Koren et al. (1992); Kapoor et al. (1995); Hu et al. (2015); Santos et al. (2015); Staicu et al. (2015a, 2015b); He et al. (2018b)
Reduction-adsorption				
Reduction techniques Ferrous hydroxide Reduction-adsorption Reduction-adsorption-precipitation Adsorption	Reduction of selenium, uptake and separation of the products formed A two-step process: ferrous iron is added resulting in the reduction of selenate to selenite and the subsequent adsorption and/or coprecipitation of selenite by ferric hydroxide or ferrihydrite	Relatively simple and low cost method Well-known technology similar to the coprecipitation method Widely implemented in industry Efficient to treat water or wastewater: chemical reduction of Se(IV) to Se(0)	Chemical consumption pH-dependent: optimal pH between 8 and 9 Ineffective in removal of selenium at low concentration (less than 5 µg/L) Not as effective at the reduction of selenate to selenite as zero-valent iron Presence of dissolved oxygen, bicarbonate and nitrate can interfere with reduction High sludge production, handling and disposal problems (management, treatment, cost) Toxicity of sludge considered as hazardous waste	Zingaro et al. (1997); MSE (2001); Geoffroy and Demopoulos (2011); Sharrad et al. (2012); Ling et al. (2015); Stefaniak et al. (2018)

(continued)

Table 3.3 (continued)

Chemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Zero-valent iron				
Reduction-adsorption Redox reactions	Chemical reduction and adsorption-coprecipitation Oxyanions are converted to elemental selenium by redox reactions Zero-valent iron used as reducer and catalyst	A relatively inexpensive and moderately strong reducing agent Efficient to remove selenite and selenate from different salt containing solutions to low concentrations For wastewaters, Se(IV) is favored over Se(VI) Adapted to low pollutant loads although kinetics are slow Well established procedures (temperature, pH, residence time) and maintenance Relative easy physicochemical monitoring of the effluent: efficiency is a function of pH (optimal pH between 6 and 7) and equilibrium concentrations of ferrous and ferric iron Well-known reduction mechanisms; also provides ferric and ferrous iron products for precipitation and adsorption of selenium Significant reduction of other contaminants Used as pre-treatment for constructed wetlands	Laboratory scale Technology is temperature and pH dependent: temperature strongly affects the reaction kinetics; in some cases, pH adjustment may be necessary with longer residence times The reduction of selenium is highly dependent on the surface characteristics of iron and dissolved oxygen concentration in groundwater Presence of other oxyanions such as sulfate, phosphates, nitrates, nitrites and carbonates can interfere with reduction The presence of oxygen can compete with reduction of selenium Requires tertiary treatment to remove ferrous iron: aeration followed by clarification for example; generation of a large sludge volume (management, cost); spent zero-valent iron must be removed, replaced and disposed (hazardous waste)	MSE (2001); Sandy and DiSante (2010); Tang et al. (2014a, b); Ling et al. (2015); van Hullebusch (2017); Gingerich et al. (2018); He et al. (2018b); Stefaniak et al. (2018); Das et al. (2019); Sharma et al. (2019)

Cementation				
Catalyzed reduction Galvanic cementation Modified zero-valent technology Enhanced cementation	Catalyzed reduction	Efficient to remove selenite and selenate to low concentrations Well-known technology similar to the zero-valent iron method Significant reduction of other contaminants	Long residence times In some cases, pretreatment (pH) is required Cost of maintenance (sacrificial anodes) The presence of high concentrations of interfering anions can be a problem Media requires periodic replacement and disposal (hazardous waste) Sludge volume generation (management, cost) Requires tertiary treatment to remove copper or nickel discharges	MSE (2001); Twidwell et al. (2005); GOLDER (2009); Shamas et al. (2009); van Hullebusch (2017); He et al. (2018b)
Electrocoagulation				
Electrochemical method Electrolysis	Electrolysis Ferrous iron is produced by applying direct electrical current to the effluent where an iron anode oxidizes to form ferrous iron that can reduce selenate and the resultant ferric iron can coprecipitate selenite	Effective treatment for the reduction, coagulation and separation of selenate Generation of coagulants *in situ* without chemical addition (iron or aluminum sacrificial anodes) pH control is not necessary Adaptation to different pollutant (including Se) loads and different flow rates May coagulate other colloids further enhancing the coprecipitation of selenium Efficient elimination of suspended solids and metals Effective in treatment of drinking water supplies for small or medium sized communities Widely used in the mining industries	Initial cost of the equipment Cost of maintenance (sacrificial anodes, requires an electrical current, cleaning of cathodes plates) Requires addition of chemicals (salts, flocculants) in polymetallic wastewaters Variability in wastewater salinity vary the oxidation of the iron anode to ferrous ion resulting in potential perturbations Anode passivation and sludge deposition on the electrodes that can inhibit the electrolytic process in continuous operation Cost of sludge treatment Requires post-treatment to remove high concentrations of iron	Mollah et al. (2004); Mavrov et al. (2006); GOLDER (2009); Sandy and DiSante (2010); Gingerich et al. (2018); He et al. (2018b); Stefaniak et al. (2018); Hansen et al. (2019); Kazeem et al. (2019)

(continued)

Table 3.3 (continued)

Chemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Electrochemical methods				
Electro-remediation	As in electrocoagulation, ions released from sacrificial electrodes react with selenium to form insoluble precipitants The technique uses a low-level direct current as cleaning agent through several transport mechanisms and electrochemical reactions to form ferrous hydroxides	Oxidation of iron anode prevents water oxidation and formation of oxygen, and produces ferrous and ferric ions leading to the formation of hydroxides in a mixed cell Not dependent on dissolved oxygen The method can be applied to both anoxic and oxic system to remove selenate	Laboratory scale Emerging technology High electricity consumption Not effective in removing high selenate concentrations	Sandy and DiSante (2010); Baek et al. (2013); Gingerich et al. (2018)
Photoreduction				
Chemical reduction and adsorption advanced oxidation	A two-step process: chemical reduction by irradiation and adsorption method	Efficient to remove selenite and selenate to low concentrations Method uses irradiation of ultraviolet at a certain wavelength and in presence of titanium dioxide to convert oxyanions into elemental selenium	Laboratory scale Emerging technology Formation of toxic hydrogen selenide gas	MSE (2001); GOLDER (2009); Shamas et al. (2009); Sandy and DiSante (2010); Labaran and Vohra (2014); He et al. (2018b); Mohapatra and Kirpalani (2019); Sharma et al. (2019)

Biological technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Biological methods				
Biological conversions Biological volatilization Biological reduction Bioreduction Microbial reduction Heterotrophic microbial Reduction Bioremediation Bioreactors Biofilm reactors Sludge-based Bioreactors Activated sludge Constructed wetlands Phytoremediation	Use of biological cultures: anaerobic or aerobic bacteria, algae, fungi, plants On basis of conversion of soluble oxyanions to elemental insoluble selenium Uptake, reduction and volatilization processes	The application of microorganisms for the biodegradation of contaminants, including oxyanions, is simple, economically attractive and well accepted by the public High treatment efficiency: effective in reaching regulatory limits for selenium discharge into the aquatic environment Large number of species used in mixed cultures (consortiums) or pure cultures (white-rot fungus) Biological conversions using communities of microorganisms or biofilms can reduce selenium to low target levels Provides as polishing of chemical precipitation effluents Different types of reactors are commercialized: continuously stirred tanks, packed-bed reactors, sequencing batch reactor, up-flow anaerobic sludge blanket reactor, membrane biofilm bioreactor, fluidized bed, etc.	Necessary to create an optimally favorable environment Requires management and maintenance of the microorganisms and/or physicochemical pretreatment Large space requirements High operating time Performance is difficult to control (e.g. treatment of flue gas desulfurization effluents) Some systems have low chloride tolerance (<25 g/L) A solid-liquid separation step is often needed in the downstream of biological systems Generation of biological sludge	MSE (2001); Yee et al. (2007); GOLDER (2009); Hunter and Manter (2009); Zhu et al. (2009); Vriens et al. (2014); Dessì et al. (2016); Tan et al. 2016); Mal et al. (2017); van Hullebusch (2017); He et al. (2018b); Stefaniak et al. (2018); Tan et al. (2018); Gebreeyessus and Zewge (2019); Paul and Saha 2019); Rene et al. (2019); Zhang et al. (2019a); Zeng et al. (2019)
Microbial reduction				
Enhanced *in situ* reduction	Reduction of oxidized forms of selenium using inoculated microorganisms in anoxic conditions	Low-cost approach with low maintenance Adapted for large volumes of effluents	Long retention times Requires post-treatments: aeration-settling	MSE (2001); GOLDER (2009); Hunter and Manter (2009); Sandy and DiSante (2010); van Hullebusch (2017); Stefaniak et al. (2018)

(continued)

Table 3.3 (continued)

Biological technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Bioreactors				
Biological adsorption Biological reduction-adsorption Bioremediation	Adsorption of selenium, biological reduction and separation of the products formed A two-step process: adsorption on a granular activated carbon bed filter and reduction using a biofilm or a layer of microorganisms that grow on the surface of the adsorbent	Technological simple Both economically advantageous and efficient (to treat wastewater) Integrated physicochemical and biological processes Widely implemented in industry Uses naturally occurring microorganisms and molasses-based nutrient Very efficient for selenite with levels of less than 5 µg/L Significant reduction of other contaminants	Pretreatment of the effluent to remove suspended solids Physicochemical monitoring of the effluent: pH adjustment, temperature control Addition of nutrients Addition of carbon in proportion to oxyanions to prevent sulfate reduction The presence of high concentrations of nitrates can be a problem (generation of additional biomass) Requires post-treatments: media for selenium filtration, pH adjustment, re-aeration, BOD removal High sludge production, handling and disposal problems (management, treatment, cost)	Fujita et al. (2002); Espinosa-Ortiz et al. (2015); van Hullebusch (2017); Stefaniak et al. (2018); Tan et al. (2018); Paul and Saha (2019)

Fluidized bed reactor				
Aerobic systems Anoxic systems	Effluent is passed through a granular solid media (sand, activated carbon) at enough velocities to suspend the support creating a completely mixed reactor configuration for attached biofilm	Low-cost approach with low maintenance Process uses naturally occurring microorganisms and biodegradable carbon source to maintain biomass The small fluidized media provide an extremely large active surface area upon which microorganism can grow while treating contaminants proven effective technology for the production of elemental selenium nanoparticles (integrated into the media) under controlled anaerobic conditions No pretreatment of suspended solids No backwash water required Biomass separated from centrifugal separator on reactor effluent Process has a smaller site footprint than other biological treatment systems	Presence of nitrates can be a problem with an additional generation of biomass Physicochemical monitoring of the effluent: pH adjustment, temperature control, addition of nutrients External carbon source is required if soluble influent organic content or chemical oxygen demand is insufficient Addition of carbon in proportion to oxyanions to prevent sulfate reduction Media must be replaced periodically Post-treatment: pH adjustment, re-aeration to increase dissolved oxygen, BOD removal Toxicity of sludge	GOLDER (2009); van Hullebusch (2017) Sandy and DiSante (2010); Sinharoy et al. (2019)
Upflow anaerobic sludge blanket bioreactor				
	The effluent flows upward through a granular sludge at high velocity to keep the sludge suspended without washout	A well-known technology: the upper part of the bioreactor contains a gas/solid separator to allow the produced gases to be discharged and the solids entrained by the gases to be recovered Method uses naturally occurring microorganisms and biodegradable nutrients to maintain biomass Requires no attached growth media and therefore no media replacement Proven effective technology for the production of elemental selenium nanoparticles (integrated into the media) Requires little to no pretreatment for suspended solids	Temperature-dependent process Addition of carbon in proportion to oxyanions is required Competition between oxyanions and other ions present in water The presence of high concentrations of nitrates can be a problem (generation of additional biomass)	GOLDER (2009); van Hullebusch (2017); Paul and Saha (2019); Sandy and DiSante (2010)

(continued)

Table 3.3 (continued)

Biological technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Passive biochemical reactor				
Sulfate-reducing bioreactor	Reactors consists of an excavated lined area that has been filled with an organic substrate	Low capital and operation and maintenance costs: minimal operator supervision, process operate without energy or chemicals Two configurations: reactors can operate in a gravity down-flow mode or in up-flow mode Efficient method for the treatment of mining wastewaters	Large surface required Frequent replacement of organic substrate due to its degradation over time Requires the removal of suspended solids	Hockin and Gadd (2007); Conley et al. (2009); GOLDER (2009); Tan et al. (2018); Sandy and DiSante (2010)
Permeable reactive barriers				
	A passive, *in situ* treatment for shallow groundwater	A low-cost technology with low maintenance Two configurations: funnel-and-gate design and continuous mode	Finite life span Potential to be clogged due to precipitation of other ions such as metals	MSE (2001); GOLDER (2009); Sandy and DiSante (2010)
Hydrogen-based membrane biofilm reactor				
Bioreduction Autotrophic reduction	Hydrogen is used as electron donor and the membrane is used to directly supply dissolved gas to biofilm growing on the surface	Efficient method for the reduction of selenate, selenite, sulfate and nitrate Due to its very low water solubility, no residual hydrogen donor carries over in the treated water	Laboratory scale Sparging is required to supply hydrogen gas pH-dependent process (optimal pH between 7 and 9) Performance depends on hydrogen gas pressure and selenate concentration	MSE (2001); Chung et al. (2006); Rittmann (2007); Sandy and DiSante (2010)

Algal-bacterial removal				
Microalgal and bacterial pond Algal-pond systems	Biological process where bacterial growth is stimulated by the addition of algae as a food source	Relatively low cost and efficient method Can be applied as an *in situ* approach High removal is achieved when an external organic electron donor is added to the bacterial pond and combined with a post-treatment Solar ponds can remove selenium to below 5 µg/L under optimal conditions High-potential research topic: opportunities include harvesting algae and bacteria as a source of protein and selenium to supplement livestock feed and harvesting biofuel algae	Large surface required as algae growth is limited to the upper surface of the effluent due to light penetration limits Requires excess nutrients that can create eutrophic condition Seasonally limited: method affected by duration of solar light and ambient temperature High residence times The need for spatial separation can increase the capital and operational costs Not suitable for wastewaters with high concentrations of sulfates Requires post-treatments: selenium and algae removal (coagulation-flocculation, sand filtration, dissolved air flotation) Bioavailability of selenium towards aquatic invertebrates	Lundquist et al. (1994); Lin and Terry (2003); GOLDER (2009); Sandy and DiSante (2010); Liu et al. (2019)
Algal assimilation				
Biological assimilation	Assimilation of selenium by algae and/or volatilization	Relatively simple and efficient to treat effluents: selenium is assimilated by algae (as selenoproteins) Harvest of algae for biofuel or nutritional supplement	Laboratory scale High residence times Requires excess nutrients that can create Eutrophic condition Large footprint required Difficulty to remove algae from effluent Requires solids dewatering systems	GOLDER (2009); Sandy and DiSante (2010)

(continued)

Table 3.3 (continued)

Biological technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Algal volatilization				
Biological volatilization	A two-step process: selenium biomethylation and volatilization	A low-cost method Can be applied as an *in situ* approach high-potential research topic: opportunities include harvesting algae as a source of protein and selenium to supplement livestock feed and harvesting biofuel algae	Laboratory scale Large surface required as algae growth is limited to the upper surface of the effluent due to light penetration limits Requires excess nutrients that can create Eutrophic condition High residence times Seasonally limited: method affected by duration of solar light and ambient temperature Cost treatment depends on land requirements Requires post-treatments: algae removal (coagulation-flocculation)	GOLDER (2009); Sandy and DiSante (2010)
Phytoremediation				
Constructed wetlands Phytostabilization approach Phytoextraction-phytovolatilization	A green biotechnology using phytoextraction and phytovolatilization The plants are used to immobilize contaminants and store them belowground in roots and/or rhizomes	A low-cost, eco-friendly, effective and feasible approach to remove selenium Low construction, operation and maintenance costs Plant families for selenium removal: *Astragalus racemosus*, *Astragalus bisulcatus* Remove other contaminants	Emerging technology; laboratory scale Costs are highly site-specific Performance depends on several factors: environmental conditions, biological activity, competition between metals and metalloids A lack of performance data	Shardendu et al. (2003); Azaizeh et al. (2006); Pilon-Smits and LeDuc (2009); Zhu et al. (2009); Sandy and DiSante (2010); Wu et al. (2015); Dhillon and Bañuelos (2017); He et al. (2018b); Stefaniak et al. (2018)

Constructed wetlands				
Phytoremediation reduction-adsorption-volatilization Phytostabilization approach Biological volatilization selenium biomethylation	A natural process using vegetation, soil, rock and other civil structures to promote appropriate microbial and plant activity The aquatic system supports the growth of bacteria specialized in utilizing oxyanions as an energy source	A natural, low-cost and efficient method to remove selenium at low concentrations: low construction, operation and maintenance costs Adapted for large volumes of effluent; a practical alternative to the chemical treatment of drainage wastewater or in removing selenium from selenite-contaminated oil refinery wastewater Different configurations available, depending upon selenium ecological requirements Process requires minimal operator supervision No chemicals used Subsurface flow wetlands can operate in cold climates Oxyanions are reduced to elemental selenium (sequestered in the wetland sediment) and organic forms of selenium Significant reduction of other contaminants, including metals and metalloids	Large and flat area is required High residence times Pretreatment to remove suspended solids Temperature-dependent technology: selenium removal is greater in summer Performance can also be affected by the density of plant growth pH adjustment Potential ecological risk due to the bioaccumulation of selenium; possible toxicity to aquatic life and animals (birds) Potential for groundwater contamination	Gao et al. (2003); Lin and Terry (2003); Shardendu et al. (2003); Azaizeh et al. (2006); Kadlec and Wallace (2009); Johnson et al. 2009); Huang et al. (2012); Vriens et al. (2014); Stefaniak et al. (2018)
Enzymatic reduction				
Biological reduction	Use of enzyme extracts for selenium reduction	Efficient method Nutrient addition is not required for selenium reduction	Laboratory scale Not economically viable	Hockin and Gadd (2007); GOLDER (2009); Sandy and DiSante (2010); Stefaniak et al. (2018)

(continued)

Table 3.3 (continued)

Physical and physicochemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Activated alumina				
Adsorption using oxides and hydroxides of aluminum	Adsorption of selenium using granular, porous oxides and hydroxides of aluminum	Porous materials with large surface area Technological simple and adaptable to many treatment formats Both economically advantageous and efficient (to treat wastewater) Integrated physicochemical and biological processes; efficient when coupled with other pretreatments (e.g. with a pre-coagulation step) Fast kinetics Excellent quality of the treated effluent Interesting for the simultaneously treatment of arsenic and phosphates Significant reduction of other contaminants (other anions such as fluorides) simplicity of regeneration	Relatively high investment Initial cost of material Physicochemical monitoring of the effluent: pH adjustment; pretreatment of the effluent to remove suspended solids Non-selective method Possible rapid saturation and clogging of the reactors; requires a pre-treatment to prevent clogging of the filter when the water contains suspended solids or to remove certain ions Regeneration is often required to make the technology cost-effective Can accumulate bacteria Elimination of the adsorbent (regeneration or replacement)	Kosmulski (2001); Jeqadeesan et al. (2003); Sandy and DiSante (2010); Su et al. (2008, 2010); He et al. (2018b); Ji et al. (2019)
Iron oxides				
Goethite Hematite Magnetite	Adsorption of oxyanions using oxides and oxy-hydroxides of iron	Simple and adaptable to many treatment formats Economically feasible Efficient adsorbents due to their high surface area Rapid kinetics	Technological problems due to the small particle size of the metal oxides; not adequate to use in a continuous flow system pH-dependence Performance depends on the presence of minerals (phosphates, sulfates, chlorides)	Duc et al. (2006); Rovira et al. (2008); Sandy and DiSante (2010); Sharrad et al. (2012); Simeonidis et al. (2016); Kalaitzidou et al. (2019); Kawamoto et al. (2019); Matulova et al. (2019); Rene et al. (2019); Sharma et al. (2019)

Activated carbon				
Commercial carbons Non-conventional carbons from solid wastes	Adsorption of selenium using carbons (e.g. granular or powdered) having high surface area	Well-known technology, relatively simple Widely implemented in industry for metals and metalloids Highly porous materials with large surface area Versatile materials (use in batch or column) Interesting properties in terms of surface chemistry and surface charge Efficient when coupled to coagulation/ precipitation Efficient to treat water or wastewater Significant reduction of other inorganic and organic contaminants	Relatively high initial investment; cost of materials Pretreatment of the effluent to remove suspended solids Physicochemical monitoring of the effluent: pH adjustment Non-selective technology Possible rapid saturation and clogging of the reactors Can require the use of complexing agents to improve performance Elimination of the adsorbent Regeneration results in loss of material	Jadhav et al. (2000); Jeqadeesan et al. (2003); Zhang et al. (2008); Sandy and DiSante (2010); Dobrowolski and Otto (2013); Kwon et al. (2015); Santos et al. (2015); Bakather et al. (2017); He et al. (2018b); Tan et al. (2019a)

(continued)

Table 3.3 (continued)

Physical and physicochemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Other adsorbents				
Zeolites Supported magnetite Modified sand Modified bentonite Clay Composites Titanium Graphene oxide	Adsorption of selenium using other conventional adsorbents or supported materials	Zeolites: easily available and relatively cheap; high capacity and high selectivity; a high capacity to be easily regenerated (while keeping their initial properties); ion-exchange mechanism Clays: natural and low-cost minerals, abundant on most continents; layered structures with large surface area and high porosity, and high chemical and mechanical stability; they also can adsorb cationic and neutral species	Laboratory scale Can requires chemical modification Clays: results are pH-dependent	Lo and Chen (1997); Kuan et al. (1998); El-Shafey (2007a, 2007b); Zhang et al. (2009); Bleiman and Mishael (2010); Hasan et al. (2010); Pal and Rai (2010); Tuzen and Sari (2010); Mane et al. (2011); González-Acevedo et al. (2012); Li et al. (2013); Nettem and Almusallam (2013); Verbinnen et al. (2013); Khakpour et al. (2014); Yamani et al. (2014); Johansson et al. (2015); Kieliszek et al. (2015); Kwon et al. (2015); Roberts et al. (2015); Santos et al. (2015); Wang et al. (2015); He et al. (2018b); Tan et al. (2018); Bandara et al. (2019); Zhang et al. (2019b)

Biosorbents				
Peanut shell Modified rice husk Wheat Chitosan Marine algae Anaerobic granular sludge Dried biomass Yeast cells Water hyacinth Wastes	Biosorption of selenium using other non-conventional biosorbents or biomasses	Low-cost materials; readily available resources Effective technology to remove selenium and also many types of other contaminants Availability of different biomasses in large quantities and at low-cost Efficiency in removing selenium in dilute or concentrated waters Regeneration is not necessary Well-known chemical mechanism	Laboratory scale Performance depends on the different materials and on some external factors (pH, salts, competitive adsorption, temperature) Slow process and limiting pH tolerance (algae) Materials with low surface area and low mechanical strength; variability in the materials used (chitosan) Not appropriate for column systems (except granular sludge) Mechanisms must be clarified Can requires pre-treatment to improve the performance	Lo and Chen (1997); Kuan et al. (1998); El-Shafey (2007a, b); Zhang et al. (2009); Bleiman and Mishael (2010); Hasan et al. (2010); Pal and Rai (2010); Tuzen and Sari (2010); Mane et al. (2011); González-Acevedo et al. (2012); Li et al. (2013); Nettem and Almusallam (2013); Verbinnen et al. (2013); Khakpour et al. (2014); Yamani et al. (2014); Johansson et al. (2015); Kieliszek et al. (2015); Kwon et al. (2015); Roberts et al. (2015); Santos et al. (2015); Wang et al. (2015); Crini et al. (2017); He et al. (2018b); Tan et al. (2018); Minzatu et al. (2019)

(continued)

Table 3.3 (continued)

Physical and physicochemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Ion exchange				
Anion exchange resins Chelating resins Selective resins Zeolites	Exchange of oxyanions using resin beads, releasing a weakly attached co-ion	Technological simple Large range of commercial products Rapid and efficient technology with well-established and tested procedures; easy control and maintenance Easy to use with other techniques (e.g. precipitation and filtration in an integrated wastewater process) Can be applied to different flow regimes (continuous, batch) Se(VI) is slightly favored over Se(IV) Produce a high-quality treated effluent; can remove selenium to below 5 μg/L under optimal conditions Significant reduction of other contaminants High regeneration with possibility of external regeneration of resin	Economic constraints (initial cost of the selective resin, maintenance costs, regeneration time-consuming) Large volume requires large columns Rapid saturation and clogging of the reactors Pretreatment of the effluent to remove suspended solids and organic load Physicochemical monitoring of the effluent: pH adjustment Performance can be greatly reduced by competing anions Degradation of the resins over time elimination of the resin	Suzuki et al. (2000); Jelas Haron et al. (2001); Dzul Erosa et al. (2009); Sandy and DiSante (2010); Santos et al. (2015); Staicu et al. (2017); Kawamoto et al. (2019); Sharma et al. (2019); Zhang et al. (2019b)

Evaporation				
Evaporation pond Evaporation basin Solar evaporation Mechanical evaporation Enhanced evaporation Crystallization	Natural evaporation of water to various levels of salinity based on the prevailing climate conditions Elimination by the use of an external heart source, mechanical mixing and/or pressure or vacuum Concentration technique an enhanced evaporation system increases the rate at which water evaporates mechanically spraying water in the air using a blower	A low-cost and simple approach based on solar radiation Increased evaporation efficiency when using mechanical spraying Efficient to treat a reduced volume of effluent that has been pretreated by ion exchange of membrane filtration Produce a high-quality treated effluent the method produces a concentrated selenium salt cake In an enhanced evaporation system, the performance is more important due to mechanical spraying	Large space requirements due to efficiency decline as the total dissolved solids increases Strongly temperature-dependent Expensive costs for high volumes of wastewater (energy consumption, volume of the concentrate and costs of disposal) Investment costs are often too high for small and medium industries Risk of infiltration to groundwater (depending on the liner type), potential risk to wildlife The mechanical equipment may require maintenance High pollution load in the concentrates Crystallization due to the concentration of the wastewater and corrosion of the heating elements in the evaporator due to the chemical aggressiveness of the concentrated effluent Problem with the evaporation of effluents containing free cyanide requires the installation of a cleaning circuit (to prevent atmospheric pollution) Potential contamination of the distillate preventing reuse (due to the presence of some VOC or hydrocarbons in the effluent)	Gao et al. (2007); GOLDER (2009); Sandy and DiSante (2010); Tan et al. (2018)

(continued)

Table 3.3 (continued)

Physical and physicochemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Nanofiltration				
	A pressure driven membrane filtration limited by the pore size being in the molecular weight cut-off range that is similar to size of oxyanions	Large range of membrane and module configurations Small space requirement and modular type configuration simple, rapid and efficient for all divalent ions No chemicals required Operates at one-third of the pressure requirement of reverse osmosis technology Efficient to remove all salts between 0.001 and 0.01 microns Well-known separation mechanisms	Investment costs are often too high for small and medium industries High energy requirements The design of membrane filtration systems can differ significantly Depending upon the membrane used, performance may not be as effective as reverse osmosis High maintenance and operation costs Frequent membrane maintenance Pretreatment of solids/colloids is necessary to reduce scaling/fouling Rapid membrane clogging (fouling with high concentrations) Disposal of the concentrate	Kharaka et al. (1996); GOLDER (2009); Sandy and DiSante (2010); He et al. (2016a, b, 2018a, b, c)

Reverse osmosis				
	A pressure driven membrane filtration using high pressure using a semi-permeable membrane	Efficient to remove all salts less than 0.001 microns with levels of selenium and other oxyanions less than 5 µg/L Produce a high-quality treated effluent; removes all ions Small space requirements and modular type configuration Can also remove high levels of total dissolved solids Well-known separation mechanisms	Investment costs are often too high for small and medium industries Higher capital cost to purchase, install and operate than nanofiltration The design of membrane filtration systems can differ significantly High maintenance and operation costs Rapid membrane clogging (fouling with high concentrations) Pretreatment of solids/colloids is necessary to reduce scaling/fouling May require temperature control to minimize viscosity effects and/or chemical addition to reduce scaling/fouling Frequent membrane maintenance Requires tertiary treatment before the water is discharged (pH, re-constituted as ions) Elimination of the concentrate	Marinas and Selleck (1987, 1992); Kharaka et al. (1996); GOLDER (2009); Sandy and DiSante (2010); He et al. (2018a, b)

(continued)

Table 3.3 (continued)

Physical and physicochemical technologies				
Technology	Main characteristic(s)	Advantages	Disadvantages	References
Electrodialysis				
Electrodialysis reversal Electrosorption	Electrically controlled membrane using the same current flow direction Reversal method uses a difference in electrical potential to induce dissolved ions to pass through a water-impermeable membrane where the direction of current flow is reversed several times by reversing the voltage polarity applied to the electrodes	Very efficient when paired with a microfiltration step Well-known technology, applied for mining industry and agricultural water; relatively insensitive to levels of flow and of total dissolved solids Also efficient in reducing total dissolved solids and in removing other inorganic and ionized contaminants Low operating and maintenance costs (no chemical feeds) but more expensive than reverse osmosis Electrodialysis reversal is tolerant to moderate suspended solids; can extend the time between membrane cleanings High silica levels do not impact performance	Laboratory scale Performance is pH-dependent (change in speciation) Can require a chemical precipitation pretreatment; membranes can become fouled when the pores are clogged by salt precipitation or blocked by suspended particulates Competition with other contaminants	AWWA (1999); Mollah et al. (2004); Mavrov et al. (2006); Sandy and DiSante (2010); Hassanvand et al. (2017); Onorato et al. (2017); Gingerich et al. (2018); He et al. (2018b)

Fig. 3.2 An iron coprecipitation unit at an industrial scale (Copyright: G. Crini, Besançon, France)

et al. 2018; He et al. 2018b). Indeed, the method is a two-step physicochemical treatment consisting of (1) the addition of ferric salts such as ferric chloride or ferric sulfate to the effluent at proper conditions such as pH adjustment, rapid mixing and/or flocculant addition, and (2) simultaneously adsorption of selenium onto the precipitated iron hydroxide and ferrihydrite surfaces, here the contaminants are sequestered into the mineral matrix during crystal growth. Specifically, amorphous iron(III) oxyhydroxide (ferrihydrite) is formed when the ferric salt is added to the waste. Ferrihydrite Fe_2O_3-$0.5H_2O$, a poorly soluble crystalline form of ferric hydroxide ($Fe(OH)_3$), matures to more crystalline ferrioxyhydrites FeO(OH) and ferrioxides Fe_2O_3. Both dissolved and particulate elements are adsorbed onto and trapped within the precipitate, which is then settled out to leave a clarified effluent.

Iron coprecipitation is able to remove trace elements such as selenium and arsenic in complex mixtures, with elimination efficiencies for selenium – as selenite form – between 50% and 80% (Koren et al. 1992; Kapoor et al. 1995). Selenite is strongly adsorbed on the ferrihydrite floc, whereas selenate is more loosely bound. By comparison, arsenic removals are higher, of 90% and above, under comparable conditions with iron dosages of 14–28 mg/L. In some effluents, the technology is also able to remove other metals at neutral to alkaline pH. However, iron coprecipitation is not an effective treatment for removal selenate, because adsorption depends on the oxidation state of the selenium. In addition, the presence of other anions such as sulfate can strongly reduce the effectiveness of coprecipitation of selenate by ferrihydrite (Merrill et al. 1986, 1987; Koren et al. 1992; Kapoor et al. 1995; MSE 2001; Twidwell et al. 2005; Gingerich et al. 2018; He et al. 2018b).

The two outstanding characteristics of iron coprecipitation are simplicity and selectivity (Table 3.3). In a comprehensive pilot study, Merrill et al. (1986, 1987) demonstrated the technical and economic feasibility of iron coprecipitation for the

removal of Se(IV) from the ash pond effluent of a coal-fired power plant. Other contaminants can also be removed simultaneously. However, the removal performance of all trace elements is strongly affected by the pH of the solution. This treatment is inefficient for selenate due to the competition of sulfates for the same adsorption sites, selenate and sulfates have similar chemical properties. Major elements such as calcium, magnesium and bicarbonate do not compete with trace elements for adsorption sites. The mechanism of iron coprecipitation-adsorption is described in Merrill et al. (1986, 1987). The main disadvantages included the consumption of reagents, e.g. $FeCl_2$ and $FeSO_4$, adjusting the pH at optimal values between 4 to 6, the sludge volume creating handling and disposal problems) and the difficulty to obtain concentrations below 5 µg/L for treated wastewater.

Later, iron coprecipitation has been tested at full-scale in a variety of industries, for example to treat coal-mining pond water, mining wastewater, gold mine effluents, and petrochemical wastewater (Koren et al. 1992; Kapoor et al. 1995). Iron coprecipitation was efficient to treat selenite but not able to remove selenate, yielding selenocyanate-laden effluents. Kashiwagi and Kokufuta (2000) and Fujita et al. (2002) also demonstrated that, after reducing of Se(VI) to Se(IV), selenium can be removed from agricultural and industrial wastewater by coprecipitation, decreasing concentrations below 50 µg/L. The technology involved a three-step physicochemical process in which an oxidant and a ferric salt were added to the effluent under appropriate conditions. If the effluent contains selenocyanates, the technology requires pre-treatment by oxidation.

The US Environmental Protection Agency, in the Reference Guide to Treatment Technologies for Mining Influenced Water, EPA 542-R-14-001, 2014, recommends the iron coprecipitation method as the best available technology for selenite removal. In France, iron precipitation is widely implemented in the industry. Advantages and disadvantages are presented in Table 3.3.

3.4.3 Reduction Techniques

Unlike Cr(VI)/Cr(III) systems where only Cr(VI) species can be converted to less soluble species and the precipitated form Cr(III), the two prevalent forms of selenium Se(IV) and Se(V) are highly soluble, which renders separation difficult. For selenium species, a possible solution is to use reduction coupled with precipitation. Reduction techniques can be chemical or biological, and involve the use of a strong reducing agent or a selenium-reducing bacteria. The precipitation step uses a precipitant or coagulant (Zingaro et al. 1997; MSE 2001; Geoffroy and Demopoulos 2011; Sharrad et al. 2012; Ling et al. 2015; Stefaniak et al. 2018).

Reduction to metallic selenium and subsequent precipitation can be used to remove selenium as reported by Geoffroy and Demopoulos (2011). The authors proposed chemical precipitation with sodium sulfide. Here, synthetic weak sulfuric acid streams containing 300 mg/L of Se(IV) were used to simulate the typical conditions encountered in acidic effluents from industrial zinc refineries. High levels of

selenium removal were observed. The precipitate of selenium sulfide obtained from sodium sulfide was extremely stable at pH 7 but partially dissolved at pH values of 3, 5 and 10. Besides, the removal of selenium by precipitation using dithionite – $H_2S_2O_4$ or hydrosulfite – has also been tested, but in this case the resulting selenium sulfide precipitate was unstable and decomposed into several sulfur species of variable oxidation states. Other strong reducing chemical agents such as carbohydrazide and hydrazine have been proposed. These chemicals remove oxygen from oxyanions under basic conditions, effectively reducing oxyanions to elemental selenium. However, carbohydrazide and hydrazine are toxic and must be handled properly. In addition, their anhydrous forms are volatile, corrosive and form explosive mixtures with air. In France, their use is strictly controlled (Crini 2017).

Another reducer is ferrous hydroxide. This technology, referred as reduction-adsorption, reduction-adsorption-precipitation or simply adsorption process with ferric hydroxide as adsorbent, is similar to the coprecipitation method. It is widely implemented in the industry due to its simplicity and relatively low-cost. The process involves two steps: ferrous iron is first added to the water in a nearly neutral medium, e.g. addition of sodium hydroxide to ferrous sulfate, which then induces the reduction of selenate to selenite and the subsequent adsorption and/or coprecipitation of selenite by ferric hydroxide or ferrihydrite under reducing conditions at an optimal pH of 8-9. The technology is highly pH-dependent; other disadvantages, similar to the ferrihydrite adsorption technology, are mentioned in Table 3.3.

Another process involves the use of zero-valent iron as reducer in an oxidation-reduction process to remove selenium by chemical reduction of its oxidized forms and then the implementation of adsorption/coprecipitation of the reduced elements. The aim is the formation of green rust, a complex ferrous ferrihydroxide coprecipitate, which reduces selenate to selenite and selenite to elemental selenium. A similar technology uses elemental iron in the form of filings, steel wool or iron impregnated foam forms to reduce selenate and selenite. Elemental iron as low-cost reducer is easily available, easy to handle, and can produce a low reduction potential in aqueous solution (Table 3.3).

The mechanisms for selenium removal using zero-valent iron are well-known. In this technology, iron acts as a catalyst and an electron donor for the reaction. Iron also produces a variety of ferrous and ferric iron products that can provide both additional reduction, e.g. to reduce selenate to selenite then to elemental selenium, and adsorption, e.g. ferrihydrite amorphous solids adsorb selenite. The elemental form of selenium, as insoluble nanoparticles, is embedded in the iron solids. The presence of other oxyanions such as carbonate and sulfate in wastewater can contribute to the oxidation of the zero-valent media. Zero-valent iron materials can be in the form of powder, granules or fibers used in tanks or filter vessels. This form is important for the effectiveness of the reactions. Depending on the pH, between 4 and 5, and redox potential, selenium can be reduced to selenite, elemental selenium or selenide.

In water and wastewater treatment, the use of zero-valent iron is advantageous due to its non-toxic nature, abundance, relatively low-cost, easy preparation, moderately strong reducing properties and availability (MSE 2001; Sandy and DiSante

2010; Tang et al. 2014a, b; Ling et al. 2015; van Hullebusch 2017; Gingerich et al. 2018; He et al. 2018b; Stefaniak et al. 2018; Das et al. 2019; Sharma et al. 2019). For wastewater treatment, Se(IV) is favored over Se(VI). The main characteristics of the zero-valent iron method are its simplicity as a simple and combined process with minimal monitoring and maintenance, its adaptability with materials in powder, granular or fibrous forms, and its effectiveness in removing selenium. The main disadvantage is the fact that the reduction of selenium is highly dependent on the surface characteristics of iron and dissolved oxygen concentration in groundwater. Here, it is also important to control wastewater and reactor characteristics, e.g. pH, temperature, ionic strength, dissolved oxygen, suspended solids, and oxyanions. Other disadvantages are explained in Table 3.3.

In recent years, zero-valent iron nanoparticles of specified size, high large surface area and exceptional performances have been proposed to remove not only metals but also organics because of their capability to oxidize and degrade contaminants (Ling et al. 2015; van Hullebusch 2017; Gingerich et al. 2018; He et al. 2018b; Stefaniak et al. 2018; Sharma et al. 2019). Ling et al. (2015) reported that Se(IV) can be easily separated from water, reduced and encapsulated by nanoscale zero-valent iron. For example, 1.3 mM selenite was quickly removed from water within 3 min with 5 g/L of nanoscale zero-valent iron. An interesting mechanism of selenite in a single core-shell structured material particle was suggested using the method of spherical aberration corrected scanning transmission electron microscopy integrated with X-ray energy dispersive spectroscopy.

Chemical reduction techniques such as cementation and photoreduction have been proposed to convert selenate and selenite to elemental selenium (Table 3.3). These technologies are also two-step processes, combining reduction and adsorptio n/coprecipitation methods (MSE 2001; Twidwell et al. 2005; GOLDER 2009; Shamas et al. 2009). Cementation is a catalyzed reduction, consisting in the recovery of an ionized metal from effluents by spontaneous electrochemical reduction to its elemental metallic state, with oxidation of a sacrificial metal. The technology has been widely used in hydrometallurgy and in the purification process of stream and wastewaters. Some authors refer to it as galvanic cementation or modified zero-valent treatment. Indeed, the technology is similar to the zero-valent iron method and is efficient to remove selenite and selenate. The addition of copper or nickel to a zero-valent iron technology is used to catalyze the reduction of selenium by creating a greater electrochemical potential between the elemental iron and soluble selenium. The cementation process has several advantages such as recovery of metals in essentially pure metallic form, simple control requirements and low energy consumption (Table 3.3). The main disadvantages are excess sacrificial metal consumption and sludge volume generation (MSE 2001; Twidwell et al. 2005; GOLDER 2009; Shamas et al. 2009; van Hullebusch 2017; He et al. 2018b).

Photoreduction combines a chemical reduction and the adsorption technology. Photoreduction uses ultraviolet irradiation at a certain wavelength in presence of titanium dioxide to convert oxyanions to elemental selenium (MSE 2001; GOLDER 2009; Shamas et al. 2009; Sandy and DiSante 2010; Labaran and Vohra 2014; He et al. 2018b; Sharma et al. 2019). Titanium dioxide is used as photocatalyst for the

reduction of selenium forms. Contaminants that adsorb to the surface of the photocatalyst undergo chemical oxidation-reduction and adsorption reactions induced by the electrons and holes created by ultraviolet exposure. The elemental forms of the treated species are then desorbed and the surface of the photocatalyst is regenerated. Photoreduction is an effective method to reduce selenate and selenite but its main disadvantage is the formation of toxic hydrogen selenide gas (Table 3.3).

3.4.4 Coagulation-Flocculation Processes

Ferric salts are cationic coagulants. Their addition to water and wastewater at pH 7 and above forms iron hydroxides capable of removing selenium by adsorption via coprecipitation. Further bonding of iron hydroxides together by addition of a flocculant forms larger, denser aggregates that settle rapidly and are easier to separate. However, this flocculation step is not systematically necessary. As in all coagulation processes, the contaminant removal efficiency depends on the coagulant used, its dose and the pH of the water to be treated (Koren et al. 1992; Kapoor et al. 1995; Hu et al. 2015; Santos et al. 2015). Performance also depends on the oxidation state and concentration of selenium in raw water. Coagulation-flocculation separation processes are widely implemented in the industry with a coprecipitation technology. They are effective in removing selenite ions but much less effective in removing Se(VI). Coagulation by ferric salts is much more effective than by aluminum salts such as aluminum sulfate, aluminum chloride and polyaluminum chloride (Hu et al. 2015). Apart from the classical theories of coagulation and flocculation, the mechanisms described in the literature mainly involve adsorption phenomena on the hydroxide flocs formed, particularly for Se(VI) species coagulated by Fe(III). The main disadvantage is the large volume of sludge generated due to the high consumption of chemical substances (Table 3.3).

To improve performance, a pre-chlorination step can be done, during which chlorine will tend to oxidize Se(IV), thus decreasing Se in drinking water. Yet the results are highly dependent on pH and free chlorine concentration. In the case of wastewaters enriched in Se(VI), a pre-step of reduction to Se(IV) is also required. Lime softening is another treatment effective in removing Se(IV) with yields close to 50% for treatments at pH higher than 11.5 (Santos et al. 2015). However, this treatment has no effect on Se(VI) and is strongly influenced by pH. There are also soda decarbonation processes, which are technically simpler, but less efficient than lime, and more expensive. These two selenium removal processes, coagulation and lime softening, are considered as roughening processes and are generally used as pre-treatments just before the main treatment step, by adsorption for example. They are not economically interesting to eliminate selenium at trace levels.

3.4.5 Electrocoagulation

Electrocoagulation is an effective electrochemical treatment for the reduction, coagulation and separation of selenate (Mavrov et al. 2006; Mollah et al. 2004; GOLDER 2009; Sandy and DiSante 2010; Gingerich et al. 2018; He et al. 2018b; Stefaniak et al. 2018; Hansen et al. 2019). This technology is based on an electrolysis consisting of creating metallic hydroxides flocs within the water or wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum, by applying direct electrical current to an electrochemical cell. This involves *in situ* generation of coagulants by dissolving electrically either iron or aluminum ions from iron or aluminum electrodes, respectively. The generation of metallic cations takes place at the anode due to the electrochemical oxidation of the metal, whereas at the cathode the production of hydrogen gas typically occurs. H_2 gas would also help to float the flocculated particles out of the water. The technology, sometimes called electroflocculation, requires simple equipment with different possible configurations, e.g. iron in plate form or packed form of scraps, small retention time and is easy to operate, contributing to the reduction of operating costs. Figure 3.3 shows an electrocoagulation unit at the industrial scale. The mechanisms of electrode oxidation, gas bubble generation, flotation and sedimentation of flocs formed, are well known. Aluminum is usually used for water treatment, and iron for wastewater treatment. Other advantages are mentioned in Table 3.3. The main disadvantage is the large quantities of sludge that require disposal of as hazardous waste.

Fig. 3.3 Electrocoagulation unit at the industrial scale (Copyright: G. Crini, Besançon, France)

3.4.6 Metal Oxides

Liquid/solid adsorption is one of the most frequently used techniques for the decontamination of aqueous media worldwide. Adsorption is a method of separation in which substances such as selenium present in a liquid become bound to the surface of a solid material. It is a process of partition of the substance to be removed, called adsorbate, between the aqueous solution and the solid, named adsorbent. This surface phenomenon involves complex interactions between the adsorbent and adsorbate. The performance of an adsorbent depends primarily on its physical and chemical properties. Environmental parameters such as temperature, pH and competitive contaminants also play a role in determining the adsorption capacity of an adsorbent (Crini and Badot 2007, 2010).

There are two main types of adsorption, physical and chemical, yet some authors mention another type of adsorption, ion-exchange. Some authors consider ion-exchange as a chemical mechanism, named 'chemisorption', while others consider ion-exchange as a physical treatment, named 'physisorption'. In the industry and literature, coagulation using aluminum or ferric salts for selenium removal is considered as an adsorption-oriented technology, the application of aluminum salts being similar to that of ferrihydrite systems. Adsorption treatment technologies are now preferred because of their simplicity (technologically simple, easy of use), efficiency, residence times of less than a few minutes, and low-cost (minimal labor cost) for point-of-use applications (Simeonidis et al. 2016; Kalaitzidou et al. 2019). However, although extensive experimental studies on selenium removal have been reported, the mechanisms are not fully understood and there is still much debate.

Many natural and synthetic materials have been proposed for the removal of selenium from water, the most commonly used being metal oxides, ferric hydroxide, activated alumina and activated carbons. These adsorbents are interesting because they are very broad spectrum materials that also remove efficiently other metals and metalloids present in water and wastewater. Due to their great capacity to adsorb contaminants, metal oxides are the most effective adsorbents if the adsorption system is properly designed they give a good-quality output (Balistrieri and Chao 1987, 1990; Hayes et al. 1987; Zhang and Sparks 1990; Glasauer et al. 1995; Lo and Chen 1997; Zingaro et al. 1997; Su and Suarez 2000; Peak and Sparks 2002; Duc et al. 2006; Sandy and DiSante 2010; Rovira et al. 2008; Simeonidis et al. 2016; Kalaitzidou et al. 2019; Sharma et al. 2019). This advantage of metal oxides is mainly due to their structural characteristics, porous texture and high specific surface area. From literature data, the adsorption of Se(IV) onto metal oxides is effective over a wide range of pH, whereas the removal of Se(VI) is more difficult. In general, adsorption processes are ineffective at pH values greater than 10. The dominant selenium form in acidic pH is selenious acid (H_2SeO_3). Between pH 3.5 and 9, mostly biselenite $H_2SeO_3^-$ anion exist, while at pH higher than 9 selenite SeO_3^{2-} are predominant.

Granular ferric hydroxide is an iron-based adsorbent substrate commonly used to remove arsenic from drinking water (Crini and Badot 2010). Studies have shown

that this material can also be interesting to remove selenium. Adsorption on various metal oxides, especially iron and aluminum, at pH between 6 and 8 is also possible and always leads to greater efficiency in the case of Se(IV) removal. Iron is widely distributed in soil and it is well known that iron-based oxides can act as adsorbents for pollutant removal. In addition, using iron compounds is an environment-friendly method due to low Fe toxicity. However, some competing ions such as silica and phosphate can cause problems and reduce the adsorption capacity of these oxides.

The two forms of selenium display different degree of adsorption to iron and aluminum oxides: oxides adsorb Se(IV) more easily than Se(VI). The most studied iron-based materials are two oxides, hematite Fe_2O_3 and magnetite Fe_3O_4, and an oxy-hydroxide, goethite (FeOOH), a most stable varieties of iron(III) oxy-hydroxide with surface area lower than 20 m^2/g. These oxides are natural, inexpensive and effective (Balistrieri and Chao 1987, 1990; Hayes et al. 1987; Zhang and Sparks 1990; Glasauer et al. 1995; Lo and Chen 1997; Zingaro et al. 1997; Peak and Sparks 2002; Su and Suarez 2000; Duc et al. 2006; Rovira et al. 2008; Sandy and DiSante 2010; Sharrad et al. 2012; Simeonidis et al. 2016; Kalaitzidou et al. 2019; Kawamoto et al. 2019; Matulova et al. 2019; Rene et al. 2019; Sharma et al. 2019). The affinity for Se(VI) is always greater than for Se(IV) and the mechanisms are mainly due to surface complexation by formation of Lewis acid-base complexes, and precipitation, e.g. as ferric selenite. For hematite and goethite, the performance decreases at high pH due to the predominance of selenium species (Zhang and Sparks 1990; Peak and Sparks 2002; Duc et al. 2006; Rovira et al. 2008; Kawamoto et al. 2019; Rene et al. 2019). Curiously, it was reported that even at high selenium concentrations, not all active sites are occupied (Rovira et al. 2008). In general, to avoid generating a large amount of sludge, the column method is preferable.

Sharrad et al. (2012) evaluated the FeOOH performance on selenium reduction. Their study clearly demonstrated that this commercial adsorbent was a viable alternative to conventional oxides and other adsorbents due to its high surface area, large particle size (an important filter media quality requirement), relatively low cost, and rapid kinetics. However, the adsorption of selenite is significantly affected by both pH and coexisting contaminants such as phosphates; the maximal performance was achieved at pH 5. The adsorption capacity was explained by the increase of positive charge density with decreasing pH. Sharrad et al. (2012) concluded that this technology is promising for selenium removal.

FeOOH showed higher uptake capacities for Se(IV) than for Se(VI) since FeOOH forms inner-sphere complexes with Se(IV), while complexes formed with Se(VI) are outer-sphered in nature. Recently, Kalaitzidou et al. (2019) also pointed out that FeOOH reuse for Se(VI) removal was economically feasible and the recovery of selenium by this technology contributed to green chemistry. The high affinity of this iron oxy-hydroxide with oxyanions is promising for selenium removal from drinking water in full-scale water treatment plants. Matulova et al. (2019) demonstrated that goethite, one of the most common oxy-hydroxides in the environment, is efficient as adsorbent to remove selenite; this method is viable although the performance depend on the pH and the presence of anions such as sulfate and chloride.

The main problem with metal oxide adsorption is the difficulty of using metal oxides in a continuous flow system due to their small particle sizes. For this reason, many studies have proposed the use of other adsorbents such as aluminum oxides/oxy-hydroxides, e.g. activated alumina and gibbsite, and carbons. Others have proposed various iron-coated materials for the adsorption of selenium from water, such as iron-oxide-coated sand, iron-coated granular activated carbons, and zeolite-modified adsorbents (Lo and Chen 1997; Kuan et al. 1998; Zhang et al. 2008; Kwon et al. 2015). Lo and Chen (1997) studied the adsorption of selenite ions on sand coated with ferric oxide: by using 100 g of material per liter of 10 mg/L selenium solution, they obtained a 100% reduction in 10 min. Kuan et al. (1998) proposed sand coated with aluminum oxide and found similar results. Kwon et al. (2015) studied the impregnation of magnetite nanomaterials onto carbonaceous supports. These composites represent a unique material with tunable uptake properties for removing inorganic selenite in aqueous solutions. Evans et al. (2019) proposed magnetic adsorbents for selective removal of selenite from contaminated waters. Meso- and microporous tire-derived carbon frameworks as a support for magnetic iron oxide nanoparticles has been developed. Carbon-supported magnetic adsorbents displayed higher performance compared to conventional oxides. Minzatu et al. (2019) proposed a new technique to produce an ecofriendly composite material by doping graphite with iron oxide, which was used for retention of selenium and arsenic from aqueous solutions; the maximum adsorption capacity was 625 μg Se(VI) and 400 μg As(V) per gram of adsorbent.

3.4.7 Activated Alumina

Aluminum oxides/oxyhydroxides such as activated alumina γ-Al_2O_3 and gibbsite $Al(OH)_3$ are commonly used for selenium removal due to their large surface area of about 300 m^2/g, size and particular porosity (Kosmulski 2001; Jeqadeesan et al. 2003; Sandy and DiSante 2010; Su et al. 2008, 2010; He et al. 2018b; Ji et al. 2019). Processes using these materials are versatile due to their efficiency, low-cost and overall technological simplicity. Selective adsorption of selenium from drinking water by activated alumina adsorbents shows removal higher than 90% (Kosmulski 2001; Su et al. 2008, 2010; Ji et al. 2019). Coupled with a pre-coagulation step, this is one of the most effective methods. Adsorption-oriented processes using alumina are also used in water treatment because they make it possible to eliminate other oxyanions and contaminants such sulfate, arsenate, fluoride and silica, at the same time. Activated aluminum oxides can be used in different techniques (Crini 2017; Ji et al. 2019): in batch, in resins or in beds arranged in series or in parallel, where raw water continuously flows through the beds.

Alumina preferably adsorbs Se(IV) mainly by physicochemical mechanisms involving surface adsorption and ion exchange. Since Se(VI) has a low affinity for activated alumina relative to other ions, Se(VI) adsorption is likely to be hindered by interference from other ions. The adsorption capacity of alumina for Se(VI) is

approximately 1/13 of the capacity for Se(IV) under similar conditions. Sulphate ions significantly interfere with the removal of Se(VI) by activated alumina, whereas the presence of calcium and magnesium may improve the adsorption of Se(VI) by a secondary adsorption phenomenon, which involves simultaneous adsorption of multivalent cations by anions or simultaneous adsorption of multivalent anions by cations. Since activated alumina is amphoteric, adsorption depends on pH. At a pH below 8.2, the surface of activated alumina displays a positive net charge and will thus adsorb the anions present in the water. Other factors to be taken into account are the oxidation state of the contaminants, contact time, competing ions, as well as the concentration of the regenerant and its flow rate. Regeneration techniques are simple, they consist of rinsing the beds with successive washes, e.g. rinsing with a sodium hydroxide solution, rinsing with water and treating with sulphuric acid for the recovery of Se(IV), and with hydrochloric acid for the recovery of Se(VI). In addition to its cost, other disadvantages should be considered, including fouling of the activated alumina bed and degradation of the alumina during regeneration, which leads to an increased pressure drop in the substrate bed (Table 3.3).

3.4.8 Activated Carbons

Due to their large specific surface area, higher than 1000 m^2/g, microporosity and the occurrence of diverse surface functional groups, commercial activated carbons, in raw, modified or supported forms, are also proposed to remove selenium, although their efficiency is lower than that of aluminas (Sorg and Logsdon 1978). The two most commonly used techniques are the batch method, using carbon in powdered form, and percolation in reactors with the granular form. The surface chemistry of carbons, e.g. isoelectric point and acid-base properties, is the key element for the performance of the materials. In general, in a decontamination system, activated carbons are used in pre-treatment to remove as many pollutants as possible, including selenium. Therefore this is not a selective adsorption but rather a global adsorption (Jadhav et al. 2000; Jeqadeesan et al. 2003; Zhang et al. 2008; Sandy and DiSante 2010; Dobrowolski and Otto 2013; Kwon et al. 2015; Santos et al. 2015; Bakather et al. 2017; He et al. 2018b). Granular activated carbons are the most promising adsorbents, particularly iron-coated carbons due to their applicability to continuous processes.

Zhang et al. (2008) studied the removal of selenite from aqueous phase using iron-coated granular activated carbons. The commercial Darco® carbon coated with 0.1 M ferrous chloride achieved the highest selenite removal, above 97%. High removal efficiency of selenite occurred in a wide range of pH, i.e., 2–8, but the efficiency decreased above pH 8. Adsorption kinetics showed that selenite removal efficiency reached more than 90% after 6 h adsorption for initial selenium concentration of 2 mg/L and equilibrium was obtained after 48 h. The adsorption capacity reached 2.5 mg Se/g adsorbent at equilibrium for an initial concentration of 2 mg/L at 25°C. Oxyanion competitive adsorption showed that 0.1–5 mM sulfate barely

affected selenite adsorption. Other anions such as phosphate, silicate and carbonate impacted selenite adsorption to various degrees, with phosphate completely excluding selenite adsorption.

3.4.9 Others Conventional Adsorbents

Adsorption of selenium species using other conventional adsorbents such as zeolites, supported magnetite, sand, bentonite, titanium and clays was studied (Lo and Chen 1997; Kuan et al. 1998; Lenz et al. 2006; El-Shafey 2007a, b; Zhang et al. 2009; Bleiman and Mishael 2010; Hasan et al. 2010; Pal and Rai 2010; Tuzen and Sari 2010; Mane et al. 2011; González-Acevedo et al. 2012; Li et al. 2013; Nettem and Almusallam 2013; Verbinnen et al. 2013; Khakpour et al. 2014; Yamani et al. 2014; Johansson et al. 2015; Kieliszek et al. 2015; Kwon et al. 2015; Roberts et al. 2015; Santos et al. 2015; Wang et al. 2015; He et al. 2018b; Tan et al. 2018).

For example, Bar Yosef and Meek (1987), and more recently Wang et al. (2015) have proposed raw or modified clays as effective materials for selenium removal. The results are explained by the predominance of complexation phenomena on the surface of the materials due to their large surface area and high porosity. Clays are also considered as natural and low-cost minerals and efficient to adsorb cationic and neutral species. However, clay performance is highly pH-dependent. Shi et al. (2009) studied the adsorption of Se(IV) on titanium dioxide (rutile). Other hybrid materials have been proposed such as zeolite-modified magnetite (Verbinnen et al. 2013) and polymer-clay composites (Santos et al. 2015).

3.4.10 Ion-Exchange Resins

More than 80% selenium removal efficiency can be achieved in drinking water using strongly basic anion exchange resins (Tanaka et al. 1983). This technology is based of exchange of oxyanions using resin beads, releasing a weakly attached co-ion. Indeed, the resin carries a positive chemical group covalently bonded to the support and the exchangeable counter-ion carries a negative charge: we speak of anion exchangers. Commercial resins of the cross-linked polymer type grafted by tertiary amine functional groups (and/or primary and secondary amines) such as Amberlite® IRA-67 (cross-linked acrylic gel) or Duolite® A7 (phenol-formaldehyde polycondensed gel) have particular chemical structures in the form of highly porous spherical balls. These resins offer excellent stability (physical, mechanical), fast kinetics, remarkable resistance to clogging and a high exchange capacity (Tanaka et al. 1983). In general, Se(VI) is slightly favored over Se(IV). Nevertheless, conventional ion exchangers are not selective with respect to a single ion to be exchanged. This may induce preference by affinity, and therefore competition, which is often the case for industrial effluents, as well as for groundwater rich on

sulphates, phosphates and others. In that case, one can either use a chain of several ion exchangers with weak and strong anions, or use chelate resins.

Ion-exchange using anion exchange resins, chelating resins, selective resins or zeolites is technological simple, rapid with well-established and tested procedures (Table 3.3). The technology can be easily integrated in a wastewater process and can be applied to different flow regimes (batch, column). The main disadvantage of the ion-exchange technology is economic constraints, including initial cost of the resin, maintenance costs, and regeneration time-consuming. This regeneration of the resins is essential because resin capacity is gradually and rapidly exhausted. In addition to the cost of the resin process, resins are fragile and very sensitive to the presence of organic contaminants, suspended solids, calcium or iron, which can clog and clog reactors in the long term; pre-precipitation and filtration steps are thus necessary.

Commercial resins have a low selectivity for Se(IV) compared to other ions. For example, since the affinity for sulfate is almost as high as that for Se(VI) and since sulfate is generally present in much higher concentrations, this results in competition with Se(VI) for binding at ion exchange sites. More generally, strongly basic anion exchange resins have a lower affinity for Se(IV) anions than for Se(VI) anions, nitrate and sulfate. The pH of the treated water is an important factor affecting ion exchange for the removal of Se(IV). Other factors influencing performance are the oxidation state of selenium, the concentration of anions in competition and the type of resin chosen (Suzuki et al. 2000; Jelas Haron et al. 2001; Dzul Erosa et al. 2009; Sandy and DiSante 2010; Santos et al. 2015; Staicu et al. 2017; Kawamoto et al. 2019; Sharma et al. 2019). Indeed, the exchange behavior of the hydrogen selenite ion ($HSeO_3^-$) and the selenite ion (SeO_3^{2-}) must also be taken into consideration, as the selectivity towards the monovalent anion is lower than that towards the divalent anion. In addition, since selenium is usually present at trace levels in drinking water, Se removal efficiency depends on the concentration of other anions, e.g. sulphate, nitrate, chloride and bicarbonate. Dzul Erosa et al. (2009) showed that the commercial resins were effective in removing Se(IV) and Se(VI) but that the results were highly dependent on competition with other species present in the solution, especially sulfates, and also on pH. A solution is to combine a chlorine oxidation step from Se(IV) to Se(VI) with an ion exchange treatment. More specific resins, so-called chelating resins, can also be used. Chelating resins are made of a functionalized polymer support with more specific groups, hence their greater selectivity. The disadvantage of chelating resins remains their cost, which is 4–5 times higher than for conventional resins.

Much research is being conducted on the chemical modification of commercial resins. A practical and effective method removing Se(IV) from water using a Fe^{3+} type cation exchange resin was recently proposed by Kawamoto et al. (2019). The first step consisted in the addition of ferric ions $FeCl_3$ onto a commercial strong acid-type cation exchange resin, e.g. sodium type. In this process, called coadsorption, the anion was also adsorbed. Then, in a second step, the availability of the resin was studied for selenium removal at pH 3, 0.1 M NaCl. A column in which 12.8 g of resin was packed was able to remove 0.1 mg/L selenium in 3 tons of synthetic

solution. Surprisingly, the amount of Se(IV) adsorbed onto the resin increased with the increase of ionic strength. Indeed, this trend is opposite compared to selenium adsorption on ferric oxides and hydroxides. Another advantage of their method was the easy desorption of ferric ions as $FeCl_4^-$ complex ion using a small amount of hydrochloric acid and the quick regeneration of the resin. However, the method did not allow Se(VI) removal and the performance was also dependent of the presence of phosphate ions. Staicu et al. (2017) studied for the first time selenium removal from real flue gas desulfurization wastewater generated by a coal-power plant using a commercial iron oxide impregnated strong base anion exchange resin combined with barium precipitation. Their study clearly showed that a combined technology was efficient in removing selenium from effluents despite the high presence of sulfates and other ions.

3.4.11 Membrane Filtration

Membrane techniques such as nanofiltration (Kharaka et al. 1996; GOLDER 2009; Sandy and DiSante 2010; He et al. 2016a, b, 2018a) and mostly reverse osmosis (Marinas and Selleck 1987, 1992; Kharaka et al. 1996; GOLDER 2009; Sandy and DiSante 2010; He et al. 2018b) are effective techniques for removing ionic species Se(IV) and Se(VI). They rely on filtration and separation processes on micropores, with diameter lower than 2 nm, by hydrostatic pressure. Efficiency depends mainly on the quality of the water to be treated, the type of membrane, and the recovery capacity of the system (Marinas and Selleck 1992; Kharaka et al. 1996; Santos et al. 2015). Generally, cellulose acetate membranes are used which give the best abatement. Marinas and Selleck (1987, 1992) previously reported that the technologies achieved more than 99.5% rejection for selenium oxyanions and 99% for nitrates.

Reverse osmosis allows Se concentrations below 5 μg/L to be reached. Since reverse osmosis treatment systems generally produce high quality drinking water, the ability to mix treated water with raw water to produce treated water of acceptable quality can be a factor in the choice of treatment (Crini 2017). Filtration technology has also been applied in the treatment of selenium contaminated agricultural drainage waters (Marinas and Selleck 1987; Kharaka et al. 1996). However, filtration techniques generate only small volumes of concentrate, yet the total volume in case of agricultural drainage waters is immense. Filtration technologies are expensive and limited by different constraints such as gypsum precipitation observed at higher water recoveries. Other disadvantages are reported in Table 3.3.

Nanofiltration process works at low pressure, about 1/3 of that of traditional reverse osmosis, and is effective for all divalent ions. Reverse osmosis is much more efficient at removing all ions than nanofiltration, but at a much higher cost. Nanofiltration and reverse osmosis require pretreatment of solids and colloids to reduce membrane scaling and fouling, and therefore regular maintenance. For example, the presence of impurities, e.g. iron, manganese, silica and scale producing compounds, and the turbidity, are impacting process performance. The

processes also pose the problem of concentrate disposal. The cost of the process is a real disadvantage, not only in terms of initial investment and maintenance, but also through the elimination of the waste generated. Finally, treated water generally requires post-treatment, which consists of adjusting the pH and alkalinity.

3.4.12 Electrodialysis and Reverse Electrodialysis Processes

Electrodialysis is an electrochemical separation process in which charged species from water pass through a semi-permeable membrane under the influence of an electrical potential (AWWA 1999; Mollah et al. 2004; Strathmann 2004; Mavrov et al. 2006; Sandy and DiSante 2010; Hassanvand et al. 2017; Onorato et al. 2017; Gingerich et al. 2018; He et al. 2018b). The membranes form parallel stacks, and each successive membrane carries a direct electrical current. Cations and anions migrate through cationic and anionic membranes, respectively. In the reverse electrodialysis process, the polarity of the electrodes changes regularly on either side of the ion exchange membranes, causing an inversion of ion displacement, minimizing scale accumulation on the membranes (Mollah et al. 2004; Mavrov et al. 2006). These processes are efficient, fully automated and suitable for any volume to be processed (Table 3.3). However, pre-treatment is essential because membranes get fouled when the pores are clogged by salt precipitation or blocked by suspended particulates. Another problem is competition with other contaminants.

3.4.13 Biological Techniques

In the biological approach to water treatment, many terminologies are used, including biological conversion, biological volatilization, biological reduction, bioreduction, microbial reduction, microbial metabolism, heterotrophic microbial reduction, biotransformation, biomineralization, bioaccumulation, bioreactors, algal-bacterial technology, enzymatic processes, biosorption, bioremediation, phytoremediation, phytotechnology, agro-remediation, mycoremediation, phycoremediation, phytostabilization, rhizofiltration, rhizodegradation, phytodegradation, phytoextraction, phytoaccumulation and phytovolatilization. Some terms can also be classified into sub-classes. A review of the literature on these terms reveals that their definition has evolved over the years, which can be attributed to the diversity of the mechanisms involved and the techniques uses (Lundquist et al. 1994; Parker and Page 1994; Cantafio et al. 1996; Carvalho et al. 2001; MSE 2001; Yee et al. 2007; GOLDER 2009; Hunter and Manter 2009; Zhu et al. 2009; Vriens et al. 2014; Santos et al. 2015; Dessì et al. 2016; Tan et al. 2016; Terry 2016; Mal et al. 2017; van Hullebusch 2017; He et al. 2018b; Stefaniak et al. 2018; Tan et al. 2018; Calix et al. 2019; Gebreeyessus and Zewge 2019; Paul and Saha 2019; Rene et al. 2019; Zhang et al. 2019a; Zeng et al. 2019). However, all the biological approaches are based on the

use and growth of microorganisms, algae or plants. Each biological technology has its own advantages and disadvantages (Table 3.3).

Bacteria, microbes, algae and fungi are capable of reducing metals including selenium and thus produce insoluble forms that can be eliminated from contaminated water by precipitation or adsorption mechanisms. Biological community analysis shows that various selenium-reducing microorganisms contribute to the selenium cycle. Similar oxidation-reduction reactions of selenium are observed in chemical and biological reactions, yet microorganisms mediate reactions using their metabolic pathways. Microorganisms receive energy by transfer of electrons from an electron donor, i.e. food organic carbon, to an electron acceptor, which represents respiration of the microorganism with production of carbon dioxide and biomass. There are generally two main types of environments, those rich in oxygen and those where oxygen and oxidized nitrogen are absent. Oxygen is the most favorable electron acceptor for microorganisms, e.g. for microbial aerobic oxidation of organics for energy production resulting in the energy source and electron acceptor being converted to carbon dioxide and water. Microorganisms can be heterotrophs, obtaining energy from the oxidation of organic compounds, or autotrophs, where energy comes from the oxidation of inorganic compounds.

Nitrate-reducing bacteria are heterotrophic bacteria that use organic carbon as electron donor and selenate or selenite as their acceptor. Thus, they obtain both their energy and cellular growth from reaction with selenite and selenate. In some cases the environment must be controlled to exclude oxygen. For example, in an anoxic environment, bacteria called denitrifiers can use oxidized inorganic compounds, e.g. selenate or selenite, as electron acceptors, but only in the absence of oxygen. In this case, bacteria will use nitrate as an electron acceptor. This is why, in general, biological methods for treating selenium are classified into aerobic, e.g. microbial aerobic oxidation, and anaerobic techniques: denitrifying bacteria, bioreactors and constructed wetlands.

A simple classification makes it possible to distinguish biological treatments either in active technologies such as microbial reduction or in passive technologies, for example aerobic wetlands and biochemical reactors. Active treatment is subject to relatively constant monitoring to control and enhance the environment. Active treatment also requires chemical and physical monitoring, e.g. pH, chemical oxygen demand, biochemical oxygen demand, and total organic carbon. Active treatment also consumes energy. Whereas passive treatment has advantages such as little or no energy input, minimal monitoring and maintenance, natural processes and materials, suitable for low flows, but passive treatment generally requires more land and isolated locations. This classification is controversial since, for example, bioreactors can be either active or passive processes.

Typical conventional biological technologies that have been applied for the removal of selenium include created wetlands involving phytoremediation, volatilization, reduction and adsorption in sediments, algal-bacterial removal, and biological removal using dissimilatory metal reducers. These techniques can be classified as biological conversions, i.e. uptake, reduction and volatilization processes.

Biological conversions using microorganisms can be used to remove selenate and selenite oxyanions from wastewater and water (Santos et al. 2015). Microorganisms act to reduce, oxidize, precipitate, absorb and adsorb contaminants from effluents. Similarly to chemical treatment, challenges of biological treatments include low selenium concentrations in the effluent to be treated, presence or absence of nitrate, and competition from other oxyanions, e.g. sulfate. Many factors such as pH, temperature and salinity of the effluent are influencing microbial reduction. Biological reduction is currently the subject of intense research for the elimination of selenium. Typically, a biological technique is combined with other conventional physicochemical processes such as coagulation, adsorption and filtration. When the biological route for selenium-loaded wastewater is implemented, the main objective is to obtain biogenic selenium Se(0) as a solid end product. However, this element has colloidal stability between pH 2–12 due to its surface charge and nanometric size, making it difficult to remove from the effluent (Staicu et al. 2015a, b). It is thus necessary to couple the biological treatment with a coagulation-flocculation or filtration step.

The algal-bacterial technology is interesting because it avoids the commonly encountered competitive inhibition of nitrate on selenate reduction (Lundquist et al. 1994; Lin and Terry 2003; GOLDER 2009; Sandy and DiSante 2010). Microalgae are grown in a first step to reduce nitrate concentrations, and subsequently the settled algal biomass is used as a carbon source for selenium reducing bacteria in a spatially separated treatment step.

Phytoremediation is a process allowing the removal of contaminants from contaminated soils, air and water by plants (Harvey et al. 2002; McGrath et al. 2002). Selected plants can either accumulate or detoxify the contaminants (Terry 2016; Gebreeyessus and Zewge 2019; Rene et al. 2019). Phytoremediation is perceived as a simple, acceptable, cost-effective and effective cleanup technology. Phytoremediation comprises several techniques that use plants and associated microorganisms to remediate contaminated environments and matrices. These techniques can be divided into four types, i.e. phytoextraction, phytofiltration, phytostabilization and phytovolatilization, depending on the plants and the conditions used, and on the type of contaminants to remove and the level of cleanup required. Phytoremediation is carried out *in situ* and this may reduce the exposure of the contaminated substrate to humans, wildlife and the environment. To remove selenium, recent data from constructed wetlands showed that phytoremediation appears attractive due to its field scale application advantage (Gebreeyessus and Zewge 2019). Flow-through or subsurface wetlands provide an inexpensive and efficient technology for the treatment of selenium in large volume of agricultural drainage waters and flue gas desulfurization effluents. Soluble selenium is removed by different processes such as uptake by plants (phytoextraction), volatilization by plants, fungi and bacteria and microbial and geochemical reduction. However, the main disadvantage is that it is a very slow process. Another problem is the bioaccumulation of selenium and its exposure to wildlife (Table 3.3).

3.4.14 Emerging Non-conventional Adsorbents

Currently explored methods include biosorption on non-conventional adsorbent materials, named biosorbents due to their biological origin. Biosorption uses natural, low-cost materials from renewable resources, generally agricultural or marine, as an alternative in water treatment. This process takes advantage of the presence of many reactive groups on the surface of these materials, which are generally polysaccharides. Biosorbents include chitosan, biomass (microorganisms), and agricultural wastes, e.g. peanut shells and rice husks. These materials are capable of complexing contaminants, including selenium species, present in trace amounts in complex mixtures, to meet the regulatory limit in wastewater (Kidgell et al. 2014; Crini 2017). In general, kinetics are fast and retention capacities are high. The mechanisms are explained mainly by ion-exchange.

One of the biosorbents proposed is chitosan, a biopolymer obtained from chitin, the most abundant polysaccharide after cellulose. As a cationic polyelectrolyte, chitosan behaves as a polycation with a high charge density in an acidic environment, which is a very interesting property for water treatment. In addition, chitosan is known for its versatility and can be used both in solution and in the solid state under different forms, e.g. powders, beads and fibers. Chitosan can act both as an adsorbent and a flocculant, and is currently the subject of extensive research to remove contaminants. Chitosan is used in particular to prepare composite materials of high mechanical stability for use in continuous or batch reactors. Several studies have proposed coating chitosan on materials such as clay or oxides (Bleiman and Michael 2010; Yamani et al. 2014). For example, the use of chitosan-clay composites has resulted in an absorption capacity of 18.4 mg Se(VI) per g of substrate. This composite had an affinity for selenium compared to other ions present, and was able to reduce a Se(VI) concentration from 0.64 mg/L to a level below 0.01 mg/L in groundwater (Bleiman and Michael 2010).

The use of microorganisms such as fungi, yeasts, bacteria and algae, as biosorbents has proven to be a cost effective, efficient to reduce selenium species to their elemental forms, and a safe technique for metal and metalloid removal. Dead biomass is preferred to avoid toxicity and the requirement of growth medium that would increase the operational costs. Application of bacteria for the reduction of selenium oxyanions is interesting because the process takes less time and is easy to manage. It is also possible to use different types of heterotrophic aerobic and anaerobic and chemotropic bacteria. Even if selenium concentration is very low, the process is efficient, reaching final concentration bout 5 µg/L or even less, and is technically and economically viable. Fungi and yeasts such as *Aspergillus niger*, *Rhizopus arrhizus*, *Saccharomynces cerevisiae* or *Phanaerochaete chrysosporium* are able to bind selenium in its organic and inorganic forms. They can bioaccumulate selenium intracellularly by active transportation of selenium in the cells, and extracellularly by interactions with proteins, phospholipids and polysaccharides. Several varieties of marine algae have the ability to interact with selenium, even in

trace amounts. This capacity is due to the presence of polysaccharides, proteins and lipids at cell surface, capable of complexing selenium (Tuzen and Sari 2010).

Many studies are available in the literature although there is not yet an industrial sector for the production of dedicated materials for water treatment (Lo and Chen 1997; Kuan et al. 1998; El-Shafey 2007a, b; Zhang et al. 2009; Bleiman and Mishael 2010; Hasan et al. 2010; Pal and Rai 2010; Tuzen and Sari 2010; Mane et al. 2011; González-Acevedo et al. 2012; Li et al. 2013; Nettem and Almusallam 2013; Verbinnen et al. 2013; Khakpour et al. 2014; Kidgell et al. 2014; Yamani et al. 2014; Johansson et al. 2015; Kieliszek et al. 2015; Kwon et al. 2015; Roberts et al. 2015; Santos et al. 2015; Wang et al. 2015; He et al. 2018b; Tan et al. 2018). Nevertheless, pilot tests are currently emerging at the industrial stage (Santos et al. 2015; Crini 2017), which suggests that this technology will be developed. All the results described have been obtained on polycontaminated groundwater and synthetic solutions of selenium. Indeed, there is little work on complex real industrial effluents. In addition, the mechanisms of elimination are still poorly understood. Further research and optimization are needed to determine the feasibility of using non-conventional adsorbents in applications to remove selenate and selenite from water/wastewater.

3.5 Examples of Treatment for Selenium Removal

3.5.1 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). As already stated, zero-valent iron 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. 2017; 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. 2017) while the metallic core acts as an electron donor (reductant) (Eq. 3.1) (Li and Zhang 2006; Liu et al. 2017).

The reduction process in equation (3.1) 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. 3.2) and anoxic (slow process) (Eq. 3.3) 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, b; Das et al. 2019) conditions. The formation of OH^- and H_2, as in Eqs. 3.2 and 3.3, 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 Se species such as Se(IV) and subsequent reduction to insoluble Se species such as elemental selenium [Se(0)] and or selenide [Se(-II)] (Genin et al. 1998; Murphy 1988; Yoon et al. 2011; Gibson et al. 2012; Liang et al. 2013; Yoon et al. 2016) (Eqs. 3.4 and 3.5). Figure 3.4 shows Se(VI) adsorption and subsequent reduction to Se(IV), Se(0), Se(-I) and Se(-II) by zero-valent iron.

$$Fe^0 = Fe^{2+} + 2e^- \tag{3.1}$$

$$2Fe^0 + 2H_2O + O_2 = 2Fe^{2+} + 4OH^- \tag{3.2}$$

$$Fe^0 + 2H_2O = Fe^{2+} + 2OH^- + H_2 \tag{3.3}$$

$$HSeO_4^- + 3H^+ + 2e^- = H_2SeO_3\left(aq\right) + H_2O \tag{3.4}$$

$$H_2SeO_3\left(aq\right) + 4H^+ + 4e^- = Se\left(s\right) + 3H_2O \tag{3.5}$$

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 but 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;

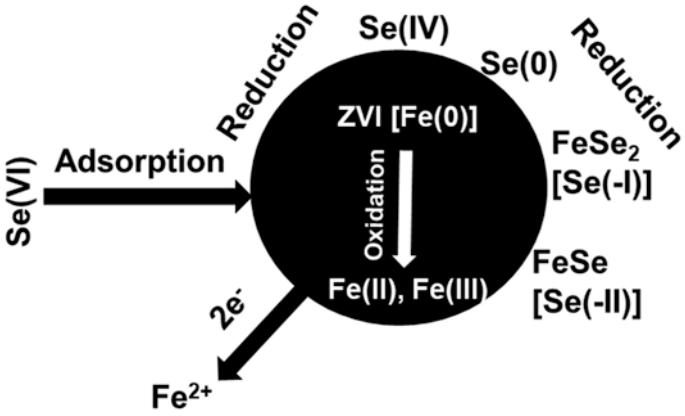


Fig. 3.4 Se(VI) adsorption and subsequent reduction to Se(IV), Se(0), Se(-I), and Se(-II) by zero-valent iron. (Adapted from Shrimpton et al. 2015)

Tang et al. 2014a; Shrimpton et al. 2015). Spectroscopic analyses also demonstrate that Se(VI) adsorption and subsequent reduction to other Se species is not only dependent on reaction time but also 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 but by both Se(VI) and Se(IV) at dissolved Se(VI) concentrations higher than 50 mg/L, signifying 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 its rate of removal (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 noted for SO_4^{2-}, PO_4^{3-}, or HCO_3^-. NO_3^- does not hinder 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 passivates the zero-valent iron surface for Se(VI) removal (Reinsch et al. 2010). The presence of dissolved Cl^- demonstrates 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 as discussed above; nonetheless, the kinetics of Se(VI) removal can be best described by either a first-or pseudo-first-order reaction pathway 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 dominant 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 solution chemistry (e.g. presence of dissolved SO_4^{2-}, NO_3^-, or both) (Das et al. 2019). In 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) resulted in more Se(0) as a reduction product 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 (magnetite, hematite, lepidocrocite, wüstite, ferrihydrite, schwertmannite, vivianite, mikasaite, etc., depending on solution chemistry) can decrease the Se(VI) removal efficiency of zero-valent iron due to passivation effects caused by these oxide/hydroxides coating onto the 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. 2017; Das et al. 2017, 2019). In addition, particle agglomeration of nano-scale zero-valent iron results in a decrease in the reactive surface areas and a lowering of the reactivity for contaminant removal (Ezzatahmadi et al. 2017). As such, 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, b), clay minerals such as bentonite (Li et al. 2015; Dong et al. 2016), and a weak magnetic field (Liang et al. 2014a, b) 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 represent an alternative to other approaches, e.g. adsorption onto iron oxide and hydroxides, co-precipitation with ferrihydrite, membrane separation.

3.5.2 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 Se 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). As such, a large number of laboratory studies spanning the last five decades have investigated the adsorption behavior and mechanism of two major Se species-Se(IV) and Se(VI)-onto iron oxides/oxy-hydroxides, including ferrihydrite ($5Fe_2O_3.9H_2O$), 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; Hayes et al. 1987, 1988; Balistrieri and Chao 1990; 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. 2009a, b; 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 a variety of factors, such as solution pH, selenium species, strength of electrolytes, concentrations of selenium species, types of adsorbate, concentrations of adsorbate, presence of competing ions, and more. Fig. 3.5 present a simplified diagram of both selenate and selenite adsorption onto iron oxide and hydroxides (Hayes 1987). 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 these two selenium species is strongly dependent on solution pH, with greater sequestration occurring at lower *versus* higher pH conditions (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; thus, 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).

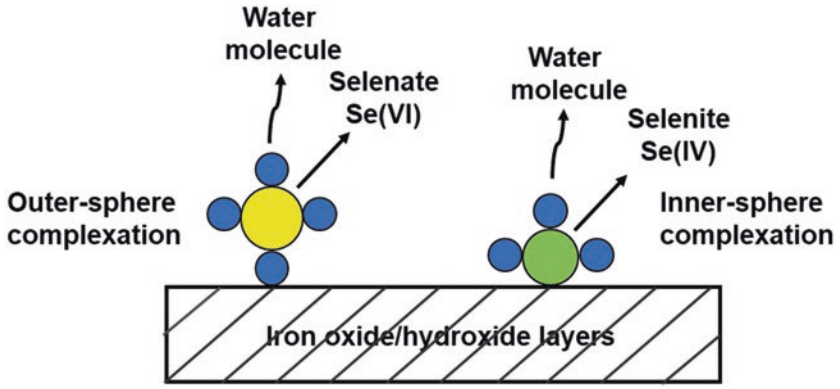


Fig. 3.5 Selenate and selenite adsorption onto iron oxide and hydroxides. (Adapted from Hayes 1987)

So, 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 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 percent 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, 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 Se sequestration by iron oxides and hydroxides. For instance, Se(IV) adsorption did not noticeably affect onto the surface of either amorphous iron hydroxide or goethite; however, a remarkable decrease in Se(VI) adsorption occurred when the ionic strength increased by an order of magnitude from 0.01 to 0.1M (Su and Suarez 2000). Adsorption of selenium also depends on the concentration of sorbate, with higher 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 Se 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 obtained from laboratory tests on selenium adsorption behavior onto iron oxides and hydroxides have been successfully evaluated 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) demonstrate 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 Se(VI) forms a weakly bound outer-sphere complex on goethite even in highly acidic conditions (pH = 4), as reflected by the absence of a second shell (Se-Fe) in the absorption spectra (Hayes et al. 1987). However, results also demonstrate the nature of Se(VI) complexation onto goethite is pH dependent, with outer-sphere surface complexes dominating at pH values ≥6 and inner-sphere surface complexes at pH values ≤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 values below 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 Se(VI), similar 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 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 Se(VI) adsorption on goethite is dependent on the electrolyte strength, with lower adsorption at greater ionic strengths signifying an ion-pair type complex (outer-sphere) on goethite surfaces [shell of hydration of Se(VI) was 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), electrophoretic study indicate Se(VI), similar to Se(IV), has lowered electrophoretic mobility and point of zero charge on the goethite surface (Su and Suarez 2000). The shift in the both electrophoretic mobility and extended X-ray absorption fine structure spectroscopy towards lower values signifies inner-sphere complexation of Se(VI) on the goethite surface as chemically or specifically bound ions accumulate 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- vs 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 discussed above, 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, surface loadings, etc.; as such, Se(IV) adsorbs more

strongly onto iron oxide/hydroxide surfaces compared to Se(VI) for given geochemical conditions (Balistrieri and Chao 1987; Su and Suarez 2000).

3.5.3 Supported Materials for Selenium Removal

As noted in Table 3.3, there are conventional inorganic materials (metal oxides/oxyhydroxides, zero-valent iron) and organic materials (activated carbons, synthetic resins) and non-conventional materials (biosorbents) that have utility for adsorption-based application. The adsorption-based removal of selenium species from aqueous media can be either physisorption or chemisorption in nature, depending on the nature of the adsorbent. Based on the foregoing discussion, the various inorganic and organic adsorbents have a wide range of efficiency, according to the external conditions, e.g. 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 a range of selected examples of adsorbent preparation that illustrate the use of various types of conventional and unconventional substrates.

An example of the latter was shown by Kong and Wilson (2017), where they report on the preparation of goethite and its supported forms onto cellulose supports and to examine their utility as adsorbents for the uptake of 4-hydroxy-3-nitrobenzene arsenic acid (roxarsone) from aqueous media. A key result obtained in this work reveals that while iron oxide materials such as goethite are considered as efficient adsorbents for inorganic/organic oxyanions of arsenic, the supported nanomaterials had reduced iron leaching whilst maintaining comparable uptake of arsenic species at fractional (30%) iron oxide content. 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, where it was proposed 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).

A further illustration of the role of supported materials can be ascertained 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_4NPs) and supported forms. An approximate 18-fold increase was observed for the uptake of Cr(VI) between MoS_2@Fe_3O_4NPs and 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 5-fold increase was noted for ferric ion-impregnated biochar over that of 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, but 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. 2009a, b; 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).

Yamani et al. (2014) demonstrated the utility of chitosan supports for metal oxide adsorbent materials. Nanocrystalline metal oxide impregnated chitosan beads were successfully developed with nanocrystalline aluminum oxide (n-Al_2O_3) to form n-Al_2O_3 impregnated chitosan beads. These impregnated beads were able to simultaneously adsorb inorganic aqueous selenite and selenate more effectively than n-Al_2O_3 or chitosan alone.

Verbinnen et al. (2013) reported that a zeolite-supported magnetite was found to be suitable as an adsorbent for the simultaneous adsorption of oxyanions from wastewater. In this study, it was shown that at the ideal pH (3–3.5), the adsorption capacities for Mo, Sb and Se oxyanions are high (18–23 mg/g). Anions like 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 (inner-sphere complex formation) for all studied oxyanions, except for selenate, that forms outersphere complexes, as supported by modeling results.

Li et al. (2015) reported on 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, where the removal efficiency was 95.7%. By comparison, this removal exceed that for the sum

(72%) of either single component (nano-zero valent iron, 62.1%) and non-supported Al-bent adsorption (9.86%).

Tan et al. (2019a) carried out a study where biochar and activated carbon were both produced from corn straw. The 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 reported at 62.52 and 35.39 mg/g. 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. The higher iron content and more positive charges of biochar-zero valent iron provided and account for the difference with activated carbon-zero valent iron, in spite of it much lower BET surface area and pore volume of the former. The mechanism of removal of Se(IV) and Se(VI) from wastewater in the case of zero valent iron occurs via co-precipitation, 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 on the preparation of activated carbon-supported Fe(II) and nano-zero valent iron were prepared 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; activated carbon/nano-zero valent iron, 46.5 mg/g.

Svecova et al. (2011) carried out an adsorption study of selenite and selenate ions onto rutile using batch and column method. In conjunction with X-ray absorption spectroscopy results, evidence of surface complexes, where both inner- and outer-sphere complexes were proposed. At pH 3, the column method yielded an adsorption capacity of 2.1 μmol/g for selenate and 14.8 μmol/g for selenite onto rutile. Jordan et al. (2014) used X-ray absorption spectroscopy to study the adsorption of selenite onto maghemite and concluded the formation of bidentate inner-sphere complexes. Tridentate complexes were favored for arsenite or antimonite species over selenite due to the incompatible smaller size of selenite.

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 showed that the polysulfide-nano-zero valent@biochar (PS-nZVI@BC) is more effective for the control of selenium (selenite) over that of 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 more accessible selenium (water-soluble and exchangeable fractions) into the less accessible forms via a range of surface process (precipitation, reduction, complexation and surface adsorption), where the latter three were dominant mechanisms for Se 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 hierarchical porous structured polysulfide supported nano-zero valent iron/biochar and efficient immobilization of selenium in the soil.

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, and materials stabilization toward leaching and oxidation.

3.5.4 Selenium Rejection with Nanofiltration and Reverse Osmosis Membranes

From all pressure-driven membrane separation technologies, which includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis, only nanofiltration and reverse osmosis membranes were found to be effective for the treatment of selenium contaminated water (Santos et al. 2015; Stefaniak et al. 2018). Nanofiltration and reverse osmosis membranes 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).

Operating Principles of Nanofiltration/Reverse Osmosis Nanofiltration and reverse osmosis are membrane separation processes in which the driving force is the transmembrane pressure applied on a liquid to pass through a so-called semipermeable membrane. The target contaminant size in nanofiltration is in the nanometer range (e.g. multivalent ions and micropollutants), which corresponds to the approximate pore size of the membrane. In osmosis membrane, which is a typical process for seawater desalination, is used for the rejection of monovalent ions. The separation process for inorganics in nanofiltration/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 predominant by the size exclusion giving the high molecular weight and hydrated radius of both Se 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, Donnan exclusion mechanism, which represent the electrostatic interactions between the charged membrane surface and ions present in solution, is a further mechanism that contributes to the rejection of selenium species (He et al. 2016a, b). Schematic presentation of the main rejection mechanisms in nanofiltration/reverse osmosis membranes are shown in Fig. 3.6.

Variation of Selenium Rejection with Membrane and Water Type Various nanofiltration/reverse osmosis membranes were investigated for Se rejection from laboratory to full pilot scale and for different water types (Kharaka et al. 1996; He et al. 2016a, b, 2018c; Chung et al. 2010; Richards et al. 2011; Chehayeb and Lienhard 2017; Cingolani et al. 2018; Malhotra et al. 2020). Table 3.4 summarizes the work

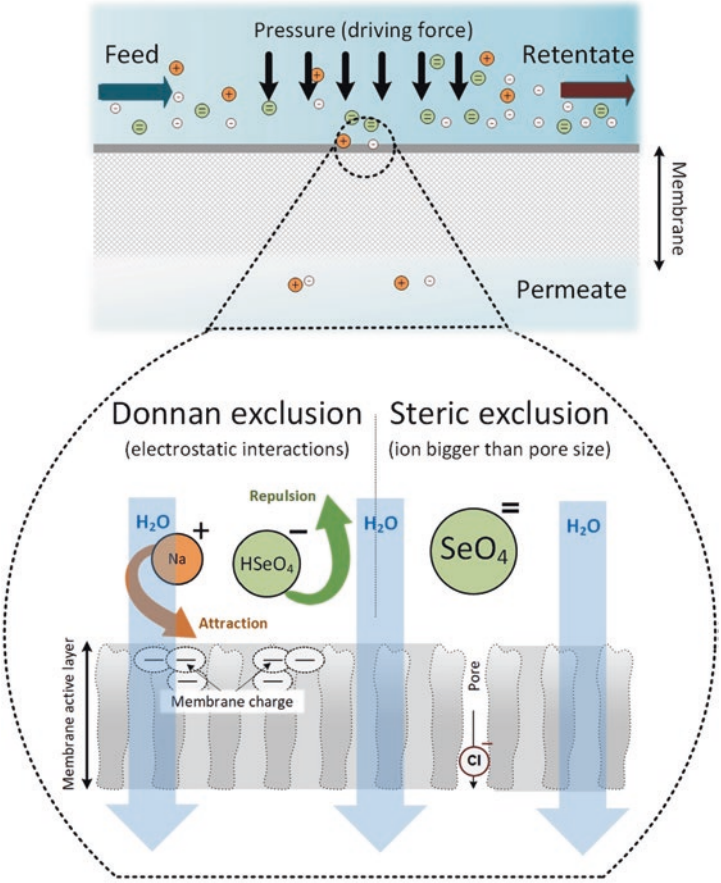


Fig. 3.6 Mechanisms of ion rejection in nanofiltration/reverse osmosis. (Source: Youssef-Amine Boussouga, Eggenstein-Leopoldshafen, Germany)

that has been reported to date on selenium rejection with nanofiltration/reverse osmosis. The rejection of selenium is generally higher with tight membranes (e.g. nanofiltration (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 as in water and given the importance of size exclusion and charge repulsion this may be an important contributing factor in retention.

Table 3.4 Selenium rejection with different nanofiltration/reverse osmosis membranes. Pressure in bar; flux in L/m^2 h; selenium rejection in %

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. (2016a, b)
POSS-PA TFN[b]	Synthetic solutions; 1000 mg/L, pH 7.5	10	54.0	96.5 for Se(IV) species	He et al. (2016a, b)
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, b, c)
TFC-50[b]		10	85.0	99.1 for Se(IV) species	He et al. (2018a, b, c)
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)

[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

Effect of Speciation on Selenium Rejection 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 Se forms in water (Chand and Prasad 2009). Se(IV) species are found in moderately oxidizing environment (moderate

concentration of dissolved O_2 as electron acceptor), while Se(VI) species are mostly present in oxidizing environment of 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) would be 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 Se is shown in Fig. 3.7. He et al. (2016a, b) have investigated the effect of the speciation on Se(IV) and Se(VI) rejection by varying pH during the filtration experiments with a laboratory made nanofiltration membrane (see Fig. 3.7). Higher rejection (>90%) of Se(IV) was observed at pH > 9, where the divalent SeO_3^{2-}

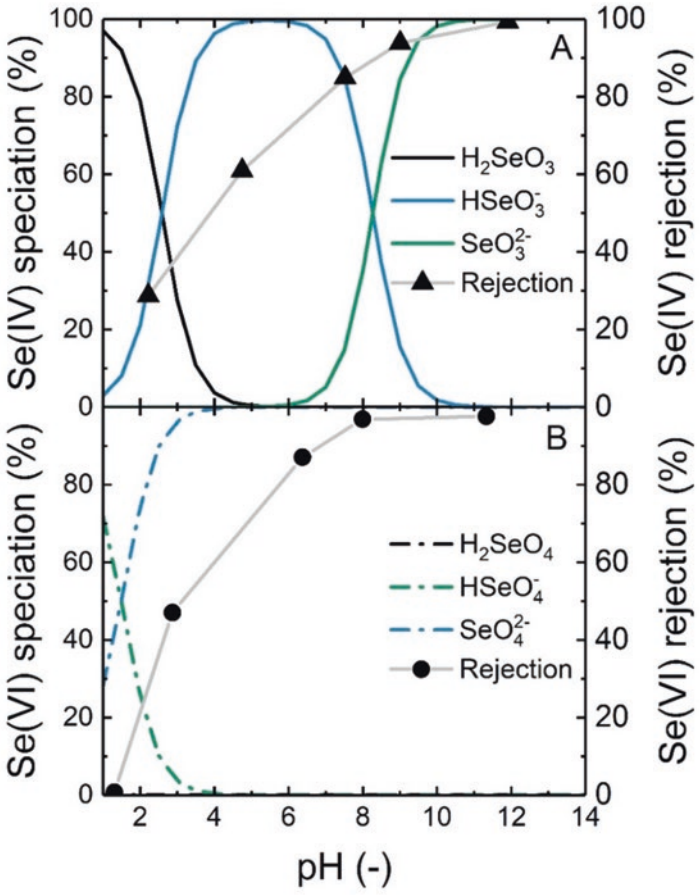


Fig. 3.7 Speciation of selenium (Se) and its rejection with laboratory-made TFN membrane, adapted from He et al. (2016a, b); speciation of Se(IV) and Se(VI) was calculated at 25°C and CO_2 partial pressure of $3.9 \cdot 10^{-4}$ bar, by using the software MINTEQ v.3.1, KTH, Sweden

becomes the dominant species as shown in Fig. 3.7a. In the other hand, the rejection of Se(VI) was higher than in the case of Se(IV) at all pH values due to the presence of the divalent SeO_4^{2-} species in water from pH > 4 (see Fig. 3.7b). Similar behavior was observed with commercial nanofiltration membranes used to remove Se(VI) (Malhotra et al. 2020). Further, it is noted that the increase in Se(VI) rejection with pH is influenced by the surface charge characteristic of the membrane that becomes more negative with increasing the pH, like 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 that are reviewed in the subsequent section.

Effect of Operating Conditions – Transmembrane Pressure and Recovery In addition to water chemistry, nanofiltration/reverse osmosis performance is also influenced by the 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. Regarding the recovery, which is the ratio of permeate production by feed volume, is also known by its influence on permeate quality and membrane fouling/scaling (Lee et al. 2015). Malhotra et al. (2020) have investigated the effect of transmembrane pressure on the Se(VI) rejection with loose (NF2) and tight (NF2) nanofiltration 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. 3.8. Results shows that, the rejection of Se(VI) increased with the transmembrane pressure and from 15 bar the rejection remained constant for both nanofiltration membranes (Fig. 3.8a). This behavior is explained by 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 (see Fig. 3.8b) has been attributed to the increase of Se(VI) concentration at the membrane surface (concentration polarization) which enhances the solute transport through the membrane (Chung et al. 2010). In addition, at higher recovery, the rejection of Se(VI) with the nanofiltration was more affected than with the reverse osmosis membrane where the ions transfer is known to be less convective and more diffusive (Pontié et al. 2008). In summary, the rejection of Se with nanofiltration/reverse osmosis membranes increases with transmembrane pressure whereas it decreases with the recovery. However, further in-depth investigations are still needed to work at high recovery and thus to decrease the retentate quantity without affecting the efficiency of the nanofiltration/reverse osmosis process.

Gaps in Knowledge in Selenium Removal by Nanofiltration/Reverse Osmosis Besides the studies on the effect of pH and ultimately the speciation on the rejection of selenium with nanofiltration/reverse osmosis, future studies that

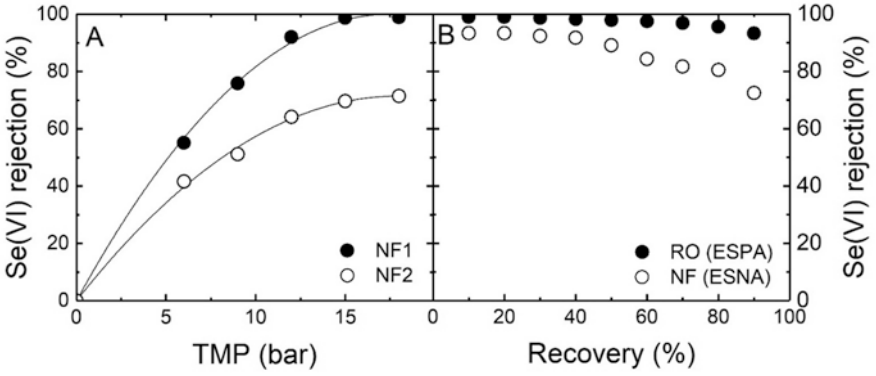


Fig. 3.8 Rejection of Se(VI) with nanofiltration/reverse osmosis membranes as a function (**a**) the transmembrane pressure (TMP) and (**b**) the recovery (source: (a) adapted from Malhotra et al. (2020): Se(VI) 1600 μg/L and pH 8; (b) adapted from Chung et al. (2010): S(VI) 326 μg/L, pH 7.2 and pressure 8 bar)

investigate the impact of the 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 Se and the complex transport mechanisms 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 (in case of cross flow systems) that effect mass transfer. For the process itself, much more dedicated work focused on system design and the optimization of the operating parameters to achieve zero liquid discharge and eventually lower specific energy consumption.

3.5.5 Selenium Removal Using Electrodialysis

Operating Principles of 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 are moved from the cathode to the anode, while cations move in the other direction. While counter-ions can pass through the ion exchange membranes, co-ions are repulsed from similarly charged membranes and cannot be transported across. The target in electrodialysis is to only remove charged ions, therefore electrodialysis is generally incapable of removing non-charged elements from water streams. Figure 3.9 shows the basic concept of an electrodialysis process. Electrodialysis is more energy efficient compared to reverse osmosis for desalinating brackish water. Specifically, in desalinat-

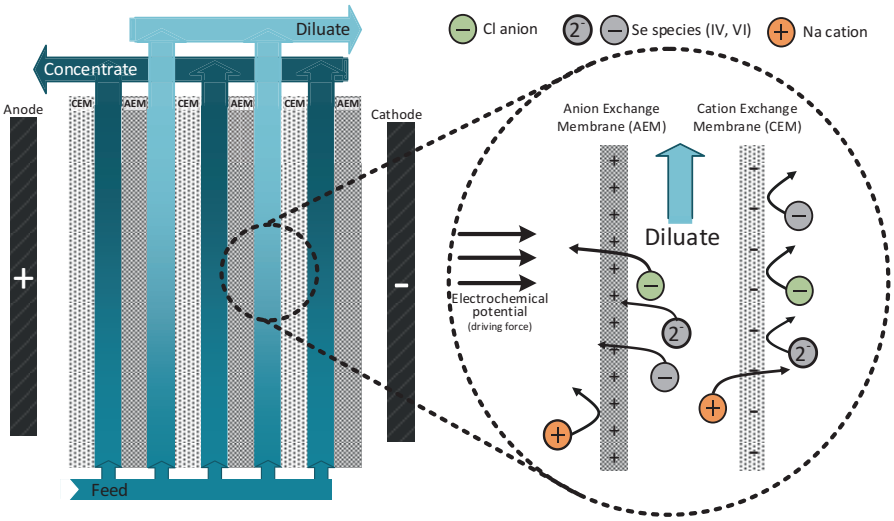


Fig. 3.9 Principle of an electrodialysis process. (Source: Mehran Aliaskari, Eggenstein-Leopoldshafen, Germany)

ing brackish water with salinity of 4 g/L total dissolved solids or less; this higher efficiency also depends on the recovery of the process and extent of salt removal (Karimi et al. 2015; Patel et al. 2021). Both selenium species, selenite (Se(IV)) and selenate (Se(VI)) are anions in the neutral pH range. In 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.

Effect of Operative Parameters on Selenium Removal by Electrodialysis 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 in different flowrates. The results suggest that at higher flowrates, double-charged ions show a somewhat increased transport compared to single charged ions. The higher transport of double-charged ions in higher flowrates is attributed to the thinner boundary layer, as the limiting factor for ion transport in electrodialysis is this layer, in which diffusivity and mobility of the ions play an important role in transport. Selenate is analogous to sulfate and has similar chemistry and diffusivity in water (see Table 3.5), therefore similar removal by electrodialysis can be expected for them. Sosa-Fernandez et al. (2019) show that an increase in current intensity had little impact on the final sulfate removal, and high sulfate removals up to 97% can be achieved when diluate solution is depleted of other anions such as chloride. However, Onorato et al. (2017) have investigated the effect of applied electrical potential on selenium removal. By an increase in electrical potential from 12 to 18 v, selenium removal is improved from

Table 3.5 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]	Nitrate[c]	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 Engineering Inc (2002)

33% to 48%. Karimi and Ghassemi (2015) have shown that electric potential has a bigger impact on divalent ions compared to monovalent ions. Figure 3.10 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 reported at 7 to 9, selenium is divalent in this pH.

Effect of Speciation on Selenium Removal with Electrodialysis In a general study with brackish water that contained some Se, Onorato et al. (2017) have also investigated Se removal as a function of pH. The brackish water had an electric conductivity of 8290 µS/cm (≈5.3 g/L NaCl). In this, selenate (Se(VI)) was the dominant Se species at a relatively low concentration of 20 µg/L (WHO guideline: 40 µg/L (WHO 2017)), while no data for selenite Se(IV) was reported. Removal of Se(VI) is shown in Fig. 3.10, along with speciation simulation for both Se(VI) and Se(IV) in 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. However, Based on the speciation of Se(IV) in Fig. 3.10, it is expected that Se(IV) removal would be maximum in between 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) in pH 8 to 11 (see Fig. 3.10) was attributed to the presence of calcium, which may have caused a co-precipitation 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 from these results. In the case of specific wastewaters that require pretreatment steps before the electrodialysis process, the pH of the feed must be considered as 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).

Effect of Competing Anions on Selenium Removal by Electrodialysis While electrodialysis can in principle remove trace selenium concentrations, presence of other anions in water may hinder Se removal through competition. While there is no data available for Se, this process is likely from observations with other similar ions. For

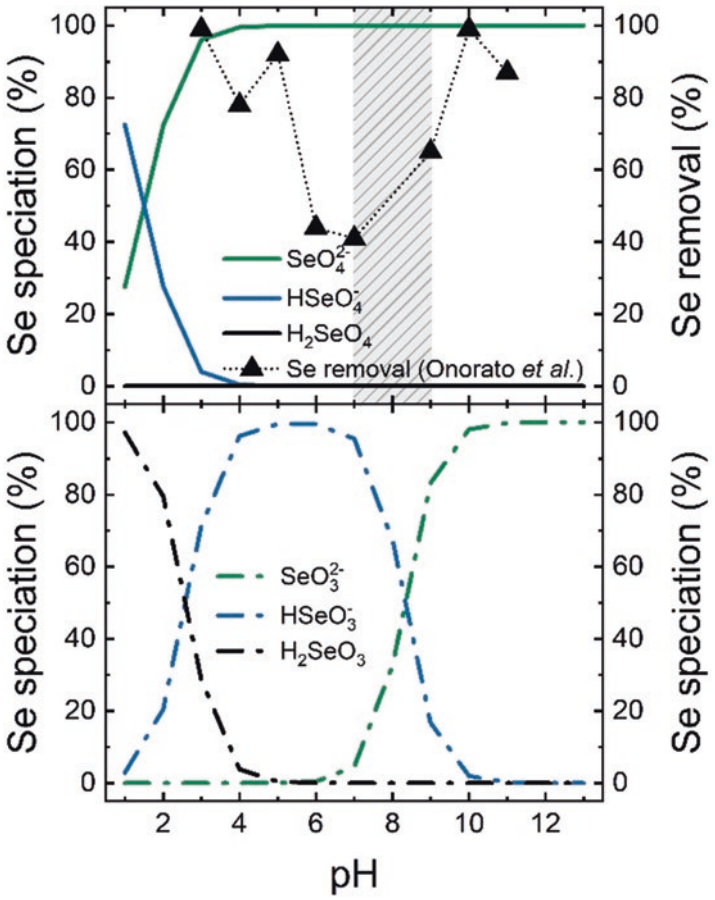


Fig. 3.10 Speciation of selenium VI (top) and IV (bottom) over pH 1 to 13 and removal of selenium VI, adapted from Onorato et al. (2017); electric potential 12 V; feed salinity 5.3 g/L; membranes Neosepta CMX-SB & AMX-SB, Tokuyama Soda Ltd., Japan; the highlighted pH range shows the real pH of sample water used which was then modified by adding HCl and NaOH)

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 expected that oxoselenium anions removal follow 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 in Table 3.5. Ionic mobility and diffusion coefficient of selenium species and different anions are presented in Table 3.5. 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.

Gaps in Knowledge in Selenium Removal by Electrodialysis Very few studies on Se removal by electrodialysis have been reported to date. Several handbooks (HDR Engineering Inc 2002) and patents (Wallace 2013a, b) mention electrodialysis as a process to remove selenium from water, 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 mentioned patents (Wallace 2013a, b), it is suggested to have 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 (Onorato et al. 2017) makes it difficult to conclude 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 Se removal.

3.5.6 Remediation of Solutions Containing Selenium 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, which are determined by their diffusivity and solubility in the membrane material. In nanofiltration, the separation of solutes results from a complex mechanism including steric hindrance dependent on the relative sizes of the pores and the solutes (Ferry 1936), Donnan exclusion resulting from the Coulomb interaction between charged solutes and the membrane fixed charge (Donnan 1995), dielectric exclusion in terms of both 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 (Table 3.6), which result in a high energy cost. Oppositely, ultrafiltration requires lower applied pressures while providing higher permeation fluxes, but the small solute removal performances are much lower due to larger pores.

Table 3.6 Comparison of different pressure-driven membrane processes

	Reverse osmosis	Nanofiltration	Ultrafiltration	References
Molecular weight cut-off (kDa)	<0.1	0.1-1	1-300	
Pore diameters (nm)	<0.5	0.5-2	2-100	
Transmembrane pressure (bar)	80-30	40-10	5-1	Aimar et al. (2010)
Permeation flux (L/hm^2)	10-60	50-100	50-500	Aimar et al. (2010)
Exclusion mechanisms	Solution-diffusion	Steric, electric and dielectric effects	Steric and electric effects	

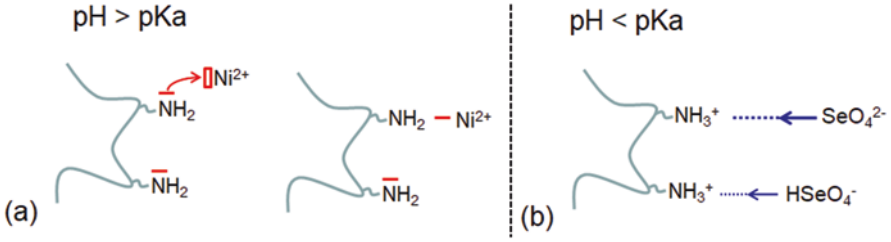


Fig. 3.11 (**a**) Complexation mechanism with metal ions, and (**b**) electrostatic attraction with oxyanions of Se(VI) by amine groups of polymers

However, the range of use of ultrafiltration can be enlarged towards solutes smaller than membrane pores by means of pretreatments such as micellization (Kryvoruchko et al. 2002; Witek et al. 2005; Chhatre et al. 2008) or complexation (Rumeau et al. 1992; Kryvoruchko et al. 2002; Mimoune et al. 2007). This preliminary treatment aims at increasing the effective size of ions for improving their rejection due to steric effects. This step is implemented by complexation of metal ions with either synthetic polymers, such as polyethylenimine (Molinari et al. 2004) poly(acrylic acid) (Cojocaru et al. 2007) and macrocycle and macromolecular compounds (Walkowiak et al. 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) (Fig. 3.11a) 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, as it is depicted in Fig. 3.11b.

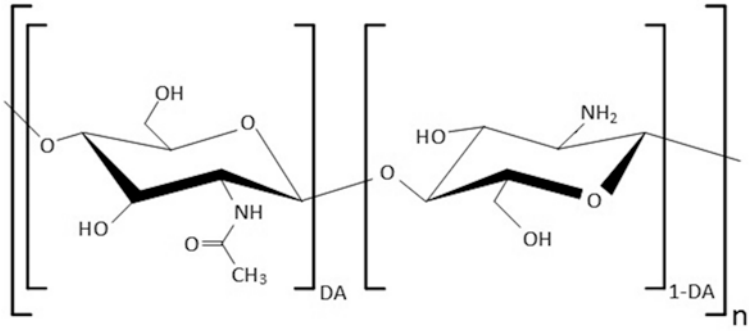


Fig. 3.12 Chitosan molecule. DA: degree of acetylation

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 its 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 (1-DA in Fig. 3.12) were protonated. Polymer then behaved like 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 the latter can be present in different forms depending on pH value. As shown by Fig. 3.13, for acid pH, Se(IV) can 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 Figs. 3.14a and b, respectively. It clearly appears 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 (pH = 4). In this pH condition, electrostatic attraction between the positive $–NH_3^+$ groups of chitosan and the negative charge of oxyanions allows 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. 3.14b). 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 ($HSeO_3^-$). Figures 3.14a and b also show that the permeation flux notably decreases when 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

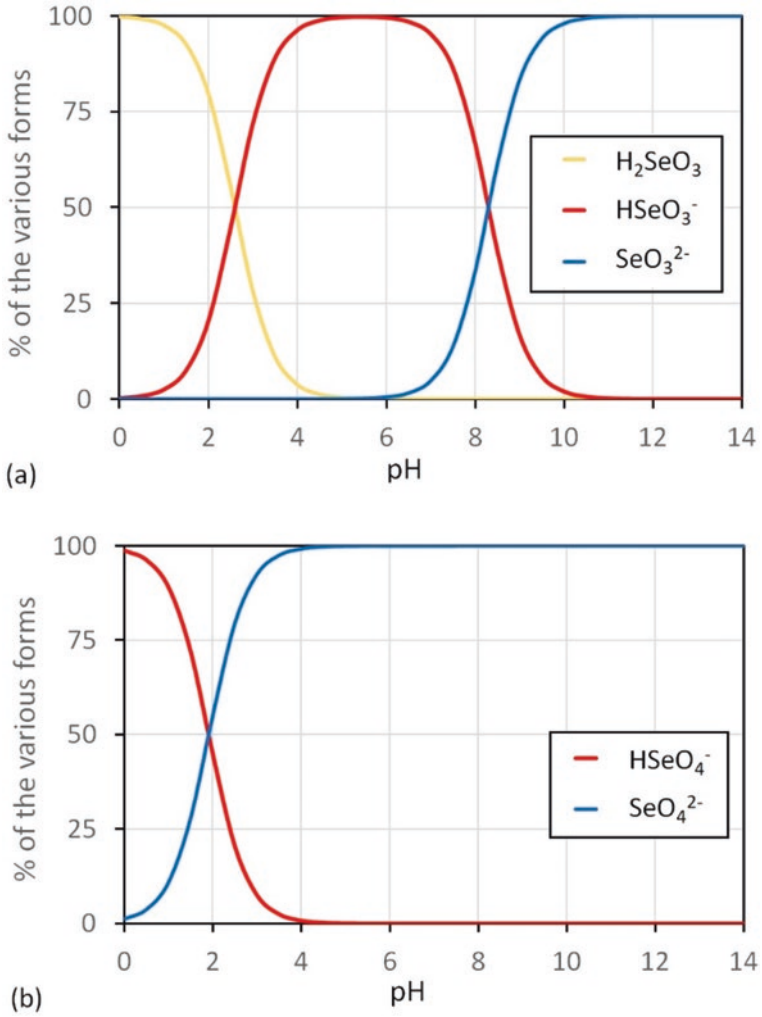


Fig. 3.13 Distribution diagrams of the various forms of a) Se(IV) and b) Se(VI)

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 on condition that polymer and selenium species have opposite charges and the ionic strength is sufficiently low in order not to screen the electrostatic interactions between oxyanions and polymer. Polymer-enhanced ultrafiltration appears as a potential option to remove anionic pollutants from wastewaters.

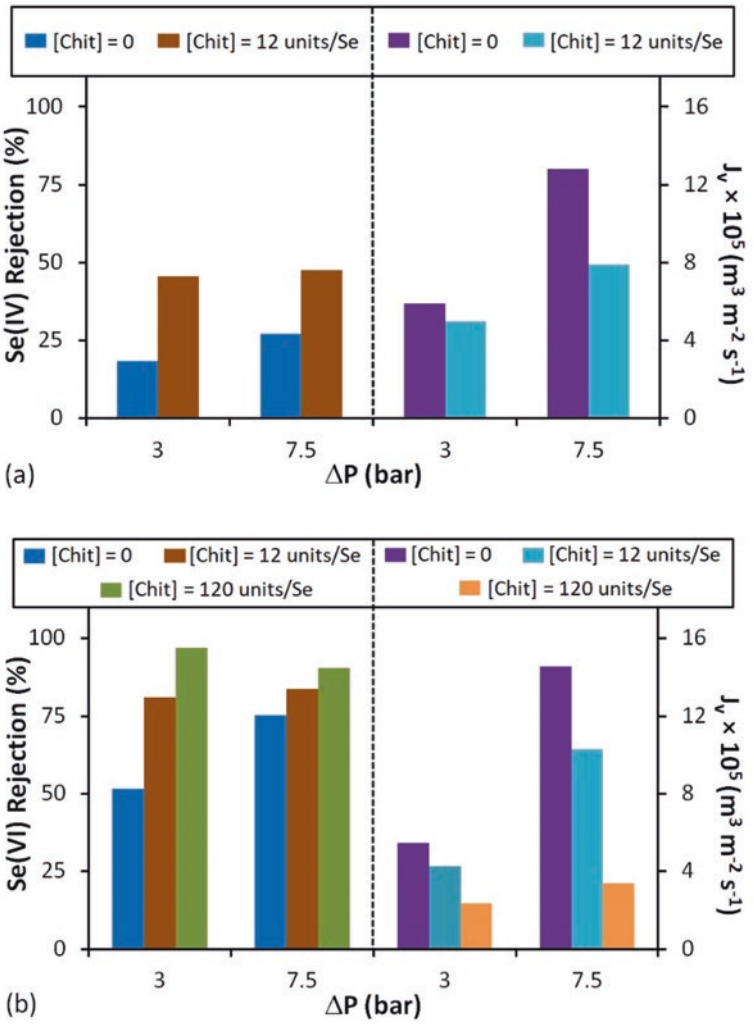


Fig. 3.14 Rejection and permeation flux obtained by ultrafiltration (CERAM 60 membrane, molecular weight cut off: 8 kDa) of solutions containing 1.7 mmol/L of (**a**) Se(IV) and (**b**) Se(VI) with and without chitosan at pH = 4

3.5.7 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 elimination of soluble Se 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/wastewater (Fig. 3.15). Such microbial Se metabolisms are mediated by different types of

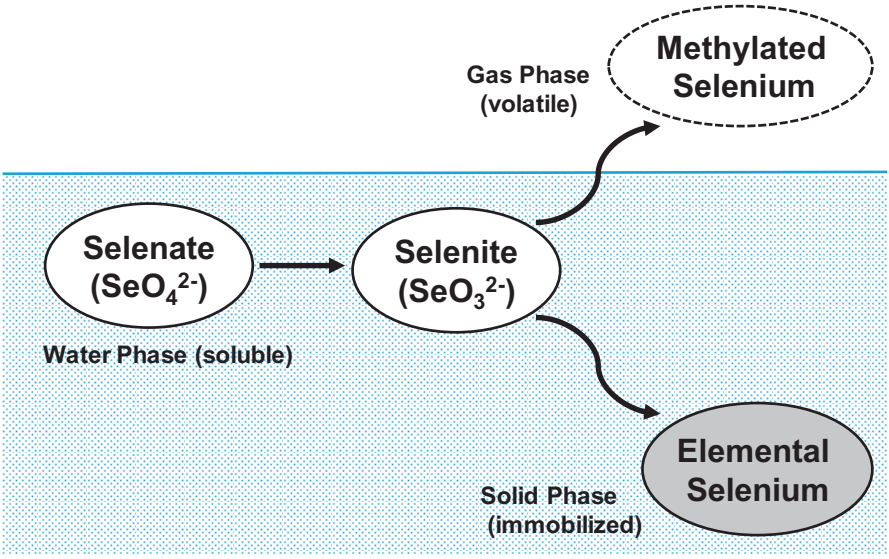


Fig. 3.15 Microbial selenium metabolism enabling the removal of soluble Se as selenate and selenite from the water phase. Selenate reduction into selenite proceeds mainly under anoxic conditions; selenite volatilization occurs mostly under aerobic conditions, while selenite reduction into elemental Se proceeds under both aerobic and anoxic conditions

microbes and are known to proceed under both aerobic and anaerobic conditions. Since various kinds of aerobic and anaerobic microbes exist in activated sludge, it possesses 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. 2019a). 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 they are considered the main contributors to selenate reduction (startup period; phases I and II). After almost complete removal of soluble Se 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 Se removal.

The selenium treatment performance of the sequencing batch reactor is shown in Fig. 3.16. In all treatment phases, selenate concentration in the effluent was maintained below the detection limit, and soluble Se was almost completely removed (>97%) without significant accumulation of selenite, independent of the length of the aeration step. However, a considerable amount of solid Se was found in the effluent as suspended solid-Se, and consequently removal of total Se was much lower than that of soluble Se. The suspended solid-Se concentration was maintained at relatively low levels, and the average total Se removal during the anoxic operation (phase III) was 88%. On the other hand, during alternating anoxic/oxic conditions (phases IV to VI), total Se 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 Se particles in the sequencing batch reactor and make them remain in the effluent.

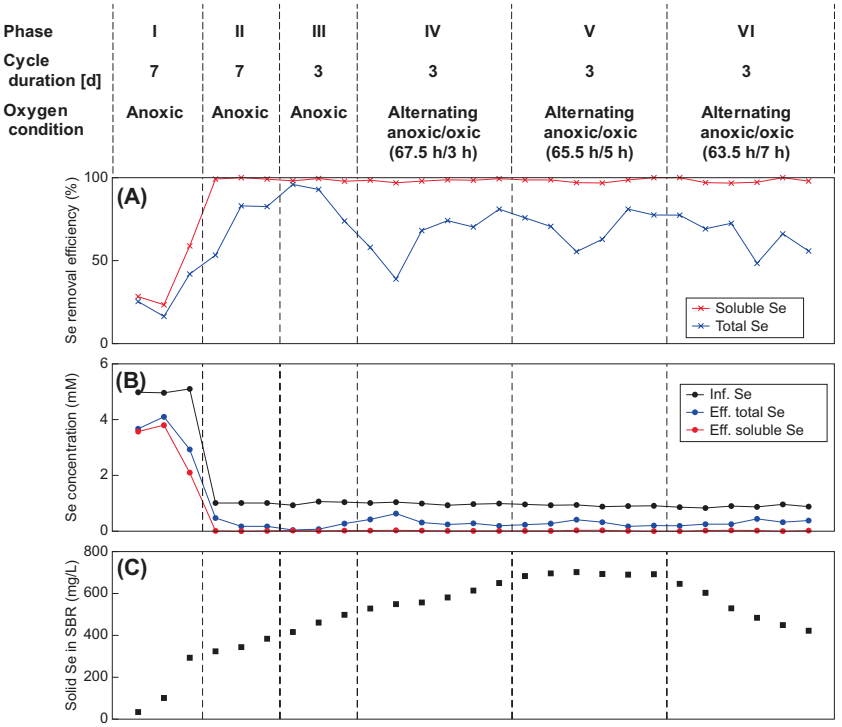


Fig. 3.16 Se removal performance of the sequencing batch reactor: (**a**) Se removal efficiencies; (**b**) Se concentrations in the influent and effluent; and (**c**) solid Se in the reactor. (Adapted from Zhang et al. 2019a)

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 Se, most likely elemental Se (bioimmobilization/bioprecipitation). The extension of the aeration period in phases V and VI clearly changed the fate of Se in the sequencing batch reactor; specifically, the amount of Se in the sequencing batch reactor was kept constant during phase V, and the amount of Se decreased during phase VI. Based on the selenium mass balance calculation, the disappearance of Se 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 (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 Se 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), 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 Se. Further, activated sludge can convert selenate to both solid Se and volatile Se, depending on the duration of the aeration period. Under anoxic conditions, selenate was reduced into elemental Se, which should be removed and disposed of as waste sludge, while biovolatilization of Se became efficient under prolonged oxic conditions and Se 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).

3.6 Conclusion

During the Renaissance, the Swiss physician and alchemist Paracelsus wrote: “All things are poison, and nothing is without poison; only the dose determines what is not a poison”. In other words, substances considered beneficial at low doses can be toxic in too large quantities. This is the case of selenium, which is considered an important trace element and at the same time a potentially dangerous emerging substance. At low doses, selenium is an essential nutrient for animal and human life. However, at high doses, it becomes toxic. Selenium is naturally present in the environment but it also has an anthropogenic origin (coal combustion, mining activities, phosphate fertilizer production, etc.). We can be exposed to selenium through its presence in soil, (drinking) water, air and food. One of the main sources of selenium exposure is tap water. In Europe, the maximum level to be respected at the

consumer's tap has been set at 10 µ/L, a threshold that is exceeded in many countries, including France. In general, it is drilling water from seleniferous areas that poses treatment problems. Selenium is currently the subject of much research both in terms of its chemistry (speciation), impact and toxicity, and also its elimination. However, in the field of water treatment, the problem is not simple. Indeed, when Se is present at trace levels, below 50 µg/L, in complex waters due to the presence of other substances, Se is a chemical substance very difficult to eliminate.

There are several treatment methods, each with its advantages and disadvantages, such as chemical precipitation, adsorption on conventional materials (metal oxides, alumina, coal), coagulation, electrocoagulation, ion exchange, membrane filtration (reverse osmosis, nanofiltration) or biological pathways (microbial reduction, phytoremediation, etc.). In France, for selenium removal to produce drinking water, adsorption treatment technologies are now preferred because of their efficiency, simplicity, residence times of less than a few minutes, and low-cost for point-of-use applications. For the treatment of industrial wastewaters, a combination of several processes is often necessary for reasons related to the different nature of the pollutants (including selenium) to be treated and especially to economic problems. Indeed, there is no single, low-cost process that can effectively and selectively remove selenium. At industrial scale, the coupling between coprecipitation and coagulation-flocculation process is used to remove selenium present in polycontaminated effluents. However, the scientific community remains interested in the development of new technologies for the elimination of selenium. The development of new processing methods is a topical issue, as evidenced by the many publications published in recent years. Among the new processes proposed, biosorption on non-conventional materials such as chitosan seems to be a promising way forward because this agri-food industry co-product is cheap and effective in eliminating trace forms of selenium.

Selenium will undoubtedly be one of the next priority substances to be addressed in the coming years, from a chemical, biological, ecotoxicological, health, economic and industrial point of view!

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