

Industrial Selenium Pollution: *Wastewaters and Physical–Chemical Treatment Technologies*

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Abstract Industrial activities including mining, metal and petrol refining, coal-fired power generation, and intensive agriculture may generate wastes and effluents loaded with selenium (Se). Currently, even if Se discharge is strictly regulated in North America, the large volumes of selenium-laden effluents produced represent a critical problem for both industry and environmental agencies. Numerous treatment technologies for Se removal based on physical and chemical processes have been tested at bench scale, pilot scale, and full scale, and several are commercially available. Physical treatment (e.g., membrane filtration and evaporative systems) can be effective in bringing the Se levels below the discharge standards, but it entails prohibitive operational costs due to high-energy consumption. Adsorption is a less financially demanding alternative treatment option; however, the competition with other anions present in real industrial effluents severely limits the Se removal performance. Chemical treatment has been tested for selenium removal, being mainly founded on the redox change of this element. Various reducing agents (e.g., zero-valent iron and sodium dithionite) have been tested mostly for synthetic wastewaters. pH plays a critical role in the effectiveness of the chemical treatment and, similarly to adsorption, the competition with other anions limits its performance. Several studies have coupled physical and chemical treatment systems in order to attain higher Se removal efficiencies. Residual products of Se treatment are generated by all physical–chemical treatment systems, incurring additional treatment and disposal costs.

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List of Abbreviations

AA	Activated alumina
BDAT	Best demonstrated available technology
COD	Chemical oxygen demand
DO	Dissolved oxygen
EC	Electrocoagulation
EES	Enhanced evaporation system
EP	Evaporation
EPRI	Electric Power Research Institute
Fe ⁰	Elemental (zero-valent) iron
Fh	Ferrihydrite
FGD	Flue gas desulfurization
GAC	Granular activated carbon
HRT	Hydraulic residence time
IEA	International Energy Agency
NAMC	North American Metal Council
NF	Nanofiltration
NSMP	Nitrogen and selenium management program
nZVI	Nanoscale zero-valent iron
ORP	Oxido-reduction potential
pH _{PZC}	Point of zero charge
RO	Reverse osmosis
SSW	Stripped sour water
Se	Selenium
Se ⁰	Elemental (zero-valent) selenium
SeO _x	Selenium oxyanions (selenite and selenate)
TCLP	Toxicity characteristic leaching procedure
TDS	Total dissolved solids
TOC	Total organic carbon
TSS	Total suspended solids
USBR	United States Bureau of Reclamation
USEPA	United States Environmental Protection Agency
ZLD	Zero liquid discharge
ZVI	Zero-valent iron

1 Introduction

Selenium (Se) is an element of concern that has caused several environmental disasters. Selenosis (i.e., *Se poisoning*) was first recognized as affecting terrestrial ecosystems, where plants growing on seleniferous soils accumulate Se to levels that become toxic for animals feeding on them (Raisbeck 2000). The medical condition known as ‘alkali disease’ leads to necrotic hooves, hair loss, poor growth, and even death of the exposed ruminant and monogastric animals (Hartikainen 2005). Starting mid-1970s, evidence also accumulated on the deleterious effects that Se oxyanions can exert to aquatic ecosystems. Several lakes were severely impacted by industrial Se discharge. Combustion ash from coal-fired power plants was deposited in the vicinity of Lake Belews, NC, USA (Lemly 2002) and Martin Lake, TX, USA (King et al. 1994). Selenium leached gradually in the lake leading to mass mortality of local fish populations. Selenium also caused congenital deformities and reproductive failures in migratory bird populations surrounding Kesterson Reservoir (San Joaquin Valley, CA, USA) (Ohlendorf 1989). The mechanism of Se toxicity has still to be clarified. Some of its pathogenesis indicators are glutathione depletion and secondary lipid peroxidation, alongside reactive oxygen species (ROS) (Reilly 2006).

Selenium concentrations in the environment vary greatly from region to region and are mainly associated with fossil fuels (e.g., petroleum, coal, and bituminous shales), sulfidic minerals, and seleniferous soils (Chapman et al. 2010). Due to anthropogenic activities such as mining, coal-fired power generation, metal and oil refining, and crop irrigation, the presence of Se in aquatic and terrestrial ecosystems increases at an accelerating pace. A variety of wastewaters related to industrial activities contain concentrations of Se that greatly exceed the discharge limits (e.g., $5 \mu\text{g L}^{-1}$) (see Sect. 3.5). As a solution to the environmental disasters triggered by Se (e.g., Lake Belews and Kesterson Reservoir), industry and academia proposed a number of physical and chemical treatment processes attempting to decrease Se levels present in wastewaters below the set limits.

This chapter begins with a brief introduction into the aquatic chemistry of selenium, followed by a detailed presentation of the main types of Se-laden industrial wastewaters. It then provides an overview of the physical and chemical systems employed for treating these effluents. We discuss the mechanistic bases and advantages and disadvantages of each treatment technology presented.

2 Aquatic Chemistry of Selenium

Speciation plays a critical role in the environmental mobility and toxicity of selenium. Table 1 presents the main inorganic Se species, their water solubility, and ecotoxic potential. Selenium species with the highest valence states, selenate (Se

Table 1 Inorganic species of the element selenium (modified from Fernandez-Martinez and Charlet 2009)

Species	Chemical formula	Solubility in water	Toxicity
Selenate [Se(+VI)]	$\text{H}_2\text{SeO}_4^0, \text{HSeO}_4^-, \text{SeO}_4^{2-}$	High ^a	High
Selenite [Se(+IV)]	$\text{H}_2\text{SeO}_3^0, \text{HSeO}_3^-, \text{SeO}_3^{2-}$	High ^b	High
Elemental selenium [Se(0)]	Se^0	Insoluble	Low*
Selenides [Se(-II)]			
Hydrogen selenide	H_2Se	Low	High
Metal selenides (e.g., CdSe)	$\text{M}^{2+}\text{Se}^{2-}$	Insoluble	High
Selenocyanate	SeCN^-	Soluble	High**

Notes ^a58.5 g 100 mL⁻¹ (as Na₂SeO₄); ^b89.8 g 100 mL⁻¹ (as Na₂SeO₃) (Lide 2004)

*Toxicity in relation to ecological receptors

See **Box for more details

[+VI], SeO_4^{2-}), and selenite (Se[+IV], SeO_3^{2-}) are highly water-soluble, bioavailable, and toxic (Simmons and Wallschlaeger 2005). Both are oxyanions, or SeO_x , and are the main forms present in industrial effluents. Additional characteristics, such as limited interaction with cations (entailing limited precipitation potential) and high stability over the entire pH range, make SeO_x persistent in aquatic solutions/ecosystems (Chapman et al. 2010).

Elemental selenium (Se^0), having a solid state and negligible water solubility, is considered practically non-toxic (Lenz and Lens 2009). However, several studies reported its adverse effects against ecological receptors including filter-feeding mollusks and fish (Chapman et al. 2010). The bioremediation approach employed by various bioreactor systems relies on the microbial conversion of SeO_x into Se^0 (Staicu et al. 2015a).

Selenide, Se[-II], is the most reduced valence state of Se, being only found under strongly reducing conditions. Among inorganic selenide compounds, H_2Se , metal selenides, and selenocyanate (SeCN^-) are highly toxic. Metal selenides can form when SeO_x are reduced to Se[-II] and metal cations are available, since selenides display high reactivity. In contrast to hydrogen selenide and metal selenides, selenocyanate is water-soluble and, therefore, more environmentally mobile. Energy and oil processing industries generate wastewaters containing H_2Se and SeCN^- (NAMC 2010). Organic selenides including methylated species (e.g., dimethylselenide, DMSe), amino acids (e.g., selenocysteine and selenomethionine), and metabolic products (e.g., trimethylselenonium) also exist, but they are not the focus of this chapter.

3 Industrial Pollution Associated with Selenium

Anthropogenic activities involving Se-rich materials result in the liberation of Se as gaseous (e.g., volatile coal combustion products), solid (e.g., coal ash), and liquid (e.g., industrial wastewaters) wastes. Of these, wastewaters are the greatest challenge for industry and the focus of this chapter. Tables 2, 3, and 4 provide information on the characteristics of common Se-containing wastewaters, which are highly variable in their composition due to differences in the levels of Se and other elements in the raw material, variability of the feedstock, the technology used to

Table 2 Characteristics of the main types of Se-laden wastewater

Parameter	FGD ^a	Mine water ^b	Oil refinery (SSW) ^c	Agriculture drainage ^d
pH (s.u.)	6.39–7.71 (7.07)	7.7–7.9 (7.8)	6.4–8.3 (7.25)	7.7–7.9 (7.8)
Conductivity (mS cm ⁻¹)	8.19–39.6 (20.5)	0.5–3	2.8–8.5 (3.4)	14.2–19 (17.2)
ORP (mV)	140–539 (289)	120–380	-227–63 (-58)	n/a
Alkalinity* (mg L ⁻¹)	37.5–165 (60)	55–160	180–210 (200)	250–301 (279)
Hardness* (mg L ⁻¹)	n/a	993–1120 (1060)	250–330 (298)	2.3–2.46 (2.4)
TSS (mg L ⁻¹)	9–68 (31)	5–100	11–102 (46)	41.4–61.8 (49.5)
TDS (g L ⁻¹)	13–29 (19.7)	<20	1.4–2.3 (1.96)	10.7–17 (13.3)
COD (g L ⁻¹)	31–57 (44)	<50	60–648 (225)	18.2–58 (35.5)
Ca ²⁺ (g L ⁻¹)	(3.7)	(0.42)	(0.1)	(0.5)
Mg ²⁺ (g L ⁻¹)	(0.64)	(0.4)	(0.02)	(0.3)
Na ⁺ (g L ⁻¹)	(0.05)	(0.014)	n/a	(4.33)
F ⁻ (mg L ⁻¹)	3.9–24.5 (8)	0.1–10 (0.8)	n/a	n/a
Cl ⁻ (g L ⁻¹)	3.7–15.3 (7.5)	(0.02)	0.67–0.80 (0.73)	1.9–3.4 (2.9)
Br ⁻ (mg L ⁻¹)	24.8–130 (45)	0.5–5 (1.6)	n/a	n/a
HCO ₃ ⁻ (mg L ⁻¹)	62**	579**	n/a	286–301 (292)
NO ₃ ⁻ (mg L ⁻¹)	11.4–45.2 (25.7)	(218)	1.8–11 (5.5)	174–212 (193)
SO ₄ ²⁻ (g L ⁻¹)	0.8–1.3 (1.46)	1.8–2.1 (1.9)	0.20–0.52 (0.37)	5.5–7.4 (6.6)

^a*n* = 158 (sampling period: 06/16/2014–05/27/2015); ^b*n* = 11 (21/06/2015–08/09/2015)

^c*n* = 84 (08/03/2011–10/24/2011); ^d*n* = 17 (06/18/2014–10/07/2014)

*As CaCO₃ (mg L⁻¹)

**determined on a representative sample

Note In brackets is presented the average value, n/a not-available

Acronyms FGD: flue gas desulfurization, SSW: stripped sour water, ORP: oxido-reduction potential, DO: dissolved oxygen, TSS: total soluble solids, TDS: total dissolved solids, and COD: chemical oxygen demand

Table 3 Elements present in trace amounts in the main types of Se-laden wastewater

Trace element*	FGD ($\mu\text{g L}^{-1}$)	Mine water ($\mu\text{g L}^{-1}$)	Agriculture drainage ($\mu\text{g L}^{-1}$)
Al	2343	400	0.8
As	1172	100	24
B	179.6	100	45
Cd	110	10	0.2
Hg	57	n/d	0.1
Mn	2564	10	0.1
Ni	242	30	4.1
Pb	97	50	n/d
Si	22.7	4700	46
Sr	9606	220	6973
Zn	1682	10	0.3

Note *average values, n/d not-detected

Table 4 Selenium speciation in the main types of Se-laden wastewater

Se species	FGD ($\mu\text{g L}^{-1}$)	Mine water ($\mu\text{g L}^{-1}$)	Oil refinery (SSW) ($\mu\text{g L}^{-1}$)	Agriculture drainage ($\mu\text{g L}^{-1}$)
SeO_4^{2-}	2778	389	20.9	185
SeO_3^{2-}	26.2	14	112	1.15
SeCN^-	25	n/a	0.26	n/a

process/transform the material, and the way the effluent is managed. This variability is a challenge for effective treatment.

3.1 Wastewaters Associated with Coal Combustion

Coal combustion in power generation facilities results in the production of Se-enriched solid wastes (e.g., bottom ash and fly ash) and flue gas emissions (including volatile selenium species) to the atmosphere. Coal is currently the source of $\sim 40\%$ of the world's primary energy (IEA 2014). China, in particular, is increasingly relying on coal to fuel its economic development (IEA 2013). The most studied Se-laden effluents generated by coal combustion are *ash pond water* and *flue gas desulfurization water*.

3.1.1 Ash Pond Water

The ash resulting from coal burning is sluiced into settling basins. The water from settling basins is alkaline and contains mainly selenite and selenate (Liu et al. 2013). Apart from pH, redox potential is also a key parameter controlling Se mobilization

from ash (Schwartz et al. 2016). The enrichment factor (ratio of initial Se in coal to Se in ash) can be up to 800 (Table 1). This Se-bearing water is periodically discharged into the receiving natural waters or can accidentally overflow. During one such accident (December 22, 2008), 1.5 million tons of ash and around 10 million tons of slurry (a mixture of fly ash and water) from the solid-waste-containment area of a Tennessee Valley Authority (TVA) coal-fired power plant were discharged as a result of a dike failure. The slurry covered 1.2 km² of surrounding land, damaging homes and contaminating the nearby Emory River and Clinch River (TVA 2009). The environmental impact of this accident was studied in an 18-month survey. The survey showed that although the river water was relatively low in leachable coal ash contaminants, such as arsenic, selenium, boron, strontium, and barium, elevated concentrations of these contaminants were found in river sediments (Ruhl et al. 2010). This entails the potential of Se mobilization by anthropogenic or natural sediment disturbance. Other examples of Se pollution from coal ash are Martin Lake (Texas), Lake Belews, and Lake Sutton in North Carolina (Lemly 2014).

Lake Sutton was constructed in 1972 as a cooling reservoir for a coal-fired electric generating facility in North Carolina, and it became a popular fishing location. Selenium enters Lake Sutton via ash wastewater and bioaccumulates in the aquatic food networks leading to teratogenic effects in fish populations. In a recent survey, around one-third of the juvenile bluegill (*Lepomis* spp.) exhibited spinal and craniofacial malformations including permanently deformed gill cover and deformed skull (Fig. 1). The cost of fishery loss, based on *Lepomis* spp. alone, was estimated at over \$US 8.6 million annually (Lemly 2014).

3.1.2 Flue Gas Desulfurization

In order to curb acid rain occurrence, environmental authorities imposed the deployment of scrubbers for the removal of sulfur oxides from coal-fired plant exhaust flue gases (i.e., flue gas desulfurization, FGD). Wet limestone FGD is most widely used because it has a better desulfurization performance and lower operating costs compared to other FGD technologies (Cordoba 2015). Sulfur oxides react with an alkaline reagent (e.g., lime and limestone), leading to the production of gypsum (CaSO₄) solid and a process water enriched in Se. Along with Se, other major constituents are calcium (several g L⁻¹), chloride (3–20 g L⁻¹), and sulfate (several g L⁻¹) (Table 2). In addition, FGD contains a broad spectrum of toxic metals such as lead, mercury, nickel, and strontium (Table 3). Depending on the feed coal, other toxic elements are cadmium, molybdenum, and uranium (Cordoba et al. 2011). Of all the known Se-contaminated wastewaters, FGD has the highest reported electrical conductivity, up to 30 mS cm⁻¹. High conductivity increases the corrosive characteristics of the effluent.

In most FGD effluents, selenate is the main Se form present, whereas selenite and selenocyanate are minor species (Table 4; NAMC 2010). However, the type of FGD system affects the speciation of selenium in the FGD effluent. For power plants that have forced oxidation, Se is predominantly present as selenate. Conversely, in

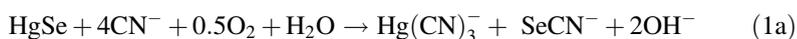


Fig. 1 Bluegill (*Lepomis macrochirus*) from Lake Sutton (North Carolina) with deformities that resulted from teratogenic effects of selenium poisoning. *Top* abnormal individual; *bottom* normal individual. Photo courtesy of A.D. Lemly and L.P. Lemly

systems that do not use forced oxidation, the selenite concentration is higher approximately equivalent to the selenate concentration (EPRI 2006). Selenium speciation in FGD is complex and involves other less common selenium forms, such as selenosulfate, selenomethionine, and methylseleninic acid (NAMC 2010).

Box 1. Selenocyanate. Toxicity and removal

Selenocyanate (SeCN^-) is a selenium species that is thermodynamically more stable than the oxyanions selenite and selenate (Kyle et al. 2012). Selenocyanate can be formed through metal selenide and Se^0 dissolution and to a lesser extent SeO_x reduction in the presence of the cyanate ion (CN^-) (Kyle et al. 2012). Metal selenide minerals (e.g., HgSe) dissolve in cyanide solutions to form metal cyanide complexes and the selenocyanate ion according to Eq. 1a:



In addition, selenite and selenate oxidize cyanide (CN^-) to cyanate (OCN^-) ions, while the two oxyanions are reduced to form SeCN^- , according to Eqs. 2a and 3a:



Selenocyanate can form complexes with cadmium, mercury, gold, zinc, and iron (Kyle et al. 2012). Because these are less stable than the corresponding cyanide complexes, they will form in significant amounts only in the presence of low cyanide concentrations (Norbury 1975; Kyle et al. 2011). Selenocyanate has been identified in oil refining and FGD wastewaters (NAMC 2010). In gold mine wastewater, SeCN^- is the main selenium species (Wallschläger and Bloom 2001). Cyanidation is currently the main metallurgical technique employed for extracting gold from low-grade ores. Although the selenocyanate ion is considerably less toxic than thiocyanate, several studies on rat metabolism have indicated adverse effects that include weight gain depression, moderate renal tubular interstitial nephritis, and moderate-to-severe hepatic hypertrophy (Conaway et al. 1992). Rats injected subcutaneously with selenocyanate excreted dimethylselenide in the breath and trimethylselenium ion in the urine. These results indicate that a substantial part of selenocyanate in the body is metabolized and excreted in methylated forms (Vadhanavikit et al. 1987). Treatment of SeCN^- can be accomplished using powerful oxidants (e.g., hydrogen peroxide, chlorine dioxide, and ozone) in a manner similar to cyanide mineralization (Kyle et al. 2012). The oxidation of selenocyanate is complicated by chemical oxygen demand and ammonia, which consume the oxidizing agent. Another challenge is controlling oxidation up to selenite only. Copper precipitation of selenocyanate has been documented at elevated pH (9–10) resulting in around 95% removal (Manceau and Gallup 1997). The removal of selenocyanate from solution by reductive precipitation to Se^0 using Fe^0 has also been investigated (Meng et al. 2002). Ion exchange has been applied, but high levels of sulfur ions and TDS reduce its effectiveness (NAMC 2010).

3.2 Mining

The mining of coal, phosphate, and sulfidic ores is a significant source of Se pollution. Mining activities are deployed as surface and pit operations, and both produce waste rock (overburden) that is the primary source of Se pollution. Surface mining involves the removal of several hundred meters of overburden to reach the deep mineral deposits, resulting in the production of huge volumes of waste rock (Griffith et al. 2012). The overburden is placed in areas called overburden disposal areas or put back in the pit. When the overburden comes into contact with air and

water (precipitation, groundwater intrusion, surface runoff, or snow melt), oxidative weathering occurs leading to Se leaching and solubilization. Seeps containing Se levels up to $2000 \mu\text{g L}^{-1}$ develop near the base of the overburden piles (Knotek-Smith et al. 2006). A recent study indicates that the volume of mining waste rock represents roughly 80% of the Se load from the Elk Valley (Canada), and wet years contribute more than twice the Se load of dry years (Wellen et al. 2015). Other potential Se sources related to mining activities are tailings, coarse-rejects stockpiles, coal storage, breaker rejects, ash from coal-fired dryers, and coal spillage (Chapman et al. 2009). End-pit lakes are drainage collection pools (groundwater infiltration and surface runoff accumulation) that remain as a heritage of open-pit mining after the cessation of dewatering operations. These drainage basins have high Se concentrations and are of particular concern due to wildlife exposure (Luek et al. 2014).

Apart from Se, mainly found as selenate, mine waters also contain high levels of nitrate, sulfate, and bicarbonate alkalinity (Table 2) that increase the buffering capacity of the wastewater. Buffering is particularly relevant when treatment technologies require specific pH ranges to achieve optimal performance. Then, addition of acids and bases is required for pH adjustment. In addition, bicarbonate can react with products used in the pre-treatment step of the wastewater. For example, HCO_3^- reacts with BaCl_2 used for sulfate removal (Staicu et al. 2017), entailing additional costs for reagents and disposing of larger sludge volumes.

3.3 *Petroleum Refinery Effluents*

The refining of crude oil to fuels, other petrochemicals, and elemental sulfur results in the production of wastewaters. The majority of Se contained in crude oil goes into the stripped sour water (SSW) streams that result from the collection of gases associated with crude oil distillation, catalytic cracking, and sulfur recovery. At acidic to neutral pH, the predominant forms of Se in SSW are hydrogen selenide and hydrogen selenocyanate (NAMC 2010). Extremely low pH values (<1) have been reported for petroleum refinery effluents (Soda et al. 2011). A secondary source of Se is generated through the crude oil dewatering and desalting, taking place prior to the refining process. Both effluents are typically combined, resulting in a complex waste stream (Table 2). Selenium can be found in SSW in concentrations ranging from 1000 to $5000 \mu\text{g L}^{-1}$ (Twidwell et al. 2005).

Petroleum refinery wastewaters contain oil and greases, phenols, sulfides, ammonia, cyanides, nitrogen compounds, suspended solids, and metals and metalloids such as Cr, Mo, Ni, V, Zn, and Se (Wake 2005). In contrast to most Se-bearing industrial effluents, the refinery waste streams contain selenite as the main Se form, with selenate second (Table 4). Another particularity of these effluents is their negative oxido-reduction potential (ORP, -50 to -250 mV).

3.4 Agricultural Drainage Water

Extensive soil areas in California are naturally rich in selenium, and irrigation of agricultural lands has led to the mobilization of Se into subsurface drainage water. Agricultural drainage water contains selenium mainly in the form of SeO_4^{2-} (Table 4). Selenium concentrations up to $4200 \mu\text{g L}^{-1}$ (typically as selenate) were found in contaminated drainage water in western San Joaquin Valley (California) (Kharaka et al. 1996). Additionally, nitrate from fertilization is present in concentrations of $45\text{--}92 \text{ mg L}^{-1}$ (Squires et al. 1989). Sometimes high levels of sulfate ($\sim 5000 \text{ mg L}^{-1}$), chloride ($\sim 2000 \text{ mg L}^{-1}$), and HCO_3^- ($\sim 350 \text{ mg L}^{-1}$) are also present (Macy et al. 1993).

3.5 Regulatory Limits

Selenium is a freshwater priority pollutant for the existing US Water Quality Criteria, with a Criterion Continuous Concentration (or chronic level) of $5 \mu\text{g L}^{-1}$ (USEPA 2013). Recently, USEPA updated the effluent guidelines for the steam-generated power industry Se discharge to $12 \mu\text{g L}^{-1}$ (monthly average) and a daily maximum limitation of $23 \mu\text{g L}^{-1}$ (USEPA 2015). In Canada, the set limit for total selenium content in surface waters is $1 \mu\text{g L}^{-1}$ (Canadian Council of Ministers of the Environment 2007). According to European Union's environmental legislation, selenium is not listed as a priority pollutant. In Japan, irrespective of the industrial source, the discharge limit for Se is $100 \mu\text{g L}^{-1}$ (Nishimura et al. 2007).

4 Physical Treatment Technologies

Among the physical methods used for SeO_x removal, the most often used are membrane filtration, evaporation, and sorption.

4.1 Membrane Filtration Processes

4.1.1 Reverse Osmosis

Reverse osmosis (RO) is a physical separation process that uses semipermeable membranes capable of rejecting most solute ions and molecules, while allowing water of very low mineral content to pass through. RO requires high transmembrane pressures ($\sim 2 \text{ MPa}$) and is typically restricted to recoveries below $\sim 70\%$ (Chellam and Clifford 2002).

RO has been employed at pilot scale and full scale to treat mining effluents and agricultural drainage (NAMC 2010). Mine water produced at Barrick Richmond Hill Mine (South Dakota, US) was treated by RO after an iron reduction and precipitation pre-treatment stage. The final Se content was reduced from 22 to 2 $\mu\text{g L}^{-1}$ with the brine being recirculated to the iron treatment step (Alberta Environment 2013). An emergency RO treatment system was implemented to treat mine water stored in an impoundment from a former gold mine in California (Golder 2009). The treatment was effective by reducing 60 $\mu\text{g L}^{-1}$ selenium to $<5 \mu\text{g L}^{-1}$ within a 4-month operation time. A full-scale hybrid application (RO + biological treatment) was designed to reduce selenium (30 $\mu\text{g L}^{-1}$) and total dissolved solids (TDS) (5000–8000 mg L^{-1}) from a Western US metal mine waste rock leachate to be released to surface waters (Gusek et al. 2008). The Se-enriched reject stream produced by RO was further subjected to an anaerobic bioreactor treatment with the goal of dropping the selenium level to below 10 $\mu\text{g L}^{-1}$. On a pilot-scale basis, RO has been tested for agricultural drainage water in Red Rock Ranch (California) having 760 $\mu\text{g L}^{-1}$ Se in the influent and only 1 $\mu\text{g L}^{-1}$ in the effluent (USBR 2008).

RO, while being effective in the reduction of Se concentration in the final effluent (permeate), the reject stream accumulates and concentrates the contaminants, therefore requiring additional treatment. Physical, chemical, and biological treatments, alongside deep injection in stable geological formations, are employed to further treat or dispose of these rejects (NAMC 2010). The RO reject stream (concentrate) can be landfilled provided it meets the disposal requirements of the site. Paint filter testing (USEPA approved test method to determine the presence of free liquids in a waste sample) and toxicity characteristic leaching procedure (TCLP) testing (analytical method that simulates the leaching capacity of a material disposed of in a landfill) are required for waste management (NAMC 2010).

4.1.2 Nanofiltration

In nanofiltration (NF), the membrane has a higher pore size than RO, and therefore, a lower transmembrane pressure is required ($\sim 0.5\text{--}1 \text{ MPa}$) (NAMC 2010). In addition, NF can be operated at recoveries $\sim 85\%$ and are cost-competitive with conventional water treatment (Wiesner et al. 1994).

A laboratory-scale NF system was used to treat Se-containing agricultural drainage water (Kharaka et al. 1996). The authors reported over 95% removal efficiency from a 1000 $\mu\text{g L}^{-1}$ initial Se concentration. This laboratory study was followed by a pilot study in the Imperial Valley of California. The Se influent concentrations were decreased from 42–63 $\mu\text{g L}^{-1}$ to 1.0–3.2 $\mu\text{g L}^{-1}$ (USBR 2002). Another laboratory-scale study treating uranium mill wastewater by iron coagulation at pH 10 followed by NF reported a 96–98% Se removal efficiency from an initial selenium load of 550 $\mu\text{g L}^{-1}$ (Chellam and Clifford 2002).

One of the main limitations of using membrane filtration (RO and NF) is scaling. Hard waters containing Ca^{2+} and Mg^{2+} ions form salts, thereby damaging or

impairing the function of the membrane. In addition, other parameters should be considered, including TDS, total soluble solids (TSS), alkalinity, total organic carbon (TOC), sulfate, silica, chloride, iron, and the bacterial–algal fouling potential. To overcome fouling, a filtration pre-treatment stage is necessary, but this will add 10–20% to the overall cost of the treatment (Alberta Environment 2013). A marked difference between NF and RO is the amount of hydraulic pressure put to achieve the same separation efficiency, NF requiring one-third of the pressure needed by RO (Alberta Environment 2013). Also, less wastewater pre-treatment is required for NF than conventional RO membranes (Kharaka et al. 1996).

4.2 Evaporation

4.2.1 Evaporation Ponds

Evaporation ponds (EP) are used in arid regions where the annual potential evaporation exceeds the annual precipitation, thus creating a water deficit (NAMC 2010). Solar radiation is used as the main energy source, and the wastewater is stored in lined ponds. EP have been employed to treat selenium-bearing agricultural drainage water in Tulare Lake Drainage District (California, US), but this approach achieved only limited success (NSMP 2007). An investigation of selenium sinks in EP systems showed its preferential accumulation in the sediments (Gao et al. 2007).

Drawbacks of using EP are related to the potential ecological hazard to aquatic birds and the limited use under colder and wet climate conditions. In addition, groundwater contamination events can occur, and the generated waste is considered hazardous, requiring special disposal (NSMP 2007).

4.2.2 Enhanced Evaporation Systems (EES)

Enhanced evaporation systems provide an alternative to EP, producing concentrated brines by mechanically spraying water in the air using a blower (NAMC 2010). An evaporation efficiency of around 67% has been reported (Salton Sea Restoration Program 2005). The main limitations are due to scale formation on mechanical parts, energy consumption, and air emissions that can be carried away from the treatment area.

4.2.3 Mechanical Evaporator/Crystallizer

Brine concentrators are a subtype of evaporators using a falling-film evaporator device. They use a calcium sulfate seed crystal that acts as a nucleation promoter when added to the brine. The brine concentrator can achieve 80–90% water

reduction for a concentration factor between 5 and 10 (USEPA 2009). This technology is sometimes used in tandem with other treatment methods, as a post-treatment stage aimed to further reduce the final treated volume.

Even if they are efficient, these systems are mechanically complex and expensive. In addition, they require energy and maintenance, plus steam and cooling water (NAMC 2010). Scale and corrosion are important issues to be considered, especially when dealing with high-strength effluents. Pre-treatment is often necessary, adding to the total operating costs. Nevertheless, mechanical evaporators and crystallizers can become important in the context of zero liquid discharge (ZLD) strategies. ZLD attempts at reducing significantly the outflow stream of industrial processes by returning the recovered water back into the process. As the legislation for discharging wastewater will become more stringent, the ZLD concept will considerably gain in importance.

4.3 Adsorption

Adsorption is a surface-based process wherein the adsorbate adheres to the surface of the adsorbent. While often governed by physical interactions, chemical bonding also plays an important role. In this section, we will use the term sorption that encompasses both processes (physisorption and chemisorption).

4.3.1 Ion Exchange Resins

Ion exchange is a method used to bind undesirable ions present in aqueous solutions to solid particles. The solid particle is a granular medium having a natural (e.g., inorganic zeolites) or synthetic (e.g., organic resins) origin and can be fixed in a column or stirred in a reactor. Typical ions that bind to ion exchanging resins are H^+ and OH^- , monovalent cations (e.g., Na^+ and K^+), divalent cations (e.g., Ca^{2+} and Mg^{2+}), multivalent anions (e.g., SO_4^{2-} , SeO_3^{2-} , SeO_4^{2-} , $HAsO_4^{2-}$, and PO_4^{3-}), charged organic acids, bases, and ionizable biomolecules. Several organic strong and weak base anion exchange resins were used for their higher affinity to SeO_3^{2-} and SeO_4^{2-} (Nishimura et al. 2007; Alberta Environment 2013). Polyamine-type weakly basic anionic resins adsorb selenate over a wide pH optimum range (3–12) and selenite at an optimum pH of 10 (Nishimura et al. 2007). Most Se-laden wastewaters are also rich in sulfate which is an additional challenge. Overall, the resin performed better for selenate with a maximum sorption capacity of 134 mg g^{-1} , but, when in competition with sulfate, a 50% decrease in SeO_4^{2-} removal was observed (Nishimura et al. 2007). Sulfate is a competing anion with higher affinity for active sites leading to exhaustion of the resin. In order to overcome this issue, $BaCl_2$ is used to precipitate sulfate. Figure 2 depicts an ion exchange process coupled with the evaporation of the effluent using evaporators/crystallizers. Alternatively, provided

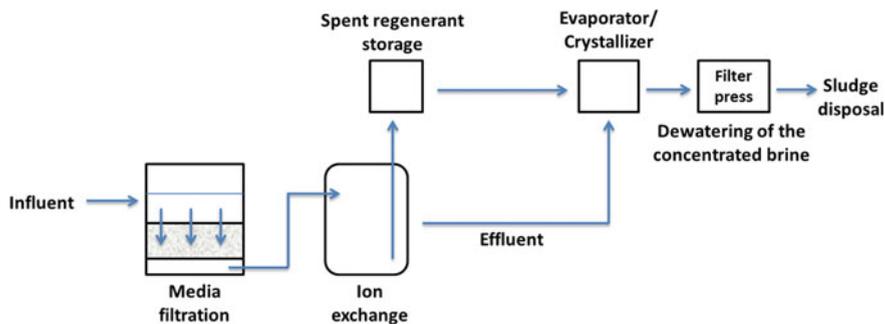


Fig. 2 Ion exchange coupled to evaporation process flow diagram of a system used to treat selenium-laden wastewaters (adapted from NAMC 2010)

the effluent meets the set discharge limits after ion exchange treatment, it can undergo pH adjustment prior to being discharged in the environment.

A laboratory-scale study investigated various types of resins treating selenium-containing oil refining SSW effluents (Montgomery Watson 1995). This type of wastewater contains hydrogen sulfide, ammonia, phenols, and chlorides and is of particular concern due to its high corrosiveness to stainless steel components. Among the resins tested, strong base anion resins showed the better performance by removing $4870 \mu\text{g L}^{-1}$ selenite down to below $50 \mu\text{g L}^{-1}$ (Montgomery Watson 1995). Another study pilot-tested mining water using a silica polyamine resin made from polyethylenimine (PEI) impregnated with zirconium. The treated effluent was acidic (pH 4) and contained both selenium ($930 \mu\text{g L}^{-1}$) and sulfate (80mg L^{-1}). Very high removal rates were achieved, with the effluent containing Se concentrations below $1 \mu\text{g L}^{-1}$ (Golder 2009).

In order to prevent issues associated with competing oxyanions that consume the exchange capacity of the resin, pre-treatment is required when applying sorption processes. Other factors to be considered are TSS-induced plugging, organic fouling, and the presence of strong oxidants that are negatively impacting the performance and the operational life of the resin (Alberta Environment 2013). In addition to these, the pH of the effluent must be adjusted before treatment because the exchange capacity of the resin varies as a function of pH. When the ion exchange sites are saturated, the resin can be regenerated using a sodium hydroxide solution. The regeneration solution being highly loaded with Se must be further treated on- or off-site.

4.3.2 Oxides

Several studies have focused on the interaction of metal oxides (e.g., aluminum, iron, and titanium) or metalloid oxides (e.g., silica) with SeO_x . Some relevant examples are presented below.

Activated alumina (AA) is an aluminum oxide (Al_2O_3) material prepared by dehydration of aluminum hydroxide at high temperatures that leads to macro and mesoporous structures with a surface area $>200 \text{ m}^2 \text{ g}^{-1}$ (Santos et al. 2015). AA shows a relatively high point of zero charge (pH_{PZC}) in the range of 8.4–9.1, meaning that below these pH values, the material has an overall positive surface charge. This is particularly relevant since SeO_x are negatively charged resulting in electrostatic interactions between the sorbent and the adsorbate. Like other sorbents that will be discussed below, AA displays a limited removal capacity for selenate, whereas selenite removal is pH dependent (2–7 optimum pH) and affected by the presence of silica, arsenic, and vanadium (Su et al. 2008).

Different iron oxyhydroxides and oxides (e.g., magnetite, Fe_3O_4 ; hematite, $\alpha\text{-Fe}_2\text{O}_3$; and maghemite, $\gamma\text{-Fe}_2\text{O}_3$) and iron oxides/hydroxides nanoparticles have been tested for SeO_x remediation. As a general conclusion, all the tested iron-based sorbents display SeO_x removal performances highly influenced by pH, ionic strength, and competing ions (Santos et al. 2015). Verbinnen et al. (2013) applied finely divided magnetite deposited on clinoptilolite, a natural zeolite used as supporting material, for the treatment of a synthetic wastewater matching the characteristics of a flue gas scrubber liquor of a waste incinerator. The synthetic wastewater contained: 4 g L^{-1} sulfate, 36.3 g L^{-1} chloride, 1.7 g L^{-1} antimonate, $950 \mu\text{g L}^{-1}$ molybdate, $175 \mu\text{g L}^{-1}$ selenate, and $75 \mu\text{g L}^{-1}$ arsenate. The best performance was recorded at pH 3.0–3.5 for a sorbent concentration of 20 g L^{-1} , with the following removal efficiencies: 99, 97, and 77% for Mo, Sb, and Se, respectively.

Other less studied metal oxides for the treatment of SeO_x are titanium dioxide (TiO_2) and manganese oxide (Mn_3O_4). Anatase is a titanium oxide polymorph with an isoelectric point of 6.3 investigated for its Se oxyanion sorption potential. Selenate sorption decreases at pH values above 6 and shows a high removal efficiency at pH 3.5 (Jordan et al. 2011). In addition, a number of studies focused on binary metal oxides such as Al(III)/SiO_2 and Fe(III)/SiO_2 , but they were conducted solely on synthetic solutions (see Santos et al. 2015).

Precipitation of ferrihydrite (Fh) followed by the sorption of SeO_3^{2-} onto its surface is EPA's best demonstrated available technology for selenite removal (BDAT) (Alberta Environment 2013). Fh is a hydrous ferric oxyhydroxide mineral used in water purification and wastewater treatment. From the mineralogical point of view, Fh is considered a form of ferric hydroxide, Fe(OH)_3 , but being metastable it will transform into more crystalline ferric oxides (e.g., goethite, lepidocrocite, and hematite) (Twidwell et al. 2000). In water treatment, ferrihydrite is formed in situ by the dissolution of ferric chloride or ferric sulfate, followed by pH adjustment, vigorous stirring, and addition of polymers and coagulants (NAMC 2010). This step is followed by SeO_x adsorption onto the ferrihydrite surface.

The sorption capacity of Fh varies as a function of the pH and the valence state of Se. The best pH range for effective selenite remediation is between 4 and 6 (85–90% removal), the efficiency decreasing with increasing pH, 80–85% at pH 7, and 20–40% at higher pH values (Twidwell et al. 2000). Selenite is strongly adsorbed onto Fh, while selenate is only loosely bound onto Fh

(Twidwell et al. 2000). The reason behind this difference in sorption has a mechanistic explanation: Selenite is adsorbed to the ferrihydrite matrix through an inner-sphere complex, whereas selenate forms an outer-sphere complex and can be more easily replaced by other ions present in solution and strongly impacted by water ionic strength (Hayes et al. 1987). Inner-sphere complexes are characterized by covalent bonds, whereas the outer-sphere complexes entail electrostatic coulombic interactions (weak bonds) between the adsorbent and the adsorbed entity.

Merrill et al. (1986) performed an early field study on Se treatment using iron co-precipitation in a continuous-flow system. They treated a Se-bearing effluent (ash pond effluent from a coal-fired power plant) containing 40–60 $\mu\text{g L}^{-1}$ Se down to below 10 $\mu\text{g L}^{-1}$ using 14 mg L^{-1} iron at an optimum pH of 6.2. A higher Se removal efficiency could not be achieved because of the presence of sulfate which outcompeted selenate.

Another important issue is related to the metastability of ferrihydrite over time which can mature to the more thermodynamically stable goethite or hematite, accompanied by a large decrease in surface area and the potential release of co-precipitated contaminants including Se (Twidwell et al. 2000).

4.3.3 Carbon-Derived Sorbents

Activated carbon is traditionally a sorbent of choice for drinking water purification and to a much lesser extent for the treatment of industrial effluents (Santos et al. 2015). The activation process (carbonization or pyrolysis of carbonaceous materials in the presence of various acids, strong bases, and salts) results in the production of highly porous ($>1000 \text{ m}^2 \text{ g}^{-1}$) sorbents. Only a limited number of studies investigated the removal of SeO_x by activated carbon. Some reports proposed the functionalization of granular activated carbon (GAC) with iron in order to achieve superior performance. Zhang et al. (2008) showed that Fe-GAC performs well for selenite removal in a wide pH range (2–8) and the principal competing ion is phosphate, whereas sulfate had only a limited impact.

4.3.4 Biosorbents

In recent years, as an alternative to conventional and commercial products, the use of biologically derived sorbents (i.e., *biosorbents*) for the treatment of industrial wastewaters has gained in popularity (see Santos et al. 2015 for a full review). Biosorbents offer the advantage of availability, cost-effectiveness, and environmental compatibility. One such biosorbent that attracted much attention is chitosan, a partially deacetylated biopolymer obtained through the alkaline deacetylation of chitin (Renault et al. 2009). The remediation of metal cations and anions using various forms of chitosan (e.g., powder, flakes, and beads) has been investigated in a number of studies. A major drawback related to biosorbents is their poor regeneration capacity and the potential bacterial and fungal contamination.

5 Chemical Treatment

Chemical treatment typically relies on the redox change of Se valence states and includes, but is not restricted to, (i) reactions of SeO_x with ferrous hydroxide, sodium dithionite, or zero-valent iron, (ii) catalyzed cementation, and (iii) electrochemical processes.

5.1 Ferrous Hydroxide

Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is used to reduce selenate to selenite, which is subsequently adsorbed onto ferrihydrite monohydrate amorphous solids. $\text{Fe}(\text{OH})_2$ is precipitated at neutral pH by the addition of NaOH to FeSO_4 solutions (Lalvani 2004). The reduction of selenate and the sorption of selenite are best accomplished under reducing conditions at a pH of 8–9 (Twidwell et al. 2000).

Figure 3 presents an FGD wastewater treatment using ferrous hydroxide. FeCl_2 is used to generate $\text{Fe}(\text{OH})_2$ at pH 8. Polymers were added to the effluent and allowed to settle in a clarifier for 3 days. Next, the overflow from the clarifier was passed through a media filter. A treatment efficiency of 84% has been reported, but the final total Se concentration was still $55 \mu\text{g L}^{-1}$ (NAMC 2010).

5.2 Zero-Valent Iron

5.2.1 Iron-Based Processes

Selenium remediation using the zero-valent iron (ZVI) technology involves the complex redox and sorption interactions between metallic iron (Fe^0) and SeO_x present in wastewater (Zhang et al. 2005). ZVI acts as an electron donor for the

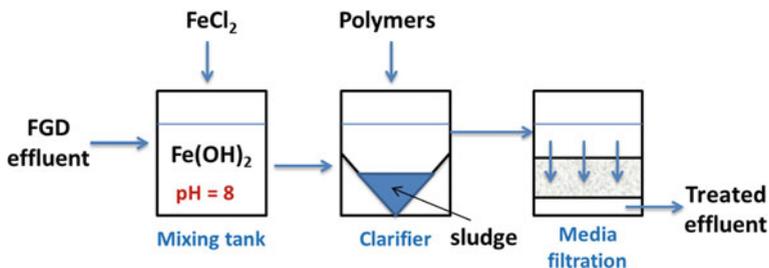
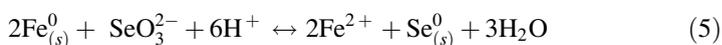
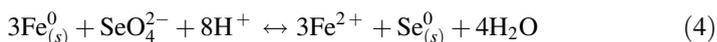


Fig. 3 Process flow diagram of an FGD effluent treatment using ferrous hydroxide precipitation, coagulation, and media filtration (NAMC 2010)

reduction of oxyanions (Frankenberger et al. 2004). Water solutions containing dissolved oxygen (DO) corrode Fe^0 by forming ferrous and ferric hydroxides. In addition to DO, oxyanions (e.g., NO_3^- , CO_3^{2-} , PO_4^{3-} , SeO_3^{2-} , and SeO_4^{2-}) have their contribution to the overall oxidation (corrosion) of iron. In solution, nanoscale zero-valent iron (nZVI) develops a core-shell structure: The layered structure of nZVI consists of a metallic iron core encapsulated by a thin amorphous oxide shell (Yan et al. 2010). Using 5 g L^{-1} nZVI particles, 1.3 mM selenite from a synthetic solution was removed from water within 3 min forming a core-shell structure. Selenite was reduced to selenide and elemental selenium, which then formed a 0.5 nm layer of selenium at the iron oxide- Fe^0 interface (Ling et al. 2015). Selenium was encapsulated in the nZVI particles at a depth of 6 nm from the surface (Ling et al. 2015).

By mixing $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ at an optimal pH range (4–5), green rust is formed. Green rust is a complex iron compound co-precipitate that sequentially reduces selenate to selenite and subsequently to Se^0 (NAMC 2010). ZVI has also the potential to directly reduce SeO_x to elemental Se (Eqs. 4 and 5). Alternatively, selenite can be adsorbed onto amorphous solids formed as by-products of ZVI oxidation.



FGD wastewater generated in a coal-fired power plant was treated by Fe^0 powder with a significant Se removal: from 7270 to $159 \mu\text{g L}^{-1}$. Nitrate co-present in the FGD under investigation was found to participate to the oxidation of elemental iron, thus contributing to its passivation (EPRI 2009).

A mining wastewater containing selenate was treated sequentially using elemental iron to reduce Se(VI) to Se(IV), followed by $\text{Fe}_2(\text{SO}_4)_3$ addition and selenite precipitation at pH 4.5, a reaction catalyzed by CuSO_4 . Even if the treatment process was optimized, the final Se effluent concentrations ($12\text{--}22 \mu\text{g L}^{-1}$) were still above the discharge limits. In order to further decrease the effluent Se concentration, the treatment was complemented by a reverse osmosis unit (Alberta Environment 2013). ZVI suffers from passivation which impacts the reducing power of iron, therefore the durability of such treatment could be problematic.

5.2.2 Hybrid Processes

Huang et al. (2013) reported the use of hybrid zero-valent iron (containing magnetite and ferrous iron) at circumneutral pH for removing Se, mercury, and nitrate from a real FGD wastewater on a field demonstration project. The prototype (bed system) was operated at $5\text{--}21 \text{ }^\circ\text{C}$, pH 7.5–8.5, and a total hydraulic residence time (HRT) of 24 h with the following results: selenate reduction from 3000 to $<7 \mu\text{g L}^{-1}$, mercury

from 50 to $0.005 \mu\text{g L}^{-1}$, and nitrate from 25 down to $<0.2 \text{ mg L}^{-1}$. Other metals/metalloids such as As, Cd, Cr, Ni, Pb, and Zn were also efficiently removed.

For a higher efficiency, ZVI can be employed in tandem with other treatment techniques. To treat mining wastewater, ZVI was used to reduce selenate to selenite, followed by the reduction to elemental selenium using iron co-precipitation. Because the initial $100 \mu\text{g L}^{-1}$ Se was reduced to only $12\text{--}22 \mu\text{g L}^{-1}$, RO was implemented as a polishing step prior to effluent discharge (Alberta Environment 2013).

5.2.3 Catalyzed Cementation

Catalyzed cementation is used for the removal of metal cations and oxyanions by enhanced cementation on the surface of Fe^0 particles using a metal catalyst. Catalyzed cementation is more specifically a ZVI treatment variation developed at Montana Tech (USA), wherein the copper or nickel coating is used to increase the electrochemical potential and thus to improve the reduction of SeO_x by Fe^0 (MSE 2001; Alberta Environment 2013). A copper–iron (Cu–Fe) or nickel–iron (Ni–Fe) galvanic cell couple induces an accelerated dissolution of iron which functions as an anode and concomitantly to an increased production of electrons (Twidwell et al. 2005). This in turn increases the current density available on the surface of the Fe^0 particles making them more reactive toward selenate, in particular. However, it is not clear to what extent the Fe^0 particles are coated with the catalyst in order to ensure the contact of the solution to be treated with both metals.

An USEPA sponsored demonstration project was implemented at the Kennecott Utah Copper Corporation site to treat selenate-bearing wastewater (around $1600 \mu\text{g L}^{-1}$) using catalyzed cementation. The treatment was effective in producing low-level Se effluent ($3 \mu\text{g L}^{-1}$) (Golder 2009).

5.3 Sodium Dithionite

A number of reducing agents (e.g., ascorbic acid, citric acid, and glutathione) can be used for the conversion of selenite into Se^0 , but they have been reported mainly for the production of Se^0 nanoparticles from synthetic solutions. Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is a reducing agent with multiple industrial applications (e.g., dyeing processes and water treatment). A full-scale treatment system was installed at a zinc refinery (Quebec, Canada). Selenium in the form of selenite is retained in a weak sulfuric acid solution during the off-gas treatment of a roaster plant (NAMC 2010). The system is a two-stage process: (1) dissolved mercury is removed by sodium sulfide; (2) selenite is reduced to Se^0 using sodium dithionite (Geoffrey et al. 2008). Following these stages, the effluent is combined with other plant effluents and treated by lime addition prior to discharge. The system uses a 20-h HRT, acidic pH (<1.7) and a molar $\text{S}_2\text{O}_4:\text{SeO}_3$ ratio in excess of 2 (Geoffrey et al. 2008).

5.4 Electrochemical Processes

Baek et al. (2013) investigated the removal of selenate from synthetic water using iron and mixed metal oxide (titanium coated with IrO_2 and Ta_2O_5) electrodes. They found that selenate removal was not directly proportional to the applied current, but dependent on the concentration of $\text{Fe}(\text{OH})_2$, proposed as the reducing agent for SeO_x . Ferrous oxide undergoes oxidation under the action of the DO present in solution, whereas SeO_4^{2-} was reduced sequentially to SeO_3^{2-} and then to Se^0 or Se (-II). Even if the removal efficiencies were high, the residual selenium (0.79 mg L^{-1}) at the end of the treatment was still above the discharge limit. No investigation on the electrochemical removal of selenite has been reported to date.

Colloidal biogenic Se^0 poses solid–liquid separation problems in biological post-treatment stages. Electrocoagulation (EC) using iron and aluminum sacrificial electrodes has been successfully employed to remove residual Se^0 from solution (Staicu et al. 2015b). EC relies on the electrogeneration of the coagulating agent by passing an electric current through an electrolytic cell containing metal sacrificial electrodes (e.g., iron, aluminum) (Fig. 4a). The electrogenerated coagulants (e.g., Al^{3+} , $\text{Al}(\text{OH})_3$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, or $\text{Fe}(\text{OH})_3$) react with negatively charged biogenic Se^0 leading to its sedimentation and separation from the treated solution (Fig. 4b).

TCLP tests showed that the Fe–Se sediment released Se below the regulatory waste disposal level (1 mg L^{-1}), whereas the Se concentration leached from the Al–Se sediment was 20 times in excess. This is particularly important given the

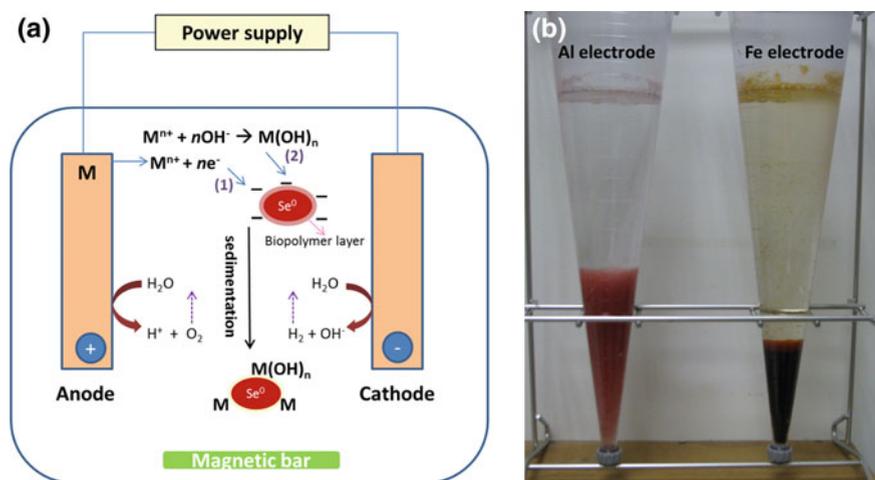


Fig. 4 Electrocoagulation of biogenic colloidal Se^0 : **a** Electrocoagulation setup. M = metal (e.g., Al, Fe) and **b** Colloidal Se^0 treated by electrocoagulation with aluminum and iron electrodes (Staicu et al. 2015b). *Note* Mechanisms (1) and (2) from Fig. 2a represent charge repression and sweep flocculation, respectively

management and safe disposal of the generated sludge resulting from the treatment of Se-contaminated wastewaters.

Alternative solid–liquid separation strategies such as filtration and chemical coagulation have been proposed (Staicu et al. 2015c). Sometimes, a media filtration polishing stage is deployed downstream of biological reactors treating SeO_x -laden effluents (NAMC 2010).

6 Physical–Chemical Processes

Due to the complexity of industrial effluents, a joint approach using both physical and chemical treatment systems can be employed. The place of each treatment system in the overall process flow sheet depends largely on the wastewater type and the treatment technologies employed (NAMC 2010). Certain physical processes such as membrane filtration require a pre-treatment of the wastewater for the reduction of TDS and organic load that would lead to the fouling of the membrane and to the reduction of its lifetime. Adsorption using various adsorbents also requires a pre-treatment stage since the co-founded anions and cations from the effluent matrix are involved in competitive adsorption reactions with the target selenium oxyanions. This aspect is particularly problematic because wastewaters contain sulfate, nitrate, carbonate, and chloride in concentrations significantly higher than SeO_4^{2-} and SeO_3^{2-} (see Sect. 3). On the other hand, chemical treatment systems such as precipitation cannot be used alone for an efficient wastewater treatment. The low discharge limits set for Se entail the need of a polishing step downstream in the treatment process scheme.

An example depicting the use of a mixed physical–chemical approach for the treatment of a real industrial effluent is shown in Fig. 5. The wastewater under investigation was generated by the electro-refining of copper and contained both selenite and selenate with a total dissolved Se concentration of around $1500 \mu\text{g L}^{-1}$. The treatment was performed in three stages, the first two using selective precipitation and the final one using ion exchange resins as a polishing step (Nishimura et al. 2007). The first stage was performed at pH 3–4 and required the addition of ferric sulfate and calcium hydroxide for the precipitation of selenite and sulfate, respectively. In the second stage, barium chloride was used to further precipitate sulfate and selenate at pH 5–6. An ion exchange resin was used in the final stage as a polishing step to lower the Se concentration below $100 \mu\text{g L}^{-1}$. The resins can then be regenerated, but the elution solution needs further treatment. Evaporative processes can be used for the concentration of the elution solutions, provided the high-energy requirements are economically sound (see Fig. 2). Alternatively, reduction–precipitation of selenate with $\text{Fe}(\text{OH})_2$ at pH 9, 70°C , and under nitrogen atmosphere was also proposed, but these experimental conditions are more difficult to attain than the ion exchange resin-based approach (Nishimura et al. 2000). The residuals management is also an important issue to be considered since precipitation produces sludge requiring dewatering, transport, and disposal.

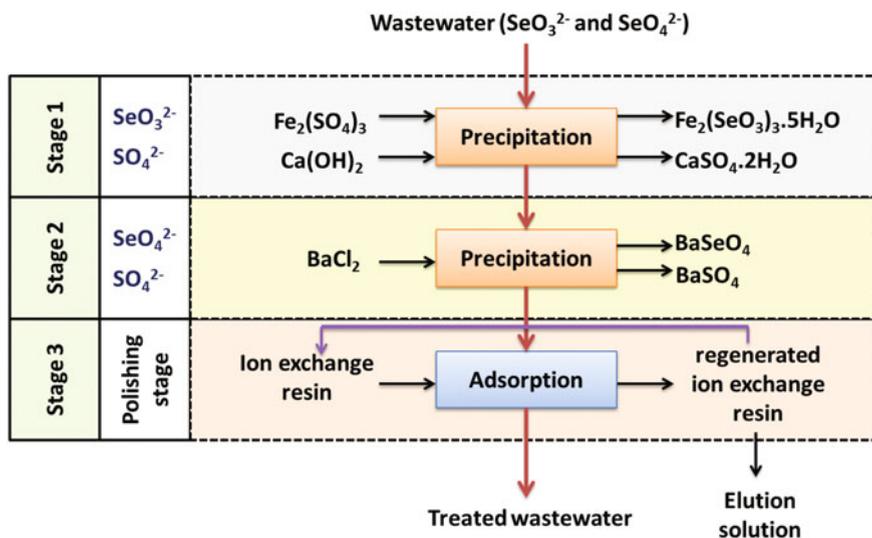


Fig. 5 Flow sheet of process for SeO_x removal from copper electro-refining wastewater (adapted from Nishimura et al. 2007)

The financial aspect, apart from the strict environmental regulations, plays an important part in designing the wastewater treatment scheme. Total installed costs include direct costs (e.g., equipment, installation costs, taxes, and other) and indirect costs (e.g., engineering, construction, and startup) (NAMC 2010).

7 Conclusions

An overview of the main sources of industrial Se pollution and the physical treatment technologies is presented in this chapter. Selenium is found in a variety of wastewaters resulting from mining (as SeO_4^{2-}), energy generation (FGD type, as SeO_4^{2-}), petrochemical (SSW type, mainly as SeO_3^{2-}), metal refining, and agricultural activities (as SeO_4^{2-}). Selenocyanate, SeCN^- , is typically associated with FGD and SSW, but in low amounts. The main challenges encountered in the treatment of Se-containing wastewaters are: (1) the presence of Se in relatively low concentrations and under several valence states (e.g., SeO_4^{2-} , SeO_3^{2-} , Se^0 , SeCN^- , and others); (2) the complex wastewater matrix containing other oxyanions (e.g., nitrate and sulfate) in significantly higher concentrations that behave as strong competitors for SeO_x remediation; (3) some treatment systems generate residual by-products in need of additional treatment or safe disposal; and (4) some wastewaters (e.g., mining and agriculture) are produced in very large amounts and have a diffuse source.

Among the physical treatment options, membrane filtration processes (e.g., reverse osmosis and nanofiltration) and evaporation systems show high Se removal efficiency, but suffer from high operational costs (energy consumption). Adsorption onto various materials (e.g., ion exchange resins, oxides, carbon-, and biologically derived sorbents) is cost effective. However, due to the non-selective action of the sorbents, the removal efficiency for SeO_x is diminished by the presence of competing anions (e.g., SO_4^{2-} , CO_3^{2-} , NO_3^- , and Cl^-) often found in industrial effluents.

Chemical treatment typically relies on the redox change of high Se valence states. Various chemical treatment systems using ferrous hydroxide, sodium dithionite, zero-valent iron, catalyzed cementation, and electrochemical processes have been tested for synthetic and real wastewaters. While efficient, they are also affected by pH sensitiveness, poor efficiency for SeO_4^{2-} removal, and competition with other anions. Both physical and chemical treatment systems generate residual products needing further treatment and safe disposal in order to comply with the environmental regulations. Some of the treatment options remain unproven for real selenium-containing effluents, and more research on them is required.

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