Opportunities and threats of selenium supply from unconventional and low-grade ores: A critical review

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Graphical abstract
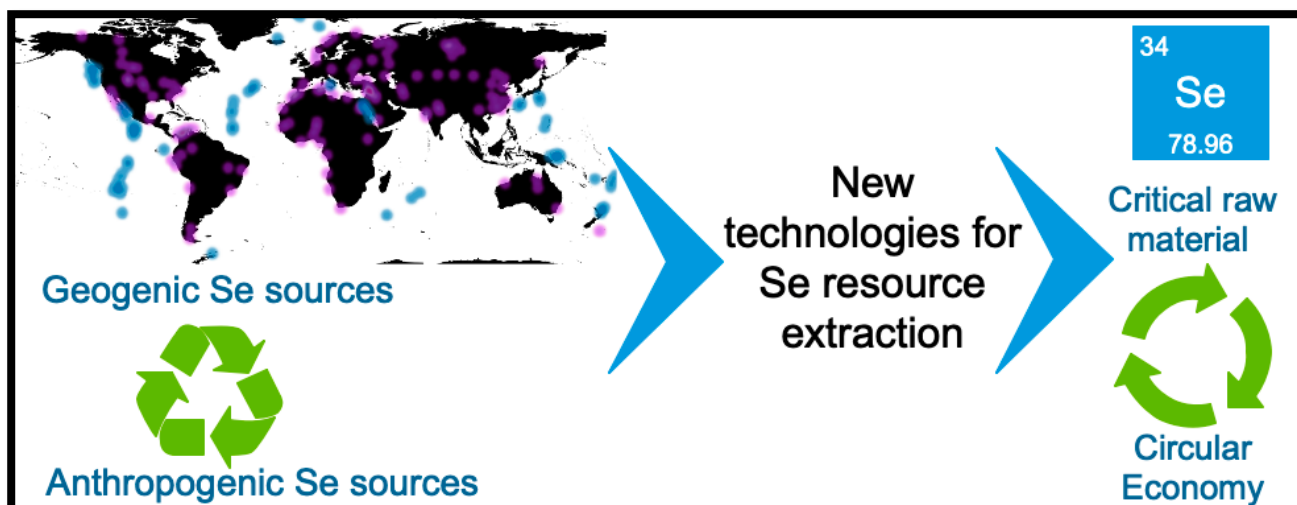
Abstract

Research on selenium has increased in recent years due to its extensive use in electronic applications, solar cells, glass industry, photocopying, cosmetic industry, and as a dietary supplement. New data and discoveries on the importance of this metalloid in the fields of medical biotechnology and human health have further increased its commercial value. This paper identifies challenges associated with selenium recovery from geogenic ores and topical unconventional ores such as marine geo-resources and anthropogenic stocks. Emphasis is given on opportunities and challenges of non-commercial processes for selenium resource extraction that may be developed at full-scale soon. Characteristics and global uses of selenium are also described to help predicting future scenarios of alternate supply. Considering the scarcity of increasingly wanted selenium metal and the recent advancements that have been made in mining from alternative and urban ores, it is possible that selenium can be effectively recovered from other sources to secure a stable and diversified supply.

1. Introduction

Selenium is a non-metal occurring at trace levels in different environmental compartments due to geogenic and anthropogenic causes. On the Earth's crust, it ranges from 0.05 to 0.2 mg/kg being relatively enriched in the Lower Crust. Average values for Se in waters, sediments, and rocks point to a limited abundance in the natural environment (Table 1). Selenium is also present in food, especially in protein-rich products like eggs, meat, fish (0.05-20 mg/kg), legumes (up to 80 mg/kg), and cereals (0.1-10 mg/kg) (Fairweather-Tait et al., 2010). Fruits and vegetables generally contain lower Se concentrations (10–20 µg/kg) (Santos et al., 2015). Selenium and its compounds with other constituents (e.g., Na, Cu, Cd, and Te) are highly required in Industry (Langner, 2003), with the global Se production reaching 2710 Mg in 2017, according to the U.S. Geological Survey (Stillings, 2017). Selenium use in everyday products and goods allows a Se cycle sustained by anthropogenic materials (Kavlak & Graedel, 2013).

Selenium has a twofold character to health as it can be toxic at high concentrations but also an essential macronutrient. At low levels of intake, Se has physiological importance for humans and animals and a critical role in cancer prevention (Bartolini et al., 2017). However, exposure to higher concentrations can lead to different severity diseases, with Se toxicity depending on multiple factors such as the oxidation state (Lenz & Lens, 2009). The complex behavior of Se depends on the diverse chemical forms and associations with inorganic phases but also with organic phases, allowing Se to occur under different species at the same time in one environment.

Selenium mining districts are widely distributed, mainly on land, and of geogenic origin. The natural occurrence of Se depends upon the composition of the ore, the stratigraphic position of ore minerals, and the tectonic setting. The majority of Se occurrences (as ore minerals of economic and sub-economic interest) are associated with igneous rocks, including porphyry type deposits and Iron Oxide Copper Gold (IOCG) deposits, volcanogenic sulfides, including volcanogenic massive

sulfides (VMS) and native sulfur, and epithermal/sedimentary sources, including phosphorites, shales, polymetallic nodules, and marine seafloor sediments. Also, numerous materials enriched in organic carbon can be a source of Se, e.g., coal averagely contains between 0.5 and 12 mg/kg Se (Table 1). However, although technically possible, Se recovery from coal is not economically viable (Kogel, 2006; Hoffmann & King, 2010). This is because Se chemical affinity to coal can be controlled by biogenic and authigenic matter (Ketris & Judovich, 2009) with metabolic reactions at the mineral-biosphere interface explaining Se depletion/enrichment. For instance, different (micro)organisms are acknowledged as Se bio-accumulators because they are compelling receptors of available Se in various processes and media (Nancharaiah & Lens, 2015 a, b).

Unconventional Se sources such as those from its anthropogenic cycle are virtually undefined while prospective offshore resources of rare and technology-critical metals are meticulously studied to counteract the supply risk (Rogers et al. 2014; Bullock et al., 2018; Li et al., 2019). Mineral predictivity flow by Li et al. (2019) for skarn-type mineralization exemplifies the exploration of magmatic-hydrothermal deposits tied to endogenic processes. For Se prospecting, the insight from Presser et al. (2004) substantiated by Stillings (2017) pointed out that organic matter can be a proxy of new resources. Therefore, mapping the global distribution of Se-rich rocks in sedimentary basins enriched in organic carbon, such as petroleum basins and marine phosphate deposits, can identify potential exploitation sites.

Under these circumstances, we interrogate if Se sources of supply should rely on unconventional and low-grade ores recovery. By comparing commercial routes of Se supply and recovery, we interlayered pathways still under development. The opportunities and threats associated with Se recovery are discussed, overviewing mineable Se resources that wait for the development of viable routes of exploitation and innovative metallurgical solutions. Final remarks are given based on the authors' personal perspective.

Table 1. Se abundance in some surficial environmental media.

Type		Mean value (range)	Number of observations	Reference
Upper Continental Crust	mg/kg	0.09	-	Rudnik & Gao (2013)
Coal (average)	mg/kg	1.6	18801	Ketris & Yudovich (2009)
U.S. coals	mg/kg	3.6 (0.02-75)	304	Coleman et al. (1993)
Finnish coals	mg/kg	3.0	-	Koljionen, (1992)
British coals	mg/kg	4.9 (0.3-62)	61	Bullock et al. (2019)
Iranian coals	mg/kg	1.39 (0.01-31)	478	Pazand (2015)
Chinese coals	mg/kg	3.13 (2.97-3.28)	33	He et al. (2002)
Soil (average)	mg/kg	0.44 (0.05-1.5)	-	Kabata-Pendias (2011)
European soils	mg/kg	0.4 (<0.01-16)	24491	Reimann et al. (2018, 2015, 2014, 2003, 1998, 1997); Petrik et al. (2018); Beone et al. (2018); Perez-Sirvent et al. (2010); Rawlis et al. (2012); De Temmerman et al. (2014)
Australian soils	mg/kg	0.06 (<0.01-2)	1314	Reimann & de Caritat (2017)
Asian soils	mg/kg	0.33 (<0.01-128)	8197	Xie & Cheng (2001); Chen et al. (1991); Cheng et al. (2014); Yanai et al. (2012);
U.S. soils	mg/kg	0.2 (<0.2-8.3)	4841	Smith et al. (2019)
South-American soils	mg/kg	0.12 (0.01-0.7)	30	Rodrigues Nogueira et al. (2018)
Leaves, Europe	mg/kg	0.1 (<0.1-0.5)	182	Reimann et al. (2015)
Grass, Europe	mg/kg	0.005 (<0.001-0.02)	-	Kabata-Pendias (2011)
Lake sediments, Europe	mg/kg	(0.27-3.64)	-	Parkman & Hult-berg (2002)
Lake water, Europe	mg/kg	(<0.043-0.209)	-	Parkman & Hult-berg (2002)
Surface water (average)	µg/l	0.07 (0.01-0.3)	-	Gaillardet et al. (2005)
Surface water, Europe	µg/l	(0.01-15)	807	Salminen et al. (2005)
Groundwater, Europe	µg/l	1.83 (<0.015-247)	577	Shand and Edmunds (2008)
Seawater (average)	µg/l	0.08	-	Mitchell et al. (2012)

2. Global demand and sustainability of the supply chain

Selenium plays a critical role in technological production chains. Along with Te, Se maintains a place of relevance as a primary component in different high-tech and green applications. Selenium is gaining increasing attention in the production of solar cells and finds applications in electronic devices, glass industry, cosmetics, and as a dietary supplement, so it is considered a high commercial value element (Naumov, 2010; Schulz et al., 2017). Selenium is highly required also because it can replace strategic metals (European Commission, 2014) in some applications with comparable performances. Selenium substitutes Sb for hardening of materials and alloys; it can be used in bimetallic catalysts to decrease the need for Re, or replace Te in metallurgy. Cu-In-diselenide can replace Cd-telluride in photovoltaic power cells providing good substitutability for expensive Te compounds. In the high-purity form, usually available as shot or powder, Se is used

for thermoelements and xerographic materials in electronics due to remarkable photoelectric characteristics. Further research material on Se uses in Appendix A.

Due to the close connection to major metal deposits, minor resources like Se depend heavily on the production of element primarily mined (e.g. Cu), resulting in complex demand/supply and price patterns (Hageluken & Meskers, 2010). Minor metals like Se are not traded on the London Metal Exchange. The market Se price reached its all-time heights in 2011 (Stillings, 2017), which would correspond today to \$170,000 per Mg. Currently, high purity Se powder costs around 16-18 US\$/kg, according to the Shanghai Metals Market, and the main chemical suppliers sell it about a thousand times its value. The dramatic price volatility of Se is related to its application for strategic energy technologies (Lenz & Lens, 2009) and the highest substitutability index compared to Ag, Au, As, Cu, and Te combined with its vulnerability to potential supply restriction higher than Te (Nassar et al., 2012). Materials containing > 99.5 wt. % Se are commercially available as powder, granules, and lump. Pigment grade Se is typically used in coloration and has a purity of 99.7 wt. %. The high grade is ranking third about purity with 99.999 wt. % minimum Se. The ultrahigh grade is claimed to contain from 99.999 % to 99.9999 wt. % Se (Hoffmann & King, 2010). The refined grade is 99.5 wt. % minimum Se with Te, Fe, Pb, and Cu as the main impurities, which likely complicate matters during analytical determination and metal recovery/purification.

Selenium supply is an everlasting challenge given the rare presence of this element in the continental crust as to question whether its use is sustainable. However, in many areas of the world, as Europe, recovery of minor by-products like Se has minimal infrastructure, low efficiencies, and represents a small contribution to revenues, typically less than 5% (European Union, 2017). Secondary Se is processed by a small number of primary Se refiners. No secondary Se sources have in situ production. The anode mud deposited during the electrolytic refining of Cu and Mn and other processes can generate potential losses of Se in effluent wastewaters that likely need post-

treatment to avoid that this secondary resource becomes inaccessible. Putting more efforts into mining from unconventional and low-grade ores is vital to secure a stable supply and diversifying sourcing.

The exploration of marine environments has resurged a circumstantial interest in secondary metal production. For example, phosphatic rocks mining is generally limited to P extraction, a critical and non-renewable element for fertilizer production, but these deposits are enriched in Rare Earth Elements (REE) (sum of REE + Yttrium ranging 161-1000 mg/kg; Hein et al., 2016) and other elements of economic interest including Se (up to 300 mg/kg Se; Stillings, 2017). Ore minerals from VMS are a global source of Cu, Pb, Zn, Au, Ag, PGE, and other trace elements of critical economic interest such as Be, Bi, Co, In, Ge, and Se (Shanks et al., 2012). With secondary low-grade ores (e.g., lateritic soils, fayalitic slags, metal-rich tailings, and landfilled sludge) starting to be effectively looked for alternate supplies, conventional methods for prospecting and recovery borrowed from primary mining need to be rethought, providing solutions tailored for complex materials and different ore arrangements. Innovative strategies for different materials at variable Se concentrations like those coming from biotechnologies are wanted because they can help to uncouple demand/supply and price patterns from major metals extraction. Environmental microorganisms can transform selenium species, and their dissimilatory reactions can be exploited to enhance sustainability indicators and in the production of micronized elemental Se (e.g., Eswayah et al., 2016). This, in turn, will open novel recycling possibilities, which may be overlooked for merely technical reasons.

Since Se obtained from either conventional and unconventional sources relies on advanced treatments and demanding purification steps, comment upon most methods currently at the commercial or prototype scale and others under development is given, with a focus on unconventional ores and biological reactions possibly relevant to Se supply and recovery.

3. Conventional Se supply

There is no preferred source of Se for industrial extraction, but commercial resources of Se are mostly geogenic, mined from a variety of ore minerals, with mining districts widely distributed mainly on land (Figure 1).

Generally produced as a mining by-product from deposits mined for other major constituents (e.g. Cu, Ag, Pb, Mn, U), refinery production of Se is reported by 14 countries with more than 130 companies trading the metal at a different level of purity. Although the efforts to standardize the Se estimate in sulfide ores, the variable host minerals and measured concentrations hinder the definition of Se grades and cut-off values in ore mining. Typical Se ore concentrations in exploited mines ranged 20000-250000 mg/kg according to the available references (Hyvaerinen, 1990; Halada et al., 2001). However, low-grade deposits averaging 20-40 mg/kg Se are commercially treated (Appendix B), especially when metal recovery meets remediation purposes and restoration of waste legacy sites.
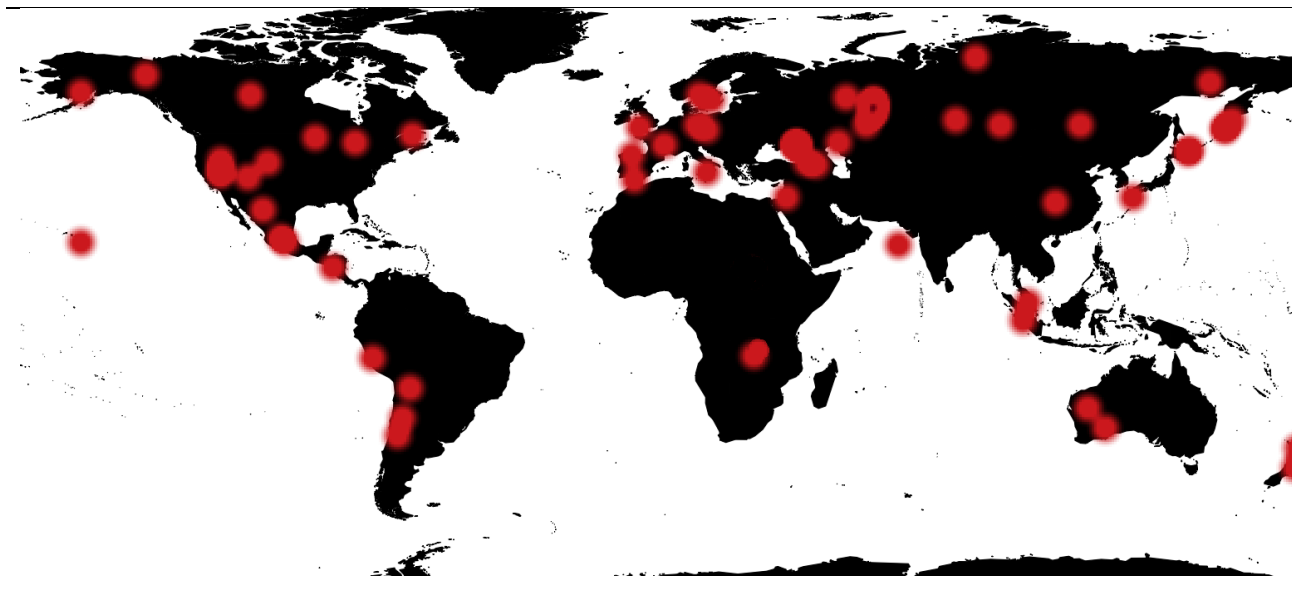

Figure 1. Clusters of distribution of Se mining districts (in red). World map is from www.thematicmapping.org; source data from Butterman & Brown, 2004; Kogel, 2006; Stillings, 2017; and retrieved from www.mindat.org.

3.1. Geogenic deposits

Selenium is primarily found substituting S in sulfide veins, matching S behavior especially at high temperature (magmatic/hydrothermal environments), but also segregates at lower temperatures depending on pH, oxygen fugacity, and its different affinities for other elements (Huston et al., 1995). The primary supply of Se comes from sulfide ores present in Canada, United States, Bolivia, China, and Russia. In intrusive rocks, the most considerable Se resources relate to mafic and ultramafic rocks of chalcopyrite-pentlandite-pyrrhotite deposits. The mean Se/S ratio is generally low (≈ 0.1) in magmatic sulfides so their primary ore deposits bearing Se are rarely considered high-grade. Earlier estimates reported an average Se content of 0.02 wt. % in magmatic and associated hydrothermal sulfides as mineral ores (Hutchinson, 1973). Where recent reviews exist, Se concentrations may vary from 0.2 to 220 mg/kg in igneous rocks (Queffurus & Barnes, 2015). Conversely, selenide ore minerals are rare but of critical importance as Se can spot locally at elevated concentrations up to 3 wt. % (Stillings, 2017).

Selenium is also exploited from tuffaceous rocks and other exogenic deposits such as phosphate rocks. Concentrations of hundreds of mg/kg are frequent in other volcanogenic sedimentary rocks, including sporadic depositions of sulfur. Further research material on active and abandoned mines untapped for Se is in Appendix C.

3.2. Anthropogenic stocks

The most significant anthropogenic source of Se economic recovery is waste from electronic and electric equipment (WEEE), where Se is an essential component required at high concentration and purity, and it can be easily separated from the inert material. Although there is potential for Se recovery from anthropogenic materials (i.e., urban mining), limited examples were found: factory scrap generated during the manufacture of Se-based rectifiers, burned-out rectifiers, spent catalysts, used xerography-copying cylinders and heat-generators, unused sensors, printed circuit boards

(especially advanced microdevice's graphics cards), relays, Cd-Se resistors, advanced optical stores (Schrauzer, 2004; George & Wagner, 2009). Further research material on the anthropogenic Se cycle is gathered in Appendix D.

3.3. Commercial processes for Se recovery

More than 90% of the U.S. Se output and more than 8% of the world Se production are derived from the anode mud deposited during the Cu electrolytic refining. Typically, only a fraction of Se is recovered from Cu anodes that can contain between 0.5 and 280 kg Se per Mg of copper, generating a potential loss of Se in effluent wastewaters that likely undergo further post-treatment. Soda ash roasting, roasting with sulfuric acid, wet chlorination, and alkaline autoclaving are primary recovery processes for Se developed at the full scale (Hoffmann & King, 2010; Stillings, 2017). They typically work well for pre-treated (with H_2SO_4 for the total removal of Cu and Pb) slimes of Cu and Pb refinery waste and slag. In soda ash roasting (Figure), once the major constituents (Cu or Pb) are leached out, the slimes are mixed with Na_2CO_3, clay, and water, then pelletized, dried, and roasted at 530-650 °C to convert Se and Te to the hexavalent state. Selenium is thereby separated from Te and other impurities. After water leaching, Se solubilizes as Na_2SeO_4 in alkaline conditions; then Na-selenate is precipitated by mixing with charcoal and heated to convert it into Na_2Se. The resulting selenide is put in water and oxidized by blowing air into the solution to precipitate Se^0. Another configuration relies on sulfur dioxide blowing as a final recovery step after reducing the hexavalent Se using concentrated HCl or ferrous iron salts catalyzed by chloride ions (Figure). All industrial processes to produce Se involve a finely tuned combination of fundamental methods, such as chemical treatments, physical separation methods, thermal treatments, and electrodeposition. Electrowinning is a compelling option for the final recovery of elemental Se, especially from Cu-Ni ores, but also from fly dust and slag of metal foundries (Langner, 2003). Generally, the final product of recovery is an amorphous or nanocrystalline phase of Se recovered by deposition/sedimentation, anodic electrodeposition, flue-gas condensation (at the scrubber where

usually halogens or other absorbers are added), vacuum distillation, or other phase separation methods (Hoffmann & King, 2010).

Abiotic treatments may apply for dissolved or insoluble Se. The Se-loaded by-product is either electro-coagulated (i.e. aggregation of the destabilized phases forming flocs) (Mollah et al., 2004; Santos et al., 2015), or reacted with alkaline and sulfide solutions (e.g. Na_2SO_3 or $NaHSO_3$), or iron salts (e.g. ferric sulfate or chloride) (e.g. CH2MHILL, 2010; Overman, 2000) or dithionite ion and sodium sulfide (Geoffroy & Demopoulos, 2009, 2011), followed by solid/liquid separation. Cementation of Se nanoparticles generated at some processing steps can be operated onto iron surfaces with zero-valent iron acting as a reductant or using advanced carbon-based adsorbents such as magnetic graphene (Fu et al., 2014; Santos et al., 2015). Also, organic reactants are highly regarded; carbohydrazide is known to cause Se reduction to elemental Se from dissolved Se in an aqueous solution only if Na concentration is maintained as low as 500 mg/l (Goodman et al., 2000). The recent advances of membrane separation technologies are adding new perspectives for Se recovery from very fine precipitates (and different mineralogical phases) using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), being the latter, RO and NF, most effective among the others (CH2MHILL, 2010; Santos et al., 2015).

The WEEE showing high Se contents like scraps from document copiers and laser printers are the focus of urban mining. The Se layer from xerographic photocopier drums is either broken up mechanically, then cleaned and remelted; or dissolved in sodium sulfite or other solvents, then precipitated and eventually purified, generating no more than 50 Mg secondary Se annually (Butterman & Brown, 2004). Other residual streams for practical urban mining are waste solutions from the production of trigonal Se (used in photosensitive or photoconductive components) where Se oxide may be in the form of sodium selenite and sodium selenate and for which patented processes may apply (e.g., Goodman et al., 2000). As Se rectifiers and photocopiers have been

almost phased out, the secondary recovery of Se appears to be plausible mostly for solar cells (Kavlak & Graedel, 2013). However, limited amounts of solar cells reach end-of-life to justify Se recovery, which depends clearly on developing and deploying end-of-life recovery and recycling programs for these products (Kavlak & Graedel, 2013).
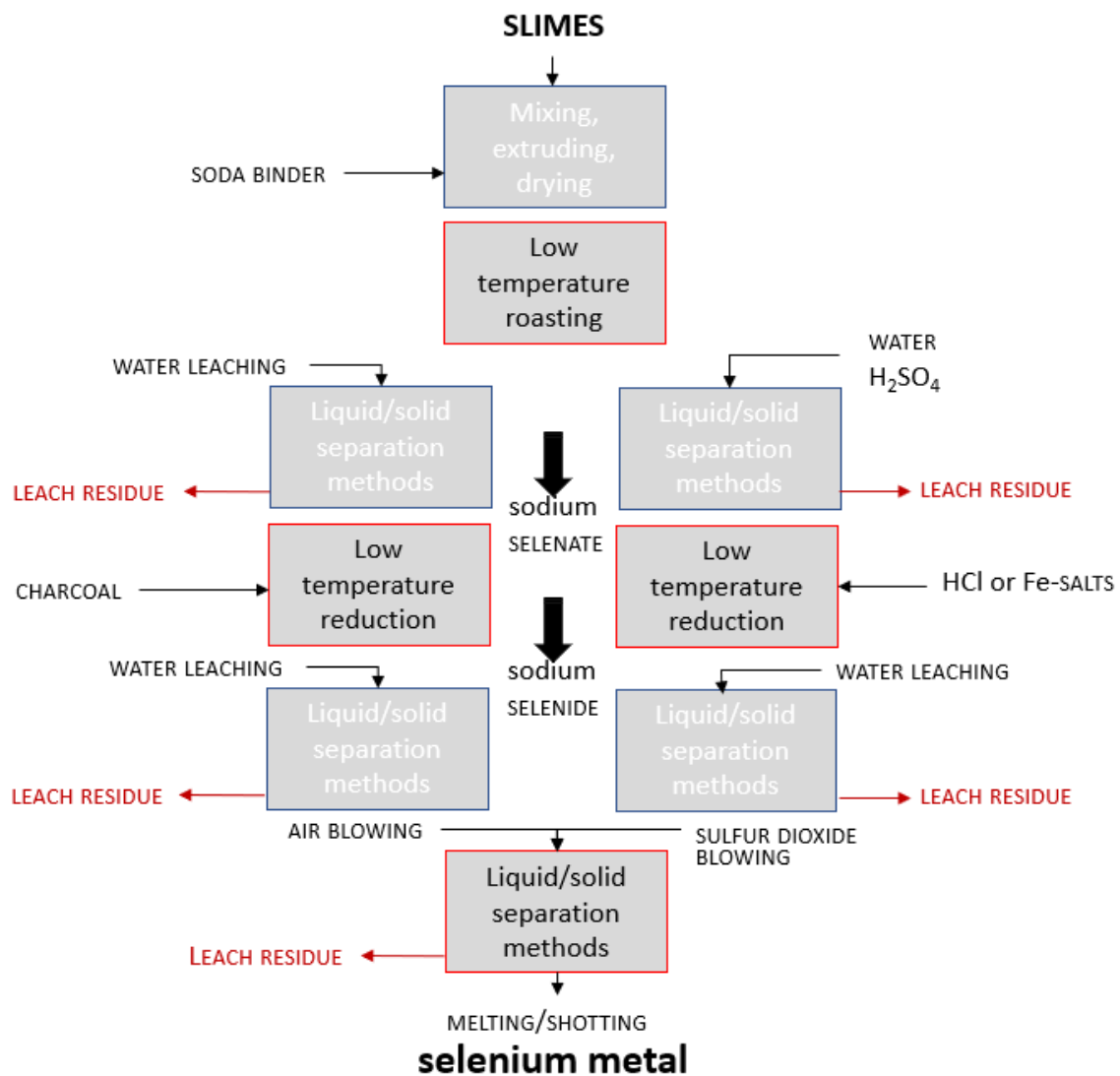

Figure 2. Soda ash roasting industrial process for Se recovery from slimes of Cu and Pb refinery residues. Demanding tasks and process wastes are shown in red.

4. Unconventional Se supply

4.1. Prospective geogenic sources

There is no indication about cut-off values in the recent scientific literature so different deposits can be identified both onshore and offshore (Table 2). Igneous rocks, such as layered intrusions, and VMS can be considered potential alternate sources for Se supply though very little explored so far, especially offshore (Figure 3). From a mining perspective, the preference towards sulfides for the occurrence of seleniferous ores complicated the definition of correlation between Se and any of the associated elements (e.g., Cu, Pb, Ni, S, Te, and precious metals). In hydrothermal settings, Se distribution within sulfide minerals is directly dependent on changes in fluid Se/S ratio, temperature, redox, and pH (Layton-Matthews et al., 2005). At ambient seafloor temperatures, reduced forms of Se are relatively immobile. Therefore, Se preferential deposition occurs when relatively hot, acidic, reduced hydrothermal fluids mix with cold oxidized ambient seawater. High Se/S ratios and low δ^{34}S values generally reflect magmatic fluids, whereas the opposite is true for sedimentary or evaporitic sources (Fitzpatrick, 2008).

Natural resources for economic Se extraction are some phosphate deposits and organic-rich shales (Presser, 1999). Sedimentary bedrock units can show high Se concentration due to Se depositional pathway in marine basins with high primary biological productivity (Presser et al., 2004; Figure 3). In general, high- and low-temperature systems can provide conditions for Se occurrence (Table 2). Geogenic deposits are active or fossilized, however, with prevailing land-based operations, commercial-scale exploitation of offshore sources seems unfeasible due to technical reasons. In the next sections, geogenic sources untapped for Se like VMS, shales, and other polymetallic nodules and crusts are analyzed.
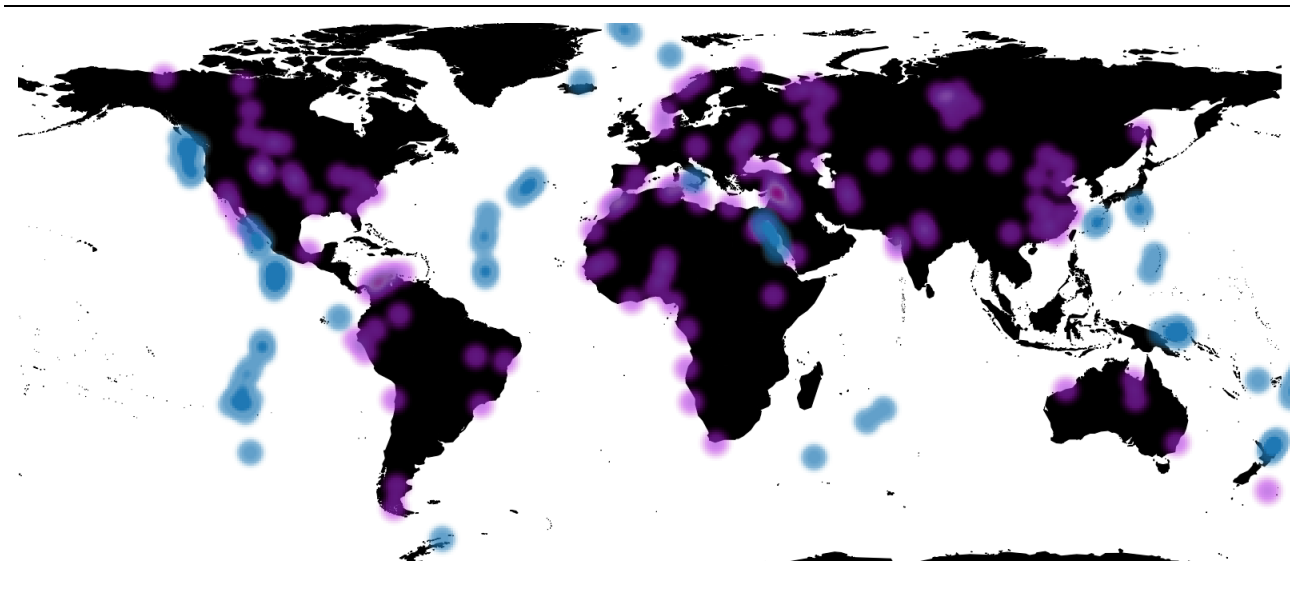
Figure 3. Clusters of distribution of Se inferred sources tied to organic-rich sediments (in purple; from Presser et al., 2004) and modern volcanogenic massive sulfides (in blue; from Boschen et al., 2013) as perspective deposits identified both onshore and offshore. World map is from www.thematicmapping.org.

Volcanogenic massive sulfides

Despite their growing economic importance, the distribution and concentration of trace elements in VMS remain poorly constrained. The number of chemical analyses for Se is much lower than that for base and precious metals, but an overall mean concentration of 128 mg/kg is reported (Geomar, 2013). Table 2 compiles the available data. High Se concentrations are typically associated with sulfides (pyrite, chalcopyrite, and sphalerite) like in the Troodos ophiolite complex in Cyprus, where hematite-rich breccias contain 3956 mg/kg Se in euhedral pyrite and up to 4953 mg/kg in chalcopyrite (Martin et al., 2018).

Upper Jurassic-Lower Cretaceous ophiolites of the Balkan Peninsula host Cu–Zn–Pb VMS deposits (*sensu* Hutchinson, 1973) where the massive sulfide ores (including pyrite, chalcopyrite, and minor sphalerite) are characterized by an increased content of Se in selenides (from 6000 mg/kg up to 24 wt. %). These deposits differ from Cyprus-type deposits and resemble those of polymetallic sulfides forming at the modern seafloor (Economou-Eliopoulos et al., 2008).

In modern VMS of the East Pacific Rise, Se-rich mineralization occurs in the inner part of the deposit in equilibrium with hydrothermal fluids and is influenced by the mixing with seawater (Auclair et al., 1987). Here, where active venting at chimneys is present, Se substitutes S in solid solution in all sulfide minerals. The highest Se content is found in chalcopyrite (2500 mg/kg) and euhedral pyrite (1500 mg/kg) (Auclair et al., 1987). At Lucky Strike along the Mid Atlantic Ridge near the Azores Triple Junction, Se values range 213-1640 mg/kg in chalcopyrite, whereas low concentrations characterize pyrite and marcasite (< 50 mg/kg). Shreds of evidence suggest two sources for S and Se. The hydrothermal fluid represents the first source; however, another source may come from bacterial reduction of seawater sulfate and inorganic reduction of Se oxyanions in the subsurface environment (Rouxel et al., 2004a). Right in the interior of active chimneys chalcopyrite-isocubanite lining reaches a maximum value of about 1500 mg/kg Se (Rouxel et al., 2004b).

In the Logatchev hydrothermal field, along the South Atlantic branch of the Mid Atlantic Ridge, Se content of copper sulfides found in the active chimneys is high, typically between 1000 and 1500 mg/kg (Rouxel et al., 2004b). Offshore northern Papua New Guinea, in the Manus Basin, an actively venting hydrothermal field has been under prospecting for mining base and precious metals for quite a long time by Nautilus Minerals Inc. (Solwara 1 project). Mass-balance calculations show that S and chalcophile trace elements, including Se, typically associated with magmatic Cu-Au mineralization, are enriched by several orders of magnitude relative to country rock, with Se concentration as high 166 mg/kg in hydrothermally altered dacites (Yeats et al., 2014). Concentrations of Se are sometimes higher in the weathering products than in the sulfide ore due to oxidation processes of sulfides from the primary ore and the formation of authigenic minerals (Bullock et al., 2018). Modern hydrothermal analogs exhibiting advanced alteration are the Valu Fa Ridge and West Mata Seamount in the Lau Basin, the Desmos Caldera in the eastern Manus Basin, the Yonaguni Knoll IV in the Okinawa Trough, the Brothers Cone site of the

Kermadec Arc, NW Rota-1 Seamount in the Mariana Arc, and the Palinuro Volcano in the Aeolian Arc (Yeats et al., 2014; Figure 3).

Phosphorites

Phosphorite slabs and nodules may be enriched in REE, V, U, F, Ag, Cd, Cr, Mo, As, Se, Sr, Te, Zn and other trace elements (González et al., 2016). In regular (land-based) mining operations, elements such as U, Th and their decay products and Cd, Tl, Se and Hg are closely monitored. If found in excessive concentrations, these elements are recovered to mitigate environmental risks linked to fertilizer use or phosphate tailings disposal (Notholt, 1994; Trappe, 1998).

The P mineralization is generally characterized by discrete laminae and nodules, which require specific conditions to form, such as sustained organic matter burial flux, changes in redox conditions, little terrigenous input, and bottom current or wave winnowing (Filippelli, 2011). Marine settings characterized by upwelling conditions, high biological productivity, little riverine discharge, and alongshore currents are ideal for phosphate-rich sediment formation. This setting is typical, for example, of the Peru and Chile continental shelf and upper slope (Kudrass et al., 2017) and the middle and outer shelf of Namibia (Compton & Bergh, 2016) (Figure 3). Phosphorites or their precursor sediments form here, with an average concentration of 13.8 mg/kg Se, hardly due to large terrigenous inputs (Borchers et al., 2006).

Offshore Baja California in Mexico, at the top of isolated plateaus in water depths of 50–100 m, phosphatization has cemented dolomite and Miocene foraminiferal limestone interpreted as long-term residual deposits, concentrated during periods of sea-level lowstands (Föllmi & Garrison, 1991; Kudrass et al., 2017). In Africa and the Middle East, phosphorites show the highest concentrations (Table 2). On the Galicia Bank, Iberian margin, at water depths from 1200 to 700 m, Se concentrations peaked 21 mg/kg in phosphorite nodules comparatively higher than in other types of phosphorite mineralization (González et al., 2016).

Phosphorite nodules are composed of a dense carbonate fluorapatite nucleus interlayered by Fe-Mn oxides. Pure phosphorites comprised of carbonate fluorapatite are believed to form on seamounts rather than along continental margins (Hein et al., 2016). One of the best-studied seamount-related phosphorite deposit in the world forms an area of about 400 km^2 in the 400 m-deep saddle on the crest of the Chatham Rise, 1000 km east from the South Island of New Zealand. The phosphorites of the Chatham Rise consist of carbonate fluorapatite, which replaced early to middle Miocene nannochalk. Large phosphorite nodules (> 8 mm) usually have a core with lower phosphatization and higher Ca-carbonate component; the smaller ones (1-8 mm) are completely phosphatized, but with decreasing grain size, the relative portion of the elements associated with the glauconitic cover, such as Si, Al, Fe, K, many trace metals, including REEs, increases (Kudrass et al., 2017).

Black shales and organic-rich sediments

Black shales are admixtures of organic and inorganic materials, enriched in P, U, Mo, V, Re, Zn, Hg, and other trace elements including Se (Table 2). Black shales are typically deposited during Phanerozoic oceanic/anoxic events wherein the observed $\delta^{82/76}$Se excursion is due to substantial availability of volcanogenic Se accompanied by reduction of excess Se oxyanions in the euxinic water column (Mitchell et al., 2012). Marine and subaerial highly organic shales contain as much as 1500 mg/kg Se closely associated with detrital organic matter (Parnell et al., 2016). For black shales of UK and Ireland, Parnell et al. (2016) reported a range of 1.3-42 mg/kg Se. Black shales of the late Neoproterozoic Gwna Group (570-580 Ma) located on the NW coast of Wales contain Se between 47-116 mg/kg (Armstrong et al., 2018). Thousands mg/kg Se have also been reported for soils developed on black shales (e.g., Chang et al., 2019). In metalliferous black shales of Brooks Range, Alaska, average authigenic contents of Se (and other trace elements) show enrichment factors of up to 1.2×10^6 compared to modern seawater, like the enrichments in phosphorites (Slack et al., 2015).

Brumsack et al. (1989) reported an average of 2.2 mg/kg Se in Gulf of California's recent sediments. In marine coring samples, a sharp maximum in Se concentration (lower than 60 mg/kg) occurs immediately below the inferred depth of oxygen penetration, followed by Ag and C (Crusius & Thomson, 2003). In sediments deposited in upwelling area offshore Namibia, high average concentrations are reported (13.8 mg/kg Se; Borchers et al., 2005) as well as in sediments offshore Peru (8.6 mg/kg Se; Baturin, 2017) and Chile (maximum of 3.26 mg/kg Se; Böning et al., 2005) and other settings such as in the sapropelitic sediment of the Black Sea (6.5 mg/kg Se, Baturin, 2017).

Polymetallic nodules

During the first ventures of deep seabed mining exploration, Se concentrations in marine ferromanganese concretions and nodules were estimated between 0.02 and 1.2 mg/kg, with an average of 0.6 mg/kg (Takematsu et al., 1990; González et al., 2016). Se content in nodules and ferromanganese crusts is still considered of commercial interest, but literature data report actual concentrations of 0.6 mg/kg on average (Table 2). Available figures include mean concentrations of 0.8 mg/kg in the Cook Islands continental shelf (Hein et al., 2016); 0.5 mg/kg in the Northeast Atlantic Ocean (Muiños et al., 2013); 1.73 mg/kg in the Indian Ocean; 5.06 mg/kg in the South Pacific Ocean; 2 mg/kg in the California continental margin; 0.72 mg/kg in the Clarion Clippertone Fracture Zone (Conrad et al., 2017); 15 mg/kg in the Shatsky Rise, NW Pacific Ocean (Hein et al., 2012); 8.7 mg/kg on the Mendeleev Ridge in the Western Arctic Ocean (Kostantinova et al., 2017); a mean range of 2-7 mg/kg in the South China Sea (Guan et al., 2017). Assessment of modern polymetallic crusts and nodules remains scarce, with few sites worldwide.

Table 2. Selenium abundance in other potential geogenic sources (in mg/kg). Explicit averages and italicized entries can be taken as a reference for the different metallogenetic settings.

Type	Mean value (max. value)	Number of observations	Reference
Marine pelagic clay (average)	0.2	-	Li (1991)
Marine Shale (average)	0.6	-	Li (1991)
Marine Sediments, Bohai Sea	0.16 (1.5)	405	Li et al. (2016)
Marine Sediments, Tyrrhenian Sea	0.3 (48)*	-	Emelyanov and Shimkus (1986)
Marine Sediments, Jobos Bay	1.17 (2.74)	43	Apeti et al. (2012)
Marine Sediments, Gulf of California	2.2 (3.3)	50	Brumsack (1989)
Marine Sediments, Caspian Sea	1.6	15	Baturin (2017)
Marine Sediments, Baltic Sea	2.3	15	"
Marine Sediments, Chilean margin	2.33 (3.78)	38	Böning et al. (2005)
Marine Sediments, Black Sea	5.38 (6.5)	60	Baturin (2017); Duliu et al. (2019)
Mediterranean Sapropel	24 (44)	-	Nijenhuis et al. (1999)
Massive sulfides or VSM	128 (2500)	> 200	Juliani and Ellefmo (2018); Queffurus and Barnes (2015); Geomar (2013); Rouxel et al. (2004 a,b); Auclair et al. (1987)
Black smokers, East Pacific Rise	(2500)	> 50	Auclair et al. (1987); Stillings (2017)
Manganese crusts and nodules (average)	0.6 (15)	> 200	Conrad et al. (2017); Konstantinova et al. (2017); Hein et al. (2016, 2012); Muinõs et al. (2013); Li (1991); Takematsu et al. (1990)
North American Shale Composite (NASC)	0.08	-	Morgan et al. (1978)
Shale (average)	0.4 (42)	-	Bowen (1979); Koljionen, (1992)
Carbonaceous shale (average)	0.77 (4.6)	12	Wen and Carignan (2011)
Phosphorite (average)	4.6 (13)	6	Altschuler (1980)
Phosphorites, Peru	2.38 (6)	13	Bech et al. (2010)
Phosphorites, U.S.	7.39 (23)	9	"
Phosphorites, Africa and Middle East	7.93 (44)	14	"
Black shale (average)	18.7 (42)	44	Parnell et al. (2016)
Carboniferous Bowland shales	19.7	15	"
Black shales, U.S.	225 (1200)	-	Stillings (2017)
Black shales, Northern Europe	74.5 (1590)	> 50	Parnell et al. (2016); Bullock et al. (2018)
Gwna Group shales	61.5 (116)	12	Armstrong et al. (2018)
Volcanic ashes	1.1 (7)	37	Floor and Román-Ross (2012)
Localized epithermal deposits	48700 (213700)	1221	Števko et al. (2018)
Terrigenous/volcanic sedimentary shales (average)	6.0	550	Ketris and Yudovich (2009)

* maximum from an ISMAR-CNR collection of 158 samples (average 0.68 mg/kg) analyzed by X-Ray Fluorescence

4.2. Prospective anthropogenic sources

Selenium sourced from the atmosphere (and technosphere) re-accumulates in environmental compartments or is taken up by plants and generally converted into fuels (Appendix D). Except for Se enriched process solution from mining of major ore minerals like Cu, other sinks for Se of anthropogenic origin are not accounted for recovery. Potentially available Se can be sourced from anthropogenic supplies such as flows of substance from power plants and smelters (Kogel, 2006; Hoffmann & King, 2010), contaminated sediments, and electronics post-consumption (e.g., WEEE) and other wastes (Table 3).

Mininni et al. (2019) reported chemical data of sewage sludge from Italy, where Se concentrations can also be significant. Most Se consumed domestically is dissipated into the environment and believed to be not recoverable. From 1940 to 2010, about 60 Gg Se was used once and then dispersed worldwide (Kavlak & Graedel, 2013). Se-bearing post-consumer products consumed in everyday life may end up in landfills considering 1 mg/kg Se is the hazardous waste limit due to Se toxicity (Table 3), likely causing Se leaches out into complex, metal-loaded leachates and also pollution transfer by volatilization. Contaminated sediments from superphosphates and soils associated with coal mine environments can show high Se concentrations (Stillings, 2017). In China, several areas show Se values higher than 2000 mg/kg, as a secondary effect of the anthropic activity (Zhu et al., 2008).

Kogel (2006) has suggested a moderate enrichment factor for Se calculated for the crustal abundance similar to the enrichments observed in fly ash from coal-fired power plants and refuses from incinerators. According to Cornelis et al. (2008), Se is almost completely volatilized from slag and bottom ash of metallurgical and municipal incineration residues. However, when metal oxides absorb volatile Se^{IV} compounds, Se remains quite stable and, consequently, trace amounts of Se can be found (as Se^{IV} as the dominant species) in fly ash and air pollution control (APC) residues and

their leachates. Trace amounts of Se^{IV} and Se^{VI} have been reported in fly ash leachates (van der Hoek et al., 1996). Some traces of Se^{0} or even insoluble Se^{-II} may also be found due to the reduction of Se^{IV} by SO_2 at temperatures < 150 °C, as reported during coal combustion (Yan et al., 2001). Meawad et al. (2010) reported Se concentration of the residues from thermal power plants burning fossil fuels, such as bottom ashes (0.007-9 mg/kg Se), fly ashes (0.0003-49.5 mg/kg Se), boiler slag (0.1-14 mg/kg Se), and desulfurization residues (0.015-162 mg/kg Se). Jones et al. (2012) further elucidated that Se is leached from fine-grained coal fly ashes easier than coarse ones, but Se leaching is lower in fly ashes than bottom ashes.

In municipal solid waste incinerators (MSWI, including Waste to Energy systems), the temperature profile is retained too high in the combustion chamber for marketable Se to remain in the residue. In municipal incineration bottom ashes, Se ranges 0.05-10 mg/kg (Allegrini et al., 2014 and reference therein). In reference materials of municipal solid waste incineration ash, BCR-CRM176, and its replacement, BCR-CRM176R, Se concentration is 41.2 mg/kg and 18.3 mg/kg, respectively. Municipal incineration fly ashes generally show higher Se contents, and Huang et al. (2007) reported concentrations as high as 160 mg Se per kg of incineration fly ash.

In 2010, an estimate pointed to 2.7 Gg Se present in electrical and electronic devices globally (Kavlak & Graedel, 2013). Despite the general lack of information concerning Se contents in WEEE, Ma et al. (2020) reported a Se concentration as high as 49.77 wt. % from Cu-In-Ga diselenide chamber waste of solar cells. The potential Se in spoil tip from glass and free-machining alloys industry are generally not considered for neither beneficiation nor recycling, because it probably volatilizes during melting operations.

Table 3. Selenium abundance (in mg/kg) in selected anthropogenic samples, including regulatory limits of environmental leachates from different waste types. (MSWI: Municipal Solid Waste Incineration; FGD: Flue gas desulphurization).

Type	[Mean value] range (max. value)	Number of observations	Reference
Toxicity characteristic leaching procedure (TCLP)	(1)	*Regulatory limit of leachates*	US: USEPA (1992); China: Li et al. (2017); Yu et al. (2013); Taiwan: Liu et al. (2015); Singapore: Guo and Wu (2017)
Inert waste	(0.01)		EN (2002), B. S. 12457-2; EC (2013)
Non-hazardous waste	(0.05)		EN (2002), B. S. 12457-2
hazardous waste	(0.7)		"
Steel Slag	(0.01)		Italian Ministerial Decree 186/2006
Soils in Chinese cities	[0.23] 0.03-10.8	3799	Cheng et al. (2014)
Soils of London	[0.67] <0.2-19.6	6288	Scheib et al. (2011)
Cerrado Soils, Brazil	0.022-0.072	45	Carvalho et al. (2019)
Seleniferous soils, U.S.	2.7-90	-	Trelease & Beath (1949)
Seleniferous soils, Central China	20-95 (7007)	-	Dhillon et al. (2019); Zhu et al. (2008); Chang et al. (2019)
Superphosphates	(20)	-	Stillings (2017)
Landfill leachates	0.005-0.05	-	Lemly (2004)
Sewage sludge	2.6-4.3	84	Mininni et al. (2019)
Urban landfill	0.145-1.26	34	Roessler et al. (2017)
WEEE	(498000)	-	Ma et al. (2020)
Coal combustion fly ash	[11.7] (31)	10	Huggins et al. (2007)
FGD effluents	[1]	-	Cordoba and Staicu (2018)
MSWI Bottom Ash	0.05-10	78	Allegrini et al. (2014); Morf et al. (2013); Fedje et al. (2012)
MSWI Fly Ash	0.5-160	-	Huang et al. (2007); Morf et al. (2013); Funari et al. (2015)
MSWI Molten Fly Ash	0.05-11	-	Alorro et al. (2008); Hasegawa et al. (2014)
Arsenic-alkali residue from Sb smelting	[1800]	-	Long et al. (2020)
Ladle Steel slag	[22.7]	6	Mäkelä et al. (2013)
Non-Fe metallurgical slag	50 - 3000	-	Johnson et al. (1984), Hasegawa et al. (2014)
Mining wastes and tailings	1.55-173	12	Ziemkiewicz et al. (2011), El Amari et al. (2014), Bullock et al. (2017)
Metal foundries residue	0.10-61100	-	Bożym (2020), Shirmehenji et al. (2020)

4.3. Biological systems

Microorganisms, especially bacteria, seem craving Se in their metabolic reactions (Figure 4). Se oxyanions, selenate and selenite, are transported into bacterial cells by different processes and converted through microbial assimilatory reduction to selenide (Karle & Shrift, 1986) for the synthesis of selenoproteins. Selenium in microorganisms is essential as they use selenocysteine in various prokaryotic enzymes, including glycine reductase in several clostridia, dehydrogenases in

diverse prokaryotes, such as *Enterobacter*, *Salmonella*, *Clostridium*, and *Methanococcus*, hydrogenases in *Methanococcus* and other anaerobes. Moreover, in certain clostridial species, other bacterial Se-dependent enzymes were identified, like nicotinic acid dehydrogenase and xanthine dehydrogenase, in which the Se is part of the active site molybdenum-containing cofactor (Johansson et al., 2005; Eswayah et al., 2016). Currently, several other genera are known for producing selenoproteins, including *Clostridium*, *Bacillus*, *Shewanella*, *Salmonella*, *Enterobacter*, *Vibrio*, *Actinobacteria*, and *Pseudomonas* (Dungan & Frankenberger, 1999; Johansson et al., 2005; Zhang et al., 2006). Moreover, the recent analysis of bacterial selenoproteomes revealed the presence of a new selenoprotein-containing phylum and several species (Peng et al., 2016).

Se oxyanions-reducing microorganisms are not limited to any particular group of prokaryotes and are mainly distributed in bacteria and archaea. Major identified Se-reducing prokaryotes and their properties are reviewed by Eswayah and collaborators (2016). Some bacteria can convert both selenate and selenite to elemental Se, while others can only reduce selenate to selenite (Blum et al., 1998), or selenite to elemental Se (Eswayah et al., 2016; Piacenza et al., 2018). However, the number of isolated microorganisms that reduce selenate is relatively small compared to that of microorganisms capable of reducing selenite.

Moreover, Se is also efficiently accumulated in several plants. Significantly high Se concentrations are also reported in some legumes, nuts, and mushrooms. Accumulator plants can incorporate from 1000 to 10000 mg/kg Se: they include: *Astragalus L.*, *Conopsis* (Nutt.) *Greene*, *Oryzopsis Michx.*, *Xylorhiza* (Nutt.), *Mentzelia* L., and *Stanleya* (Nutt.) (Presser, 1999). Several species are labeled as hyperaccumulators as they can store over 1000 mg/kg Se dry weight (Bodnar et al., 2012). Selenium uptake in plants primarily occurs in the roots where it is carried out more efficiently, starting from selenate then selenite, thanks to its higher solubility in water; but also their concentration and several environmental and physicochemical properties. Furthermore, Se

oxyanions uptake depends on sulfate presence because selenate is driven into the plants through a mechanism mediated by sulfate transporters while selenite is carried through phosphate transporters (Sors et al., 2005; Gupta & Gupta, 2017).

Also, both microorganisms and plants can biomethylate Se. It represents a fundamental process in the biogeochemical cycle of Se (also critical to losing the Se in the atmosphere), converting selenate and selenite to volatile compounds, such as dimethyl selenide (DMeSe) and dimethyl diselenide (DMeDSe) (Figure 4). Cultured microorganisms that produce methylated Se species are reported by Eswayah et al. (2016). The predominant groups are bacteria and fungi found in soils and sediments, or bacteria in aquatic environments. In particular, they include bacteria such as *Aeromonas* sp. VS6, *Citrobacter freundii* KS8, and *Pseudomonas luorescens* K27 (Chasteen & Bentley, 2003), *Clostridium collagenovorans*, *Desulfovibrio gigas*, *Desulfovibrio vulgaris* (Michalke et al., 2000), *Enterobacter cloacae* SLS1a-1 (Dungan & Frankenberg, 2001), *Rhodobacter sphaeroides*, *Rhodospirillum rubrum* S1 (Van Fleet-Stalder & Chasteen, 1998), *Stenotrophomonas maltophilia* (Dungan et al., 2003; Cox & Alexander, 1974), and several fungi such as *Fusarium* spp. (Barkes & Fleming, 1974), *Penicillium spp.* (Fleming & Alexander, 1972; Chasteen et al., 1990), and *Candida humicola* (Cox & Alexander, 1974). Moreover, the algal methylation of Se compounds can volatilize a substantial amount of Se oxyanions (Oyamada et al., 1991; Fan et al., 1997; Neumann et al., 2003), offering a possible way to remove Se from the aqueous phase. Recently, the microalgae ability to biomethylate Se was also demonstrated in *Chlamydomonas reinhardtii* (Vriens et al., 2016).
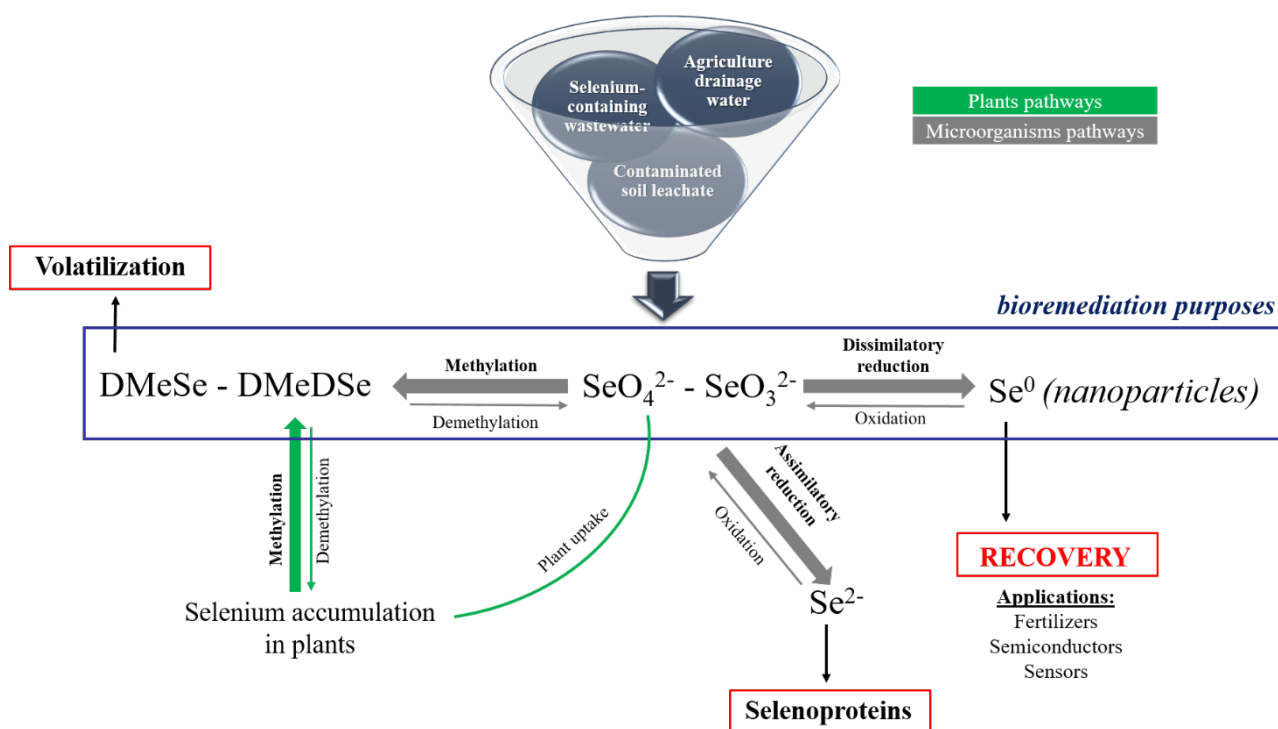
Figure 4. Se cycle sustained by plants and microorganisms can follow selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) pathways, leading to the reduction to elemental Se and the formation of volatile methylated products, respectively.

4.4. Other processes for Se recovery

Non-commercial processes are considered inadequate to meet the financial requirements of metal recovery at a large scale due to technical reasons or low concentration in the ore mineral. Processes devoted to secondary Se recovery are essentially unidentified, but they have to be considered on a case-specific basis. Besides the commercially available processes, other processes currently under investigation and some already patented rely on coagulation-based and biological methods (Baldwin et al., 1985; Goodman et al., 2000; Overman, 2000; Kashiwa et al., 2000; Fujita et al., 2002; Mollah et al., 2004; El-Shafey 2007a, b; Geoffroy & Demopoulos, 2009, 2011; CH2MHILL, 2010; Hoffmann & King, 2010; Soda et al., 2011; Pickett & Sonstegard, 2012; Fu et al., 2014; Mierzejewski et al., 2017). Membrane separation technologies are typically deployed at the final recovery stage to separate Se crystalline nanoparticles or amorphous aggregates, being MF, NF, and RO most used. Numerous oxidizers/adsorbents have been tested to biotic and abiotic

processes such as Al, Fe, Ti, Si oxides (e.g., anatase), manganese oxide, binary metal oxides ($Al(III)/SiO_2$, $Fe(III)/SiO_2$, $Fe(III)$ and $Mn(III)$ hydrous oxides), layered double hydroxides (i.e., nanostructured anionic clays, mostly Mg-Al, Mg-Fe, and Zn-Al based), graphene and magnetic graphene oxide nanocomposite, and even peanut shell and rice husk (Kashiwa et al., 2000; Mollah et al., 2004; El-Shafey, 2007a, b; Geoffroy & Demopoulos, 2009, 2011; CH2MHILL, 2010; Soda et al., 2011; Fu et al., 2014; Santos et al., 2015).

Synthetic Se nanoparticles, e.g. produced by laser ablation, are used in agriculture and hi-tech applications (Appendix A), while nature-based solutions for fixed-size particles are still developing (Figure 4). Prototyped biotechnology can be operated both in suspended-growth or packed-bed systems (Figure 5). Here, microorganisms can reduce available Se into insoluble forms, then the sludge containing the biomass is treated to recover Se (Baldwin et al., 1985; CH2MHILL, 2010). The soluble ionic Se species turn into insoluble Se metal, which can be recovered from the porous matrix and biomass using physical separation methods, e.g., differential filtration or membrane separation technology. The remaining sludge can be processed further for recovery of other metals.

There are exciting options but still immature for industrial implementation. Nonetheless, the presence of bio-accumulators and Se-tolerant plants prompted the use of different (micro)organisms for bio-recovery and bioremediation that might be adapted to sustain alternate Se supply.
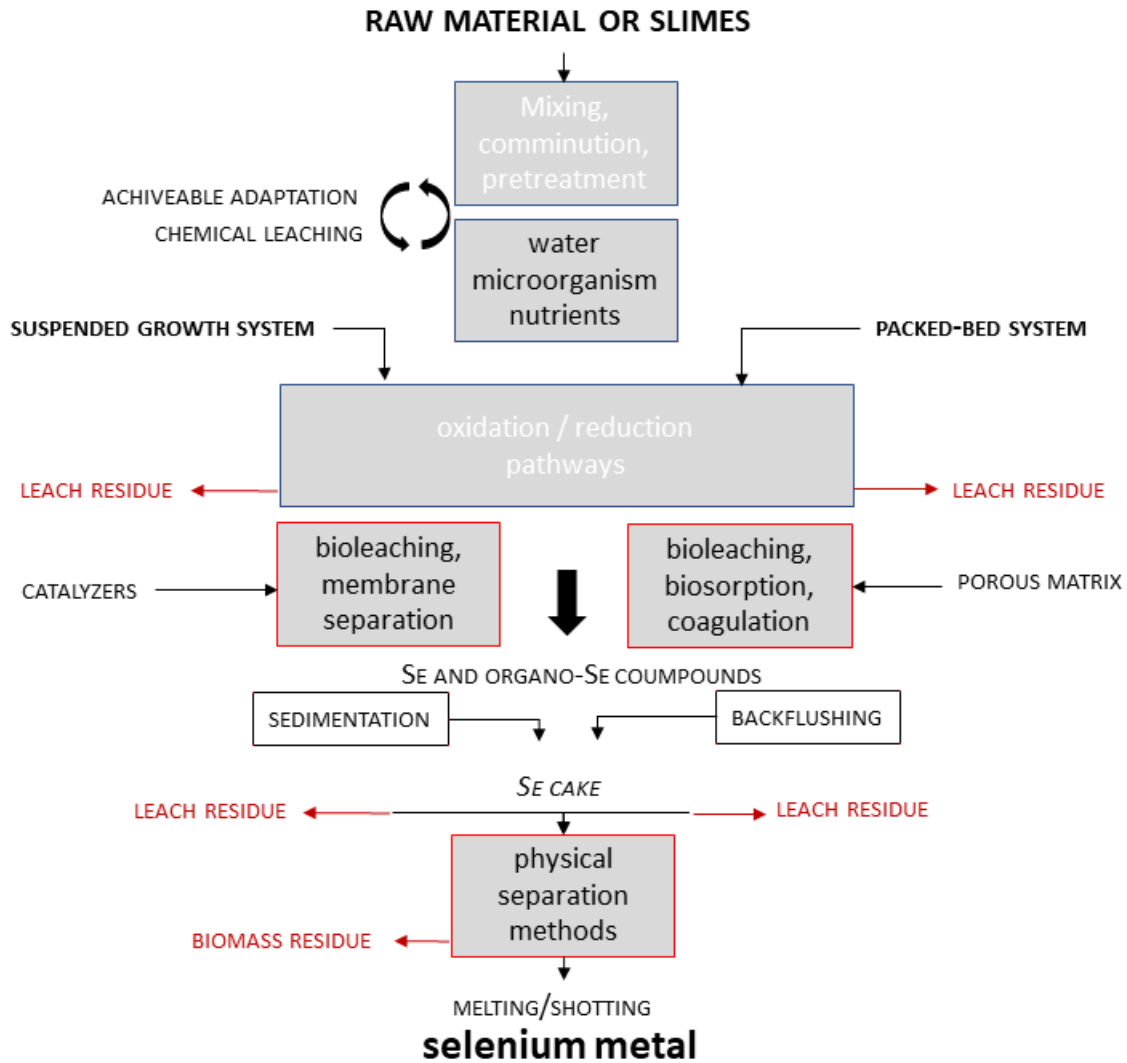
RAW MATERIAL OR SLIMES

Figure 5. Simplified process flow for Se recovery using suspended-growth and packed-ped systems in biological methods. The management of some tasks and process wastes are tough (shown in red).

Nature-inspired processes

Biological methods inherently include bacterial leaching, phytovolatilization, or deployment of biogenic metabolic substances. Mainly anaerobic or facultative-anaerobic bacteria capable of growing phototrophycally or chemotrophycally have been used for Se-decontamination purposes, thanks to their metabolic potential in bioconverting Se-oxyanions (Figure 4). The reactions of reduction of Se oxyanions, not linked to respiration or assimilation, are highly active among many

different bacteria, that can play an essential role in the environment (Eswayah et al., 2016). Instead, much less is known about the bioconversion by strictly aerobic or microaerophilic microorganisms (Tan et al., 2016), which also presents disadvantages, including the competition between the dissolved oxygen and the Se-oxyanion as terminal electron acceptor (Seghezzo et al., 1998; Chan et al., 2009), and the additional energetic cost needed to aerate a bioreactor (Tan et al., 2016).

The reduction and methylation processes involved in the Se bioremediation are thermodynamically favored compared with their inverse reactions, oxidation and demethylation, respectively, which only occur in particular situations. Therefore, microbial bioremediation truly represents a "cost-effective green alternative solution" to the conventional processes involved in the detoxification of soils and wastewaters (Oremland & Zehr, 1986; Oremland et al., 1994; Losi & Frankenberger Jr, 1998). Through bacterial leaching and phytovolatilization, substantial amounts of Se may be removed from Se-contaminated soil. Wetlands are a positive example of demonstrated biological passive treatment for Se (CH2MHILL, 2010; Huang et al., 2013). Numerous methods from soil bioremediation can apply to Se bio-recovery (Appendix D).

The degree of recovery and purification depends on Se yields. Although rapid Se recovery from biomass is practically unfeasible, several technologies based on bacterial metabolism and fungal systems have been tested in the laboratory. For example, *Agaricus bisporus* (edible basidiomycete mushroom), *Clostridium* genus, *Ganoderma lucidum* (fungus), *Eichhornia crassipes* (water hyacinth), *Lemna minor* (lesser duckweed), *Saccharomyces cerevisiae* (baker's yeast), *Cladophora hutchinsiae* (green marine alga), marine *Aspergillus terranea* have been tested for Se enrichment and subsequent extraction (Dernovics et al., 2002; Santos et al., 2015; Nancharaiah & Lens, 2015a). Furthermore, photobioreactors are emerging to include microalgae as part of integrated algal-bacterial Se removal systems, wherein Se oxyanions are removed by volatilization and bioreduction. Several algae and microalgae species can uptake different Se forms

(Doucha et al., 2009; Umysová et al., 2009; Araie et al., 2011). However, contrary to land plants, not much is known on pathways of aquatic ones, although microalgae seem to use similar sulfate and phosphate transporters for selenate and selenite uptake, respectively (Araie & Shiraiwa, 2016).

Selenate reduction has been investigated under methanogenic, sulfate-reducing, denitrifying, and hydrogenotrophic conditions (Nancharaiah & Lens, 2015a). Different bioreactor configurations have been adopted, such as up-flow anaerobic sludge blanket reactors (Seghezzo et al., 1998), sequencing batch reactors (Mal et al., 2017), fluidized bed reactors (Soda et al., 2012), plug flow reactors (Fujita et al., 2002), membrane biofilm reactors (Lay et al., 2016; Van Ginkel et al., 2011), and bioelectrochemical systems (Opara et al., 2014) capable also of retaining Se-reducing microorganisms as flocs (Mollah et al., 2004; Santos et al., 2015). To separate granular sludge or biofilms from the biomass, different types of soil, sand, cellulose, glass wool, and glass beads are used as a porous matrix for retaining microorganisms with satisfactory economic and environmental performances (Baldwin et al., 1985; Soda et al., 2011) (Figure 5). The use of microbial consortia over pure cultures in removing of toxic Se-species from environmental matrices contaminated particularly from wastewaters, is of great interest for researchers (Tan et al., 2016), as it has several advantages, including the larger volumes of wastewaters treatable, high adaptability of microbial communities to diverse conditions, the presence of synergic interactions among different microorganisms within the consortium. Moreover, it allows working in non-aseptic conditions (Tan et al., 2016), facilitating process control and reducing maintenance and operational costs (Rashamuse et al., 2007).

Different technologies and reactors have been used with microbial consortia to treat wastewaters contaminated with a large amount of Se-oxyanions. The ABMetR biofilter system from North Carolina resulted in a highly efficient biological system able to remove 99.3% Se-oxyanions, by using anaerobic microbial communities (Sonstegard et al., 2007). Moreover, an on-

site pilot-scale study was performed by an electro-biochemical reactor that was able to reduce the Se-oxyanions concentration from over 500 to 5 µg/l in coal mine wastewaters in British Columbia (Canada) (Opara et al., 2014), representing an emerging strategy for Se recovering from wastewaters (Nancharaiah & Lens, 2015a).

Recently, a multispecies biofilm consisting of several strains adapted to high Se-oxyanions concentration, including *Rhodococcus* sp., *Pseudomonas* sp., *Bacillus* sp., and *Arthrobacter* sp., was grown on granular activated carbon in anaerobic fixed-film reactors (Yang et al., 2016). It converted both selenate and selenite, with high bioprocess proficiency and led to the recovery of approximately 97% of elemental Se from agriculture drainage wastewater (Garfield Wetlands-Kessler Springs, Utah, USA) (USEPA, 2001).

Moreover, a membrane biofilm reactor, which consists of autohydrogenotrophic bacteria (e.g., *Cupriavidus metallidurans*) (Van Ginkel et al., 2011), resulted in 94% of selenate removal from low-Se solutions, with elemental Se retained inside the microbial biofilm (Chung et al., 2006) as crystalloid aggregates. Another example of hydrogen-based membrane biofilm reactor showed that biofilms exposed to a high load of selenate ranged from 1000-11000 µg/l (more than 20-200 times the maximum contaminant level for drinking water), were composed principally by denitrifying bacteria belonging to the genera of *Denitratisoma* and *Dechloromonas* (Ontiveros-Valencia et al., 2016). The complete selenate bioreduction in a membrane biofilm reactor can also be achieved using methane gas as an electron donor, instead of hydrogen. The microbial consortium was mainly composed of a specific methanotrophic genus (*Methylomonas*). Once again, the final product of the process were Se-nanospheres accumulated in the microbial biomass that could be easily recovered from starting Se concentrations as low as 1 mg/l (Lay et al., 2016). However, although these membrane biofilm reactors seem promising, the high cost of electron donors in the systems prohibits large-scale applications.

5.   Opportunities and threats of Se supply and recovery

5.1. Prospecting alternate sources

With the general advancements in mining low-grade or complex anthropogenic ores, the global anthropogenic Se cycles may experience a renaissance, especially from the recovery of selected WEEE streams such as photovoltaic panels. It has been demonstrated that the treatment of Cu-In-Ga diselenide waste chamber from solar cells can produce up to 99.96 % of recoverable Se dioxide (Ma et al., 2020). When the in-use Se stock from such a waste category can be accounted for (considering an approximate 25-year lifespan), Se outflows are best counteracted by enhanced recycling, and the estimate from Klavak and Graedel (2013) can update to reach higher sustainability indicators. The major threats for the implementation of new technologies for Se recovery are statutory and financial factors, such as the volatility of markets and metal prices, the low mineral extraction costs ("mineralogical barrier"), and the current low cost of landfill deposition; all of which are generally not favorable to resource recovery (Gomes et al., 2020). Therefore, mining low-grade deposits and marine geo-resources can find consensus if the technology readiness will be pursued for offshore extraction.

The lack of accurate models based on quantitative analysis hinders predicting new Se resources. A comparative review for dissolved Se analysis is available in Santos et al. (2015). Summarizing, beside the ineluctable flaws amongst different analytical techniques, the goodness of determination methods for Se depends on several factors: Se speciation in the test sample; type of environmental matrix (e.g., organic vs inorganic material); proper conversion of Se after distillation in the coordination compound wanted (that is, suitable to analytical measure); effective reduction/deposition to elemental Se when a gravimetric determination is desired; presence of interfering substances left behind in the sample preparative.

The prospecting of new and alternative Se resources increases even though, e.g., in dynamic hydrothermal systems, fluid flux is episodic and cyclic, and fluctuations in fluid chemistry result in heterogeneous chemical contents (i.e., zoned compositions of some smokers). Moreover, the scientific community is tenaciously against seabed mining of VMS and active hydrothermal vents because of the rare ecosystems hosted in these environments (Van Dover et al., 2018). Marine exploitation of mineral resources underpinned in different locations worldwide halted several times for major environmental concerns. Private holdings have sought mining licenses for marine phosphates with little fortune. The phosphorite-rich segment of the Baja California shelf was investigated by Odyssey Marine Exploration Inc., which received an exploration license for an area 40 km offshore from Ulloa Bay in water depths of 70–90 m. However, the Mexican government canceled the project in 2018 after the company submitted the Environmental Impact Assessment (EIA). Chatham Rock Phosphate Ltd. received a mining permit 450 km east of Christchurch in New Zealand, water depths of 400 m on the Chatham Rise, however, after public consultation and discussion of the EIA, the environmental consent required to mine the deposit was declined in 2015. Phosphates in Namibia are being targeted by Namibian Marine Phosphate (Pty) Ltd 60 km off the coast and south of Walvis Bay in water depths of 180–300 m. After a public hearing in 2013, the Namibian government issued a moratorium to perform the EIA with emphasis on the marine ecosystem before allowing mining to proceed, and the project is currently on hold.

Indeed, environmental impacts arising from commercial-scale exploitation spark concerns for the marine environment. Impacts include interferences and overlaps with fishing grounds and the tourist industry, damage to the pelagic ecology, loss of benthic fauna, increased turbidity and disturbance of the water column due to mobilization of bottom sediments and re-deposition of fine-grained particles, including heavy metals and pollutants loads. For examples, this is observed in large sediment plumes arising from the tailings discharge during the collecting of seafloor phosphates with conventional trailing suction hopper dredges (Kudrass et al., 2017). Therefore,

offshore-mining of phosphate rocks has not been attempted due to environmental concerns, the sparse distribution of marine phosphorites, prevailing economic conditions with rock phosphates prices plummeting after a brief spike in the late 2010s, and the availability of phosphates from non-marine sources.

5.2. Metal recovery

The metallurgical purification of Se requires outstanding efforts and is comparably energy demanding and less environmental friendly among the other processing stages (compare similar steps highlighted in red in Figures 2 and 5). As such, the main drawbacks threatening an effective Se recovery are drawn:

(1) the primary objective is the recovery of precious metals.

(2) Tellurium is typically co-precipitated in most sulfidic ores, being Te-Se separation a significant challenge.

(3) Pb refinery residues contain less Se than Cu, so Pb-bearing materials are typically mixed to copper slimes to lessen melting temperatures (Hoffmann & King, 2010) increasing the heterogeneity of Se phases, which, in turn, affects overall recovery.

(4) At the purification stage, gas blowing may demand high oxygen or generate dangerous sulfur dioxide emissions, or high-pressure filtration is not affordable (CH2MHILL, 2010; Hoffmann & King, 2010; Santos et al., 2015; Stillings et al., 2017)

(5) Corrosion issues and unstable precipitates are frequent (Hoffmann & King, 2010; Geoffroy & Demopoulos, 2009, 2011)

(6) Selenium yields should be elevated, and impurity level kept as low as possible in commercial products to avoid the simultaneous presence of metals like As, P, Cu, Pb, Zn, Cd, Te, and other rare metals.

(7) In the electro-coagulation process, intricate patterns of pH-dependency of Se species in solution might limit the recovery efficacy (Fu et al., 2014).

(8) Partial knowledge on Se phases precipitating in the different processing stages may lead to inaccurate yield estimation.

The numerous reactants, including organic resins, oxides and minerals (as single and mixed oxides and hydroxides), carbon-based absorbents (activated carbons and graphene), biosorbents, and adsorbents derived from natural wastes, have advantages and disadvantages depending on the targeted Se compound (Kashiwa et al., 2000; Soda et al., 2011). Regeneration and disposal of exhausted adsorbents can level the revenues, while suitability for continuous treatment should be demonstrated at least at the pilot scale for effective industrial roll-out.

For Se recovery, the most significant environmental burden is attributable to the purification and refining stages required to obtain the final metal product. The majority of Se metal is mainly obtained together with Te and Ag in the anode slimes from copper refining. The anode slimes contain 2–25 wt. % Se, on average (Hoffman & King, 2010). The recovery rate during concentration (or upgrading), processing, refining, and purification concentration is increasingly high (up to 90 % during anode slimes refinement) (Kavlak & Gradel, 2013), generating, however, significant losses of Se resource at the first stages. Life cycle assessment allows delineating that high global warming potential is associated with Ag, Te, Se, Cd, and As in decreasing order from anode slime during the primary production of Cu and Ag with higher impacts allocated to Ag depending on the metal price (Nuss & Eckelman, 2014). The by-product Se in the anode slime from Cu production shows a production factor four orders of magnitude smaller than that for Cu. Nonetheless, Se production contributes to the revenue allocation more than Te production because Se's output mass is comparably higher by a factor of two (Nuss & Eckelman, 2014).

Selenium is sold in four commercial or refined grades, even though the industry has no specifications for the several classes and some producers provide customers with their specifications. Common contaminants like Ca, Al, Si, Fe, Na, Mg, and possible hazardous impurities (e.g. As, B, Pb, Te, Hg) must be removed to reach higher purification levels. Generally, the concentration of sulfur, oxygen, and halogens must be ensured as low as possible for high-purity Se powders.

Analytical difficulties for accurate Se quantification, especially from unconventional sources, should reliably inform when estimating grades, elemental purity, and recovery process optimization. The good coverage of sequential extraction procedures on geochemical samples, in turn, facilitates identifying alternate supplies and stepwise improvements during process optimization. For Se, these procedures generally allow differentiation of five forms of Se bound after five steps of extraction, where the final separation generally relies on P-buffers at circumneutral pH (Hagarova et al., 2005; Lu et al., 2015). Biohydrometallurgical recovery of Se from polymetallic ores can be supported by evaluating sequential extraction (Dernovics et al., 2002). The Se recovery from process by-products (Cabrera et al., 2011) or low-grade and dispersed sources such as marine geo-resources and several anthropogenic materials, has the potential to be embraced by a combination of abiotic and biotic treatments, especially biological methods given the suitability of bioleaching towards recovery from low-grade ores and wastes (Gomes et al., 2020). Biological methods also serve to offset remediation (legacy sites) and operation costs by valorising wastes. This can also contribute to minimizing the environmental impacts of raw materials extraction, providing appropriate treatment for spoil tip and gangue from primary ore mining. Technology readiness level (TRL) of biological methods are comparably lower than other processes. However, as the role of Se in biological systems is better understood, Se recovery options become available and trusted. Future genetic studies and biochemical characterizations of the Se methylation and demethylation pathways could allow their modification by overexpressing the necessary enzymes, with the consequent acceleration of these

essential biological processes. With the overcoming of the limitations due to low reaction rates, these methods could become fundamental for both the bioremediation of Se compounds in Se-polluted soils and aquatic environments, as they may be removed entirely in the vapor phase and recover vapor-phase Se (Eswayah et al., 2016). Besides, the identification of proteins or other biomolecules involved in the size and surface properties of biogenic Se in bacterial cultures and/or microbial communities could be used to develop intelligent biomineralization systems essential for Se recovery, in which it is possible to induce or stop the crystallization process by using different concentrations of these molecules (Nancharaiah & Lens, 2015a). Moreover, culture-independent studies will allow understanding of the diversity and distribution of organisms able to convert Se compounds and their role in the global Se cycle to improve their use in large-scale bioreactors (Eswayah et al., 2016). The importance of resource recovery in reducing carbon emissions could receive increased attention and further contribute to leveraging the development of TRL of bioleaching shortly.

However, the current lack of work practices in the biotechnological process applied to metal recovery can lead to poor reproducibility of biological methods. There is a need to account for the effect of each porous matrix adopted (e.g. soil, sand, cellulose, glass wool, glass beads, electrolytic adsorbers) to ore minerals bioleaching or for retaining the microorganisms as well as for that of nutrient feed, essential in mine water/porous matrix to provide energy for cell growth. Such data needs integration with the negative impacts of effluent wastewaters and eventual losses of inaccessible Se in detailed life-cycle assessment to provide stakeholders with facts. Further research is required to satisfactory cover more substrate materials and inocula requirements. There is also a need to assess the after-use if excessive biomass is produced in the process. Finally, the possibility of biological hazard needs accurate assessment at the prototype phase via standardized ecotoxicity tests that still have to be fully developed and should adapt to the proposed technologies.

6. Concluding remarks

We highlight the importance of assessing potential management and prospection challenges to secure supplies from unconventional ores. Several conclusions can be made to provide a basis for further research and innovative applications for Se supply from alternate sources, including dissipated/diffuse ones:

(1) Improved data availability would improve certainty in ore prospects, given the wide variations in Se content that would be anticipated based on sulfur or organic-rich ore sources.

(2) Many technologies for Se recovery are demonstrated only at the laboratory scale and appear not economical as they present the disadvantage of the high cost related to chemicals, wastewater, and solid waste disposal. Corrosion issues can also be relevant for the factual application using currently available solutions. Detailed mineralogical investigation at the different processing steps, especially on the precipitated Se amorphous nanoparticles, should inform the recovery process.

(3) Biological methods for Se recovery are more attractive than traditional ones because of low operational costs and impacts on the environment. Still, coverage of data is necessary to increase TRL.

(4) The performance of any technology should be evaluated on a case-specific basis, optimized and demonstrated at the pilot scale before deployment. Virtually, the starting Se concentration is not a limiting factor but rather the concentration of other metals and impurities must be well-known to assure suitability of a process tailored to Se separation and purification.

A better understanding of modern metallogenic sectors and their implications with biological systems will enhance sustainable supplies.

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Opportunities and threats of selenium sources from unconventional and low-grade ores: A critical review

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A. Selenium and global uses at the glance

Selenium is a major constituent in some selenides, selenites, and selenates, compounding with Se^{2-} or $[Se_2]^{2-}$, $[Se^{4+}O_3]^{2-}$, and $[Se^{6+}O_4]^{2-}$ anions, respectively. Also, it can occur as native Se (Se^0) and in other sulfosalts at high concentrations. Selenium belongs to the group of chalcogens and displays a chemical behavior similar to sulfur; for this reason, it is a minor constituent of numerous sulfides and some tellurides. As per its many oxidation states Se can be one of the most mobile elements during rock weathering so that it can be found in a variety of environmental sinks and numerous minerals due to different authigenesis.

Regarding Se global uses, compounds of strategic importance for the industry include Se-dioxide, Se-disulfide, cadmium selenide and sulfoselenide, sodium and other selenites, and some organic Se compounds, such as phosphine selenides (Langner, 2003; Stillings, 2017). The glass industry uses approximately 25% of the total Se production (Langner, 2003). The use of cadmium sulfoselenide is predominant in inorganic pigments, plastics, paints, enamels, inks, rubber, and ceramics, while other selenides are commonly used in glassware for brown nuance coloration. Moreover, selenide minerals act as vulcanizing agents in rubber production. A fraction of 10-15% Se globally produced each year is used in accelerators, gaseous electric insulation (as Se hexafluoride), solvents, and lubricants. The remaining Se is used in metallurgy for stainless steel and refractory metals, in the electrolytic production of manganese, in medical and pharmaceutical topical preparations (e.g., against dandruff), as dietary supplements in agriculture (as a macronutrient for humans and livestock).

Numerous applications are associated with Se nanoparticles produced either synthetically (using laser ablation; Gudkov et al., 2020) or biologically (Eswayah et al., 2016). Selenium nanomaterials find extensive use in frontier technologies such as electronics, catalysis, and sensors (Chaudhary & Mehta, 2014). The application of Se zero-valent-state nanoparticles in agricultural technology is

increasing as it demonstrates beneficial as an amendment for soil or fertilizers to overcome Se imbalance problems in agricultural lands (e.g., Gudkov et al., 2020).

B. Commercial ore deposits

Commercially exploited Se belongs to no less than three types of mineral deposits models proposed by Cox and Singer (1986), namely "Deposits related to felsic porphyroaphanitic intrusions", "Deposits related to marine felsic to mafic extrusive rocks", and "Deposits in clastic sedimentary rocks". Here, a simplified classification of metallogenic deposits is deliberately adopted to give an idea of permissive levels in different environments and geographic locus (Table B.1), readapting the data from Stillings (2017) and reference therein. While the formation of sulfides of economic interest is widespread, selenides ores are infrequent and with comparably limited extent of mineralization. The local concentration of selinides occurred owing to dynamic redox environments.

Table B.1 Overview of different Se deposits around the world. Types of deposit are listed according to simplified metallogenic settings with descending Se concentrations (in mg/kg).

Type of deposit	Economic mineralization	Location	Mean value	Notable facts and figures
Magmatic/Hydrot hermal	in selenides	Australia	334700	Pilbara region, Copper Hills (up to 45 g/100g in oosterboschite)
	"	DRC	313200	Katanga Copperbelt, Musonoi Mine (up to 70 g/100g in trogtalite)
	"	N-Europe	290100	Skrikerum deposit, Småland (in selenojalpaite)
	associated with sulfides	Australia	140000	Iron Oxide Copper Gold (IOCG) dam (up to 19 g/100g)
	in selenides	Brazil	122000	Serra Pelada Au-Pd-Pt deposit (in sudovikovite)
	associated with sulfides	Spain	91200	Providencia Mine, Leon (in villamaninite)
	"	Turkey	26100	Murgul deposit, (in tetradymite)
	associated with chlorinated Au-Ag veins	USA	17400	Nevada, Humboldt County, National District, Buckskin Mountain (up to 21.91 g/100g)
	associated with sulfides	SE-Europe	2000	Glava, Grusen, Moberg, Tinnsjå, Tjøstølflaten (up to 4617 mg/kg in bornite)
	"	"	700	Banatitic Magmatic and Metallogenetic Belt (BMMB) (up to 1045 mg/kg in cretaceous skarn)

	"	Chile	600	Pascua deposit
	in chalcopyrite-molybdenite	Kazakhstan	200	Boshchekul' deposit (up to 800 mg/kg in molybdenite)
	associated with sulfides	Russia	130	Zyuzel'skoye deposit (up to 495 mg/kg in pyrite); Noril'sk, Oktyabr deposit (up to 496 mg/kg in millerite); Gay deposit (up to 550 in pyrite)
	"	Canada	20	Foudulac, Algold
Volcanic/Exogenous	associated with native sulfur	Hawaii	51800	Near Kilauea volcano
	"	Italy	11300	Lipari island
	"	Portugal	2900	Zambujal orebody (up to 3220 mg/kg)
	associated with andesite tuffs or volcanic soils	New Zealand	2500	Broken Hills deposit
	associated with native sulfur	Russia	1500	Kurile Islands, Kamchatka, Paramushir Island (up to 1900 mg/kg)
	associated with andesite tuffs or volcanic soils	USA	1200	Shoshone, Jasper, and Riverton deposits
	associated with native sulfur	Australia	240	Dry River South deposit (up to 760 mg/kg)
Hydrothermal/Epithermal	associated with other sulfides	Japan	93000	Suttsu Mine (up to 13 g/100g in kawazulite)
	"	Italy	23900	Baccu Locci Mine (up to 13 g/100g in clausthalite)
	associated with precious metals	Russia	480	Kirovskoye deposit (up to 0.33 g/100g in bismuthinite of quartz-gold ore)
	associated with other sulfides	Canada	180	Geco Mine (up to 595 mg/kg in pyrrhotite)
	in chalcopyrite-molybdenite	Armenia	120	Dzhindara deposit, Kadzharan deposit (up to 500 mg/kg in molybdenite)
	"	Canada	120	Sudbury deposit (up to 152 mg/kg in Cu-Ni ore)
	associated with other sulfides	Russia	80	Bukuka deposit (up to 175 mg/kg in pyrite)
	associated with precious metals	Brazil	40	Serra Pelada (in bulk rock of bonanza grade Au-Pd-Pt)
	"	Canada	40	McIntyre Mine (up to 110 mg/kg in low-temperature pyrite)

C. Non-commercial geogenic ore deposits

Sulfides and minerals such as pyrite should be considered a potential source of economic interest for this element. The growing necessity for Se sources has led to an increasing focus on and reviewing former ore mining sites (Bullock et al., 2018) and untapped sulfide and iron ore deposits. Sometimes altered products can be richer in Se than the primary sulfide ores due to oxidation processes and formation of goethite and haematite (Bullock et al., 2018). As such, chemogenic volcanogenic sedimentary rocks are compelling targets exemplified by jaspers, phosphorites, and depositions of sulfur, exogenic iron ores, and manganese oxides. These naturally occur within mid-

oceanic ridges and rift valley systems. Deposits of native sulfur were exploited to supply Se in the Hawaiian Islands, Lipari Islands and Mount Etna (Italy), Kunashir and Kurile Islands, and many other locations in Kamchatka (Russia), and New Zealand (e.g., The Great Barrier Islands). However, these sources are localized and do not offer suitable volumes for sustainable extraction. Even though effective sorption of Se in volcanic soils from Hawaii, Mount Etna in Italy, and New Zealand with compounds like ferrihydrite, poorly crystalline aluminosilicates, and organic matter, has been reported, the enrichment is site-specific and likely trivial because Se is not easily leachable from volcanic soils (Floor & Román-Ross, 2012).

It is also well ascertained the connection between Se and organic components with accumulation or depletion likely controlled by diagenesis, being clearest examples coals and marine shales (Presser et al., 2004; Stillings, 2017). For example, phosphogenesis involves diagenesis of P-bearing phases, chiefly from organic matter, in marine sediments, the release of P to interstitial waters, the local supersaturation of P, and authigenic minerals formation (e.g., carbonate fluorapatite, framboidal pyrites).

We can only surmise that sulfate and phosphate transporters (*sensu* Araie & Shiraiwa, 2016) may play a key role in the destiny of Se delineating hydrothermal and biogenic enrichment pathways in natural environments that may be followed in prospecting. However, for example, in modern and ancient VMS, the distribution of trace elements is ultimately a function of the temperature of precipitation of the sulfide minerals (Layton-Matthews et al., 2005). More efforts are needed to determine how the correlation between temperature and mineral assemblages of sulfides and other authigenic minerals affects Se contents.

C.1 Other geogenic deposits untapped for selenium

A former mining site near Kongsberg, Norway, is primarily composed of sulfide ore deposits of hydrothermal origin, which occur within Precambrian metamorphic basement, and has been extensively worked for Cu and Ag extraction leaving behind trace elements that are believed to

reach toxic levels when naturally released or leached out (Bullock et al., 2018). Notably, the sulfide ore contains exceptionally high concentrations of Se, hosted within selenides. Selenium is also present within the sulfide ore in pyrite and chalcopyrite, which contain up to 688 mg/kg Se. Additionally, oxidative weathering of the exposed bedrock has resulted in the accumulation of hyper-enriched, unconsolidated weathered crust deposits at the surface (up to 1590 mg/kg Se) (Bullock et al., 2018).

Also, the Neves-Corvo deposit of Iberian Pyrite Belt (Portugal) is not exploited for Se despite its significant amounts, especially in the Zambujal orebody (Table B.1). The deposit is one of the leading producers of Cu and Zn of the European Union and, despite the falling grade of Cu, the overall abundance at the deposit scale due to the small size of Se-rich galena and other sulfides implies that Neves-Corvo deposit does not represent a mineable resource (Carvalho et al., 2019). We have seen that Au–Ag epithermal deposits may be enriched in Se; generally, only the low-sulfidation types are noted for selenide mineral occurrences, though little research has been undertaken on Se-rich phases in high sulfidation epithermal deposits (Simon et al., 1997). In the Neogene Kremnica (porphyry-Cu deposit) ore district in Slovakia, the base-metal ore mineralization composed of pyrite, sphalerite, and chalcopyrite lacks Se, whereas the superimposed low-sulfidation Au–Ag paragenesis is Se-enriched, showing selenide phases. This mining district is mainly exploited for precious metals recovery, although a mean value range of 0.1-21.4 wt. % Se is reported, with maxima associated with naumannite (Ag_2Se) and clausthalite (PbSe) (Števko et al., 2018). Besides selenides, the most Se-enriched phases are miargyrite, proustite–pyrargyrite, and polybasite–pearceite. Historical gold deposits such as those of Central Slovakia Volcanic Field including Banská Štiavnica, Kremnica, Hodruša-Hámre, and Nová Baňa, were important sources of precious and base metals in the past, revealing today the highest contents of Se ever found worldwide in vein-type sulfosalts locally scattered and limited in volumes in both quartz and

dolomite (Števko et al., 2018). Similarly, the Pierina high sulfidation epithermal Au–Ag deposit in Peru (hydrothermal deposit) hosts pyrite containing 78-131 mg/kg Se (Fitzpatrick, 2008).

D. Global Se-cycle and the technospheric mining

Se is potentially mineable in contaminated sediments from superphosphates and those in the vicinity of Cu and Pb smelters and refineries, but also incineration residues (especially after combustion of organic or P-rich waste), coal ash, municipal fly ash and bottom ash, Se-rich wastewaters and sludge (e.g., from treatment plants for phosphorus production), landfill leachates, plastics and oil waste, and other mining waste dump resealing Se are compelling sources of anthropogenic Se (Kabata-Pendias & Pendias, 2011; Kogel, 2006; Hoffmann & King, 2010). The total emission into the atmosphere is higher than six kilotonnes per year, in the form of small particles and volatile compounds (Kabata-Pendias & Mukherjee 2007), mainly credited by volcanic activity. Floor and Román-Ross (2002) reported Se concentration ranging from <0.2 to 7 mg/kg in volcanic ash, substantially higher than those in rocks (Table 1; Table B.1). This let us surmise a significant contribution of the anthropic activity to the global Se budget. It is commonly believed that Se from pigments, fertilizers, animal feeds, chemicals, and pharmaceuticals, is dispersed without any possibility of avoiding loss of resource.

Depending on its bioavailability, Se is taken up by several organisms and converted into organic compounds, such as Se-containing amino acids, including selenomethionine and selenocysteine (the 21st proteinogenic amino acid), involved in the biosynthesis of a large number of selenoproteins, which have been observed in eukaryotes, archaea, eubacteria, and viruses (Yi et al., 2003; Lobanov et al., 2009; Lin et al., 2015), sometimes serving as a detoxifying mechanism.

In successful biological treatments, microorganisms can convert soluble Se oxyanions into the less toxic elemental Se paving the way to bioremediation strategies. In soil, sediment, and water, microbial dissimilatory reduction of soluble Se oxyanions is known to be an essential process for detoxification. So it might suit bioremediation purposes, unlike assimilatory reduction that is less

significant for this purpose due to the extremely low Se fluxes involved (Eswayah et al., 2016). During the dissimilatory Se reactions, certain bacteria can use Se oxyanions reduction, not only for detoxification (Losi & Frankenberger, 1998; Kuroda et al., 2011; Tan et al., 2016), but also as electron donors for anaerobic respiration and energetic purposes (Knight et al., 2002; Nancharaiah & Lens, 2015a). Reversible and irreversible redox processes must be recognized to exploit effectively electrical conduction in potentially deployable microbial recovery cells (Gomes et al., 2020). Bioleaching taking in loan bioremediation methods and electrodialytic remediation can be combined for metal recovery.

D.1 Bioremediation and wastewater treatment

Besides recovery, biological methods can, at the same time, have a considerable impact on the bioremediation of Se-contaminated environments. Although the narrow gap lining between bioremediation and biorecovery, here follows a brief description of available methods used in bioremediation and sludge/wastewater treatments not finalized to revering commercial Se.

To take advantage of bioremediation, in the last 30 years, several studies were performed, indicating that many microorganisms may be used in these treatments. For example, Se-oxyanion-containing oil refinery wastewater, at the concentration of 3.7 mg/l, was treated in a laboratory-scale bioreactor system inoculated with the selenate-respiring bacterium *Thauera selenatis*; it activated a reduction of 95% of the Se oxyanion levels that were converted to elemental Se, easily removed from the water phase because of its insoluble characteristics (Lawson & Macy, 1995). Thanks to its unique metabolism, *T. selenatis* was also employed on a pilot scale to remediate drainage water from the San Joaquin Valley, CA. The inflow through the system had a Se oxyanion concentration of 0.237 mg/l, and 97.9% was converted to recoverable insoluble Se. This high removal of elemental Se from the reactor effluent was facilitated via polymer coagulation with the commercially available Nalmet 8072, which helped to overcome the technical challenge of Se recovery (Cantafio et al., 1996).

Moreover, an anoxic continuous flow bioreactor was used for removing high concentrations of toxic soluble Se oxyanions (41.8 mg/l) by using *Bacillus* sp. SF-1, a selenate-reducing bacterium able to transform selenate into elemental Se via selenite, in the presence of lactate as the electron donor. With short cell retention times (2.9 h), the system effectively removed selenate with an accumulation of selenite, but at long cell retention times (95.2 h) both selenate and selenite (>99%) were successfully reduced into nontoxic elemental Se (Fujita et al., 2002). However, the combination of the bioreactor and different physicochemical methods useful for removing selenite (e.g. chemical precipitation, catalytic reduction, and ion-exchange) can be used as a good strategy for the treatment of selenate-containing wastewater. Moreover, the combined use of *Bacillus* sp. SF-1 and selenite-reducing bacteria could represent another efficient strategy by the bioaugmentation of *Bacillus* sp. SF-1 into an existing anaerobic wastewater treatment process, or the use of the bioreactor followed by anaerobic wastewater treatment (Fujita et al., 2002).

Also, bioaugmentation studies using *Pseudomonas stutzeri* NT-I with 256-litre pilot-scale bioreactors, under slightly aerobic conditions, were employed for the bioremediation of Se-containing refinery wastewater, demonstrating their practical potential for Se removal (Soda et al., 2012). In constructed wetland systems, a pre-treatment unit involving the use of *Chlorella vulgaris* was able to remove 96% of supplied Se oxyanions (1.58 mg/l) from river water entering the Salton Sea (California), within 72 h. This arrangement allowed up to 61% of the Se to be removed by volatilization to the atmosphere (Huang et al., 2013).

Recently, a sequencing batch reactor was used for selenate removal, in the presence of NH_4^+ and an activated sludge collected from a wastewater treatment plant; the microbial consortium removed up to 100% of selenate and 95% of ammonium (Mal et al., 2017). Moreover, a microbial consortium composed of aerobic rhizobacteria belonging to *Bacillus* genus was used for the bioremediation of Se-contaminated soils, generally less explored than wastewater treatment, showing a higher rate of

removal for selenite, due to its greater bioavailability in the soils compared to selenate (Prakash et al., 2010).

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