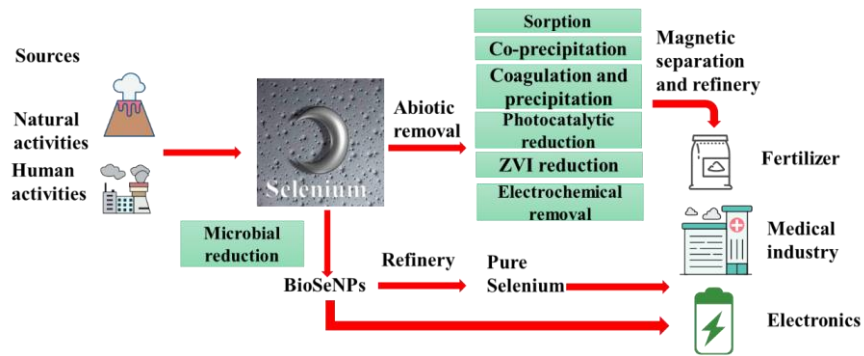


## Graphical Abstract



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**Highlights:**

- Biogeochemical cycling of Se presents opportunities for Se recovery
- Se recovery is urgent from both environmental and economic perspectives
- Bioreactor design and morphology control of BioSeNPs are critical for Se recovery
- Magnetic separation after remediation techniques is promising for Se recovery

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**Selenium (Se) recovery for technological applications from environmental matrices based on biotic and abiotic mechanisms**

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1 **Abstract:**

2 Selenium (Se) is an essential element with application in manufacturing from food  
3 to medical industries. Water contamination by Se is of concern due to anthropogenic  
4 activities. Recently, Se remediation has received increasing attention. Hence, different  
5 types of remediation techniques are listed in this work, and their potential for Se  
6 recovery is evaluated. Sorption, co-precipitation, coagulation and precipitation are  
7 effective for low-cost Se removal. In photocatalytic, zero-valent iron and  
8 electrochemical systems, the above mechanisms occur with reduction as an  
9 immobilization and detoxification process. In combination with magnetic separation,  
10 the above techniques are promising for Se recovery. Biological Se oxyanions reduction  
11 has been widely recognized as a cost-effective method for Se remediation,  
12 simultaneously generating biosynthetic Se nanoparticles (BioSeNPs). Increasing the  
13 extracellular production of BioSeNPs and controlling their morphology will benefit its  
14 recovery. However, the mechanism of the microbial production of BioSeNPs is not well  
15 understood. Se containing products from both microbial reduction and abiotic methods  
16 need to be refined to obtain pure Se. Eco-friendly and cost-effective Se refinery  
17 methods need to be developed. Overall, this review offers insight into the necessity of  
18 shifting attention from Se remediation to Se recovery.

19 ▪ **Keywords:** Biogeochemical cycling of selenium; Resource recovery; Selenium  
20 oxyanions reduction; Bioremediation.

21

## 22 1. Introduction

23 Selenium (Se) is crucial for industrial applications and an essential micronutrient  
24 for life [1]. Se semiconductor, photoconductor, photoelectrical, and catalytic properties  
25 play essential roles in the electronics industry, driving the market need for high purity  
26 Se [2, 3]. This element has a narrow range between beneficial and toxic ( $40 \mu\text{g day}^{-1}$  <  
27 beneficial <  $400 \mu\text{g day}^{-1}$  < toxic) [4]. Se deficiency increases the risk of cancer [5].  
28 However, excessive exposure to Se can cause acute poisonings, such as cardiovascular  
29 difficulties and chronic damage to mental and body health [6]. Both human and natural  
30 activities can cause Se contamination to environmental matrices, such as mining,  
31 petroleum refining, agricultural irrigation, and volcanic activities [7-9]. The extensive  
32 use of Se generated a widespread of Se contaminated wastewater, primarily containing  
33 soluble Se oxyanions, including selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ) [6, 10].

34 Se is widely distributed in the Earth crust but with a low concentration (0.05–0.09  
35  $\text{mg kg}^{-1}$ ), less than any other nutrient element. There is currently no ore from which Se  
36 can be mined as a primary product [11]. Currently, the main source of Se is the by-  
37 product of copper anode slime [12]. Prospective Se geogenic sources such as  
38 phosphorites, black shales and organic-rich sediments for Se supply have been  
39 proposed recently [13]. However, the natural occurrence of Se in these sources is not  
40 well understood, and the potential linkages between global biogeochemical Se cycling  
41 and Se recovery have received limited attention. Bridging these fields will reveal  
42 opportunities to support Se recovery and contribute to a resilient environment and  
43 circular economy thinking [14, 15].

44 Abiotic methods such as sorption, coagulation and precipitation are well  
45 recognized as effective Se removal techniques. However, they are rarely reported or  
46 discussed for Se recovery. These procedures followed by magnetic separation might  
47 provide another option for Se recovery [16]. Se removal through microbial reduction  
48 has received increased attention from researchers [17, 18]. In most studies, amorphous  
49 red Se nanoparticles in the colloidal form (BioSeNPs) were observed [19, 20].  
50 Currently, most studies addressing Se remediation concentrate on the removal

51 efficiency (the percentage of Se that is removed) and removal rate (the amount of Se  
52 that is removed in a specific time) of Se but ignore characterization of the Se containing  
53 product, which is critical for cost-effective Se separation and recovery [21].

54 Several reviews have been published on remediation approaches for Se [22-25],  
55 or biogenic synthesis of BioSeNPs [26, 27]. However, Se recovery was not fully  
56 explored even though there is potential to offset treatment costs and support a circular  
57 economy [23]. The main goals of this work are to highlight the importance of Se  
58 recovery, review Se remediation methods and their possibility to facilitate Se recovery.  
59 Abiotic Se remediation approaches followed by magnetic separation for Se recovery  
60 are proposed, and microbial Se reduction is highlighted in this review.

## 61 **2. Se cycle, contamination, and bioaccumulation**

62 Understanding Se cycles is the basis for understanding Se's environmental impact  
63 (Figure 1). Se's biogeochemical cycling can have implications for its recovery. Se  
64 normally exists in four valence states in the natural environment: Se(VI), Se(IV), Se(0),  
65 and Se(-II). Se(VI) and Se(IV) have high mobility as they are water-soluble and thus  
66 can pose health threats, while Se(0) is insoluble and less toxic [28]. Inorganic Se(-II)  
67 can be oxidized once it contacts oxygen, and most Se(-II) exists in organic forms such  
68 as selenocysteine (SeCys) and selenomethionine (SeMet), or as selenide mineral [28].  
69 Three mechanisms control Se speciation (depending on microbial activities, redox  
70 conditions, pH): oxidation vs reduction, mineralization vs immobilization, and  
71 volatilization. They affect Se immobilization in the natural environment and Se  
72 remediation in wastewater [29]. Globally, 45,000 tons of Se is released into the  
73 environment from natural activities per year [30]. Natural sources of Se mainly include  
74 volcanic eruptions and biogeochemical processes of Se containing rocks [31].  
75 Volcanoes eject massive amounts of toxic metal elements, including Se, into soils,  
76 water and the atmosphere [32]. About 76,000-88,000 tons of Se is released into the  
77 environment by human activities each year [30]. Major anthropogenic activities causing  
78 Se contamination are mining, fossil fuel combustion, fertilization, and precious metals  
79 processing such as copper, silver, and gold [33-36].

80 The lithosphere is the origin of Se (Figure 1). Rocks contain about 40% of the  
81 Earth's crust's total Se, mainly in sandstone, quartzite, and limestone [37]. Se can also  
82 be found in phosphatic rocks (e.g., phosphate rocks) and sulfur (S) containing rocks  
83 (e.g., chalcopyrite, pyrite) due to structural similarities between Se and P or S oxyanion  
84 [30, 38, 39]. Biogeochemical processes of rocks such as weathering, rock-water  
85 interactions, and biological activities can control Se migration from rocks to other  
86 phases and its distribution around the Earth [39]. Se concentration is elevated in the soil  
87 as Se fertilizer is adopted for tackling Se deficiency [36]. Some Se hyperaccumulating  
88 plants native to seleniferous soils accumulate Se up to 100-fold greater than other plants  
89 (15,000 mg·kg<sup>-1</sup> dry weight) [40]. Various Se tolerant organisms may utilize Se rich  
90 plants, thereby facilitating Se transport into the food webs with subsequent cycling in  
91 other phases [40].

92 Annually, 14,000 tons of Se flow from the terrestrial system into the marine system  
93 through surface and groundwater [30, 41]. Mediated by microorganisms, Se(0)  
94 nanoparticles coated by biopolymer with colloidal stability (BioSeNPs) can be  
95 produced. In seawater, the presence of counter cations can substantially decrease the  
96 colloidal stability of BioSeNPs in contrast to freshwaters, which results in the  
97 concentration of Se on the sediment surface, representing an eventual sink for Se mobile  
98 pool [29]. Compared with surface water, groundwater normally contains higher  
99 concentrations of Se due to contact with rocks [30, 42]. Besides, Se in the deposited ash  
100 from volcanoes, mining and combustion would permeate into the water system through  
101 surface runoff and penetration.

102 Cases of Se pollution around the world and its threat to wildlife are listed in Table  
103 1. In China, the biggest coal producer and consumer, Se released by coalfired power  
104 plants in 2020 was estimated to be 459.57 tons [43]. In industrial effluents and process  
105 wastewaters, Se concentrations ranging from 0.03 to 1.4 mg L<sup>-1</sup> were detected due to  
106 its presence in crude oil [44]. In mining wastewaters, Se was found with concentrations  
107 up to 12 mg L<sup>-1</sup> [45]. Se biofortification in agriculture for increasing human intake of  
108 Se was proposed and proved to be the most viable method for increased human  
109 consumption [40]. Se fertilizers have been adopted and increased the Se concentration

110 in the soil, as not all added Se in the soil can be absorbed and used by plants [36]. Plants'  
111 uptake efficiency of Se varies from <1% to >50%, which is affected by Se speciation  
112 and soil properties [29]. Most of the Se in fertilizers remains in the soil and enters water  
113 bodies through soil leaching and surface runoff. Therefore, Se in wastewater increases  
114 Se concentration in aquatic or other compartments of the ecosystem without proper  
115 treatment. Many studies have reported that fish and birds die due to excessive intake of  
116 Se [29]. For example, 19 of the 20 fish species in a Se polluted lake in the US were  
117 eliminated [46]. In addition, animals with greater nutritional requirements in aquatic  
118 and terrestrial food webs may be overexposed to Se and poisoned [29]. Se  
119 contamination has become a concern because of its toxicity and bioaccumulative  
120 character in food webs. Thus, Se remediation is imperative [47].

### 121 **3. Increasing market demand of Se and its circular economy**

122 Due to its photosensitivity and semiconductor properties, Se is widely used in  
123 electronics, such as photocells and solar cells which represent about 30% of total Se  
124 demand [2, 3, 48]. High-purity Se is the primary and essential light-absorbing medium  
125 in photocopiers [49]. Se is also an important physical decolorizer and stain in the glass  
126 manufacturing industry, e.g., red lights at intersections are made with Se amended glass  
127 [50]. As a result of the continuous improvement in low-carbon energy development,  
128 there is an increasing demand for pure Se [51, 52]. For example, magnesium (Mg)-Se  
129 batteries have been developed to boost the kinetics of magnesium ions inside Se-based  
130 cathodes, as the electric conductivity of Se ( $1 \times 10^{-3} \text{ S m}^{-1}$ ) is 25 orders of magnitude  
131 greater than that of S ( $5 \times 10^{-28} \text{ S m}^{-1}$ ) [53]. BioSeNPs synthesized through microbial  
132 reduction have recently received increasing attention [26], and have been reported to  
133 be antibiotic, antimicrobial and anticancer agents [54, 55], adsorbent for metal, e.g., Cu,  
134 Zn, Cd, dyes and fertilizer, which can immobilize mercury (Hg) [56].

135 Se is an essential nutrient for humans and animals [36]. Selenoproteins and  
136 selenoenzymes are vital in thyroid hormone metabolism [57], immune function [58],  
137 and antioxidant defenses [59]. Oral supplements containing Se are popular, with  
138 various brands offering different dosages and Se species. Se effectively reduces cancer



139 risk, inhibits oxidation, and supports the immune system [60]. Soil fertilization is one  
140 of the major agronomic practices for Se biofortification and plays an essential role in  
141 agriculture [61]. Se deficiency has been considered a global health issue that causes  
142 endemic diseases, e.g., Kashin-Beck disease in Eastern Siberia, Northern China and  
143 North Korea [62, 63]. A survey showed that half to one billion people are Se-deficient  
144 around the world [64]. For example, Denmark, Finland, New Zealand, eastern and  
145 central Siberia (Russia), and China contain minimal average amounts of Se in their soils  
146 [64]. Thus, agronomic biofortification through soil or foliar Se fertilizers has been  
147 studied and applied. For example, almost all fertilizers used in Finland since 1985 have  
148 Se because of a deficient Se intake in the 1970s ( $0.025 \text{ mg day}^{-1}$ ). Before Se  
149 supplementation of fertilizers started, the mean human plasma Se concentration in  
150 Finland was  $0.89 \mu\text{mol L}^{-1}$ , with the mean plasma Se level reaching  $1.4 \mu\text{mol L}^{-1}$  in the  
151 2010s [65]. The reference range in the United States for plasma Se is about  $0.87\text{-}2.14$   
152  $\mu\text{mol L}^{-1}$  [66]. Serum or plasma Se concentrations are believed to achieve maximum  
153 glutathione peroxidases expression at  $1.14\text{-}1.27 \mu\text{mol L}^{-1}$  [67]. Se fertilizers can  
154 increase the nutritional quality, including vitamin C, soluble protein, which has also  
155 been associated with antiviral resistance [68, 69].

156 Due to increased market demand, Se resources have become critical in recent years  
157 [13, 70]. Between 2002 and 2005, Se's (temporary) scarcity had a huge impact on  
158 market prices when the price of Se skyrocketed by a factor of 12 [71, 72]. Currently,  
159 according to the Shanghai Metals Market, the leading chemical supplier, high purity Se  
160 powder costs around  $16\text{-}18 \text{ US\$ kg}^{-1}$  [13]. However, Se cannot be exploited through  
161 conventional ore exploration as it is extremely scattered. Currently, primary sources of  
162 Se are extraction from copper anode slimes and flue gas desulfurization effluents [48,  
163 73]. Se concentrations can be as high as  $12 \text{ mg L}^{-1}$  in mining wastewater. If a median  
164 is taken to be  $6 \text{ mg L}^{-1}$ , with a recovery efficiency of 83.2%, 5 g Se could be obtained  
165 from  $1 \text{ m}^3$  wastewater [48]. The motivation for a cost-effective alternative resource of  
166 Se is evident, and economically feasible Se recovery technology is urgent.

#### 167 **4. Se remediation techniques and potential recovery**

168 Se remediation techniques in wastewater can be classified into abiotic and biotic  
169 according to whether microorganisms are involved [74-76]. Abiotic Se remediation  
170 techniques, including sorption, co-precipitation, coagulation and precipitation, are well-  
171 recognized and can be combined with reduction in photocatalytic, zero-valent iron  
172 (ZVI), and electrochemical systems. In microbial Se remediation, different mechanisms  
173 such as sorption, reduction, transfer to organic materials, and volatilization by  
174 microorganisms coexist [77, 78]. Microbial reduction of soluble Se oxyanions to  
175 insoluble Se(0) is the dominating microbial Se removal mechanism. It has attracted  
176 increasing attention from researchers due to the formation of BioSeNPs and its low cost  
177 [74, 79].

178 Product separation is an indispensable step for achieving Se recovery. Two factors  
179 can be optimized for cost-effective BioSeNPs (product of microbial reduction) recovery.  
180 These are (1) the morphology of BioSeNPs through adjusting operating conditions of  
181 bioreactors and (2) settling by gravity through the configuration design of bioreactors  
182 [21]. Compared with BioSeNPs recovery, less attention has been paid to products  
183 obtained via the above abiotic Se remediation techniques, mainly because the  
184 BioSeNPs from microbial reduction can be applied directly as adsorbents and fertilizer  
185 [56, 80]. Combining magnetic separation is an option for achieving low-cost separation  
186 of Se containing products through abiotic techniques. However, no related work has  
187 been reported. The purity of the recovered Se containing product and its usage depends  
188 on the type of wastewater and the adopted technique. To meet the market demand for  
189 the high purity Se, recovered Se containing products from wastewater through both  
190 microbial reduction and non-biological methods need further refining.

191 There is limited information available in the literature on the capital and operating  
192 costs of Se remediation techniques. A comprehensive review from 2010 compares the  
193 available technologies at the time [79]. More recently, a cost evaluation of coagulation  
194 and precipitation for Se removal from wastewater using pre-hydrolyzed FeCl<sub>3</sub> at full  
195 scale was carried out. Reagent cost was estimated as 357 € kg<sup>-1</sup> Se(IV) with Se(IV)

196 concentration in the range of 30-100  $\mu\text{g L}^{-1}$  [81]. For microbial reduction, the cost of  
197 treating 1 kg Se in a mesophilic and thermophilic UASB (up-flow anaerobic sludge  
198 blanket) reactor, respectively, is 0.51 and 1.06 € (Se(VI) concentration ranges from  
199 0.78-3.9  $\text{mg L}^{-1}$ ) [82]. More effort is needed for the cost evaluation of Se remediation.  
200 Moreover, assessment of the whole process of Se recovery, including product  
201 separation and refining of different methods, should be carried out.

#### 202 **4.1. Abiotic techniques for Se remediation and potential recovery**

203 This review focuses on recent progress about sorption, co-precipitation,  
204 coagulation and precipitation of Se oxyanions and their removal by ZVI, photocatalytic  
205 and electrochemical systems as abiotic Se remediation techniques. Magnetic separation  
206 is an important method usually employed in combination with other separation  
207 techniques for elemental recovery (Figure 2) [83-85]. Abiotic techniques combined  
208 with magnetic separation could be an option to recover Se from Se contaminated water  
209 due to its ease of recycling by simply using an external magnetic force. Compared with  
210 microbial recovery of Se, the purity of Se obtained via abiotic techniques followed by  
211 magnetic separation will be lower. This section focuses on exploring the technical  
212 possibility for implementing Se recovery and encouraging the development of related  
213 work.

##### 214 **4.1.1. Sorption for Se removal and potential recovery**

215 Sorption based water treatment is a process through which a substance or a solute,  
216 initially present in the aqueous phase, is removed from that phase by accumulation at  
217 the interface between the aqueous phase and a solid phase [86]. Sorbents like activated  
218 aluminum, activated carbon, iron oxides, and nanoparticles, e.g., metal-organic  
219 frameworks and layered double hydroxides, are used for Se removal [87-93]. Sorption  
220 can be limited by the selectivity towards the target pollutant, as multiple pollutants exist  
221 in wastewater. For example, Se and arsenic (As) always coexist in the leachates of  
222 sedimentary rocks, and  $\text{SeO}_4^{2-}$  is more difficult to remove due to its more stable  
223 structure in aqueous solutions than  $\text{SeO}_3^{2-}$  [94-96]. Selectivity of the branched

224 glutaraldehyde immobilized polyethyleneimine (PEI-GA) resins for Se(VI) in the  
225 Se(VI)-As(V) system has been studied [97]. These sorbents can selectively recover  
226 Se(VI) from the Se(VI)-As(V) system, especially at pH 2 (i.e., within 50 min, the  
227 sorption capacity reached 4.5 mmol g<sup>-1</sup> PEI-GA (PEI/GA at a weight ratio of 4:1) resin  
228 for Se(VI)).

229 From environmental and circular economy perspectives, the use of Se saturated  
230 sorbent needs to be further processed, e.g., separating the saturated sorbent from water  
231 for Se recovery. Recently, the application of magnetic sorbent has drawn considerable  
232 attention because of the easy recycling by simply using an external magnetic force [98].  
233 Se oxyanions sorption by magnetic sorbents is listed in Table 5, which shows the  
234 reported magnetic sorbents have better sorption capacity for Se(IV) than Se(VI). This  
235 might be due to the surface properties and functional group of sorbent [99]. In a reported  
236 work about the sorption of Se(IV) and Se(VI) at the goethite-water interface, it was  
237 suggested that Se(IV) forms a strongly bonded, innersphere bidentate complex [100].  
238 In contrast, Se(VI) forms a weakly bonded, outersphere monodentate hydrated complex  
239 [100]. Six different hematite nanoparticles (na-Fe<sub>2</sub>O<sub>3</sub>), in terms of shape, size, and  
240 surface area, were used to assess how particle morphology affects the sorption capacity  
241 of nano-metal oxides for Se(VI) [93]. The results showed that surface area and size  
242 alone do not regulate the na-Fe<sub>2</sub>O<sub>3</sub> sorption capacity of Se oxyanions. In contrast, the  
243 crystal surface structure affects both the adsorption capacity and mechanism. Explicitly,  
244 {0 1 2} facets (a crystal surface structure) promote adsorption of Se(VI) and Se(IV)  
245 over {1 1 0} facets. The absence of the {1 1 0} facet has a greater effect on Se(VI)  
246 adsorption than that of Se(IV). {1 1 0} and {0 1 2} facets bind Se(IV) via inner-sphere  
247 complexes with albeit {1 1 0} binds bidentate binuclear complexes, while {0 1 2} binds  
248 via bidentate mononuclear complexes. Se(VI) binds to na-Fe<sub>2</sub>O<sub>3</sub> primarily through  
249 outersphere complexes with some proportion of innersphere complex dependent on the  
250 specific facet [93].

251 A strategy to enhance sorbents' capacity for Se(VI) to achieve efficient removal  
252 of total Se from wastewater containing both Se(VI) and Se(IV) is to combine selected  
253 sorbents with a material with a higher association constant for binding Se(VI), such as

254 chitosan ( $3.048 \times 10^{-3}$  for Se(VI) and  $1.990 \times 10^{-4}$  for Se(IV), respectively).  
255 Impregnating aluminum oxide (n-Al<sub>2</sub>O<sub>3</sub>) on chitosan beads (AICB, 0.0903 g n-Al<sub>2</sub>O<sub>3</sub> g<sup>-1</sup>  
256 chitosan) allowed to improve the adsorption capacity for Se(VI) from 9.35 mg g<sup>-1</sup> n-  
257 Al<sub>2</sub>O<sub>3</sub> to 20.11 mg g<sup>-1</sup> AICB [91]. Further studies should be carried out for enhancing  
258 Se(VI) sorption by different magnetic sorbents. Moreover, whether chitosan affects  
259 magnetic sorbent's magnetic characteristics needs to be verified to achieve Se recovery  
260 via sorption combined with magnetic separation.

261 From the Se resource recycling perspective, biochar is an excellent sorbent and an  
262 agent for agricultural and environmental applications [94-96]. Compared with N and P,  
263 the sorption of Se by biochar has not received enough attention. Present studies using  
264 biochar for Se sorption aim to optimize the immobilization of Se in soil [101], and  
265 sorption of Se from aqueous solutions [102]. Several recent works focused on Fe-  
266 biochar for Se removal from water and soil [95, 101, 103]. In these studies, the  
267 modification of biochar by Fe(III) or ZVI considerably improves the sorption capacity  
268 of Se(VI) and Se(IV) from the water phase to the modified biochar. The application of  
269 Se saturated magnetic biochar as fertilizer might be an ideal solution as the recovery of  
270 high purity Se is challenging due to the presence of competitive anions such as PO<sub>4</sub><sup>3-</sup>,  
271 SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>. However, no work focused on the application of Se saturated biochar  
272 as fertilizer has been reported.

273 A Se saturated sorbent-iron(III) modified zeolite (Fe(III)-MZ) has been tested as  
274 a soil supplement to cultivate *Pleurotus ostreatus* mushrooms [104]. In this work, the  
275 dried mushrooms showed that the amount of sorbed and organically transformed Se is  
276 greater (>200 µg g<sup>-1</sup>) than in a control system ( $0.071 \pm 0.01$  µg g<sup>-1</sup>). This finding proves  
277 that certain Se saturated sorbent can promote the sorption of Se by plants. However,  
278 factors such as the presence of other (toxic) pollutants and whether the sorbent is an  
279 environmentally friendly material must be carefully considered [105]. To achieve the  
280 application of recovered Se through adsorption/desorption, the desorption ability of Se  
281 saturated sorbents should be considered and evaluated in water/soil systems. However,  
282 the desorption ability of Se saturated sorbent, especially in soil, has received less  
283 attention than sorbents' adsorption ability.

284 Se release by Se loaded Fe(III)-MZ has been investigated in water and soil at  
285 different pH [105]. The results showed that the pH does not affect the Se release trend  
286 from Fe(III)-MZ in an aqueous solution. In contrast, the Se release proportion from  
287 Fe(III)-MZ increases with lower soil pH (the content of Se in the soil was 0.82 mg kg<sup>-1</sup>  
288 and 0.67 mg kg<sup>-1</sup>, and the release proportion was 13.84% and 11.39% when 0.50 g Se  
289 saturated Fe(III)-MZ was added into the soil at pH was 7.8 and 10.8, respectively).  
290 Another critical parameter is the amount of Se saturated Fe(III)-MZ applied. In this  
291 study, the content of Se in the applied soil reached 0.82 and 1.13 mg kg<sup>-1</sup>, and the  
292 release proportion was 13.84% and 9.52 % when 0.50 and 1.00 g Se saturated Fe(III)-  
293 MZ was added at pH 7.8. This work demonstrated that Se release from a sorbent is  
294 affected by the conditions of desorption. However, Se's mobility in soil is complex.  
295 Many unanswered questions remain, e.g., how is it affected by the soil properties such  
296 as organic matter, texture, and microbial structure after its release from sorbents. Before  
297 actual application, the release of Se loaded on the sorbent must be evaluated.

#### 298 **4.1.2. Co-precipitation for Se removal and potential recovery**

299 Co-precipitation, in this review, refers to the immobilization of a trace element in  
300 a mineral during the crystal growth of other elements. Barite (BaSO<sub>4</sub>) can work as a  
301 host phase of Se in the natural environment [106, 107]. Se(IV) uptake by barite depends  
302 on pH, coexistent calcium ions (Ca<sup>2+</sup>), and SO<sub>4</sub><sup>2-</sup> concentration in the initial solution,  
303 possibly due to the effects on the chemical affinity and structural similarity of SO<sub>4</sub><sup>2-</sup>  
304 and SeO<sub>3</sub><sup>2-</sup>. Se(VI) uptake by barite is strongly inhibited by SO<sub>4</sub><sup>2-</sup> in the initial solution  
305 due to the structural similarity of SO<sub>4</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup> [106, 107]. Se species' incorporation  
306 into barite formed in marine sediment was discovered in a hydrothermal vent system  
307 near Okinawa [107]. This also explains why marine sediment is a pool of Se resources.

308 Se species' co-precipitation has also been reported during the formation process of  
309 minerals such as hematite (iron(III) oxide, Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub>), goethite (α-FeO(OH)),  
310 magnetite (iron(II, III) oxide, Fe(II)Fe(III)<sub>2</sub>O<sub>4</sub>), and green rust [108-110]. Mineral  
311 phases containing reduced iron species (i.e., Fe(II)) can reduce Se oxyanions under  
312 anoxic conditions [111]. The Se and Fe(II) interaction leads to a nanoparticulate iron

313 selenide phase (FeSe), which is oxidized and transformed into trigonal elemental Se  
314 during the gradual oxidation process of the aquatic system [111]. Se is retained  
315 regardless of whether the oxidation of the unstable iron oxides leads to the formation  
316 of pure magnetite or other iron oxide phases, e.g., goethite [111]. The possibility of Se  
317 incorporation into magnetic minerals followed by magnetic separation should be  
318 studied for Se recovery, especially for *in-situ* Se recovery. This will provide new insight  
319 into geochemical Se immobilization and mobilization.

#### 320 **4.1.3. Coagulation and precipitation for Se removal and potential recovery**

321 Se removal can be achieved by coagulation and precipitation, a widely used water  
322 treatment process in drinking water plants to allow flocculation for precipitation [112].  
323 The addition of a coagulant to the water will promote coagulation. Dissolved Se can be  
324 sorbed by destabilizing stabilized charged particles and forming agglomerates [86].  
325 Aluminum (Al) and iron (Fe) salts, e.g., aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), ferric sulfate  
326 ( $\text{Fe}_2(\text{SO}_4)_3$ ) and ferric chloride ( $\text{FeCl}_3$ ), are the most used coagulants. The Fe(III)-based  
327 coagulant was more effective than the  $\text{Al}^{3+}$ -based one in removing Se [113]. For  
328 example, the removal efficiency of Se(IV) by  $\text{FeCl}_3$  can reach above 98% at dosages  
329 of more than  $0.4 \text{ mmol Fe L}^{-1}$  when the initial Se(IV) concentration was  $250 \mu\text{g L}^{-1}$ . In  
330 comparison, the maximum removal efficiency of  $\text{AlCl}_3$  was about 80% at the dosage  
331 of  $1.2 \text{ mmol Al L}^{-1}$  [113]. The removal of Se(IV) by coagulation was much more  
332 effective than that of Se(VI) [113]. For example, at the dosage of  $0.4 \text{ mmol L}^{-1}$  Fe or  
333 Al, the removal efficiencies of Se(IV) were twice as high as those of Se(VI) [113]. High  
334 coagulant dosage and weakly acidic pH conditions favored Se removal [113]. The  
335 coexistence of other anions impacts the removal [113, 114]. The negative influence on  
336 Se(IV) removal among the tested four oxyanions followed the order:  $\text{PO}_4^{3-} > \text{SiO}_3^{2-} >$   
337  $\text{CO}_3^{2-} > \text{SO}_4^{2-}$  due to each oxyanions' binding with the surface sites of metal hydroxides  
338 [113].

339 Electrocoagulation is a well-known technique for removing metalloids (including  
340 Se oxyanions) from wastewater [115, 116]. Electrocoagulation consists of generating a  
341 coagulant *in situ* through the dissolution of the metal anode while generating hydroxyl

342 ions ( $\text{OH}^-$ ) and hydrogen gas ( $\text{H}_2$ ) at the cathode and anode, respectively. This process  
343 produces hydrous ferric oxide (HFO). Se(IV) is sorbed by HFO and its sorption  
344 efficiency changes with pH. Se(IV) will be removed from wastewater because  $\text{SeO}_3^{2-}$   
345 can be sorbed onto metal oxyhydroxides, while  $\text{SeO}_4^{2-}$  presents low sorption and poor  
346 precipitation characteristics [117, 118]. This technique has been successfully tested in  
347 petroleum refining wastewater using a 1 L cylindrical acrylic cell [114]. Other chemical  
348 species such as  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  in the wastewater can reduce the removal efficiency of  
349 Se due to the competition for active binding sites of iron hydroxide formed in the  
350 electrocoagulation process, which lengthen the treatment time. The increased treatment  
351 time also increased the energy required per mg of removed Se. The increase in the  
352 current density has a notable effect on the removal efficiency. For 240 min of treatment,  
353 when the current density increases from  $76.7 \text{ A m}^{-2}$  to  $153.4 \text{ A m}^{-2}$ , the removal  
354 efficiency is almost doubled [114]. The next step should focus on how to upscale this  
355 technique to field application in terms of the configuration of the reactor, the applied  
356 current, and maintenance of the electrodes [119].

357         Magnetic seeding coagulation is a process where magnetic particles are added to  
358 coagulate with other particles to form magnetic flocs with improved settleability [120].  
359 Magnetic seeding combined magnetic separation techniques have been used for heavy  
360 metal removal from wastewater since the 1970s [121, 122]. Magnetite ( $\text{Fe}_3\text{O}_4$ ) is one  
361 of the most used magnetic seeds for water treatment [123]. Electrocoagulation has been  
362 reported to produce  $\text{Fe}_3\text{O}_4$  particles using steel electrodes to form magnetic flocs,  
363 lowering the operating cost and the waste volume because this avoids preparing  
364 ferric/ferrous solutions at high-pH conditions [124]. Recently, magnetic seeding of  
365  $\text{Fe}_3\text{O}_4$  followed by magnetic separation has been applied in P recovery and As removal  
366 [125, 126]. Although coagulation and electrocoagulation can effectively remove Se  
367 oxyanions, magnetic seeding combined with magnetic separation has not been applied  
368 for Se removal and recovery [127]. The obtained Se containing flocs can be further  
369 processed for pure Se.

370         Sodium sulfide ( $\text{Na}_2\text{S}$ ) is an effective precipitant for  $\text{SeO}_3^{2-}$  [128].  
371 Removal/precipitation of Se with  $\text{Na}_2\text{S}$  from weakly acidic  $\text{SO}_4^{2-}$  solutions containing



372 300 mg L<sup>-1</sup> of Se(IV) at 23 °C was achieved [128]. The precipitation reaction starts as  
373 soon as the Na<sub>2</sub>S is added to the Se-bearing synthetic wastewater and completes within  
374 10 min. The orange selenium sulfide (SeS<sub>2</sub>) precipitates were aggregated and dense in  
375 an easily filterable precipitate. Elevation of pH above 7 leads to the SeS<sub>2</sub>-n solid  
376 solution structure breakdown and the formation of individual colloidal Se(0) particles  
377 [128]. The precipitation of SeO<sub>3</sub><sup>2-</sup> by Na<sub>2</sub>S and filtration of SeS<sub>2</sub> precipitates followed  
378 by pH elevation to release elemental Se might be a solution to achieve fast Se recovery  
379 from wastewater.

#### 380 4.1.4. Photocatalytic systems for Se removal and potential recovery

381 Photocatalytic reduction is one of the most advanced wastewater treatment  
382 methods. It is potentially energy self-sufficient as it can use solar energy [129]. The  
383 mechanism of Se oxyanions reduction by TiO<sub>2</sub> is shown in Figure 3. To the authors'  
384 best knowledge, although diverse photocatalysts have been studied for aqueous  
385 oxyanions removal from water, the only well-studied photocatalyst for Se oxyanions is  
386 TiO<sub>2</sub>, which was first studied by Sauki et al., in 1999 [130-132]. The existing literature  
387 has overlooked the role of other types of photocatalysts in exploring SeO<sub>4</sub><sup>2-</sup> and SeO<sub>3</sub><sup>2-</sup>  
388 reduction. In a recently published review, studies about photocatalytic reduction of  
389 SeO<sub>4</sub><sup>2-</sup> and SeO<sub>3</sub><sup>2-</sup> were summarized. However, they did not cover Se removal or  
390 recovery [132].

391 Different types of commercially available TiO<sub>2</sub> powder: Millennium PC500 (374  
392 m<sup>2</sup> g<sup>-1</sup>), PC50 (53 m<sup>2</sup> g<sup>-1</sup>), and Degussa P25 (48 m<sup>2</sup> g<sup>-1</sup>) were tested for reduction of Se  
393 oxyanions to Se(0) [133]. Results showed that Millennium PC500, with the highest  
394 surface area, performed better sorption and photoreduction of Se oxyanions. Being  
395 sorbed on the surface of the photocatalyst is the prerequisite for photoreduction. In this  
396 process, all TiO<sub>2</sub> powders showed substantial sorption to SeO<sub>3</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup> (i.e., 12.9  
397 ±0.8 mg g<sup>-1</sup> PC500 for 20 mg L<sup>-1</sup> SeO<sub>3</sub><sup>2-</sup>, 6.4 ±0.48 mg g<sup>-1</sup> PC500 for 20 mg L<sup>-1</sup> SeO<sub>4</sub><sup>2-</sup>).  
398 Common co-existing anions, especially molybdate (MoO<sub>4</sub><sup>2-</sup>) and SO<sub>4</sub><sup>2-</sup>, can inhibit the  
399 sorption of SeO<sub>4</sub><sup>2-</sup> on TiO<sub>2</sub> by competitive sorption [134-136]. However, there is no  
400 report on the sorption of SeO<sub>4</sub><sup>2-</sup> on TiO<sub>2</sub> under the interference of other anions (e.g.,

401  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and metal oxyanions). Photocatalytic reduction of  $\text{SeO}_3^{2-}$  proceeded much  
402 faster than  $\text{SeO}_4^{2-}$  (i.e., 20 mg  $\text{L}^{-1}$  of  $\text{SeO}_3^{2-}$  needed 2 h for its complete removal from  
403 solution while 4 h were needed to remove 20 mg  $\text{L}^{-1}$  of  $\text{SeO}_4^{2-}$  with Millennium PC500  
404 in [133]). The presence of common co-existing anions such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  
405 the reduction from  $\text{SeO}_4^{2-}$  to  $\text{SeO}_3^{2-}$  are big challenges of using  $\text{TiO}_2$  for Se recovery in  
406 terms of the reduction efficiency of Se oxyanions and purity of the recovered Se product.

407 The endpoint of  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  reduction by  $\text{TiO}_2$  can be Se(0) and/or Se(-II)  
408 as shown in Figure 3 [131, 137]. A challenge for Se recovery using  $\text{TiO}_2$  is how to  
409 control the reduction's endpoint, which can be tackled by metal deposition on the  $\text{TiO}_2$   
410 surface and the addition of electron scavengers to the reaction system [137]. The noble  
411 metal deposit can affect the reduction potential of the electrons [137]. With a more  
412 positive reduction potential, the less likely the photogenerated electrons can reduce the  
413 Se(VI)/Se(0) reduction couple ( $E^0 = 0.5 \text{ V}$  vs the standard hydrogen electrode (SHE)).  
414 For example, Ag, Au, Pt and Pd have varying work functions of -0.18 eV, 0.66 eV, 0.76  
415 eV, and 1.06 eV vs SHE. Pd- $\text{TiO}_2$  catalysts allow greater product selectivity towards  
416 Se(0) than Ag- $\text{TiO}_2$ , Au- $\text{TiO}_2$  and Pt- $\text{TiO}_2$  [137, 138]. Formic acid has been reported  
417 as the most effective organic scavenger for enhancing Se oxyanions photoreduction by  
418  $\text{TiO}_2$ . Moreover, Se(0) was only produced in formic acid and was enhanced without  
419 oxygen in reported studies [131, 138, 139]. Although the final product has been proved  
420 to be controlled, the conversion efficiency of  $\text{SeO}_4^{2-}$  to Se(0) is still low, i.e., 40% for  
421 Pd- $\text{TiO}_2$  [137].

422 There is potential for Se remediation and recovery through photoreduction.  
423 However, this technique is not yet technologically and economically applicable for  
424 commercial scale as the most studied catalyst in Se removal- $\text{TiO}_2$  can only be activated  
425 by near UV irradiation (less than 5% of the total solar spectrum) [140]. Future work  
426 should explore Se reduction by different types of photocatalysts. It is also necessary to  
427 develop a photocatalytic system applied under visible and/or solar light irradiation for  
428 commercial scale Se remediation and recovery [140]. Another challenge in applying  
429 cost-effective photocatalytic reduction for Se recovery is how to improve the recovery  
430 of reduced Se products and used photocatalysts. A novel magnetic photocatalyst C-

431  $\text{TiO}_2@\text{Fe}_3\text{O}_4/\text{AC}$  was recently prepared and had both C- $\text{TiO}_2$  and  $\text{Fe}_3\text{O}_4$  loaded together  
432 onto magnetic activated carbon (AC). This magnetic photocatalyst could be an  
433 attractive choice due to its low band-gap of 2.535 eV, visible light catalytic activity,  
434 stable structure, and magnetic separation characteristics [141]. However, this  
435 photocatalyst has not been tested on Se removal and recovery.

#### 436 **4.1.5. Se removal, immobilization, and potential recovery by zero-valent iron** 437 **(ZVI) system**

438 Se removal can be achieved by chemical reduction as Se(0) is insoluble and less  
439 toxic than highly soluble Se(VI) and Se(IV) [142]. The most popular Se oxyanions  
440 reducing agent is zero-valent iron (ZVI) [142]. The application of ZVI in groundwater  
441 treatment began in the early 1990s when granular ZVI was first used in permeable  
442 reactive barriers (PRBs) systems [143, 144]. Compared to the conventional pump-and-  
443 treat technology, the ZVI-PRB technology is more efficient and substantially less  
444 expensive [145]. ZVI technology has been widely used in pilot and large scale field  
445 applications in the past few decades, as ZVI is readily available, relatively inexpensive,  
446 and nontoxic [146, 147]. Depending on the pH and redox potential, the endpoint of  
447  $\text{SeO}_4^{2-}$  reduction can be  $\text{SeO}_3^{2-}$ , Se(0), and  $\text{Se}^{2-}$  [31]. Both chemical reduction and  
448 sorption by corrosion products occur during this process (Figure 4) [142]. From an  
449 environmental perspective, the identification of Se oxyanions reduction products and  
450 ZVI oxidation products can determine the transformation of ZVI to iron oxide and  
451 immobilization of Se(VI) in soils, sediments, and aquifers [142].

452 During the Se(VI) reduction process, ZVI is oxidized to Fe(II) and reacts with  
453 hydroxide ( $\text{OH}^-$ ) to form ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) at the corroding ZVI surface  
454 [142]. The  $\text{Fe}(\text{OH})_2$  can be further oxidized to green rust, magnetite, lepidocrocite,  
455 ferrihydrite, or goethite [148-151]. It has been reported that the main factor for Se(VI)  
456 reduction, sorption and iron corrosion coating was Se(VI) concentration [142]. With 10  
457  $\text{mg L}^{-1}$  Se(VI) concentrations as the initial concentration and 1  $\text{g L}^{-1}$  ZVI as the electron  
458 donor, Se(VI) was completely reduced to Se(0)/Se(-II), and magnetite was formed.  
459 However, Se(VI)/Se(IV) was partially sorbed on the ZVI surface, and lepidocrocite was

460 formed when initial Se(VI) concentrations were  $>50 \text{ mg L}^{-1}$ . In addition, Fe(II) may  
461 have facilitated the autoreduction of lepidocrocite to magnetite [142]. From the  
462 viewpoint of electron transfer, magnetite can be considered a semiconductor ( $10^2\text{--}10^3$   
463  $\Omega^{-1} \text{ cm}^{-1}$ ) and is believed to facilitate the electron transfer from the ZVI core to the  
464 solid-liquid interface [152]. At the same time, lepidocrocite has poor conductivity  
465 (bandgap of 2.3 eV) and is mainly responsible for the passivation of ZVI [153].  
466 However, lepidocrocite shows better sorption affinity for Se(VI) in the presence of Fe(II)  
467 [153]. Excessive generation of lepidocrocite would block the electron transfer pathway  
468 [154].

469 The surface passivation of ZVI considerably restricts the application of ZVI  
470 technology. Acid washing, ultrasonication,  $\text{H}_2$  reduction, microwave, nano-sized ZVI  
471 technology, and weak magnetic field have been developed to address this issue [155-  
472 160]. However, these techniques are far from satisfactory to implement in full-scale  
473 applications due to high capital and operational costs. Recently, using  $\text{H}_2\text{O}_2/\text{HCl}$  to  
474 conduct ZVI pre-corrosion allowed  $\text{SeO}_4^{2-}$  removal efficiency to improve from 65% to  
475 95% in 8 h with Se(0) as a product [154]. In this study, the pathways of Se(VI) removal  
476 by pre-corroded ZVI were identified as the following processes in sequence: contact of  
477 Se(VI) with the solid surface, reduction of Se(VI) to Se(IV), immobilization of Se(IV)  
478 via inner-sphere complexation, further reduction of the immobilized Se(IV) to Se(0) in  
479 the solid phase. Finally, most Se (78.2%) was immobilized as Se(0) [154].

480 Based on the magnetic susceptibility of ZVI and Fe bearing minerals, several  
481 studies have assessed the suitability of magnetic separation following the ZVI  
482 amendment to remove heavy metals such as Cu, Zn, Cr from contaminated soils [161-  
483 163]. However, ZVI amendment combined with magnetic separation for Se recovery  
484 has not been reported. A magnetic separation process should be carried out to separate  
485 the residual ZVI particles and attached iron (hydr)oxides, thus minimizing the re-  
486 release risk of immobilized Se and achieving Se recovery [127].

#### 487 4.1.6. Electrochemical systems for Se removal and potential recovery

488 Electrochemical systems have been employed to transform or destroy  
489 contaminants [164]. In these systems, one or more electrons are acquired on the cathode  
490 surface during direct current flow through the system (anode, cathode, and electrolyte  
491 solution). Generally speaking, the oxidation half-reaction occurs at the anode, while the  
492 cathode is where reduction occurs and electrons are gained [165]. Se oxyanions can be  
493 removed by direct electrochemical reduction on the cathode surface or by indirect  
494 chemical or physicochemical transformations in the electrolyte, depending on the anode  
495 material [117, 166-169]. Comparison and mechanisms of direct electrochemical  
496 reduction (DER) and indirect Se removal by electrochemical systems are illustrated in  
497 Figure 5.

498 In an electrochemical system with a sacrificial iron anode, iron dissolution is the  
499 dominant reaction on the anode (Figure 5) [166]. Depending on the electrolyte pH, the  
500 ferrous ions might subsequently form ferrous hydroxides ( $\text{Fe}(\text{OH})_2$ ) in a mixed cell  
501 [166]. The basic mechanisms of indirect Se removal have been investigated in batch  
502 electrochemical systems by comparing reactive iron anode and inert anode with a  
503 copper plate as the cathode in a bicarbonate medium (pH 7) [117].  $\text{SeO}_4^{2-}$  removal in  
504 this system is due to the formation of  $\text{Fe}(\text{OH})_2$  precipitates instead of direct cathodic  
505 reduction. The  $\text{SeO}_3^{2-}$  reduced from  $\text{SeO}_4^{2-}$  can be further reduced to Se(0) or Se(II)  
506 [117]. Later, this electrochemical system was enlarged to a flow-through sand column  
507 incorporating a pair of electrodes (iron electrolysis) to simulate the *in situ* application  
508 in a permeable aquifer for  $\text{SeO}_4^{2-}$  remediation [170]. The removal rate of  $\text{SeO}_4^{2-}$  was  
509 proportional to the contact time and the yield of  $\text{Fe}(\text{OH})_2$  or ferrous carbonate. This  
510 study demonstrated the electrochemical system's effectiveness in removing  $\text{SeO}_4^{2-}$  in a  
511 single well [170]. While the indirect electrochemical method can provide reliable Se  
512 removal performance for *in situ* remediation, solids that need management are produced.  
513 Se recovery from the generated solids can be a strategy to minimize the secondary  
514 pollution. Further research should be carried out to offset the management costs.

515 Direct electrochemical reduction (DER) has been intensively used in industrial Se  
516 plating (known as electrodeposition) for decades on metal surfaces, such as gold, silver,  
517 nickel, and iron [171]. Se oxyanions in the substrate are reduced to Se(0) during the  
518 DER process, forming a thin layer on the target metal surface [172]. A soft-template,  
519 cetyltrimethylammonium bromide (CTAB), had been used and synthesized single-  
520 crystalline Se nanotubes (10-30  $\mu\text{m}$ ) on the surface of a gold sheet electrode by cyclic  
521 voltammetry [173]. The advantages of using CTAB as a template are that it can be  
522 easily washed away from the products with hot water and can modify the morphology  
523 of produced Se(0) by changing CTAB concentration and electrochemical parameters of  
524 the system [172, 174].

525 Although Se ions can be successfully electrodeposited, the recovery ratio of Se is  
526 necessarily limited by the low Se concentration in wastewater. To enhance  
527 electrochemical Se recovery performance, a cyclone electrowinning reactor was  
528 employed to treat a strongly acidic copper refining wastewater (pH 0.3 and 3.8 mM Se).  
529 In this study, 97.6% of Se(IV) was successfully recovered via DER using low-cost  
530 stainless steel cathodes in 90 min with nano-sized and mesoporous Se(0) produced  
531 [167]. However, the Se electrochemical deposition mechanism is complex due to its  
532 several oxidation states, especially for environmental applications of Se removal and  
533 recovery [172]. To understand factors affecting DER performance for Se recovery, a  
534 three-electrode electrochemical system with gold as a working electrode was employed  
535 to evaluate Se reduction's thermodynamic and kinetic performance [175]. This work  
536 found that Se reduction via DER is a robust process that can deal with weakly acidic  
537 solutions (pH 4–7) containing 0.001–10 mM Se(IV). Se(IV) can be electrochemically  
538 reduced from the aqueous phase through either a four- or six-electron pathway. The  
539 former generates Se(0) directly attached to the electrode surface, and the latter produces  
540 Se(-II) that is subsequently converted to Se(0). The four-electron pathway is a surface-  
541 limited process below 70 °C. It terminates when the cathode is fully covered with the  
542 insulative amorphous Se(0).

543 Reducing  $\text{SeO}_4^{2-}$  to  $\text{SeO}_3^{2-}$  is a critical challenge in applying DER in wastewater  
544 or natural water treatment due to the necessity of anion structure change and the high

545 activation energy required to break the Se=O double bond. Other oxyanions, e.g.,  $\text{SO}_4^{2-}$ ,  
546  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ , and metal oxyanions that complex water matrices can trigger  
547 cathodic parasitic reactions to compete with Se removal via DER or lead to co-  
548 deposition with Se [175]. However, DER approaches offer several advantages over  
549 indirect electrochemical Se removal, including selective Se removal when the cathode  
550 potential is precisely controlled, less solids generation, and direct Se recovery on the  
551 cathode.

552 The major drawback of electrochemical systems is that electricity and working  
553 electrodes generate extra operation costs [204]. For example, operating costs of landfill  
554 leachate treatment amounted to  $465.2 \text{ kWh m}^{-3}$  (240 min of reaction time at  $200 \text{ mA}$   
555  $\text{cm}^{-2}$ ) with a cost of  $55.8 \text{ € m}^{-3}$  influent, while for the combined microbial compartment  
556 with the electrochemical oxidative treatment, the total cost was  $18.7 \text{ € m}^{-3}$  [205].  
557 However, Se removal by electrochemical systems requires less time than biotic  
558 methods. Moreover, it is cleaner and environmentally friendly than other abiotic  
559 methods. Future studies about reactor design optimization, electrode modification of  
560 electrochemical systems are also needed for more energy and cost-effective Se removal  
561 and recovery [175, 176].

#### 562 **4.2. Se remediation, BioSeNPs synthesis and recovery through microbial** 563 **reduction**

564 There are different mechanisms of Se oxyanions reduction and fabrication of  
565 BioSeNPs by different bacteria. Only a few species such as *Thauera selenatis*,  
566 *Enterobacter cloacae* SLD1a-1, and *Bacillus selenatarsenatis* SF-1 have been well  
567 studied regarding the enzymes involved in  $\text{SeO}_4^{2-}$  reduction [177]. However,  
568 microorganisms' reduction shares four common steps for BioSeNPs formation (Figure  
569 6): (i) Se oxyanions transportation into the cell; (ii) Se oxyanions reduction to Se(0);  
570 (iii) the exportation of Se(0) nuclei out of the cell; (iv) BioSeNPs assembly. Steps (i)  
571 and (iii) are not essential for forming BioSeNPs when the BioSeNPs form  
572 extracellularly [178]. For extracellular Se oxyanions reduction, only steps (ii) and (iv)

573 are involved. The overall microbial Se oxyanions reduction process is illustrated in  
574 Figure 6.

#### 575 **4.2.1. Microbial Se oxyanions reduction and its affecting factors**

576 The potential of microorganisms to mediate the Se cycle was first hypothesized in  
577 1964 [179]. The reduction of  $\text{SeO}_4^{2-}$  to  $\text{SeO}_3^{2-}$  and  $\text{Se}(0)$  coupled with *Salmonella*  
578 *Heidelberg's* aerobic growth was observed in 1966 [180]. Certain  $\text{SeO}_4^{2-}$  reducing  
579 bacteria can also perform  $\text{SeO}_3^{2-}$  reduction, which has a vital role in Se remediation and  
580 recovery [181, 182]. However,  $\text{SeO}_4^{2-}$  reduction has been shown to result in  $\text{SeO}_3^{2-}$   
581 accumulation in bioreactors inoculated with certain single  $\text{SeO}_4^{2-}$  reducing bacteria  
582 [183, 184]. The understanding of bioreduction of Se oxyanions progressed in the 1980s  
583 and 1990s, with the recognition that sulfate ( $\text{SO}_4^{2-}$ )-reducing bacteria (SRB) are also  
584 able to reduce  $\text{SeO}_4^{2-}$ , due to shared analogous biochemical and geochemical reactions  
585 [25, 181]. Since then, various microorganisms with Se oxyanions reduction ability  
586 through different pathways and forming  $\text{Se}(0)$  at different locations have been identified  
587 and separated (Table 2) [23, 181, 185].

588 The reduction of  $\text{SeO}_4^{2-}$  can be inhibited by other electron acceptors, with  $\text{SO}_4^{2-}$   
589 and  $\text{NO}_3^-$  being the most studied coexistent pollutant in Se reduction [186]. It has been  
590 reported that  $\text{SO}_4^{2-}$  in wastewater inhibits  $\text{SeO}_4^{2-}$  reduction by bacteria such as  
591 *Comamonas testosteroni S44* [187]. In addition to  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  is also often abundant in  
592 wastewater [188-190]. In a study about a pure culture (though species not identified)  
593 isolated from a freshwater marsh,  $\text{SeO}_4^{2-}$  was used as an electron acceptor only when  
594  $\text{NO}_3^-$  was absent [189]. However, not all bacteria performing  $\text{SeO}_4^{2-}$  reduction can be  
595 inhibited by  $\text{NO}_3^-$ . For example, the presence of  $\text{NO}_3^-$  did not inhibit  $\text{SeO}_4^{2-}$  reduction  
596 in  $\text{SeO}_4^{2-}$ -grown *Thauera selenatis* as it synthesizes independently  $\text{NO}_3^-$  and  $\text{SeO}_4^{2-}$   
597 reductases in different locations within the cell [191]. Besides  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ,  $\text{SeO}_4^{2-}$   
598 reduction is also inhibited by the presence of other electron acceptors, such as  $\text{O}_2$ ,  
599  $\text{CrO}_4^{2-}$ , or  $\text{MnO}_2$  [186].

600 Another challenge in using a single microbial strain to remove Se from wastewater  
601 through reduction is that Se often coincides with the high salinity in industrial



602 wastewaters [77]. In Se refinery wastewater, typical concentrations of Se and salinity  
603 range from 13.2 to 74.0 mg L<sup>-1</sup> and 6-7%, respectively [192]. Inhibition of Se reduction  
604 caused by salinity was observed for *Pseudomonas stutzeri* NT-I, with reduction  
605 efficiency for SeO<sub>4</sub><sup>2-</sup> and SeO<sub>3</sub><sup>2-</sup> considerably decreased from 100 % at 0.5 % (w/v)  
606 NaCl to 40% at 2% (w/v) NaCl [193]. Thus, it is crucial to select suitable strains with  
607 Se oxyanions reduction ability in target wastewater under certain operating conditions,  
608 e.g., *Pseudomonas stutzeri* NT-I has been reported to reduce SeO<sub>4</sub><sup>2-</sup> to Se(0) efficiently  
609 without prolonged accumulation of SeO<sub>3</sub><sup>2-</sup> under aerobic conditions [193].

610 Mixed cultures from activated sludge have been adopted for treating SeO<sub>4</sub><sup>2-</sup>  
611 containing mine wastewater (containing 3 % (w/v) NaCl) with excessive acetate as the  
612 electron donor under oxygen-limited conditions, with 98% of 395 mg L<sup>-1</sup> soluble Se  
613 was removed within 7 d [19]. The composition of the microbial community shifted to  
614 overcome salinity inhibition. Besides, there is a synergy between bacteria in diverse  
615 and complex bacterial communities that resist environmental changes and reduce  
616 SeO<sub>4</sub><sup>2-</sup> reduction inhibition when multiple pollutants are present in the wastewater [194-  
617 196]. Besides activated sludge, mine site soils and sediments have also been utilized as  
618 microorganism resources [197]. Enriched mixed cultures from a metal mine site  
619 continuously receiving SeO<sub>4</sub><sup>2-</sup> containing wastewater have been studied for their ability  
620 to reduce and remove dissolved Se from a concentrated brine solution containing NO<sub>3</sub><sup>-</sup>,  
621 SO<sub>4</sub><sup>2-</sup>, and other salts (235 mg L<sup>-1</sup> N, 1730 mg L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>, and 1.87 mg L<sup>-1</sup> Se) [197].  
622 Successful Se removal with NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> present was achieved by the symbiotic  
623 relationship between the enriched microorganisms and the addition of ZVI [197]. The  
624 dominant species of the enriched microorganisms include *Clostridium*, *Sphaerochaeta*,  
625 *Synergistes*, and *Desulfosporosinus* species [197].

626 Other factors affecting microbial Se oxyanions reduction performance include pH,  
627 initial Se concentration of the wastewater, and operation conditions of bioreactors such  
628 as hydraulic retention time (HRT), dosage of electron donor (reducing agent) and  
629 temperature. Different bioreactors' operations under different conditions with their  
630 performance are listed in Table 3. However, it is hard to compare the Se oxyanions  
631 reduction performance in various types of bioreactors with different inoculum as the

632 enrichment of bacteria or the microbial community is either too complex or not well  
633 documented. The complex factors described above can affect bacteria or the microbial  
634 community in actual water bodies and must be addressed for scaling up. In extensive  
635 research on Se oxyanions reduction using mixed culture as inoculum, e.g., activated  
636 sludge, contaminated/uncontaminated soil or sediment, the structure of the microbial  
637 community changed with different operating conditions and thus affected Se oxyanions  
638 reduction performance [19, 74, 79, 81, 82, 193-197]. Compared with selecting pure  
639 cultures or specific consortia as seed for bioreactors, a preliminary work of enriching  
640 and isolating functional microbial consortium as inoculum from mixed cultures, shaped  
641 by target contaminated water under certain operating conditions that require low  
642 maintenance cost is a better solution. In this way, the inhibition effects of other  
643 contaminants in actual wastewater can be overcome, and the financial requirements can  
644 be satisfied.

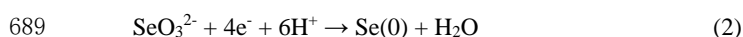
#### 645 **4.2.2. Mechanism of microbial reduction of Se oxyanions and synthesis of** 646 **BioSeNPs**

647 In this review, BioSeNPs (biologically produced Se nanoparticles coated by  
648 biopolymer) are considered Se recovery products through bioreduction without further  
649 refining treatment. Microorganisms (bacteria and fungi) have been reported in  
650 BioSeNPs synthesis and Se recovery (Table 4). Different bacteria or fungi have  
651 different Se oxyanions reduction pathways and mechanisms, which might influence Se  
652 oxyanions reduction rate, BioSeNPs formation location, size and shape, which  
653 consequently affect the separation of BioSeNPs [198, 199]. For example, extracellular  
654 polymeric substances (EPS) coated BioSe-Nanospheres (diameters between 20 and 50  
655 nm) showed a  $91.6 \pm 0.5$  % settling efficiency in fresh lake water. In contrast, EPS  
656 coated BioSe-Nanorods (lengths between 300 and 700 nm with a median of 570 nm)  
657 displayed a settling efficiency of  $97.1 \pm 0.5$  % [199].

658 The transportation of  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  into cells is the first step of Se metabolism  
659 [200]. Transporters for structurally similar oxyanions, e.g.,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , can uptake  
660 Se oxyanions [201, 202].  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  can enter the *E. coli* cells through the

661 sulphate permease system (cysA, cysU, cysW) [203, 204]. Through engineering  $\text{PO}_4^{3-}$   
662 transporters from *Saccharomyces cerevisiae* into *Rhodotorula glutinis* X-20, Se content  
663 in the cell was increased by 21.1% and reached  $5349.6 \mu\text{g g}^{-1}$  with  $\text{SeO}_3^{2-}$  as the Se  
664 source [202]. However, the Se uptake pathway is not well documented, and no specific  
665 Se oxyanions uptake system has been reported. From the perspective of Se recovery,  
666 reducing the Se uptake by cells may enhance the production of extracellular BioSeNPs,  
667 which might be achieved by gene regulation and modification.

668 Several reviews have summarised the Se oxyanions reduction processes by  
669 bacteria [182, 205, 206]. It is well recognized that microbial  $\text{SeO}_4^{2-}$  reduction to  $\text{Se}(0)$   
670 can be represented by equations (1) and (2). The reduction of  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  can  
671 occur both intracellularly and extracellularly mediated by reductase and other  
672 biomolecules (Figure 6) [177]. The bioreduction of  $\text{SeO}_4^{2-}$  to  $\text{SeO}_3^{2-}$  is primarily  
673 catalyzed by either a soluble or membrane-bound selenate reductase (Ser) [182]. In  
674 comparison, the microbial conversion of  $\text{SeO}_3^{2-}$  to  $\text{Se}(0)$  is widely recognized as a  
675 detoxification strategy, whereby the toxic and soluble Se is converted to solid  $\text{Se}(0)$ .  
676 During the detoxification process, various biomolecules, including glutathione,  
677 glutaredoxin, and siderophores, facilitate the conversion of  $\text{SeO}_3^{2-}$  to  $\text{Se}(0)$  [182]. There  
678 are also reported studies using extracted biomolecules such as cytochrome c,  
679 glutathione, and  $\beta$ -carotene as reductants to synthesize Se nanostructures at room  
680 temperature [207-209]. EPS, which contains various functional groups including  
681 carboxyl, phosphoric, amine, and hydroxyl groups, also has an unrevealed function in  
682 extracellular Se oxyanions reduction [187-191]. The reduction of  $\text{SeO}_3^{2-}$  by EPS has  
683 been confirmed [194]. However, the specific component in EPS and enzyme  
684 responsible for Se oxyanions reduction is still poorly understood and documented.  
685 Further studies should be conducted to reveal the Se oxyanions reduction enzyme,  
686 biomolecule and EPS components for low-cost Se recovery through large scale cell-  
687 free reduction of Se oxyanions.



690 For steps (iii) and (iv), there are different opinions. It has been proposed that  
691 BioSeNPs are formed by binding amorphous Se(0) and protein Se factor A (sefA)  
692 before being exported by *Thauera selenatis* (Figure 6) [210]. For *Stenotrophomonas*  
693 *maltophilia*, it has been suggested that the Se(0) is produced intracellularly and  
694 exported outside the membrane. Then amorphous BioSeNPs is formed [211]. Although  
695 some authors claim that larger selenospheres are formed through Ostwald ripening until  
696 capped by agents such as EPS and protein, larger selenosphere formation from Se(0) is  
697 not well studied [23, 178, 212]. Moreover, how the BioSeNPs are exported through the  
698 membrane is still unknown [23, 178]. Although there is not enough research  
699 concentrating on the fabrication and exporting process of BioSeNPs, protein and  
700 enzyme involvement may substantially influence the morphology of BioSeNPs [213].  
701 Bacterial SeO<sub>3</sub><sup>2-</sup> reduction by *Azospirillum brasilense* was studied using the efflux  
702 pump inhibitor carbonyl cyanide m-chlorophenylhydrazone (CCCP). In this case study,  
703 only intracellular Se crystallites were produced because CCCP blocked the membrane  
704 export of Se(0) nuclei [214]. From the perspective of Se recovery, bacteria with efflux  
705 pump overexpression can boost the presence of extracellular BioSeNPs. In the most  
706 reported cost-effective Se removal studies, mixed cultures, e.g., activated sludge and  
707 sediment, were employed as microorganism resources, especially for *in situ*  
708 remediations [215, 216]. In this case, mechanisms discussed above, including  
709 intracellular/extracellular Se oxyanions reduction and BioSeNPs assembly, occur [215,  
710 216].

#### 711 **4.2.3. BioSeNPs production and its recovery from wastewater**

712 The recovery of BioSeNPs from wastewater is attracting attention from  
713 researchers worldwide [12, 217, 218]. However, other pollutants such as PO<sub>4</sub><sup>3-</sup>, S, Ca,  
714 especially metal ions in wastewater, can be trapped with the BioSeNPs [199, 219]. The  
715 purity of the recovered Se depends highly on the type of wastewater, which might affect  
716 its application. It has also been reported that the recovered BioSeNPs produced by  
717 *Pseudomonas stutzeri* NT-I from synthetic wastewater were composed mainly of

718 organic matter and 11-14 mass% Se(0) (biomass unseparated) [219]. For obtaining pure  
719 Se, the refining of recovered BioSeNPs from wastewater is necessary.

720 The BioSeNPs are produced both intracellularly and extracellularly, especially  
721 when using mixed cultures [220]. Part of the Se will be trapped in the biomass, and  
722 separating the entrapped BioSeNPs for Se recovery can be achieved through cell lysis  
723 followed by filtration or centrifugation [221]. However, cell lysis is energy-intensive  
724 and involves chemicals that lead to further environmental contamination [220]. A  
725 solution to avoid breaking cells is using microbes to reduce Se(0) to volatile methylated  
726 selenides and then using chemicals (e.g., nitric acid) to collect the selenides [222].  
727 However, the produced selenides are toxic. To improve Se's recovery efficiency, purity  
728 and avoid cell lysis of Se accumulated in the cell or volatile methylated selenides  
729 production, maximizing the extracellular production of BioSeNPs is necessary [220].

730 Different physiological states of growing cell culture, their gradual changes, and  
731 the medium components also influence both the Se oxyanions reduction process and  
732 BioSeNPs synthesis [223]. Two *Azospirillum brasilense* strains (Sp7 and Sp245) were  
733 studied to reduce  $\text{SeO}_3^{2-}$  to BioSeNPs [214]. Extracellular BioSeNPs can be attained by  
734 using bacterial cultures at the end of the logarithmic growth phase (sometimes called  
735 the log phase or the exponential phase, a period characterized by cell doubling) [214].  
736 The obtained BioSeNPs sizes depended on the initial Se concentration (~25–80 nm in  
737 diameter at 5–10 mM selenite). This study showed that the formation of extracellular  
738 BioSeNPs requires normal bacterial metabolic activity [214]. Studies aiming at  
739 maximizing microbial Se recovery should test the microorganisms at different  
740 conditions to maximize the production of extracellular BioSeNPs.

741 Certain bacteria can produce extracellular BioSeNPs only. For example, *Bacillus*  
742 *safensis* JG-B5T was reported to reduce  $\text{SeO}_3^{2-}$  to BioSeNPs extracellularly with  
743 decreased colloidal stability than BioSeNPs produced by anaerobic granular sludge and  
744 *B. selenatarsenatis* which enables a higher settling efficiency [224]. For instance, at a  
745 Na:Se mass ratio of 23 and neutral pH, the  $\zeta$ -potential of BioSeNPs produced via  
746 anaerobic granular sludge and *B. selenatarsenatis* was -35 mV. In comparison, at a  
747 much lower Na:Se mass ratio of ~0.80 and neutral pH,  $\zeta$ -potential was close to -10 mV

748 for BioSeNPs produced by *B. safensis* JG-B5T. The lower colloidal stability of the  
749 BioSeNPs produced by *Bacillus safensis* JG-B5T has a strong relationship with the high  
750 toxicity of  $\text{SeO}_3^{2-}$  which induces stress in the microorganisms, making less extracellular  
751 protein coating on Se(0). However, in this study, no decrease of total Se and increase  
752 of  $\text{SeO}_3^{2-}$  were observed when  $\text{SeO}_4^{2-}$  was the only electron acceptor present during the  
753 incubation of *Bacillus selenatarsenatis*, which means *Bacillus safensis* JG-B5T is not  
754 capable of reducing  $\text{SeO}_4^{2-}$ . Although BioSeNPs were produced extracellularly in this  
755 study, direct cell contact was essential for  $\text{SeO}_3^{2-}$  reduction by *Bacillus safensis* JG-  
756 B5T [224].

757 A fungus isolated from a soil sample, identified as *Aspergillus terreus*, was used  
758 for cell-free extracellular synthesis of SeNPs [225]. Spherical particles with an average  
759 size of 47 nm were formed by adding a culture supernatant of *Aspergillus terreus* to  
760  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  solution [225], avoiding the intracellular reduction of Se oxyanions  
761 and the formation of SeNPs. Through this cell-free method, the purity of Se in the  
762 recovered SeNPs might be enhanced, which can reduce the cost of refining SeNPs to  
763 get pure Se [219, 224]. Moreover, the recovery of the final Se production is simplified  
764 as no biomass was present and thus no need for the separation of biomass and Se.  
765 However, the authors did not adequately describe the produced BioSeNPs, *i.e.*, purity  
766 of Se and the functioning enzymes and metabolites in the supernatant.

767 In the effluent of most studied bioreactors treating Se containing wastewater,  
768 BioSeNPs have a diameter of up to 400 nm instead of large crystals [23]. This  
769 characteristic and the coated polymer layer allow BioSeNPs to display colloidal  
770 properties and remain in the bioreactor liquid phase [23]. The colloidal stability of  
771 BioSeNPs also leads to further treatment because part of the BioSeNPs is still present  
772 in the effluent and cannot meet the discharge regulatory guidelines. The BioSeNPs from  
773 the matrix can be separated by adding chemicals through coagulation and flocculation  
774 [226, 227]. Adjusting the pH and/or addition of counter cations is a straightforward  
775 method to enhance the settleability of BioSeNPs, which can further decrease the Se  
776 concentration in the effluent [72]. For Se removal from the effluent, lower zeta potential  
777 means lower cost of chemicals for separating colloidal BioSeNPs [72]. Further research

778 on Se bioremediation should optimize BioSeNPs separation for effective Se removal.  
779 However, for Se recovery, adding chemicals will hamper the purity of recovered Se.  
780 Physical solid-liquid-biomass separation (i.e., centrifugation, filtration or gravity  
781 sedimentation) of BioSeNPs resulting from microbial reduction, which is more eco-  
782 friendly as there is no extra addition of harsh chemicals, is influenced by BioSeNPs  
783 properties such as size, density and crystal structure [21, 199]. Combining BioSeNPs  
784 sedimentation and well-designed configuration of bioreactors, enabling liquid, biomass,  
785 and BioSeNPs separation is an optimal method for low-cost Se recovery.

786 Various morphologies of BioSeNPs have been observed (Table 2) through Se  
787 oxyanions reduction by bacteria or fungi. The size of the Se(0) particles produced by  
788 microorganisms grows until capped by agents such as proteins, polysaccharides,  
789 phospholipids or EPS, which coated the Se(0) with a layer of biopolymer (BioSeNPs).  
790 The production of larger particles with higher density (crystalline Se:  $4.81 \text{ g mL}^{-1}$ ) from  
791 Se with lower density (amorphous Se:  $4.27 \text{ g mL}^{-1}$ ) is a crucial step to enable easy  
792 BioSeNPs sedimentation for Se recovery [21]. In batch and fed-batch reactors using  
793 anaerobic activated sludge, grey crystalline hexagonal acicular BioSeNPs were  
794 obtained at pH 7, 8 and  $50 \text{ }^\circ\text{C}$ , while at pH 6, 7, 8 and 9 combined with a temperature  
795 lower than  $30 \text{ }^\circ\text{C}$ , red amorphous nanospheres were dominant [21]. Relatively pure  
796 hexagonal Se(0) crystals, which can settle under gravity, were produced in a batch  
797 reactor treating an influent containing  $120 \text{ mg L}^{-1}$  Se(VI) with ethanol as the electron  
798 donor and carbon source at  $30 \text{ }^\circ\text{C}$  (pH 7) [217]. However, in this study, Se(VI)  
799 concentration is much higher than Se(VI) concentration used in other works and  
800 common wastewater (Table 1). Moreover, the presence of relatively pure hexagonal  
801 Se(0) crystals might be due to the long incubation as the morphology of the BioSeNPs  
802 was observed after 229 days [188]. Amorphous BioSeNPs ( $181 \pm 40 \text{ nm}$ ), produced by  
803 *Shewanella* sp. strain HN-41 under anaerobic conditions, were found to transform into  
804 extensive, long and thin, polycrystalline Se nanowires and nanoribbons ( $>100 \text{ nm} \times$   
805  $57 \text{ nm}$ ) rapidly in 80% DMSO, a polar aprotic solvent, after 12 h of incubation at  $30 \text{ }^\circ\text{C}$   
806 via dissolution–recrystallization processes [228]. This might be an option for

807 resembling amorphous BioSeNPs in the effluent to crystalline BioSeNPs by gravity for  
808 Se recovery.

809 To achieve low-cost Se recovery, reactor design to enable liquid-solid separation  
810 is critical. An inverse fluidized bed (IFB) reactor containing low-density floatable  
811 biosupport material was investigated [229]. In this reactor, biofilm is formed on the  
812 biological carrier material and remains on the top of the reactor. Due to fluidization,  
813 BioSeNPs are separated from the biomass and settled at the bottom, so the BioSeNPs  
814 are easy to recover. When the IFB operated with hydraulic retention time (HRT) of 24  
815 h and 48 h (influent  $\text{SeO}_3^{2-}$  concentration of 0.1 mM), 94% and 99% of Se was removed,  
816 respectively. Around 45% of Se was recovered as BioSeNPs in both cases. The  
817 extended residence time allows agglomeration of amorphous BioSeNPs into larger  
818 crystalline BioSeNPs, and the sedimentation rate to the bottom of the reactor is faster.  
819 However, small BioSeNPs (< 45 nm) generally do not settle at the bottom of the reactor  
820 and get washed out along with the effluent stream and a large part of Se was trapped in  
821 biomass, which was not determined in this work. For the separation of treated water,  
822 BioSeNPs and biomass, a system with the combination of a fixed bed biofilm reactor,  
823 a novel bacterium-nanoparticle separator containing a tilted poly-ethylene sheet, and a  
824 tangential flow ultrafiltration module was investigated [230]. The three units in the  
825 system worked in synergism to achieve separation and recovery. The tangential flow  
826 ultrafiltration module retained the biomass in the system, which increased the biomass  
827 retention time and allowed for more biomass decay through which intracellular  
828 BioSeNPs could be released and recovered. BioSeNPs aggregates were separated from  
829 bacterial aggregates due to their different interactions with a tilted polyethylene sheet  
830 in the bacterium-BioSeNPs separator. BioSeNPs aggregates stayed on the polyethylene  
831 sheet while bacterial aggregates settled to the bottom of the separator [230]. The  
832 potential of rotating biological contactor, rotating horizontal packed bed bioreactor,  
833 moving bed biofilm reactor to complete Se recovery in the single-stage process have  
834 also been discussed in a review paper [194]. However, no work on the use of these  
835 bioreactors for Se recovery has been published.



### 836 **4.3 Refinery of Se containing products**

837 To obtain pure Se, the recovered Se containing products from wastewater  
838 treatment need refining [219]. The most used method for getting pure Se from anode  
839 slime, currently the primary source of Se, is chemical Se refining. The whole procedure  
840 can be summarized into three steps: (i) characterization of the recovered product; (ii)  
841 separation of the impurities; (iii) conversion of the captured Se to Se(0) by reduction  
842 [73, 231, 232]. The aim of step (i) is to identify the elemental composition of the  
843 recovered Se containing product using X-ray diffraction analysis (XRD). Step (ii) can  
844 be achieved by adding various leaching agents such as mineral acids and sodium  
845 hydroxide [73, 232], or roasting (including oxidation, sulfate, and soda) [233-235].

846 Although as high as 99% pure Se can be obtained through chemical refining, it has  
847 the following disadvantages: complex process, large reagent consumption, low yield,  
848 and production of severe pollution [231]. Physical methods such as zone refining and  
849 vacuum distillation have been studied for Se refining [231]. However, high  
850 concentrations of volatile impurities (1.12% of Te, 0.06% of Cu, and 0.01% Pb) have  
851 hindered the purification of Se [231]. An approach combining chemical impurity  
852 separation and vacuum distillation was studied, and 70% Se was purified to 99.998%  
853 [231]. In this study, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) converted the impurity phases in the Se  
854 sludge slurry, thereby decreasing impurities' volatilization in the later distillation  
855 process. A vacuum distillation process was carried out to extract Se efficiently, and  
856 high-purity Se was collected in the volatile component [231]. These refinery methods  
857 provide the basis to develop cost-effective and eco-friendly Se refining from Se  
858 containing solids, including BioSeNPs through microbial reduction and Se containing  
859 sludge through abiotic methods followed by magnetic separation.

860 Only oxidizing roasting has been adapted for the refinery of BioSeNPs obtained  
861 through microbial reduction of Se oxyanions in synthetic wastewater by *Pseudomonas*  
862 *stutzeri* NT-I with a purity of 99% [219]. The detailed procedure is to evaporate Se to  
863 gaseous selenium dioxide (SeO<sub>2</sub>) from solid at 700 °C or higher temperature with pure  
864 oxygen, precipitate SeO<sub>2</sub> at 340 °C or lower temperature. The solid SeO<sub>2</sub> is dissolved

865 in water to produce a  $\text{SeO}_3^{2-}$  solution, then subjected to a reduction process by applying  
866 sulfite gas to obtain purified Se [219]. For other Se containing products obtained  
867 through abiotic techniques, no refinery study has been reported. More studies about  
868 eco-friendly and cost-effective Se containing product refining for high purity Se should  
869 be carried out.

## 870 **5. Conclusions and future perspectives**

871 Se is a valuable and scarce resource that plays an essential role in industries.  
872 However, it cannot be exploited through ore exploration. Because of the intensive  
873 human activity and uncontrolled natural activities, mounting Se contamination offers  
874 the opportunity to remediate and recover it for reuse, given the increasing demand for  
875 pure Se for electronics and medical applications. Microbial recovery of Se  
876 nanoparticles has gained substantial attention as BioSeNPs can be obtained. Se  
877 recovery through microbial reduction can be boosted by enhancing Se oxyanions'  
878 extracellular reduction and larger size BioSeNPs production by manipulating reaction  
879 conditions. The production of BioSeNPs with density for sedimentation by gravity,  
880 combined with well-designed bioreactors allowing liquid-solid separation, is an optimal  
881 solution to achieve low cost Se recovery. Notably, the cost-effective recovery of Se  
882 with high purity is limited by its concentration and the existence of other pollutants in  
883 wastewater. Compared with abiotic Se remediation methods, microbial reduction needs  
884 a longer time for incubation and bacterial growth. At the same time, abiotic Se  
885 remediation techniques, e.g., coagulation and precipitation, reduction by ZVI followed  
886 by magnetic separation, can be an option for Se recovery. From both Se remediation  
887 and recovery perspectives, the coexistence of other pollutants, including sulfate,  
888 phosphate, nitrate, is a major challenge. The development of cost-effective and eco-  
889 friendly refinery methods for recovered Se containing products has not received enough  
890 attention.

891 This work has reviewed the widespread microbial Se reduction, proposed abiotic  
892 Se remediation techniques in combination with magnetic separation for Se recovery,  
893 and suggested the development of refinery methods for recovered Se product. The

894 attractive microbial reduction and proposed abiotic Se remediation techniques followed  
895 by magnetic separation have shed light on Se recovery from wastewater. However, pilot  
896 and full scale applications of Se recovery from wastewater are largely absent in the  
897 literature. Only a few papers have demonstrated Se recovery at laboratory scale. To  
898 achieve and maximize Se recovery through microbial reduction, future research should  
899 consider the following points: (i) the performance of microbial Se reduction should be  
900 evaluated on a case-specific basis before scaling up as it can be affected by wastewater  
901 type, selected inoculum, and operation conditions; (ii) the mechanism of Se oxyanions  
902 reduction to BioSeNPs formation needs to be further explored, and extracellular  
903 production of BioSeNPs should be boosted; (iii) biological reduction technology and  
904 physio-chemical technology can be combined for easy separation of the formed  
905 BioSeNPs. The combination of abiotic Se remediation techniques and magnetic  
906 separation may be an option for achieving Se recovery with the following aspects  
907 needing to be addressed: (i) verification and development of the magnetic separation  
908 combined with different abiotic Se remediation techniques; (ii) identification and  
909 evaluation of the recovered Se product via different abiotic methods. To provide pure  
910 Se to the market, the produced Se containing product from wastewater needs further  
911 refining. The goal of a cost-effective and eco-friendly refinery method for recovery Se  
912 containing products requires further attention.

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920 **Declaration of Competing Interest**

921       The authors declare that they have no competing financial interests or personal  
922 relationships that could have influenced the work reported in this paper.

923

924 **References**

- 925 [1] M. Sakamoto, H.M. Chan, J.L. Domingo, M. Kubota, K. Murata, Changes in body  
926 burden of mercury, lead, arsenic, cadmium and selenium in infants during early  
927 lactation in comparison with placental transfer, *Ecotoxicology and environmental*  
928 *safety*, 84 (2012) 179-184.
- 929 [2] Y.H. Ribeiro, D.G. David, M.V. da Silva, Z.N. da Rocha, Analysis and Growth  
930 Modeling of CuInSe 2 Films by Electrodeposition for Photocell Applications, *Brazilian*  
931 *Journal of Physics*, (2021) 1-14.
- 932 [3] A. Kumar, Impact of selenium composition variation in CZTS solar cell, *Optik*, 234  
933 (2021) 166421.
- 934 [4] W.H. Organization, Trace elements in human nutrition and health, World Health  
935 Organization, 1996.
- 936 [5] L. Foster, S. Sumar, Selenium in the environment, food and health, *Nutrition &*  
937 *Food Science*, (1995).
- 938 [6] S. Etteieb, S. Magdoui, M. Zolfaghari, S. Brar, Monitoring and analysis of selenium  
939 as an emerging contaminant in mining industry: A critical review, *Science of the Total*  
940 *Environment*, 698 (2020) 134339.
- 941 [7] A.D. Lemly, Aquatic selenium pollution is a global environmental safety issue,  
942 *Ecotoxicology and environmental safety*, 59 (2004) 44-56.
- 943 [8] G.H. Floor, E. Marguá, M. Hidalgo, I. Queralt, P. Kregsamer, C. Strelí, G. Román-  
944 Ross, Study of selenium sorption processes in volcanic ash using Total Reflection X-  
945 ray Fluorescence (TXRF), *Chemical Geology*, 352 (2013) 19-26.
- 946 [9] L. Twidwell, J. McCloskey, P. Miranda, M. Gale, Technologies and potential  
947 technologies for removing selenium from process and mine wastewater, *Proceedings*  
948 *of the Recycling, Waste, Treatment and Clean Technology (REWAS)*, San Sebastian,

949 Spain, (1999) 5-9.

950 [10] A.M. Gustafsson, M.R.S. Foreman, C. Ekberg, Recycling of high purity selenium  
951 from CIGS solar cell waste materials, *Waste management*, 34 (2014) 1775-1782.

952 [11] M.M. Rodriguez, V.C. Rivero, R.J. Ballesta, Selenium distribution in topsoils and  
953 plants of a semi-arid Mediterranean environment, *Environmental Geochemistry and*  
954 *Health*, 27 (2005) 513-519.

955 [12] O. Otsuka, M. Yamashita, Selenium recovery from wastewater using the selenate-  
956 reducing bacterium *Pseudomonas stutzeri* NT-I, *Hydrometallurgy*, 197 (2020) 105470.

957 [13] V. Funari, H.I. Gomes, D. Coppola, G.A. Vitale, E. Dinelli, D. de Pascale, M.  
958 Rovere, Opportunities and threats of selenium supply from unconventional and low-  
959 grade ores: A critical review, *Resources, Conservation and Recycling*, 170 (2021)  
960 105593.

961 [14] J.T. Trimmer, D.C. Miller, J.S. Guest, Resource recovery from sanitation to  
962 enhance ecosystem services, *Nature Sustainability*, 2 (2019) 681-690.

963 [15] A.P. Velenturf, P. Purnell, Resource recovery from waste: Restoring the balance  
964 between resource scarcity and waste overload, *Sustainability*, 9 (2017) 1603.

965 [16] S.F. Evans, M.R. Ivancevic, J. Yan, A.K. Naskar, A.M. Levine, R.J. Lee, C.  
966 Tsouris, M.P. Paranthaman, Magnetic adsorbents for selective removal of selenite from  
967 contaminated water, *Separation Science and Technology*, 54 (2019) 2138-2146.

968 [17] L. Lortie, W. Gould, S. Rajan, R. McCready, K.-J. Cheng, Reduction of selenate  
969 and selenite to elemental selenium by a *Pseudomonas stutzeri* isolate, *Appl. Environ.*  
970 *Microbiol.*, 58 (1992) 4042-4044.

971 [18] J.-H. Luo, H. Chen, S. Hu, C. Cai, Z. Yuan, J. Guo, Microbial selenate reduction  
972 driven by a denitrifying anaerobic methane oxidation biofilm, *Environmental science*  
973 *& technology*, 52 (2018) 4006-4012.

- 974 [19] Y. Zhang, M. Kuroda, S. Arai, F. Kato, D. Inoue, M. Ike, Biological treatment of  
975 selenate-containing saline wastewater by activated sludge under oxygen-limiting  
976 conditions, *Water research*, 154 (2019) 327-335.
- 977 [20] S. Xia, X. Xu, L. Zhou, Insights into selenate removal mechanism of hydrogen-  
978 based membrane biofilm reactor for nitrate-polluted groundwater treatment based on  
979 anaerobic biofilm analysis, *Ecotoxicology and environmental safety*, 178 (2019) 123-  
980 129.
- 981 [21] S.P. Hageman, R.D. van der Weijden, A.J. Stams, C.J. Buisman, Bio-production  
982 of selenium nanoparticles with diverse physical properties for recovery from water,  
983 *International Journal of Mineral Processing*, 169 (2017) 7-15.
- 984 [22] L.C. Tan, Y.V. Nancharaiah, E.D. van Hullebusch, P.N. Lens, Selenium:  
985 environmental significance, pollution, and biological treatment technologies,  
986 *Biotechnology advances*, 34 (2016) 886-907.
- 987 [23] Y.V. Nancharaiah, P.N. Lens, Selenium biomineralization for biotechnological  
988 applications, *Trends in biotechnology*, 33 (2015) 323-330.
- 989 [24] E.A. Pilon-Smits, D.L. LeDuc, Phytoremediation of selenium using transgenic  
990 plants, *Current Opinion in Biotechnology*, 20 (2009) 207-212.
- 991 [25] Y. He, Y. Xiang, Y. Zhou, Y. Yang, J. Zhang, H. Huang, C. Shang, L. Luo, J. Gao,  
992 L. Tang, Selenium contamination, consequences and remediation techniques in water  
993 and soils: a review, *Environmental research*, 164 (2018) 288-301.
- 994 [26] S.A. Wadhvani, U.U. Shedbalkar, R. Singh, B.A. Chopade, Biogenic selenium  
995 nanoparticles: current status and future prospects, *Applied microbiology and  
996 biotechnology*, 100 (2016) 2555-2566.
- 997 [27] A. Sinharoy, P.N.L. Lens, Biological Removal of Selenate and Selenite from  
998 Wastewater: Options for Selenium Recovery as Nanoparticles, *Current Pollution*

- 999 Reports, 6 (2020) 230-249.
- 1000 [28] R.J.B. Reynolds, E.A. Pilon-Smits, Plant selenium hyperaccumulation-Ecological  
1001 effects and potential implications for selenium cycling and community structure,  
1002 *Biochimica et Biophysica Acta (BBA)-General Subjects*, 1862 (2018) 2372-2382.
- 1003 [29] Z. Li, D. Liang, Q. Peng, Z. Cui, J. Huang, Z. Lin, Interaction between selenium  
1004 and soil organic matter and its impact on soil selenium bioavailability: A review,  
1005 *Geoderma*, 295 (2017) 69-79.
- 1006 [30] F.M. Fordyce, Selenium deficiency and toxicity in the environment, in: *Essentials*  
1007 *of medical geology*, Springer, 2013, pp. 375-416.
- 1008 [31] S. Santos, G. Ungureanu, R. Boaventura, C. Botelho, Selenium contaminated  
1009 waters: An overview of analytical methods, treatment options and recent advances in  
1010 sorption methods, *Science of the Total Environment*, 521 (2015) 246-260.
- 1011 [32] L.H.E. Winkel, B. Vriens, G.D. Jones, L.S. Schneider, E. Pilon-Smits, G.S.  
1012 Banuelos, Selenium Cycling Across Soil-Plant-Atmosphere Interfaces: A Critical  
1013 Review, *Nutrients*, 7 (2015) 4199-4239.
- 1014 [33] F.E. Huggins, C.L. Senior, P. Chu, K. Ladwig, G.P. Huffman, Selenium and  
1015 arsenic speciation in fly ash from full-scale coal-burning utility plants, *Environmental*  
1016 *science & technology*, 41 (2007) 3284-3289.
- 1017 [34] I. Pumure, J. Renton, R. Smart, The interstitial location of selenium and arsenic in  
1018 rocks associated with coal mining using ultrasound extractions and principal  
1019 component analysis (PCA), *Journal of hazardous materials*, 198 (2011) 151-158.
- 1020 [35] A. Khamkhash, V. Srivastava, T. Ghosh, G. Akdogan, R. Ganguli, S. Aggarwal,  
1021 Mining-related selenium contamination in Alaska, and the state of current knowledge,  
1022 *Minerals*, 7 (2017) 46.
- 1023 [36] A. Haug, R.D. Graham, O.A. Christophersen, G.H. Lyons, How to use the world's



1024 scarce selenium resources efficiently to increase the selenium concentration in food,  
1025 *Microbial Ecology in Health and Disease*, 19 (2007) 209-228.

1026 [37] Z.J. Wang, Y.X. Gao, Biogeochemical cycling of selenium in Chinese  
1027 environments, *Applied Geochemistry*, 16 (2001) 1345-1351.

1028 [38] J. Bech, M. Suarez, F. Reverter, P. Tume, P. Sánchez, J. Bech, A. Lansac, Selenium  
1029 and other trace elements in phosphate rock of Bayovar-Sechura (Peru), *Journal of*  
1030 *Geochemical Exploration*, 107 (2010) 136-145.

1031 [39] A. Fernández-Martínez, L. Charlet, Selenium environmental cycling and  
1032 bioavailability: a structural chemist point of view, *Reviews in Environmental Science*  
1033 *and Bio/Technology*, 8 (2009) 81-110.

1034 [40] L.H. Winkel, B. Vriens, G.D. Jones, L.S. Schneider, E. Pilon-Smits, G.S. Bañuelos,  
1035 Selenium cycling across soil-plant-atmosphere interfaces: a critical review, *Nutrients*,  
1036 7 (2015) 4199-4239.

1037 [41] M. Ichnat, Occurrence and distribution of selenium, CRC press, 1989.

1038 [42] J.D. Hem, Study and interpretation of the chemical characteristics of natural water,  
1039 Department of the Interior, US Geological Survey, 1985.

1040 [43] H. Tian, K. Liu, J. Zhou, L. Lu, J. Hao, P. Qiu, J. Gao, C. Zhu, K. Wang, S. Hua,  
1041 Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-  
1042 Fired Power Plants □ Temporal Trends and Spatial Variation Characteristics,  
1043 *Environmental science & technology*, 48 (2014) 3575-3582.

1044 [44] R.J. Cassella, O.D. de Sant'Ana, A.T. Rangel, B. Maria de Fátima, R.E. Santelli,  
1045 Selenium determination by electrothermal atomic absorption spectrometry in petroleum  
1046 refinery aqueous streams containing volatile organic compounds, *Microchemical*  
1047 *journal*, 71 (2002) 21-28.

1048 [45] K.L. Wasewar, B. Prasad, S. Gulipalli, Removal of selenium by adsorption onto

1049 granular activated carbon (GAC) and powdered activated carbon (PAC), *CLEAN–Soil,*  
1050 *Air, Water*, 37 (2009) 872-883.

1051 [46] A.D. Lemly, Symptoms and implications of selenium toxicity in fish: the Belews  
1052 Lake case example, *Aquatic Toxicology*, 57 (2002) 39-49.

1053 [47] S.J. Hamilton, Review of selenium toxicity in the aquatic food chain, *Science of*  
1054 *the Total Environment*, 326 (2004) 1-31.

1055 [48] P. Cordoba, L.C. Staicu, Flue gas desulfurization effluents: An unexploited  
1056 selenium resource, *Fuel*, 223 (2018) 268-276.

1057 [49] X. Xia, L. Ling, W.-x. Zhang, Genesis of pure Se (0) nano-and micro-structures in  
1058 wastewater with nanoscale zero-valent iron (nZVI), *Environmental Science: Nano*, 4  
1059 (2017) 52-59.

1060 [50] Z. Xu, W. Xu, Y. Lv, S. Wang, J. Wang, Phase separation of molybdenum, cesium  
1061 and selenium from the borosilicate glass containing simulated nuclear wastes under a  
1062 CO<sub>2</sub>-rich heating atmosphere, *Journal of Nuclear Materials*, 523 (2019) 216-222.

1063 [51] T. Watari, B.C. McLellan, S. Ogata, T. Tezuka, Analysis of potential for critical  
1064 metal resource constraints in the international energy agency’s long-term low-carbon  
1065 energy scenarios, *Minerals*, 8 (2018) 156.

1066 [52] W. Berger, F.-G. Simon, K. Weimann, E.A. Alsema, A novel approach for the  
1067 recycling of thin film photovoltaic modules, *Resources, Conservation and Recycling*,  
1068 54 (2010) 711-718.

1069 [53] D. Wu, W. Ren, Y. NuLi, J. Yang, J. Wang, Recent progress on selenium-based  
1070 cathode materials for rechargeable magnesium batteries: a mini review, *Journal of*  
1071 *Materials Science & Technology*, (2021).

1072 [54] H. Abbas, D. Abou Baker, Biological evaluation of selenium nanoparticles  
1073 biosynthesized by *Fusarium semitectum* as antimicrobial and anticancer agents,

1074 Egyptian Journal of Chemistry, 63 (2020) 1119-1133.

1075 [55] D. Medina Cruz, G. Mi, T.J. Webster, Synthesis and characterization of biogenic  
1076 selenium nanoparticles with antimicrobial properties made by *Staphylococcus aureus*,  
1077 methicillin-resistant *Staphylococcus aureus* (MRSA), *Escherichia coli*, and  
1078 *Pseudomonas aeruginosa*, *Journal of Biomedical Materials Research Part A*, 106 (2018)  
1079 1400-1412.

1080 [56] X. Wang, X. Pan, G.M. Gadd, Immobilization of elemental mercury by biogenic  
1081 Se nanoparticles in soils of varying salinity, *Science of the total environment*, 668 (2019)  
1082 303-309.

1083 [57] J.R. Arthur, F. Nicol, G.J. Beckett, Selenium deficiency, thyroid hormone  
1084 metabolism, and thyroid hormone deiodinases, *The American journal of clinical*  
1085 *nutrition*, 57 (1993) 236S-239S.

1086 [58] J.R. Arthur, R.C. McKenzie, G.J. Beckett, Selenium in the immune system, *The*  
1087 *Journal of nutrition*, 133 (2003) 1457S-1459S.

1088 [59] L.J. Machlin, A. Bendich, Free radical tissue damage: protective role of antioxidant  
1089 nutrients, *The FASEB journal*, 1 (1987) 441-445.

1090 [60] K.M. Kubachka, T. Hanley, M. Mantha, R.A. Wilson, T.M. Falconer, Z. Kassa, A.  
1091 Oliveira, J. Landero, J. Caruso, Evaluation of selenium in dietary supplements using  
1092 elemental speciation, *Food chemistry*, 218 (2017) 313-320.

1093 [61] Y. Wu, P. Yang, J. Chen, J.F. Shao, R. Gui, Selenium Biofortification of Bamboo  
1094 Shoots by Liquid Se Fertilization in the Culm Pith Cavity, *ACS Food Science &*  
1095 *Technology*, (2020).

1096 [62] F. Fordyce, Selenium geochemistry and health, *Ambio*, (2007) 94-97.

1097 [63] A. Nesterov, The clinical course of Kashin-Beck disease, *Arthritis & Rheumatism:*  
1098 *Official Journal of the American College of Rheumatology*, 7 (1964) 29-40.

- 1099 [64] G.F. Combs, Selenium in global food systems, *British journal of nutrition*, 85  
1100 (2001) 517-547.
- 1101 [65] G. Alfthan, M. Eurola, P. Ekholm, E.-R. Venäläinen, T. Root, K. Korkalainen, H.  
1102 Hartikainen, P. Salminen, V. Hietaniemi, P. Aspila, Effects of nationwide addition of  
1103 selenium to fertilizers on foods, and animal and human health in Finland: From  
1104 deficiency to optimal selenium status of the population, *Journal of Trace Elements in*  
1105 *Medicine and Biology*, 31 (2015) 142-147.
- 1106 [66] U. Garg, L.D. Smith, *Biomarkers in Inborn Errors of Metabolism: Clinical Aspects*  
1107 *and Laboratory Determination*, Elsevier, 2017.
- 1108 [67] R. Stoffaneller, N.L. Morse, A review of dietary selenium intake and selenium  
1109 status in Europe and the Middle East, *Nutrients*, 7 (2015) 1494-1537.
- 1110 [68] S. Zhu, Y. Liang, D. Gao, X. An, F. Kong, Spraying foliar selenium fertilizer on  
1111 quality of table grape (*Vitis vinifera* L.) from different source varieties, *Scientia*  
1112 *Horticulturae*, 218 (2017) 87-94.
- 1113 [69] A. Gastélum-Estrada, S.O. Serna-Saldívar, D.A. Jacobo-Velázquez, Fighting the  
1114 COVID-19 Pandemic through Biofortification: Innovative Approaches to Improve the  
1115 Immunomodulating Capacity of Foods, *ACS Food Science & Technology*, (2021).
- 1116 [70] K.J. Schulz, J.H. DeYoung, R.R. Seal, D.C. Bradley, *Critical mineral resources of*  
1117 *the United States: economic and environmental geology and prospects for future supply*,  
1118 *Geological Survey*, 2018.
- 1119 [71] T. Kelly, G. Matos, D. Buckingham, C. DiFrancesco, K. Porter, C. Berry, M. Crane,  
1120 T. Goonan, J. Sznoppek, *Historical statistics for mineral and material commodities in the*  
1121 *United States: US Geological Survey*, in, 2018.
- 1122 [72] B. Buchs, M.W. Evangelou, L.H. Winkel, M. Lenz, *Colloidal properties of*  
1123 *nanoparticulate biogenic selenium govern environmental fate and bioremediation*

1124 effectiveness, *Environmental science & technology*, 47 (2013) 2401-2407.

1125 [73] Y. Kilic, G. Kartal, S. Timur, An investigation of copper and selenium recovery  
1126 from copper anode slimes, *International Journal of Mineral Processing*, 124 (2013) 75-  
1127 82.

1128 [74] Y. Zhang, J.N. Moore, Interaction of selenate with a wetland sediment, *Applied*  
1129 *Geochemistry*, 12 (1997) 685-691.

1130 [75] S.O. Okonji, G. Achari, D. Pernitsky, Environmental Impacts of Selenium  
1131 Contamination: A Review on Current-Issues and Remediation Strategies in an Aqueous  
1132 System, *Water*, 13 (2021) 1473.

1133 [76] P.N. Lens, K. Pakshirajan, Environmental Technologies to Treat Selenium  
1134 Pollution: Principles and Engineering, in, IWA Publishing, 2021.

1135 [77] Y.Y. Zhang, M. Kuroda, S. Arai, F. Kato, D. Inoue, M. Ike, Biological treatment  
1136 of selenate-containing saline wastewater by activated sludge under oxygen-limiting  
1137 conditions, *Water Research*, 154 (2019) 327-335.

1138 [78] E. Piacenza, A. Presentato, E. Zonaro, S. Lampis, G. Vallini, R.J. Turner,  
1139 Microbial-based bioremediation of selenium and tellurium compounds,  
1140 Biosorption'.(Ed. J Derco) pp, (2018) 117-147.

1141 [79] C.M. Hill, Review of available technologies for the removal of selenium from  
1142 water, Final Report, prepared for North American Metals Council (NAMC), (2010) 48-  
1143 60.

1144 [80] X. Xia, Z. Zhou, S. Wu, D. Wang, S. Zheng, G. Wang, Adsorption removal of  
1145 multiple dyes using biogenic selenium nanoparticles from an *Escherichia coli* strain  
1146 overexpressed selenite reductase CsrF, *Nanomaterials*, 8 (2018) 234.

1147 [81] K. Kalaitzidou, A. Zouboulis, M. Mitrakas, Cost evaluation for Se (IV) removal,  
1148 by applying common drinking water treatment processes: Coagulation/precipitation or

1149 adsorption, *Journal of Environmental Chemical Engineering*, 8 (2020) 104209.

1150 [82] P. Dessì, R. Jain, S. Singh, M. Seder-Colomina, E.D. van Hullebusch, E.R. Rene,  
1151 S.Z. Ahammad, A. Carucci, P.N. Lens, Effect of temperature on selenium removal from  
1152 wastewater by UASB reactors, *Water Research*, 94 (2016) 146-154.

1153 [83] T. Norgate, S. Jahanshahi, Low grade ores–smelt, leach or concentrate?, *Minerals*  
1154 *Engineering*, 23 (2010) 65-73.

1155 [84] Q. Dehaine, L. Filippov, R. Joussemet, Rare earths (La, Ce, Nd) and rare metals  
1156 (Sn, Nb, W) as by-products of kaolin production–Part 2: Gravity processing of  
1157 micaceous residues, *Minerals Engineering*, 100 (2017) 200-210.

1158 [85] G.B. Abaka-Wood, M. Zanin, J. Addai-Mensah, W. Skinner, Recovery of rare  
1159 earth elements minerals from iron oxide–silicate rich tailings–Part 1: Magnetic  
1160 separation, *Minerals Engineering*, 136 (2019) 50-61.

1161 [86] N.A. Oladoja, E.I. Unuabonah, O.S. Amuda, O.M. Kolawole, Operational  
1162 principles and material requirements for coagulation/flocculation and adsorption-based  
1163 water treatment operations, in: polysaccharides as a green and sustainable resources  
1164 for water and wastewater treatment, Springer, 2017, pp. 1-11.

1165 [87] T. Su, X. Guan, G. Gu, J. Wang, Adsorption characteristics of As (V), Se (IV), and  
1166 V (V) onto activated alumina: effects of pH, surface loading, and ionic strength, *Journal*  
1167 *of Colloid and Interface Science*, 326 (2008) 347-353.

1168 [88] M.A. López-Antón, M. Díaz-Somoano, J. Fierro, M.R. Martínez-Tarazona,  
1169 Retention of arsenic and selenium compounds present in coal combustion and  
1170 gasification flue gases using activated carbons, *Fuel processing technology*, 88 (2007)  
1171 799-805.

1172 [89] M. Matulová, M. Bujdoš, M.B. Miglierini, Z. Mitróová, M. Kubovčiková, M. Urík,  
1173 The effects of selenate on goethite synthesis and selenate sorption kinetics onto a

1174 goethite surface-A three-step process with an unexpected desorption phase, *Chemical*  
1175 *Geology*, 556 (2020) 119852.

1176 [90] H. Asiabi, Y. Yamini, M. Shamsayei, Highly selective and efficient removal of  
1177 arsenic (V), chromium (VI) and selenium (VI) oxyanions by layered double hydroxide  
1178 intercalated with zwitterionic glycine, *Journal of hazardous materials*, 339 (2017) 239-  
1179 247.

1180 [91] J.S. Yamani, A.W. Lounsbury, J.B. Zimmerman, Adsorption of selenite and  
1181 selenate by nanocrystalline aluminum oxide, neat and impregnated in chitosan beads,  
1182 *Water research*, 50 (2014) 373-381.

1183 [92] A.W. Lounsbury, J.S. Yamani, C.P. Johnston, P. Larese-Casanova, J.B.  
1184 Zimmerman, The role of counter ions in nano-hematite synthesis: implications for  
1185 surface area and selenium adsorption capacity, *Journal of hazardous materials*, 310  
1186 (2016) 117-124.

1187 [93] A.W. Lounsbury, R. Wang, D.L. Plata, N. Billmyer, C. Muhich, K. Kanie, T.  
1188 Sugimoto, D. Peak, J.B. Zimmerman, Preferential adsorption of selenium oxyanions  
1189 onto {1 1 0} and {0 1 2} nano-hematite facets, *Journal of colloid and interface science*,  
1190 537 (2019) 465-474.

1191 [94] M.B. Shakoor, Z.-L. Ye, S. Chen, Engineered biochars for recovering phosphate  
1192 and ammonium from wastewater: A review, *Science of The Total Environment*, (2021)  
1193 146240.

1194 [95] P. Godlewska, A. Bogusz, J. Dobrzyńska, R. Dobrowolski, P. Oleszczuk,  
1195 Engineered biochar modified with iron as a new adsorbent for treatment of water  
1196 contaminated by selenium, *Journal of Saudi Chemical Society*, 24 (2020) 824-834.

1197 [96] Y. Wang, F. Dang, X. Zheng, H. Zhong, Biochar amendment to further reduce  
1198 methylmercury accumulation in rice grown in selenium-amended paddy soil, *Journal*  
1199 *of hazardous materials*, 365 (2019) 590-596.

1200 [97] S. Wang, K. Xiao, Y. Mo, B. Yang, T. Vincent, C. Faur, E. Guibal, Selenium (VI)  
1201 and copper (II) adsorption using polyethyleneimine-based resins: Effect of  
1202 glutaraldehyde crosslinking and storage condition, *Journal of hazardous materials*, 386  
1203 (2020) 121637.

1204 [98] S.C. Tang, I.M. Lo, Magnetic nanoparticles: essential factors for sustainable  
1205 environmental applications, *Water research*, 47 (2013) 2613-2632.

1206 [99] Y. Fu, J. Wang, Q. Liu, H. Zeng, Water-dispersible magnetic nanoparticle–  
1207 graphene oxide composites for selenium removal, *Carbon*, 77 (2014) 710-721.

1208 [100] S. Das, M.J. Hendry, J. Essilfie-Dughan, Adsorption of selenate onto ferrihydrite,  
1209 goethite, and lepidocrocite under neutral pH conditions, *Applied Geochemistry*, 28  
1210 (2013) 185-193.

1211 [101] S. Mandal, S. Pu, X. Wang, H. Ma, Y. Bai, Hierarchical porous structured  
1212 polysulfide supported nZVI/biochar and efficient immobilization of selenium in the soil,  
1213 *Science of the Total Environment*, 708 (2020) 134831.

1214 [102] S.-H. Hong, F.N. Lyonga, J.-K. Kang, E.-J. Seo, C.-G. Lee, S. Jeong, S.-G. Hong,  
1215 S.-J. Park, Synthesis of Fe-impregnated biochar from food waste for Selenium (VI)  
1216 removal from aqueous solution through adsorption: Process optimization and  
1217 assessment, *Chemosphere*, (2020) 126475.

1218 [103] S. Satyro, H. Li, A.M. Dehkhoda, R. McMillan, N. Ellis, S.A. Baldwin,  
1219 Application of Fe-biochar composites for selenium (Se+ 6) removal from aqueous  
1220 solution and effect of the presence of competing anions under environmentally relevant  
1221 conditions, *Journal of Environmental Management*, 277 (2021) 111472.

1222 [104] S. Jevtić, I. Arčon, A. Rečnik, B. Babić, M. Mazaj, J. Pavlović, D. Matijašević,  
1223 M. Nikšić, N. Rajić, The iron (III)-modified natural zeolitic tuff as an adsorbent and  
1224 carrier for selenium oxyanions, *Microporous and mesoporous materials*, 197 (2014) 92-  
1225 100.



- 1226 [105] X. Zhang, X. Li, Z. Jin, S.H. Tumrani, X. Ji, Selenium in wastewater can be  
1227 adsorbed by modified natural zeolite and reused in vegetable growth, *Science Progress*,  
1228 104 (2021) 00368504211019845.
- 1229 [106] J. Hein, M. Stamatakis, J. Dowling, Trace metal-rich Quaternary hydrothermal  
1230 manganese oxide and barite deposit, Milos Island, Greece, *Applied Earth Science*, 109  
1231 (2000) 67-76.
- 1232 [107] K. Tokunaga, Y. Yokoyama, S. Kawagucci, A. Sakaguchi, Y. Terada, Y.  
1233 Takahashi, Selenium coprecipitated with barite in marine sediments as a possible redox  
1234 indicator, *Chemistry Letters*, 42 (2013) 1068-1069.
- 1235 [108] N. Börsig, A.C. Scheinost, S. Shaw, D. Schild, T. Neumann, Uptake mechanisms  
1236 of selenium oxyanions during the ferrihydrite-hematite recrystallization, *Geochimica et*  
1237 *Cosmochimica Acta*, 206 (2017) 236-253.
- 1238 [109] P.C.M. Francisco, T. Sato, T. Otake, T. Kasama, S. Suzuki, H. Shiwaku, T. Yaita,  
1239 Mechanisms of Se (IV) co-precipitation with ferrihydrite at acidic and alkaline  
1240 conditions and its behavior during aging, *Environmental science & technology*, 52  
1241 (2018) 4817-4826.
- 1242 [110] N. Börsig, A.C. Scheinost, S. Shaw, D. Schild, T. Neumann, Retention and  
1243 multiphase transformation of selenium oxyanions during the formation of magnetite via  
1244 iron (II) hydroxide and green rust, *Dalton Transactions*, 47 (2018) 11002-11015.
- 1245 [111] A.C. Scheinost, L. Charlet, Selenite reduction by mackinawite, magnetite and  
1246 siderite: XAS characterization of nanosized redox products, *Environmental science &*  
1247 *technology*, 42 (2008) 1984-1989.
- 1248 [112] R. Singh, *Membrane technology and engineering for water purification:*  
1249 *application, systems design and operation*, Butterworth-Heinemann, 2014.
- 1250 [113] C. Hu, Q. Chen, G. Chen, H. Liu, J. Qu, Removal of Se (IV) and Se (VI) from

1251 drinking water by coagulation, *Separation and Purification Technology*, 142 (2015) 65-  
1252 70.

1253 [114] H.K. Hansen, S.F. Pena, C. Gutierrez, A. Lazo, P. Lazo, L.M. Ottosen, Selenium  
1254 removal from petroleum refinery wastewater using an electrocoagulation technique,  
1255 *Journal of Hazardous Materials*, 364 (2019) 78-81.

1256 [115] H.K. Hansen, P. Nunez, C. Jil, Removal of arsenic from wastewaters by airlift  
1257 electrocoagulation. Part 1: Batch reactor experiments, *Separation science and*  
1258 *technology*, 43 (2008) 212-224.

1259 [116] H.K. Hansen, L.M. Ottosen, Removal of arsenic from wastewaters by airlift  
1260 electrocoagulation: Part 3: Copper smelter wastewater treatment, *Separation Science*  
1261 *and Technology*, 45 (2010) 1326-1330.

1262 [117] K. Baek, N. Kasem, A. Ciblak, D. Vesper, I. Padilla, A.N. Alshawabkeh,  
1263 Electrochemical removal of selenate from aqueous solutions, *Chemical engineering*  
1264 *journal*, 215 (2013) 678-684.

1265 [118] D. Merrill, M. Manzione, J. Peterson, D. Parker, W. Chow, A. Hobbs, Field  
1266 Evaluation of arsenic and selenium removal by iron coprecipitation, *Journal (Water*  
1267 *Pollution Control Federation)*, (1986) 18-26.

1268 [119] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke,  
1269 Fundamentals, present and future perspectives of electrocoagulation, *Journal of*  
1270 *Hazardous Materials*, 114 (2004) 199-210.

1271 [120] M. Lv, Z. Zhang, J. Zeng, J. Liu, M. Sun, R.S. Yadav, Y. Feng, Roles of magnetic  
1272 particles in magnetic seeding coagulation-flocculation process for surface water  
1273 treatment, *Separation and Purification Technology*, 212 (2019) 337-343.

1274 [121] T. Ohara, H. Kumakura, H. Wada, Magnetic separation using superconducting  
1275 magnets, *Physica C: Superconductivity*, 357 (2001) 1272-1280.

- 1276 [122] D. Feng, C. Aldrich, H. Tan, Removal of heavy metal ions by carrier magnetic  
1277 separation of adsorptive particulates, *Hydrometallurgy*, 56 (2000) 359-368.
- 1278 [123] S. Sun, H. Zeng, Size-controlled synthesis of magnetite nanoparticles, *Journal of*  
1279 *the American Chemical Society*, 124 (2002) 8204-8205.
- 1280 [124] C. Tsouris, D. DePaoli, J. Shor, M.-C. Hu, T.-Y. Ying, Electrocoagulation for  
1281 magnetic seeding of colloidal particles, *Colloids and Surfaces A: Physicochemical and*  
1282 *Engineering Aspects*, 177 (2001) 223-233.
- 1283 [125] C. Du, Y. Hu, H. Han, W. Sun, P. Hou, R. Liu, L. Wang, Y. Yang, R. Liu, L. Sun,  
1284 Magnetic separation of phosphate contaminants from starch wastewater using magnetic  
1285 seeding, *Science of the Total Environment*, 695 (2019) 133723.
- 1286 [126] Y. Li, J. Wang, Y. Zhao, Z. Luan, Research on magnetic seeding flocculation for  
1287 arsenic removal by superconducting magnetic separation, *Separation and Purification*  
1288 *Technology*, 73 (2010) 264-270.
- 1289 [127] S.O. Okonji, J.A. Dominic, D. Pernitsky, G. Achari, Removal and recovery of  
1290 selenium species from wastewater: Adsorption kinetics and co-precipitation  
1291 mechanisms, *Journal of Water Process Engineering*, 38 (2020) 101666.
- 1292 [128] N. Geoffroy, G. Demopoulos, The elimination of selenium (IV) from aqueous  
1293 solution by precipitation with sodium sulfide, *Journal of hazardous materials*, 185  
1294 (2011) 148-154.
- 1295 [129] T.T.Y. Tan, C.K. Yip, D. Beydoun, R. Amal, Effects of nano-Ag particles loading  
1296 on TiO<sub>2</sub> photocatalytic reduction of selenate ions, *Chemical Engineering Journal*, 95  
1297 (2003) 179-186.
- 1298 [130] S. Sanuki, T. Kojima, K. Arai, S. Nagaoka, H. Majima, Photocatalytic reduction  
1299 of selenate and selenite solutions using TiO<sub>2</sub> powders, *Metallurgical and Materials*  
1300 *Transactions B-Process Metallurgy and Materials Processing Science*, 30 (1999) 15-20.
- 1301 [131] S. Sanuki, K. Arai, T. Kojima, S. Nagaoka, H. Majima, Photocatalytic reduction

1302 of selenate and selenite solutions using TiO<sub>2</sub> powders, *Metallurgical and Materials*  
1303 *Transactions B*, 30 (1999) 15-20.

1304 [132] X. Zhao, G. Zhang, Z. Zhang, TiO<sub>2</sub>-based catalysts for photocatalytic reduction  
1305 of aqueous oxyanions: State-of-the-art and future prospects, *Environment international*,  
1306 136 (2020) 105453.

1307 [133] V.N.H. Nguyen, R. Amal, D. Beydoun, Photocatalytic reduction of selenium ions  
1308 using different TiO<sub>2</sub> photocatalysts, *Chemical engineering science*, 60 (2005) 5759-  
1309 5769.

1310 [134] C.-H. Wu, S.-L. Lo, C.-F. Lin, C.-Y. Kuo, Modeling competitive adsorption of  
1311 molybdate, sulfate, and selenate on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by the triple-layer model, *Journal of*  
1312 *colloid and interface science*, 233 (2001) 259-264.

1313 [135] R.P. Rietra, T. Hiemstra, W.H. van Riemsdijk, Comparison of selenate and  
1314 sulfate adsorption on goethite, *Journal of colloid and interface science*, 240 (2001) 384-  
1315 390.

1316 [136] C.-H. Wu, S.-L. Lo, C.-F. Lin, Competitive adsorption of molybdate, chromate,  
1317 sulfate, selenate, and selenite on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, *Colloids and Surfaces A: Physicochemical*  
1318 *and Engineering Aspects*, 166 (2000) 251-259.

1319 [137] A.B. Holmes, D. Khan, D. de Oliveira Livera, F. Gu, Enhanced photocatalytic  
1320 selectivity of noble metallized TiO<sub>2</sub> nanoparticles for the reduction of selenate in water:  
1321 tunable Se reduction product H<sub>2</sub>Se (g) vs. Se (s), *Environmental Science: Nano*,  
1322 (2020).

1323 [138] T. Tan, D. Beydoun, R. Amal, Effects of organic hole scavengers on the  
1324 photocatalytic reduction of selenium anions, *Journal of Photochemistry and*  
1325 *Photobiology A: Chemistry*, 159 (2003) 273-280.

1326 [139] T.T. Tan, D. Beydoun, R. Amal, Photocatalytic reduction of Se (VI) in aqueous  
1327 solutions in UV/TiO<sub>2</sub> system: importance of optimum ratio of reactants on TiO<sub>2</sub>  
1328 surface, *Journal of Molecular Catalysis A: Chemical*, 202 (2003) 73-85.

1329 [140] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, K. Ikeue, M. Anpo,  
1330 Degradation of propanol diluted in water under visible light irradiation using metal ion-  
1331 implanted titanium dioxide photocatalysts, *Journal of Photochemistry and*

1332 Photobiology A: Chemistry, 148 (2002) 257-261.

1333 [141] L. Zhu, X. Kong, C. Yang, B. Ren, Q. Tang, Fabrication and characterization of  
1334 the magnetic separation photocatalyst C-TiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>/AC with enhanced  
1335 photocatalytic performance under visible light irradiation, Journal of hazardous  
1336 materials, 381 (2020) 120910.

1337 [142] I.H. Yoon, K.W. Kim, S. Bang, M.G. Kim, Reduction and adsorption  
1338 mechanisms of selenate by zero-valent iron and related iron corrosion, Applied  
1339 Catalysis B-Environmental, 104 (2011) 185-192.

1340 [143] A. Faisal, A. Sulaymon, Q. Khaliefa, A review of permeable reactive barrier as  
1341 passive sustainable technology for groundwater remediation, International Journal of  
1342 Environmental Science and Technology, 15 (2018) 1123-1138.

1343 [144] S.J. Morrison, D.R. Metzler, B.P. Dwyer, Removal of As, Mn, Mo, Se, U, V and  
1344 Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress  
1345 modeling, Journal of Contaminant Hydrology, 56 (2002) 99-116.

1346 [145] T.M. Statham, L.R. Mason, K.A. Mumford, G.W. Stevens, The specific reactive  
1347 surface area of granular zero-valent iron in metal contaminant removal: Column  
1348 experiments and modelling, Water research, 77 (2015) 24-34.

1349 [146] T. Zeng, E.R. Rene, S. Zhang, P.N. Lens, Removal of selenate and cadmium by  
1350 anaerobic granular sludge: EPS characterization and microbial community analysis,  
1351 Process Safety and Environmental Protection, 126 (2019) 150-159.

1352 [147] W.X. Zhang, Nanoscale iron particles for environmental remediation: An  
1353 overview, Journal of Nanoparticle Research, 5 (2003) 323-332.

1354 [148] Y. Furukawa, J.-w. Kim, J. Watkins, R.T. Wilkin, Formation of ferrihydrite and  
1355 associated iron corrosion products in permeable reactive barriers of zero-valent iron,  
1356 Environmental Science & Technology, 36 (2002) 5469-5475.

1357 [149] J.-M.R. Génin, G. Bourrié, F. Trolard, M. Abdelmoula, A. Jaffrezic, P. Refait, V.  
1358 Maitre, B. Humbert, A. Herbillon, Thermodynamic equilibria in aqueous suspensions  
1359 of synthetic and natural Fe (II)- Fe (III) green rusts: Occurrences of the mineral in  
1360 hydromorphic soils, Environmental Science & Technology, 32 (1998) 1058-1068.

1361 [150] D.H. Phillips, B. Gu, D.B. Watson, Y. Roh, Impact of sample preparation on

1362 mineralogical analysis of zero-valent iron reactive barrier materials, *Journal of*  
1363 *environmental quality*, 32 (2003) 1299-1305.

1364 [151] S. Bae, W. Lee, Inhibition of nZVI reactivity by magnetite during the reductive  
1365 degradation of 1, 1, 1-TCA in nZVI/magnetite suspension, *Applied Catalysis B:*  
1366 *Environmental*, 96 (2010) 10-17.

1367 [152] Y.H. Huang, T.C. Zhang, Effects of dissolved oxygen on formation of corrosion  
1368 products and concomitant oxygen and nitrate reduction in zero-valent iron systems with  
1369 or without aqueous Fe<sup>2+</sup>, *Water research*, 39 (2005) 1751-1760.

1370 [153] Y. Mu, F. Jia, Z. Ai, L. Zhang, Iron oxide shell mediated environmental  
1371 remediation properties of nano zero-valent iron, *Environmental Science: Nano*, 4 (2017)  
1372 27-45.

1373 [154] C. Shan, J. Chen, Z. Yang, H. Jia, X. Guan, W. Zhang, B. Pan, Enhanced removal  
1374 of Se (VI) from water via pre-corrosion of zero-valent iron using H<sub>2</sub>O<sub>2</sub>/HCl: Effect of  
1375 solution chemistry and mechanism investigation, *Water research*, 133 (2018) 173-181.

1376 [155] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-  
1377 valent iron metal, *Environmental Science & Technology*, 30 (1995) 153-160.

1378 [156] C. Geiger, N. Ruiz, C. Clausen, D. Reinhart, J. Quinn, Ultrasound pretreatment  
1379 of elemental iron: kinetic studies of dehalogenation reaction enhancement and surface  
1380 effects, *Water Research*, 36 (2002) 1342-1350.

1381 [157] Y.H. Liou, S.-L. Lo, C.-J. Lin, W.H. Kuan, S.C. Weng, Effects of iron surface  
1382 pretreatment on kinetics of aqueous nitrate reduction, *Journal of hazardous materials*,  
1383 126 (2005) 189-194.

1384 [158] S. Comba, A. Di Molfetta, R. Sethi, A comparison between field applications of  
1385 nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated  
1386 aquifers, *Water, Air, & Soil Pollution*, 215 (2011) 595-607.

1387 [159] N. Remya, J.-G. Lin, Current status of microwave application in wastewater  
1388 treatment—a review, *Chemical Engineering Journal*, 166 (2011) 797-813.

1389 [160] L.P. Liang, X.H. Guan, Y.Y. Huang, J.Y. Ma, X.P. Sun, J.L. Qiao, G.M. Zhou,  
1390 Efficient selenate removal by zero-valent iron in the presence of weak magnetic field,  
1391 *Separation and Purification Technology*, 156 (2015) 1064-1072.

1392 [161] N. Feng, H. Ghoveisi, G. Bitton, J.-C.J. Bonzongo, Removal of phyto-accessible  
1393 copper from contaminated soils using zero valent iron amendment and magnetic  
1394 separation methods: Assessment of residual toxicity using plant and MetPLATE™  
1395 studies, *Environmental Pollution*, 219 (2016) 9-18.

1396 [162] H. Ghoveisi, N. Feng, A. Boularbah, G. Bitton, J.-C.J. Bonzongo, Effect of aging  
1397 and wet-dry cycles on the elimination of the bioavailable fractions of Cu and Zn in  
1398 contaminated soils by zero valent iron and magnetic separation technique, *Journal of*  
1399 *Environmental Engineering*, 144 (2018) 04018068.

1400 [163] X. Guan, H. Yang, Y. Sun, J. Qiao, Enhanced immobilization of chromium (VI)  
1401 in soil using sulfidated zero-valent iron, *Chemosphere*, 228 (2019) 370-376.

1402 [164] M. Sillanpää, M. Shestakova, Chapter 2 - Electrochemical Water Treatment  
1403 Methods, in: M. Sillanpää, M. Shestakova (Eds.) *Electrochemical Water Treatment*  
1404 *Methods*, Butterworth-Heinemann, 2017, pp. 47-130.

1405 [165] S. Vasudevan, M.A. Oturan, Electrochemistry: as cause and cure in water  
1406 pollution—an overview, *Environmental chemistry letters*, 12 (2014) 97-108.

1407 [166] A. Ciblak, X. Mao, I. Padilla, D. Vesper, I. Alshwabkeh, A.N. Alshwabkeh,  
1408 Electrode effects on temporal changes in electrolyte pH and redox potential for water  
1409 treatment, *Journal of Environmental Science and Health, Part A*, 47 (2012) 718-726.

1410 [167] Y. Wang, Y. Xue, J. Su, S. Zheng, H. Lei, W. Cai, W. Jin, Efficient  
1411 electrochemical recovery of dilute selenium by cyclone electrowinning,  
1412 *Hydrometallurgy*, 179 (2018) 232-237.

1413 [168] Y. Wang, Y. Xue, C. Zhang, S. Mo, Y. Xue, Microstructural Refinement towards  
1414 the Electrochemical Co-Deposition Recovery of Copper and Selenium,  
1415 *ChemistrySelect*, 3 (2018) 11127-11133.

1416 [169] A.S. Koparal, Ü.B. Ögütveren, Removal of nitrate from water by electroreduction  
1417 and electrocoagulation, *Journal of hazardous materials*, 89 (2002) 83-94.

1418 [170] K. Baek, A. Ciblak, X. Mao, E.-J. Kim, A. Alshwabkeh, Iron anode mediated  
1419 transformation of selenate in sand columns, *Water research*, 47 (2013) 6538-6545.

1420 [171] A. Alekperov, Electrochemistry of selenium and tellurium, *Russian Chemical*  
1421 *Reviews*, 43 (1974) 235.

1422 [172] B. Maranowski, M. Strawski, W. Osowiecki, M. Szklarczyk, Study of selenium  
1423 electrodeposition at gold electrode by voltammetric and rotating disc electrode  
1424 techniques, *Journal of Electroanalytical Chemistry*, 752 (2015) 54-59.

1425 [173] S.-Y. Zhang, J. Zhang, Y. Liu, X. Ma, H.-Y. Chen, Electrochemical synthesis of  
1426 selenium nanotubes by using CTAB soft-template, *Electrochimica acta*, 50 (2005)  
1427 4365-4370.

1428 [174] S. Chaudhary, A. Umar, S. Mehta, Selenium nanomaterials: an overview of recent  
1429 developments in synthesis, properties and potential applications, *Progress in Materials*  
1430 *Science*, 83 (2016) 270-329.

1431 [175] S. Zou, M.S. Mauter, Direct Electrochemical Pathways for Selenium Reduction  
1432 in Aqueous Solutions, *ACS Sustainable Chemistry & Engineering*, 9 (2021) 2027-2036.

1433 [176] S. Zou, M.S. Mauter, Competing Ion Behavior in Direct Electrochemical Selenite  
1434 Reduction, *ACS ES&T Engineering*, (2021).

1435 [177] Y.V. Nancharaiyah, P. Lens, Ecology and biotechnology of selenium-respiring  
1436 bacteria, *Microbiology and Molecular Biology Reviews*, 79 (2015) 61-80.

1437 [178] A.V. Tugarova, A.A. Kamnev, Proteins in microbial synthesis of selenium  
1438 nanoparticles, *Talanta*, 174 (2017) 539-547.

1439 [179] A. Shrift, A selenium cycle in nature?, *Nature*, 201 (1964) 1304-1305.

1440 [180] R. McCready, J. Campbell, J. Payne, Selenite reduction by *Salmonella heidelberg*,  
1441 *Canadian journal of microbiology*, 12 (1966) 703-714.

1442 [181] J.F. Stolz, P. Basu, J.M. Santini, R.S. Oremland, Arsenic and selenium in  
1443 microbial metabolism, *Annu. Rev. Microbiol.*, 60 (2006) 107-130.

1444 [182] Y.V. Nancharaiyah, P. Lens, Ecology and biotechnology of selenium-respiring  
1445 bacteria, *Microbiol. Mol. Biol. Rev.*, 79 (2015) 61-80.

1446 [183] M. Fujita, M. Ike, S. Nishimoto, K. Takahashi, M. Kashiwa, Isolation and  
1447 characterization of a novel selenate-reducing bacterium, *Bacillus* sp. SF-1, *Journal of*  
1448 *Fermentation and Bioengineering*, 83 (1997) 517-522.

1449 [184] I. Schroder, S. Rech, T. Krafft, J.M. Macy, Purification and characterization of  
1450 the selenate reductase from *Thauera selenatis*, *Journal of Biological Chemistry*, 272  
1451 (1997) 23765-23768.



1452 [185] K.H. Williams, M.J. Wilkins, A.L. N'Guessan, B. Arey, E. Dodova, A.  
1453 Dohnalkova, D. Holmes, D.R. Lovley, P.E. Long, Field evidence of selenium  
1454 bioreduction in a uranium-contaminated aquifer, *Environmental microbiology reports*,  
1455 5 (2013) 444-452.

1456 [186] R.S. Oremland, J.T. Hollibaugh, A.S. Maest, T.S. Presser, L.G. Miller, C.W.  
1457 Culbertson, Selenate reduction to elemental selenium by anaerobic bacteria in  
1458 sediments and culture: biogeochemical significance of a novel, sulfate-independent  
1459 respiration, *Appl. Environ. Microbiol.*, 55 (1989) 2333-2343.

1460 [187] Y.Q. Tan, Y.T. Wang, Y. Wang, D. Xu, Y.T. Huang, D. Wang, G.J. Wang, C.  
1461 Rensing, S.X. Zheng, Novel mechanisms of selenate and selenite reduction in the  
1462 obligate aerobic bacterium *Comamonas testosteroni* S44, *Journal of Hazardous*  
1463 *Materials*, 359 (2018) 129-138.

1464 [188] M. Lenz, E.D. Van Hullebusch, G. Hommes, P.F.X. Corvini, P.N.L. Lens,  
1465 Selenate removal in methanogenic and sulfate-reducing upflow anaerobic sludge bed  
1466 reactors, *Water Research*, 42 (2008) 2184-2194.

1467 [189] N.A. Steinberg, J.S. Blum, L. Hochstein, R.S. Oremland, Nitrate is a preferred  
1468 electron acceptor for growth of freshwater selenate-respiring bacteria, *Appl. Environ.*  
1469 *Microbiol.*, 58 (1992) 426-428.

1470 [190] L.C. Tan, Y.V. Nancharaiyah, S. Lu, E. van Hullebusch, G. Gerlach, P.N. Lens,  
1471 Biological treatment of selenium-laden wastewater containing nitrate and sulfate in an  
1472 upflow anaerobic sludge bed reactor at pH 5.0, in: *Anaerobic Treatment of Mine*  
1473 *Wastewater for the Removal of Selenate and its Co-Contaminants*, CRC Press, 2018,  
1474 pp. 127-152.

1475 [191] S. Rech, J. Macy, The terminal reductases for selenate and nitrate respiration in  
1476 *Thauera selenatis* are two distinct enzymes, *Journal of bacteriology*, 174 (1992) 7316-  
1477 7320.

1478 [192] S. Soda, A. Hasegawa, M. Kuroda, A. Hanada, M. Yamashita, M. Ike, Selenium  
1479 recovery from kiln powder of cement manufacturing by chemical leaching and  
1480 bioreduction, *Water Science and Technology*, 72 (2015) 1294-1300.

1481 [193] M. Kuroda, E. Notaguchi, A. Sato, M. Yoshioka, A. Hasegawa, T. Kagami, T.

1482 Narita, M. Yamashita, K. Sei, S. Soda, Characterization of *Pseudomonas stutzeri* NT-I  
1483 capable of removing soluble selenium from the aqueous phase under aerobic conditions,  
1484 *Journal of bioscience and bioengineering*, 112 (2011) 259-264.

1485 [194] A. Sinharoy, P.N. Lens, Biological removal of selenate and selenite from  
1486 wastewater: options for selenium recovery as nanoparticles, *Current Pollution Reports*,  
1487 6 (2020) 230-249.

1488 [195] S.S. Veeravalli, S.R. Chaganti, J.A. Lalman, D.D. Heath, Fermentative H<sub>2</sub>  
1489 production using a switchgrass steam exploded liquor fed to mixed anaerobic cultures:  
1490 Effect of hydraulic retention time, linoleic acid and nitrogen sparging, *International*  
1491 *journal of hydrogen energy*, 39 (2014) 9994-10002.

1492 [196] Z. Wang, B. Zhang, Y. Jiang, Y. Li, C. He, Spontaneous thallium (I) oxidation  
1493 with electricity generation in single-chamber microbial fuel cells, *Applied Energy*, 209  
1494 (2018) 33-42.

1495 [197] J. Liu, J.C. Taylor, S.A. Baldwin, Removal of selenate from brine using anaerobic  
1496 bacteria and zero valent iron, *Journal of environmental management*, 222 (2018) 348-  
1497 358.

1498 [198] F.M. Mosallam, G.S. El-Sayyad, R.M. Fathy, A.I. El-Batal, Biomolecules-  
1499 mediated synthesis of selenium nanoparticles using *Aspergillus oryzae* fermented  
1500 Lupin extract and gamma radiation for hindering the growth of some multidrug-  
1501 resistant bacteria and pathogenic fungi, *Microbial pathogenesis*, 122 (2018) 108-116.

1502 [199] R. Jain, N. Jordan, S. Tsushima, R. Hübner, S. Weiss, P.N. Lens, Shape change  
1503 of biogenic elemental selenium nanomaterials from nanospheres to nanorods decreases  
1504 their colloidal stability, *Environmental Science: Nano*, 4 (2017) 1054-1063.

1505 [200] B.P. Rosen, Z. Liu, Transport pathways for arsenic and selenium: a minireview,  
1506 *Environment international*, 35 (2009) 512-515.

1507 [201] J.-B. Vincourt, D. Jullien, F. Amalric, J.-P. Girard, Molecular and functional  
1508 characterization of SLC26A11, a sodium-independent sulfate transporter from high  
1509 endothelial venules, *The FASEB journal*, 17 (2003) 1-21.

1510 [202] T. Wang, X. Lou, G. Zhang, Y. Dang, Improvement of selenium enrichment in  
1511 *Rhodotorula glutinis* X-20 through combining process optimization and selenium

1512 transport, *Bioengineered*, 10 (2019) 335-344.

1513 [203] R.J. Turner, J.H. Weiner, D.E. Taylor, Selenium metabolism in *Escherichia coli*,  
1514 *Biometals*, 11 (1998) 223-227.

1515 [204] R.A. LaRossa, Mutant selections linking physiology, inhibitors, and genotypes,  
1516 *Escherichia coli and Salmonella: cellular and molecular biology*, 2nd ed. American  
1517 Society for Microbiology, Washington, DC, (1996) 2527-2587.

1518 [205] J.J. Ojeda, M.L. Merroun, A.V. Tugarova, S. Lampis, A.A. Kamnev, P.H.  
1519 Gardiner, Developments in the study and applications of bacterial transformations of  
1520 selenium species, *Critical Reviews in Biotechnology*, 40 (2020) 1250-1264.

1521 [206] D. Wang, C. Rensing, S. Zheng, Microbial reduction and resistance to selenium:  
1522 mechanisms, applications and prospects, *Journal of Hazardous Materials*, (2021)  
1523 126684.

1524 [207] A. Abdelouas, W. Gong, W. Lutze, J. Shelnutt, R. Franco, I. Moura, Using  
1525 cytochrome c 3 to make selenium nanowires, *Chemistry of materials*, 12 (2000) 1510-  
1526 1512.

1527 [208] X. Gao, T. Gao, L. Zhang, Solution–solid growth of  $\alpha$ -monoclinic selenium  
1528 nanowires at room temperature, *Journal of Materials Chemistry*, 13 (2003) 6-8.

1529 [209] B. Zhang, X. Ye, W. Dai, W. Hou, F. Zuo, Y. Xie, Biomolecule-assisted synthesis  
1530 of single-crystalline selenium nanowires and nanoribbons via a novel flake-cracking  
1531 mechanism, *Nanotechnology*, 17 (2005) 385.

1532 [210] C.M. Debieux, E.J. Dridge, C.M. Mueller, P. Splatt, K. Paszkiewicz, I. Knight,  
1533 H. Florance, J. Love, R.W. Titball, R.J. Lewis, A bacterial process for selenium  
1534 nanosphere assembly, *Proceedings of the National Academy of Sciences*, 108 (2011)  
1535 13480-13485.

1536 [211] S. Lampis, E. Zonaro, C. Bertolini, D. Cecconi, F. Monti, M. Micaroni, R.J.  
1537 Turner, C.S. Butler, G. Vallini, Selenite biotransformation and detoxification by  
1538 *Stenotrophomonas maltophilia* SeITE02: novel clues on the route to bacterial  
1539 biogenesis of selenium nanoparticles, *Journal of hazardous materials*, 324 (2017) 3-14.

1540 [212] S. Lampis, E. Zonaro, C. Bertolini, P. Bernardi, C.S. Butler, G. Vallini, Delayed  
1541 formation of zero-valent selenium nanoparticles by *Bacillus mycoides* SeITE01 as a

1542 consequence of selenite reduction under aerobic conditions, *Microbial cell factories*, 13  
1543 (2014) 1-14.

1544 [213] J. Dobias, E.I. Suvorova, R. Bernier-Latmani, Role of proteins in controlling  
1545 selenium nanoparticle size, *Nanotechnology*, 22 (2011) 195605.

1546 [214] A.V. Tugarova, P.V. Mamchenkova, V.A. Khanadeev, A.A. Kamnev, Selenite  
1547 reduction by the rhizobacterium *Azospirillum brasilense*, synthesis of extracellular  
1548 selenium nanoparticles and their characterisation, *New biotechnology*, 58 (2020) 17-  
1549 24.

1550 [215] S. Yan, K.Y. Cheng, M.P. Ginige, G. Zheng, L. Zhou, A.H. Kaksonen, High-rate  
1551 microbial selenate reduction in an up-flow anaerobic fluidized bed reactor (FBR),  
1552 *Science of The Total Environment*, 749 (2020) 142359.

1553 [216] L. Li, B. Zhang, C. He, H. Zhang, Hydrodynamics-and hydrochemistry-affected  
1554 microbial selenate reduction in aquifer: Performance and mechanisms, *Science of The*  
1555 *Total Environment*, 768 (2021) 145331.

1556 [217] B. Song, Z. Tian, R. van der Weijden, C. Buisman, J. Weijma, High-rate  
1557 biological selenate reduction in a sequencing batch reactor for recovery of hexagonal  
1558 selenium, *Water Research*, 193 (2021) 116855.

1559 [218] Z. Zhang, Y. Xiong, H. Chen, Y. Tang, Understanding the composition and  
1560 spatial distribution of biological selenate reduction products for potential selenium  
1561 recovery, *Environmental Science: Water Research & Technology*, 6 (2020) 2153-2163.

1562 [219] O. Otsuka, Y. Yanaba, T. Yoshikawa, M. Yamashita, Fundamental Studies on  
1563 Oxidizing Roasting of the “Bioselenium”, *Materials Transactions*, 57 (2016) 1183-  
1564 1191.

1565 [220] Z.M. Zhang, G. Chen, Y.N. Tang, Towards selenium recovery: Biocathode  
1566 induced selenate reduction to extracellular elemental selenium nanoparticles, *Chemical*  
1567 *Engineering Journal*, 351 (2018) 1095-1103.

1568 [221] P. Sonkusre, R. Nanduri, P. Gupta, S.S. Cameotra, Improved extraction of  
1569 intracellular biogenic selenium nanoparticles and their specificity for cancer  
1570 chemoprevention, *Journal of Nanomedicine & Nanotechnology*, 5 (2014) 1.

1571 [222] T. Kagami, T. Narita, M. Kuroda, E. Notaguchi, M. Yamashita, K. Sei, S. Soda,

1572 M. Ike, Effective selenium volatilization under aerobic conditions and recovery from  
1573 the aqueous phase by *Pseudomonas stutzeri* NT-I, *Water research*, 47 (2013) 1361-1368.  
1574 [223] W. Zhang, Z. Chen, H. Liu, L. Zhang, P. Gao, D. Li, Biosynthesis and structural  
1575 characteristics of selenium nanoparticles by *Pseudomonas alcaliphila*, *Colloids and*  
1576 *Surfaces B: Biointerfaces*, 88 (2011) 196-201.  
1577 [224] S. Fischer, T. Krause, F. Lederer, M.L. Merroun, A. Shevchenko, R. Hübner, T.  
1578 Firkala, T. Stumpf, N. Jordan, R. Jain, *Bacillus safensis* JG-B5T affects the fate of  
1579 selenium by extracellular production of colloiddally less stable selenium nanoparticles,  
1580 *Journal of hazardous materials*, 384 (2020) 121146.  
1581 [225] B. Zare, S. Babaie, N. Setayesh, A.R. Shahverdi, Isolation and characterization  
1582 of a fungus for extracellular synthesis of small selenium nanoparticles, *Nanomedicine*  
1583 *Journal*, 1 (2013) 13-19.  
1584 [226] L.C. Staicu, E.D. Van Hullebusch, P.N. Lens, E.A. Pilon-Smits, M.A. Oturan,  
1585 Electrocoagulation of colloidal biogenic selenium, *Environmental Science and*  
1586 *Pollution Research*, 22 (2015) 3127-3137.  
1587 [227] L.C. Staicu, E.D. van Hullebusch, M.A. Oturan, C.J. Ackerson, P.N. Lens,  
1588 Removal of colloidal biogenic selenium from wastewater, *Chemosphere*, 125 (2015)  
1589 130-138.  
1590 [228] C.T. Ho, J.W. Kim, W.B. Kim, K. Song, R.A. Kanaly, M.J. Sadowsky, H.-G. Hur,  
1591 *Shewanella*-mediated synthesis of selenium nanowires and nanoribbons, *Journal of*  
1592 *Materials Chemistry*, 20 (2010) 5899-5905.  
1593 [229] A. Sinharoy, S. Saikia, K. Pakshirajan, Biological removal of selenite from  
1594 wastewater and recovery as selenium nanoparticles using inverse fluidized bed  
1595 bioreactor, *Journal of Water Process Engineering*, 32 (2019) 100988.  
1596 [230] Z.M. Zhang, I. Adedeji, G. Chen, Y.N. Tang, Chemical-Free Recovery of  
1597 Elemental Selenium from Selenate-Contaminated Water by a System Combining a  
1598 Biological Reactor, a Bacterium-Nanoparticle Separator, and a Tangential Flow Filter,  
1599 *Environmental Science & Technology*, 52 (2018) 13231-13238.  
1600 [231] G. Zha, B. Yang, H. Luo, D. Huang, W. Jiang, B. Xu, D. Liu, Innovative green  
1601 approach for the selective extraction of high-purity selenium from hazardous selenium

1602 sludge, *Separation and Purification Technology*, 266 (2021) 118536.

1603 [232] J. Hait, R. Jana, V. Kumar, S. Sanyal, Some studies on sulfuric acid leaching of  
1604 anode slime with additives, *Industrial & engineering chemistry research*, 41 (2002)  
1605 6593-6599.

1606 [233] O. Hyvärinen, L. Lindroos, E. Yllö, Recovering selenium from copper refinery  
1607 slimes, *JOM*, 41 (1989) 42-43.

1608 [234] D.-k. Lu, Y.-f. Chang, H.-y. Yang, X. Feng, Sequential removal of selenium and  
1609 tellurium from copper anode slime with high nickel content, *Transactions of*  
1610 *Nonferrous Metals Society of China*, 25 (2015) 1307-1314.

1611 [235] M. Khanlarian, F. Rashchi, M. Saba, A modified sulfation-roasting-leaching  
1612 process for recovering Se, Cu, and Ag from copper anode slimes at a lower temperature,  
1613 *Journal of environmental management*, 235 (2019) 303-309.

1614 [236] P.M. Haygarth, Global importance and global cycling of selenium, *Selenium in*  
1615 *the Environment*, 1 (1994) 1-27.

1616 [237] M. Al Kuisi, A. Abdel-Fattah, Groundwater vulnerability to selenium in semi-  
1617 arid environments: Amman Zarqa Basin, Jordan, *Environmental geochemistry and*  
1618 *health*, 32 (2010) 107-128.

1619 [238] M. Bajaj, E. Eiche, T. Neumann, J. Winter, C. Gallert, Hazardous concentrations  
1620 of selenium in soil and groundwater in North-West India, *Journal of Hazardous*  
1621 *Materials*, 189 (2011) 640-646.

1622 [239] G. Zelmanov, R. Semiat, Selenium removal from water and its recovery using  
1623 iron (Fe<sup>3+</sup>) oxide/hydroxide-based nanoparticles sol (NanoFe) as an adsorbent,  
1624 *Separation and Purification Technology*, 103 (2013) 167-172.

1625 [240] L.E. McDonald, M.M. Strosher, Selenium mobilization from surface coal mining  
1626 in the Elk River Basin, British Columbia: a survey of water, sediment and biota, (1998).

1627 [241] A.R. Kumar, P. Riyazuddin, Speciation of selenium in groundwater: Seasonal  
1628 variations and redox transformations, *Journal of hazardous materials*, 192 (2011) 263-  
1629 269.

1630 [242] H. Zhang, C. Guo, H. Feng, Y. Shen, Y. Wang, T. Zeng, S. Song, Total mercury,  
1631 methylmercury, and selenium in aquatic products from coastal cities of China:

1632 Distribution characteristics and risk assessment, *Science of The Total Environment*,  
1633 (2020) 140034.

1634 [243] S. Soda, M. Kashiwa, T. Kagami, M. Kuroda, M. Yamashita, M. Ike, Laboratory-  
1635 scale bioreactors for soluble selenium removal from selenium refinery wastewater  
1636 using anaerobic sludge, *Desalination*, 279 (2011) 433-438.

1637 [244] S. Lawson, J. Macy, Bioremediation of selenite in oil refinery wastewater,  
1638 *Applied Microbiology and Biotechnology*, 43 (1995) 762-765.

1639 [245] S. Contreras-B, M.L. Lozano-V, Water, endangered fishes, and development  
1640 perspectives in arid lands of Mexico, *Conservation Biology*, 8 (1994) 379-387.

1641 [246] A. Lemly, Hazard of selenium to fish and migratory birds at Ouray National  
1642 Wildlife Refuge, Utah, Blacksburg, VA. US Forest Service, Southern, (1995).

1643 [247] A. Lemly, Preliminary assessment of selenium hazards on Caribou National  
1644 Forest, Idaho. Blacksburg, VA. US Forest Service, Southern Research Station,  
1645 Coldwater Fisheries Research Unit, Department of Fisheries and Wildlife Sciences,  
1646 Virginia Tech University, in, Technical Report, 1999.

1647 [248] A. Tugarova, E. Vetchinkina, E. Loshchinina, A. Shchelochkov, V. Nikitina, A.  
1648 Kamnev, The ability of the rhizobacterium *Azospirillum brasilense* to reduce selenium  
1649 (IV) to selenium (0), *Microbiology*, 82 (2013) 352-355.

1650 [249] M. Ikram, M. Faisal, Comparative assessment of selenite (SeIV) detoxification  
1651 to elemental selenium (Se0) by *Bacillus* sp, *Biotechnol. Lett.*, 32 (2010) 1255-1259.

1652 [250] Y. Yuan, J. Zhu, C. Liu, S. Yu, L. Lei, Biomineralization of Se nanosphere by  
1653 *Bacillus licheniformis*, *Journal of Earth Science*, 26 (2015) 246-250.

1654 [251] N.S. Khoei, S. Lampis, E. Zonaro, K. Yrjälä, P. Bernardi, G. Vallini, Insights into  
1655 selenite reduction and biogenesis of elemental selenium nanoparticles by two  
1656 environmental isolates of *Burkholderia fungorum*, *New biotechnology*, 34 (2017) 1-11.

1657 [252] J. Theisen, N. Yee, The molecular basis for selenate reduction in *Citrobacter*  
1658 *freundii*, *Geomicrobiology Journal*, 31 (2014) 875-883.

1659 [253] F.A. Tomei, L.L. Barton, C.L. Lemanski, T.G. Zocco, N.H. Fink, L.O. Sillerud,  
1660 Transformation of selenate and selenite to elemental selenium by *Desulfovibrio*  
1661 *desulfuricans*, *Journal of Industrial Microbiology*, 14 (1995) 329-336.

1662 [254] C.A. Watts, H. Ridley, K.L. Condie, J.T. Leaver, D.J. Richardson, C.S. Butler,  
1663 Selenate reduction by *Enterobacter cloacae* SLD1a-1 is catalysed by a molybdenum-  
1664 dependent membrane-bound enzyme that is distinct from the membrane-bound nitrate  
1665 reductase, *FEMS microbiology letters*, 228 (2003) 273-279.

1666 [255] J. Fellowes, Reductive biosynthesis of elemental selenium and tellurium  
1667 nanoparticles by *Geobacter sulfurreducens*, *The Bacterial Biogenic Synthesis of*  
1668 *Magnetic, Catalytic and Semiconducting Nanomaterials*, (2018) 174.

1669 [256] X. Xu, W. Cheng, X. Liu, H. You, G. Wu, K. Ding, X. Tu, L. Yang, Y. Wang, Y.  
1670 Li, Selenate reduction and selenium enrichment of tea by the endophytic  
1671 *Herbaspirillum* sp. strain WT00C, *Current microbiology*, (2019) 1-14.

1672 [257] J. Macy, S. Lawson, Cell yield (Y M) of *Thauera selenatis* grown anaerobically  
1673 with acetate plus selenate or nitrate, *Archives of microbiology*, 160 (1993) 295-298.

1674 [258] J. Zhang, Y. Wang, Z. Shao, J. Li, S. Zan, S. Zhou, R. Yang, Two selenium  
1675 tolerant *Lysinibacillus* sp. strains are capable of reducing selenite to elemental Se  
1676 efficiently under aerobic conditions, *Journal of Environmental Sciences*, 77 (2019) 238-  
1677 249.

1678 [259] G. Subedi, J. Taylor, I. Hatam, S.A. Baldwin, Simultaneous selenate reduction  
1679 and denitrification by a consortium of enriched mine site bacteria, *Chemosphere*, 183  
1680 (2017) 536-545.

1681 [260] M. Ike, K. Takahashi, T. Fujita, M. Kashiwa, M. Fujita, Selenate reduction by  
1682 bacteria isolated from aquatic environment free from selenium contamination, *Water*  
1683 *Research*, 34 (2000) 3019-3025.

1684 [261] R. Huber, M. Sacher, A. Vollmann, H. Huber, D. Rose, Respiration of arsenate  
1685 and selenate by hyperthermophilic archaea, *Systematic and applied microbiology*, 23  
1686 (2000) 305-314.

1687 [262] M. Roux, G. Sarret, I. Pignot-Paintrand, M. Fontecave, J. Coves, Mobilization of  
1688 selenite by *Ralstonia metallidurans* CH34, *Appl. Environ. Microbiol.*, 67 (2001) 769-  
1689 773.

1690 [263] W.J. Hunter, L.D. Kuykendall, Reduction of selenite to elemental red selenium  
1691 by *Rhizobium* sp. strain B1, *Current microbiology*, 55 (2007) 344-349.



1692 [264] R.S. Dungan, S.R. Yates, W.T. Frankenberger Jr, Transformations of selenate  
1693 and selenite by *Stenotrophomonas maltophilia* isolated from a seleniferous agricultural  
1694 drainage pond sediment, *Environmental Microbiology*, 5 (2003) 287-295.

1695 [265] S. Dhanjal, S.S. Cameotra, Aerobic biogenesis of selenium nanospheres by  
1696 *Bacillus cereus* isolated from coalmine soil, *Microbial cell factories*, 9 (2010) 52.

1697 [266] P. Narasingarao, M.M. Häggblom, *Sedimenticola selenatireducens*, gen. nov., sp.  
1698 nov., an anaerobic selenate-respiring bacterium isolated from estuarine sediment,  
1699 *Systematic and applied microbiology*, 29 (2006) 382-388.

1700 [267] W.J. Hunter, D.K. Manter, Bio-reduction of selenite to elemental red selenium  
1701 by *Tetrathio bacter kashmirensis*, *Current microbiology*, 57 (2008) 83-88.

1702 [268] Y. Zhang, M. Kuroda, S. Arai, F. Kato, D. Inoue, M. Ike, Biological removal of  
1703 selenate in saline wastewater by activated sludge under alternating anoxic/oxic  
1704 conditions, *Frontiers of Environmental Science & Engineering*, 13 (2019) 68.

1705 [269] C.-Y. Lai, X. Yang, Y. Tang, B.E. Rittmann, H.-P. Zhao, Nitrate shaped the  
1706 selenate-reducing microbial community in a hydrogen-based biofilm reactor,  
1707 *Environmental science & technology*, 48 (2014) 3395-3402.

1708 [270] T. Eregowda, E.R. Rene, P.N. Lens, Bioreduction of selenate in an anaerobic  
1709 biotrickling filter using methanol as electron donor, *Chemosphere*, 225 (2019) 406-413.

1710 [271] Z. Zhang, G. Chen, Y. Tang, Towards selenium recovery: Biocathode induced  
1711 selenate reduction to extracellular elemental selenium nanoparticles, *Chemical  
1712 Engineering Journal*, 351 (2018) 1095-1103.

1713 [272] N. Srivastava, M. Mukhopadhyay, Biosynthesis and structural characterization  
1714 of selenium nanoparticles using *Gliocladium roseum*, *Journal of Cluster Science*, 26  
1715 (2015) 1473-1482.

1716 [273] E. Vetchinkina, E. Loshchinina, V. Kursky, V. Nikitina, Reduction of organic  
1717 and inorganic selenium compounds by the edible medicinal basidiomycete *Lentinula  
1718 edodes* and the accumulation of elemental selenium nanoparticles in its mycelium,  
1719 *Journal of Microbiology*, 51 (2013) 829-835.

1720 [274] H. Zhang, H. Zhou, J. Bai, Y. Li, J. Yang, Q. Ma, Y. Qu, Biosynthesis of selenium  
1721 nanoparticles mediated by fungus *Mariannaea* sp. HJ and their characterization,

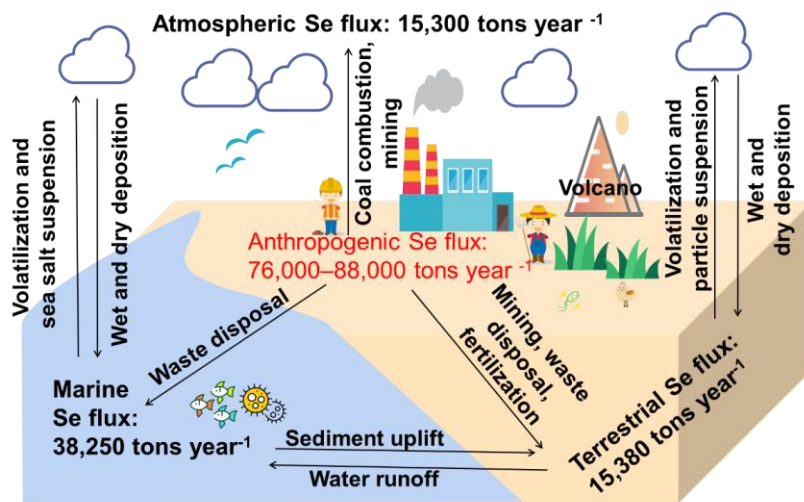
1722 Colloids and Surfaces A: Physicochemical and Engineering Aspects, 571 (2019) 9-16.  
1723 [275] T. Wang, L. Yang, B. Zhang, J. Liu, Extracellular biosynthesis and  
1724 transformation of selenium nanoparticles and application in H<sub>2</sub>O<sub>2</sub> biosensor, Colloids  
1725 and Surfaces B: Biointerfaces, 80 (2010) 94-102.  
1726 [276] Y. Cheng, X. Xiao, X. Li, D. Song, Z. Lu, F. Wang, Y. Wang, Characterization,  
1727 antioxidant property and cytoprotection of exopolysaccharide-capped elemental  
1728 selenium particles synthesized by *Bacillus paralicheniformis* SR14, Carbohydrate  
1729 polymers, 178 (2017) 18-26.  
1730 [277] S. Shoeibi, M. Mashreghi, Biosynthesis of selenium nanoparticles using  
1731 *Enterococcus faecalis* and evaluation of their antibacterial activities, Journal of Trace  
1732 Elements in Medicine and Biology, 39 (2017) 135-139.  
1733 [278] A. Presentato, E. Piacenza, M. Anikovskiy, M. Cappelletti, D. Zannoni, R.J.  
1734 Turner, Biosynthesis of selenium-nanoparticles and-nanorods as a product of selenite  
1735 bioconversion by the aerobic bacterium *Rhodococcus aetherivorans* BCP1, New  
1736 biotechnology, 41 (2018) 1-8.  
1737 [279] M.A. Ruiz-Fresneda, A.S. Eswayah, M. Romero-González, P.H. Gardiner, P.L.  
1738 Solari, M.L. Merroun, Chemical and structural characterization of Se IV  
1739 biotransformations by *Stenotrophomonas bentonitica* into Se<sup>0</sup> nanostructures and  
1740 volatile Se species, Environmental Science: Nano, 7 (2020) 2140-2155.  
1741 [280] Y.-H. Cui, L.-L. Li, N.-Q. Zhou, J.-H. Liu, Q. Huang, H.-J. Wang, J. Tian, H.-Q.  
1742 Yu, In vivo synthesis of nano-selenium by *Tetrahymena thermophila* SB210, Enzyme  
1743 and Microbial Technology, 95 (2016) 185-191.  
1744 [281] N. Srivastava, M. Mukhopadhyay, Biosynthesis and structural characterization  
1745 of selenium nanoparticles mediated by *Zooglea ramigera*, Powder technology, 244  
1746 (2013) 26-29.  
1747 [282] M. Rovira, J. Giménez, M. Martínez, X. Martínez-Lladó, J. de Pablo, V. Martí,  
1748 L. Duro, Sorption of selenium (IV) and selenium (VI) onto natural iron oxides: goethite  
1749 and hematite, Journal of hazardous materials, 150 (2008) 279-284.  
1750 [283] Z. Ma, C. Shan, J. Liang, M. Tong, Efficient adsorption of Selenium (IV) from  
1751 water by hematite modified magnetic nanoparticles, Chemosphere, 193 (2018) 134-141.

1752 [284] M. Martínez, J. Giménez, J. De Pablo, M. Rovira, L. Duro, Sorption of selenium  
1753 (IV) and selenium (VI) onto magnetite, *Applied Surface Science*, 252 (2006) 3767-  
1754 3773.

1755 [285] Z. Lu, J. Yu, H. Zeng, Q. Liu, Polyamine-modified magnetic graphene oxide  
1756 nanocomposite for enhanced selenium removal, *Separation and Purification*  
1757 *Technology*, 183 (2017) 249-257.

1758 [286] W. Cui, P. Li, Z. Wang, S. Zheng, Y. Zhang, Adsorption study of selenium ions  
1759 from aqueous solutions using MgO nanosheets synthesized by ultrasonic method,  
1760 *Journal of Hazardous Materials*, 341 (2018) 268-276.

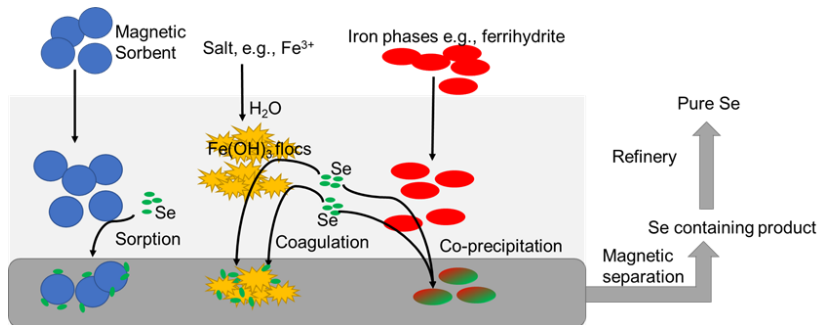
1761 [287] Y.N. Larimi, M.H. Mallah, M.A. Moosavian, J. Safdari, Fabrication of a  
1762 magmolecule using nanoparticle and evaluation of its adsorption capacity for selenium  
1763 ions from nuclear wastewater, *Journal of Radioanalytical and Nuclear Chemistry*, 298  
1764 (2013) 1511-1518.  
1765



1766

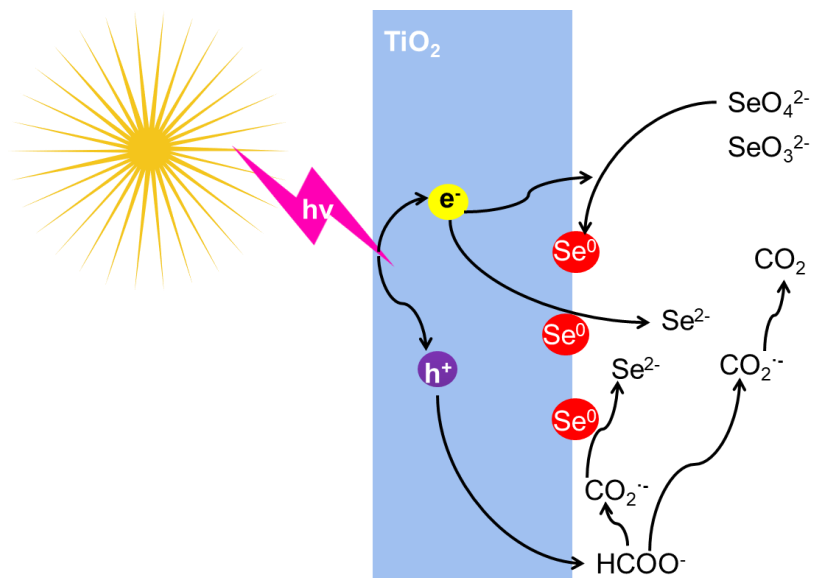
1767 **Fig. 1.** Global Se flux and cycling in the ecosystem (data from [30, 236]).

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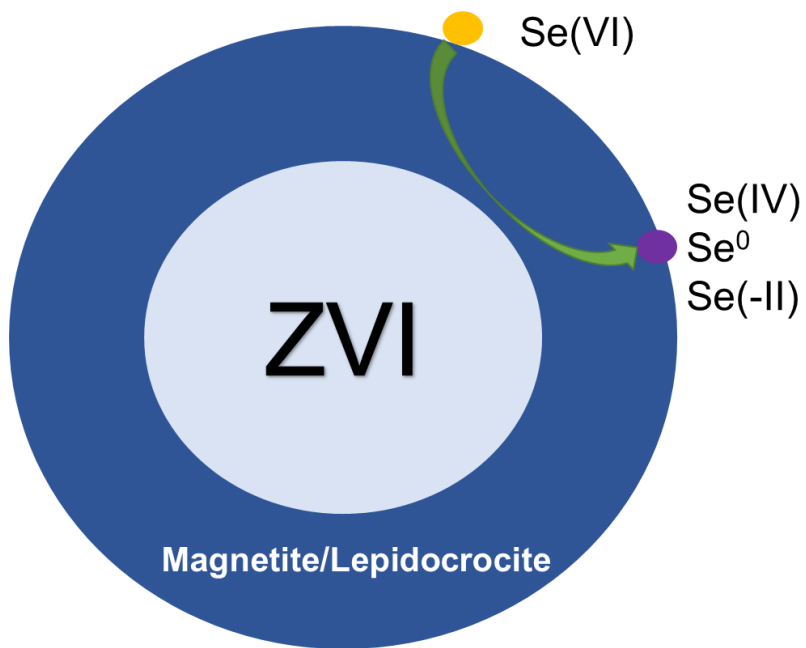
1771 **Fig. 2.** Se removal and recovery by sorption, coagulation and co-precipitation  
1772 followed by magnetic separation and product refining (mechanisms are from [86, 111,  
1773 113]).



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1775 **Fig. 3.** Photocatalytic reduction process of  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  to solid  $\text{Se}(0)$  and  
 1776 gaseous  $\text{Se}(-\text{II})$  by  $\text{TiO}_2$  in the presence of formic acid (mechanism is from [136]).

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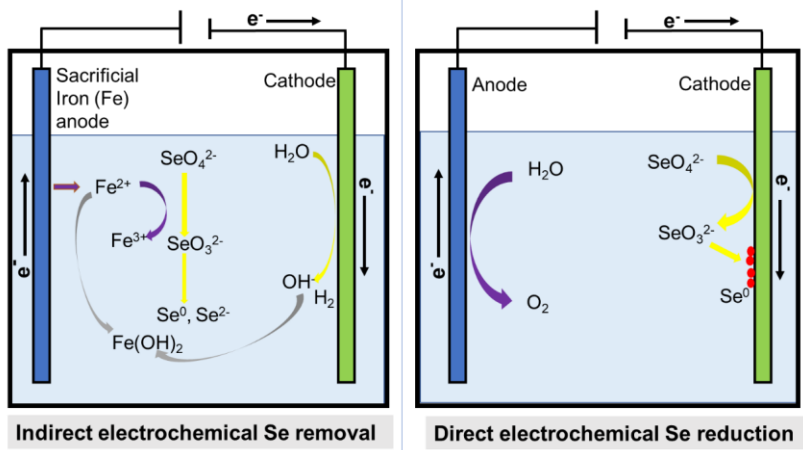


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1779 **Fig. 4.** Reduction and adsorption of selenate by zero-valent iron (ZVI) (mechanisms  
1780 are from [142]).

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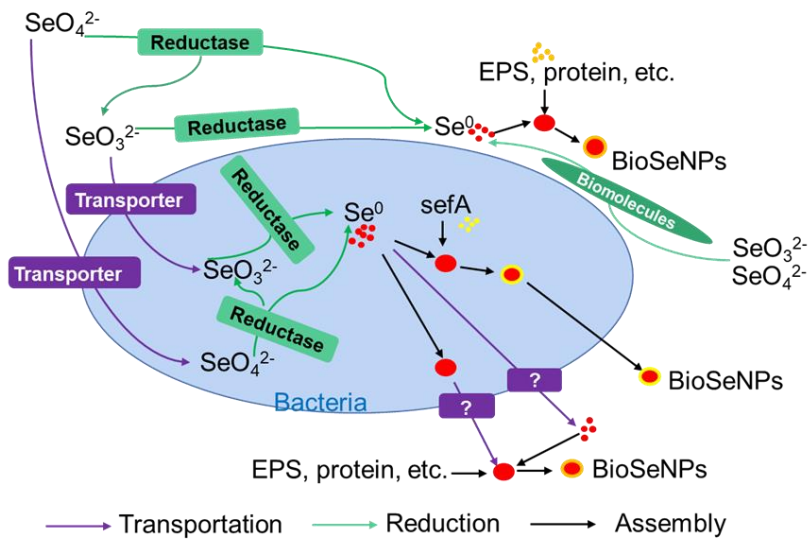


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1784 **Fig. 5.** Comparison of indirect and direct electrochemical Se removal (mechanisms are  
 1785 from [117] and [175]).

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**Fig. 6.** Schematic model for representative  $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  reduction by bacteria (summarized and adapted from [182, 205, 206]).

**Table 1.** Se concentration in contaminated location and cases for contaminated wildlife (adapted and updated from [25])

<b>Contamination</b>	<b>Se source</b>	<b>Se concentration</b>	<b>Major aquatic life contaminated</b>	<b>Ref.</b>
Amman Zarqa Basin (AZB), Jordan	Lower aquifer	1.6–30 $\mu\text{g L}^{-1}$		[237]
	Middle aquifer	1.5–742 $\mu\text{g L}^{-1}$		
	Upper aquifer	0.4–246 $\mu\text{g L}^{-1}$		
Barwa, Jainpur	Groundwater	341 $\mu\text{g L}^{-1}$		[238]
California's San Joaquin Vally	Drainage water of soils	75–1400 $\mu\text{g L}^{-1}$		[239]
Canada	Coal mining waste		Stream fish	[240]
Chandigarh, India	Groundwater	0.9 $\mu\text{g L}^{-1}$		[238]
	Groundwater	0.15–0.43 $\mu\text{g L}^{-1}$ [Se(IV)]		[241]
		0.16–4.73 $\mu\text{g L}^{-1}$ [Se(IV)]		
China	Seleniferous soils	up to 59 $\text{mg kg}^{-1}$		[238]
			Shellfish, muscles, etc.	[242]
Hisar	Groundwater	3.2 $\mu\text{g L}^{-1}$		[238]

Ireland	Seleniferous soils	up to 1200 mg kg <sup>-1</sup>		[238]
Japan	Industrial wastewater	≤ 0.1 mg L <sup>-1</sup>		[243]
	Kiln powder leachate from a cement-manufacturing plant	2–42 mg L <sup>-1</sup>		[192]
	Se refinery wastewater	13.2–74.0 mg L <sup>-1</sup>		[244]
Mexico	Irrigation drainage		Stream and river fish	[245]
	Discharge mine and process waters of the uranium mine	1.6 mg L <sup>-1</sup>		[224]
India	Groundwater	669.5 mg L <sup>-1</sup>		[238]
	Plants	3–670 mg kg <sup>-1</sup>		[238]
	Soil	6.5 mg kg <sup>-1</sup>		[238]
USA	Coal combustion waste	-	Reservoir fish	[46]
	Irrigation drainage	-	Fish, aquatic birds	[246]
	Phosphate mining waste	-	Fish, aquatic birds	[247]
	Seleniferous soils	up to 28 mg kg <sup>-1</sup>		[238]

**Table 2.** Identified microorganisms with the ability of Se oxyanion reduction.

<b>Organism</b>	<b>Origin</b>	<b>Growing condition</b>	<b>Se(0) formation location</b>	<b>Electron acceptor</b>	<b>Ref.</b>
<i>Azospirillum brasilense</i>	Culture collection of the Institute of Biochemistry and Physiology of Plants and Microorganisms	Aerobic	Intracellular	SeO <sub>3</sub> <sup>2-</sup>	[248]
<i>Bacillus cereus</i>	Inverse fluidised bed bioreactor	Anaerobic	Extracellular and intracellular	SeO <sub>3</sub> <sup>2-</sup>	[229]
<i>Bacillus licheniformis</i>	Contaminated soil and water	Anaerobic	Extracellular and intracellular	SeO <sub>3</sub> <sup>2-</sup>	[249, 250]
<i>Burkholderia fungorum</i>	Oil refinery drainage	Anaerobic	Intracellular	SeO <sub>3</sub> <sup>2-</sup>	[251]
<i>Citrobacter freundii</i>	Marine and freshwater settings	Anaerobic	Intracellular	SeO <sub>4</sub> <sup>2-</sup>	[252]
<i>Desulfovibrio desulfuricans</i>	German Culture Collection in Braunschweig,		Intracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[253]
<i>Enterobacter Cloacae</i>		Aerobic and Anaerobic	Extracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[254]
<i>Geobacter sulfurreducens</i>			Extracellular	SeO <sub>3</sub> <sup>2-</sup>	[255]
<i>Herbaspirillum</i>	Ornamental tea plant	Aerobic	Extracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[256]
<i>Thauera selenatis</i>			Extracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[257]
<i>Lysinibacillus macrolides</i> ,	Naturally occurred Se-rich soil	Aerobic	Extracellular and intracellular	SeO <sub>3</sub> <sup>2-</sup>	[258]
<i>Lysinibacillus xylanilyticus</i>	Naturally occurred Se-rich soil	Aerobic	Extracellular and intracellular	SeO <sub>3</sub> <sup>2-</sup>	[258]
<i>Pseudomonas</i>	Mine impacted natural marsh sediment			SeO <sub>4</sub> <sup>2-</sup>	[259]
<i>Pseudomonas stutzeri</i>		Aerobic		SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[260]
<i>Pseudomonas fluorescens</i>		Aerobic		SeO <sub>3</sub> <sup>2-</sup>	[260]

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<i>Pyrobaculum arsenaticum</i>	Hot spring at Pisciarelli Solfatara, Naples, Italy	Anaerobic		SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[261]
<i>Ralstonia metallidurans</i>	Metal-contaminated biotopes	Aerobic	Extracellular and intracellular	SeO <sub>3</sub> <sup>2-</sup>	[262]
<i>Rhizobium</i>	A laboratory bioreactor	Aerobic		SeO <sub>3</sub> <sup>2-</sup>	[263]
<i>Salmonella Heidelberg</i>	Alberta Provincial Laboratory of Public Health		Intracellular	SeO <sub>3</sub> <sup>2-</sup>	[180]
<i>Stenotrophomonas maltophilia</i>	Seleniferous agricultural drainage pond sediment	Aerobic	Extracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[264]
<i>Shewanella oneidensis</i>	Uranium mining waste pile	Aerobic	Extracellular	SeO <sub>3</sub> <sup>2-</sup>	[224]
<i>Shewanella putrefaciens</i>	Coalmine soil	Aerobic	Extracellular	SeO <sub>3</sub> <sup>2-</sup>	[265]
<i>Sedimenticola selenatireducens</i>	Estuarine sediment	Anaerobic		SeO <sub>4</sub> <sup>2-</sup>	[266]
<i>Stenotrophomonas maltophilia</i>	<i>Astragalus bisulcatus</i> grown in a seleniferous soil (Se hyperaccumulator plant)		Extracellular	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup>	[211]
<i>Tetrathiobacter kashmirensis</i>	Soil	Aerobic		SeO <sub>3</sub> <sup>2-</sup>	[267]
<i>Thauera selenatis</i>		Anaerobic	Extracellular	SeO <sub>4</sub> <sup>2-</sup>	[191]

**Table 3.** Se oxyanion reduction in various bioreactors.

Bioreactor	Inoculum	Se containing water	Electron donor	Dissolved oxygen	Initial pH	Temperature (°C)	HR T	Electron acceptor	Dominant bacteria	Reduction efficiency	Ref.
Sequencing batch reactor	Activated sludge	Synthetic wastewater with 3% salinity	44 mM sodium lactate	Alternating anoxic/oxic conditions	7.0–7.1	-	3.75 d	395 mg L <sup>-1</sup> Se(VI)	<i>Alcaligenes aquatilis</i> ; <i>Peptoclostridium</i> ; <i>Soehngenia</i> <i>Saccharolytica</i> ; <i>Marinobacterium halophilum</i>	97%	[268]
Batch bottle	Anaerobic granular sludge	Synthetic wastewater	20 mM Sodium lactate	Anaerobic conditions	7.5	30	7 d	10 mg L <sup>-1</sup> Se(VI)	<i>Methanobacterium</i> ; <i>Bacteroidetes</i> ; <i>Methanosaeta</i> ; <i>Anaerolinea</i> ; <i>Syntrophobacter</i>	98%	[146]
Biofilm reactor	Activated sludge	Synthetic mineral medium	2.5 psig (gauge pressure or 1.17 atm) H <sub>2</sub>	7.7 -8.0 mg L <sup>-1</sup> O <sub>2</sub>	7.0 ± 0.2	-	130 min	1 mg L <sup>-1</sup> Se(VI); NO <sub>3</sub> <sup>-</sup>	<i>Hydrogenophaga</i> ; <i>Dechloromonas</i> ; <i>Methyloversatilis</i>	60%	[269]

Biorickling filter	Activated sludge	Synthetic mineral medium	Methanol	Anaerobic conditions	7.5 ±0.1	Room temperature	18.4 min	29 mg L <sup>-1</sup> Se(VI)	-	90%	[270]
Two-chamber bioelectrochemical reactors	Activated sludge	Synthetic mineral medium	10 mg C L <sup>-1</sup> of sodium acetate	Anaerobic conditions	7.0 ±0.1	-	1.45 days	5 mg L <sup>-1</sup> Se(VI)	-	99.6%	[271]

**Table 4.** Cases for microorganisms successfully applied in nano-Se synthesis.

Microorganisms	Se Source	Operating condition	Medium	Reaction time	Observed BioSeNPs deposit location	BioSeNPs morphology description	Ref.
<b>Fungi</b>							
<i>Aspergillus terreus</i>	80 mg L <sup>-1</sup> Se(IV)	Aerobic and anaerobic; 30 °C;	Culture supernatant	1 h	Extracellular	Spherical particles with average size of 47 nm.	[225]
<i>Gliocladium roseum</i>	118.5 mg L <sup>-1</sup> Se(VI)	Aerobic; 30 °C;	Sterilized potato dextrose broth	24 h	Extracellular	Around 20–80 nm with some large particles of more than 100 nm and below 130 nm	[272]
<i>Lentinula edodes</i>	24 mg L <sup>-1</sup> Se(VI) or Se(IV)	26 °C	Beer wort	14 d	Intracellular	180.51 ± 16.82 nm Se(0) particles.	[273]
<i>Mariannaea sp. HJ</i>	79 mg L <sup>-1</sup> Se(IV)	Aerobic; 30 °C; pH at 10	Martin medium	4 d	Extracellular and Intracellular	The average size of intracellular BioSeNPs and extracellular BioSeNPs were calculated to be 45.19 and 212.65 nm, respectively.	[274]

**Bacteria**



<i>Azospirillum brasilense</i>	Se(IV)	Aerobic; pH at 6.8–7.0.	Malate salt medium	18 h	Extracellular and Intracellular	Increasing the initial $\text{SeO}_3^{2-}$ concentration resulted in smaller BioSeNPs. Their predominant size was 78–84 nm for 790 $\text{mg L}^{-1}$ $\text{SeO}_3^{2-}$ , 40-50 nm for 25 mM $\text{SeO}_3^{2-}$ , and 25-28 nm for 50 mM $\text{SeO}_3^{2-}$ .	[214]
<i>Bacillus cereus</i>	158 $\text{mg L}^{-1}$ Se(IV)	pH at 7	Tryptic Soya Broth		Extracellular and Intracellular	150-200 nm.	[265]
<i>Bacillus subtilis</i>	316 $\text{mg L}^{-1}$ Se(IV)	35 °C; pH at 7	Lysogeny broth	48 h	Extracellular	Spherical shaped with diameters ranging from 50 to 400 nm.	[275]
<i>Bacillus paralicheniformis</i> SR14	Se(IV)	37 °C; pH at 7	Synthetic medium	72 h	Extracellular and Intracellular	Particles ranged from 160 nm to 450 nm, with an average of $293.73 \pm 4.03$ nm.	[276]
<i>Enterococcus faecalis</i>	235 $\text{mg L}^{-1}$ Se(IV)	Aerobic; 37 °C; pH at 7;	Broth medium	24 h	Extracellular	Spherical in shape with a size range of 29–195 nm.	[277]
<i>Pseudomonas alcaliphila</i>	790 $\text{mg L}^{-1}$ Se(IV)	Aerobic 28 °C	Synthetic medium	48 h	-	During incubation: spherical particles with diameters from 50-500 nm. After incubation: nanorods.	[223]
<i>Pseudomonas stutzeri</i> NT-I	40 $\text{mg L}^{-1}$ $\text{SeO}_4^{2-}$	Aerobic 40 °C	Synthetic medium	24 h	Extracellular and Intracellular	-	[12]

<i>Rhodococcus aetherivorans</i>	SeO <sub>3</sub> <sup>2-</sup>	Aerobic	Extracellular	Nanoparticles and Nanorods.	[278]
<i>Stenotrophomonas bentonitica</i>	SeO <sub>3</sub> <sup>2-</sup>	Aerobic	Extracellular and Intracellular		[279]
<i>Tetrahymena thermophila</i> SB210	SeO <sub>3</sub> <sup>2-</sup>	-	Intracellular	Red spherical selenium nanoparticles with diameters of 50 – 500 nm.	[280]
<i>Zooglea ramigera</i>	SeO <sub>3</sub> <sup>2-</sup>	Aerobic	Extracellular and Intracellular	Spherical in shape with the size range of 30 nm to 150 nm	[281]

**Table 5.** Sorption of Se(VI) and Se(IV) by magnetic sorbents.

Sorbent	Sorbent dosage (g L <sup>-1</sup> )	Temperature (°C)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	pH	Sorbate	Isotherm	Kinetics	Maximum sorption capacity (mg g <sup>-1</sup> )	Ref.
Goethite	5	Room temperature	2.01	7.5	1.6 mg L <sup>-1</sup> Se(IV)	Langmuir	2nd	0.67	[282]
					1.6 mg L <sup>-1</sup> Se(VI)	Langmuir	2nd	0.22	
Hematite modified magnetic nanoparticles	0.1	25	79.0	7	0-120 mg L <sup>-1</sup> Se(IV)	Langmuir; Freundlich	2nd	25	[283]
Magnetite	0.1	Room temperature	0.89	4	0.05-39.5 mg L <sup>-1</sup> Se(IV)	Langmuir		0.25	[284]
					0.05-39.5 mg L <sup>-1</sup> Se(VI)	Langmuir		0.22	
Graphene oxide composites	1	25	NA	NA	0-100 mg L <sup>-1</sup> Se(IV)	Langmuir; Freundlich		27.5	[99]
					0-100 mg L <sup>-1</sup> Se(VI)	Langmuir; Freundlich		15	
Polyamine-modified magnetic graphene oxide nanocomposite	15.2×10 <sup>-6</sup>	Room temperature	NA	5.8	0-10 mg L <sup>-1</sup> Se(IV)	Freundlich	2nd	120.1	[285]
					0-10 mg L <sup>-1</sup> Se(VI)	Freundlich	2nd	83.7	
MgO nanosheets	0.03	25	166.44	10.5	1-100 mg L <sup>-1</sup> Se(IV)	Langmuir	2nd	103.2	[286]

					1-100 mg L <sup>-1</sup> Se(VI)	Langmuir	2nd	10.28	
Amino-functionalized magnetite nanoparticles	1	25	95.39	2.4	22.8 mg L <sup>-1</sup> Se(IV)	NA	NA	38	[287]
Fe-impregnated biochar from food waste	2	25	NA	3	10-1000 mg L <sup>-1</sup> Se(VI)	Freundlich	1st	11.7	[102]

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