

Review

# Environmental Impacts of Selenium Contamination: A Review on Current-Issues and Remediation Strategies in an Aqueous System

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**Abstract:** In both aquatic and terrestrial environment, selenium contamination may exist at concentrations above the micronutrient limit. Since there is such a narrow bandwidth between which selenium concentration is acceptable, the health of the public may be at risk of selenium toxicity once the concentration increases beyond a threshold. Selenium contamination in an aqueous environment can occur due to anthropogenic activities and/or from natural sources. This study presents a review of the forms of selenium, inorganic and organic selenium contamination, mobilization, analytical methods for various forms of selenium and remediation strategies. The review also provides recent advances in removal methods for selenium from water including bioremediation, precipitation, coagulation, electrocoagulation, adsorption, nano-zerovalent iron, iron co-precipitation and other methods. A review of selenomethionine and selenocysteine removal strategy from industrial wastewaters is presented. Selenium resource recovery from copper ore processing has been discussed. Various analytical methods used for selenium and heavy metal analysis were compared. Importantly, existing knowledge gaps were identified and prospective areas for further research were recommended.

**Keywords:** selenium; remediation; environmental; analytical techniques; water; wastewater treatment; adsorption; organoselenium



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## 1. Introduction

Selenium, a metalloid compound that possesses intermediate characteristics of metals and non-metals, was first discovered by Jons Jacob Berzelius, a Swedish chemist, in the year 1818 [1]. It belongs to the same group (chalcogen) as oxygen and is next to sulfur in the periodic table of elements. It has an atomic number of 34, and an atomic weight of 78.96. Some of the health benefits of selenium include its role in the proper functioning of the heart, as an antioxidant and for detoxification of the body system [2], its anti-cancer effect [3,4], decrease in heart disease [5], antiviral agent [6] and lower response to influenza infections [7]. It has industrial applications in the electrical and electronic industry, chemical and paint industry, glass industry and ceramics, metallurgy, and others [8]. It is estimated that the global production of selenium is more than 2500 tons per year [8].

While, selenium is considered a micronutrient essential for physiological functions, there is a narrow range between which it is considered essential. Concentrations in excess of this range is considered toxic to the human body. This narrow range between toxicity and deficiency varies among different species and organisms and is dependent on exposure and selenium speciation [9]. Recent studies have shown that selenium contamination is an increasing environmental problem globally, and is linked with a wide range of human activities, including agricultural activities and other industrial processes [10–14]. Hence,

an exhaustive understanding of the processes responsible for selenium cycling and the state-of-art remediation techniques for the treatment of selenium-contaminated water is important.

Over the decades, several review studies have documented and reviewed selenium contamination from various viewpoints. A handful of the review reports were written as technical reports that studied selenium contamination from mining sites and the available treatment technologies, such as MSE (2001) [15], Sobolewski (2005) [16], Golder (2009) [17], CH2M Hill (2010) [18] and Golder (2020) [19]. Others included a review of selenium toxicity [20]; selenium mobilization and bioavailability [21]; adsorbent production, post-treatment recovery and reuse of elemental selenium [22]. Furthermore, investigations of selenium pollution, cycling, interaction, and biological treatment approaches have been reported in literature [23–26]. Wadgaonkar et al. [27] reviewed the microbial transformation of selenium in soil and sediments and more recently, Getachew and Zewge [28] presented a scan of environmental issues caused by selenium.

Though several reviews about selenium and its impact have been published in literature, the kinetics of organic selenium removal associated with remediation techniques in an aqueous system was not reported. This paper focuses on the current understanding of selenium remediation techniques, selenium mobilization and contamination in the environment, with emphasis on organic selenium. Analytical methods for selenium speciation and quantification were compiled and analyzed. Research gaps were identified and prospective areas for future studies were recommended.

## 2. Selenium Sources in Environment

Primarily, two main sources stand apart as the origin of selenium in the environment. Firstly, the naturally occurring sources which include phosphate rocks, black shale, coal, and limestone deposits [29], and secondly, anthropogenic sources (coal combustion, agriculture, mining, oil and gas refineries, etc.). The natural biogeochemical mobilization of selenium in the environment comes from volcanic eruptions, weathering of selenium-bearing rocks, sediments and soil, volatilization/recycling via biotic activity, and sea spray [29,30]. On a global scale, selenium tends to be more concentrated in sedimentary rocks than igneous rocks [31] and can be cycled in every facet of the environment (atmosphere, hydrosphere, biosphere, and pedosphere). Ultimately, the natural sources of selenium are the origin for selenium mobilization in the environment. However, the anthropogenic sources have a faster distribution rate, therefore increasing the propensity of selenium transfer across various phases in the environment.

### 2.1. Anthropogenic Sources

Mobilization of selenium in the environment as a result of human activities is a global phenomenon [11]. Some of the anthropogenic activities that are contributing factors to selenium mobilization in the environment are discussed below.

#### 2.1.1. Coal and Mining Operations

One of the primary human activities responsible for mobilizing selenium in the environment is the procurement, processing, and combustion of coal for power generation [32]. According to Aibyeq et al. [33], the mining industry is one of the prime contributors to selenium released into the environment. Selenium from mining operations is not limited to coal mining; hard rock, mineral mining for valuable metals (gold, phosphate, copper, and silver), and metallic sulfides are also key contributors [11,18]. Selenium can be released from waste rock and tailings or excavated mining sites that contain sulfur-bearing minerals. Selenium bound to rock and tailings undergoes an oxidation reaction when exposed to air, either during materials handling activities or during the extraction process [18]. Once oxidized, it forms selenite or selenate; either of these forms can leach or migrate from the rock when it is exposed to water.

Surface coal mining where the coal-bearing strata contains selenium is often associated with selenium release in the environment. In no specific order, the potential sources of selenium in the ecosystems from mining sites include tailings, coal storage, the coarse-rejects stockpiles, coal-fired ash, and coal spillage [34]. Besides coal mining, other mining explorations, such as phosphate mining, can release selenium into the environment. From phosphate mining, selenium can leach in the form of selenate from middle waste shales of excavated waste rocks. Excess waste rock that are used for backfilling in phosphate mines are disposed of in the overburden disposal area (ODA). Selenium can leach from ODA when it comes in contact with air and water, resulting in oxidative weathering [18]. Knotek [35] shows that up to 2000 µg/L of selenium can leach from phosphate mining operations. The study of Ryser et al. [36] used micro-X-ray absorption spectroscopy to identified selenium minerals that are found in phosphate ore extraction. These minerals are ferroselite ( $\text{FeSe}_2$ ), diselenide carbon compound and pyrite [36].

#### 2.1.2. Coal-Fired Power Plants (CFPP)

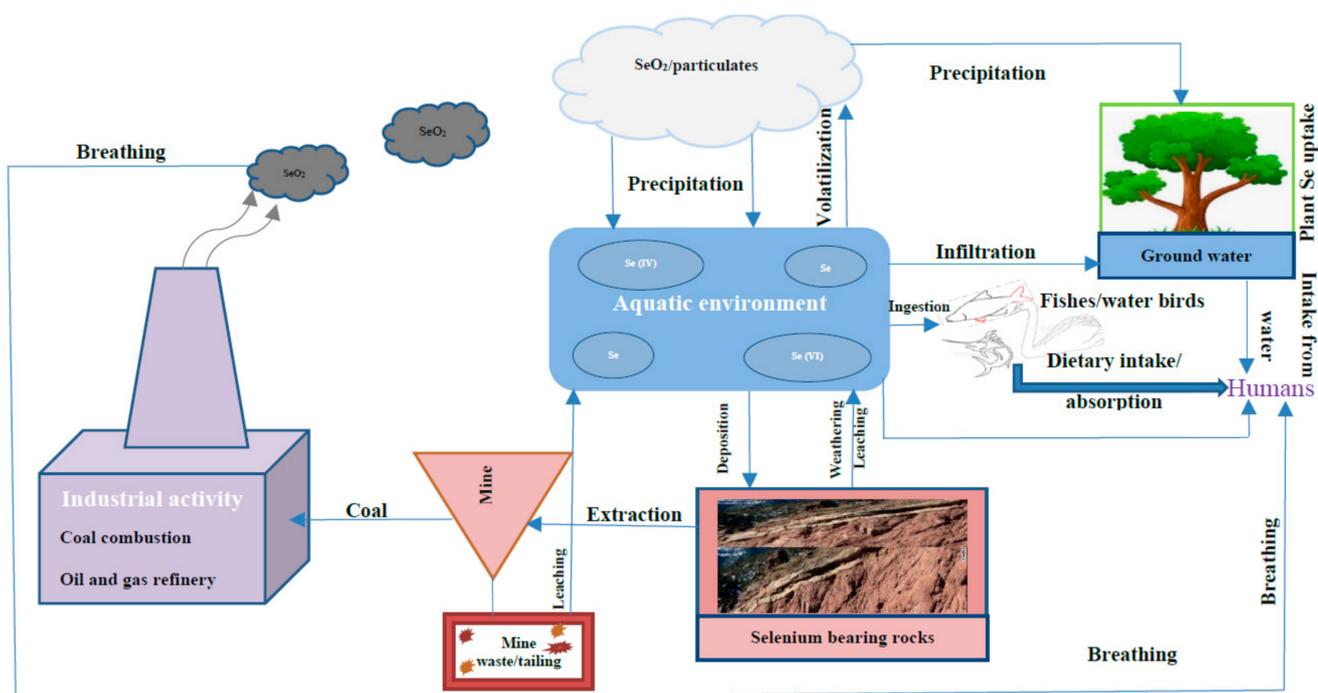
Selenium is one of the more volatile trace compounds that is released in large quantity in the vapor phase (flue gas) primarily as selenium dioxide ( $\text{SeO}_2$ ) and solid selenium species from CFPP [37,38]. Selenium emission from CFPP depends on factors such as initial concentration and composition of the coal used, and the design and operating conditions of the air pollution control equipment in the power plant facility [38]. Combustion of coal in power generation plants can generate solid waste commonly known as fly ash and bottom ash; selenium is significantly present in either of these two ashes [18,26]. A study by Andren and Klein [39] reported that selenium partitioned in the ratio of 70% fly ash and 30% vapor phase during coal combustion. Elemental selenium contained in the fly ash can be separated with the aid of electrostatic precipitators (ESP) prior to flue gas desulfurization (FGD) [18].

#### 2.1.3. Agricultural Impact

Selenium contamination in agricultural drainage runoff comes from leaching from seleniferous soils. Irrigation of seleniferous soil has been reported as a major contributor in drainage water that contains a high concentration of selenium. It is common to find selenium in shallow wells near irrigated land where the soil contains selenium [40]. There are several factors that favor selenium leaching into agricultural runoff. These include soil alkalinity that stimulates selenate formation as well as saline groundwater aquifers situated in alluvial clay layers, which prevent downward migration of irrigation water [11,41]. It is believed that selenium concentrations that are released from irrigation vary from time to time in seleniferous soils as a result of rainfall. Depending on the time of the year, the selenium concentrations fluctuate, being low during the wet season due to dilution effects [40]. Overall, from the various discussions presented on selenium fate and transport in the environment, a combination of inputs from water and mining activities can be responsible for selenium cycling and being present in the aquatic environment.

### 3. Mobilization of Selenium in the Environment

Selenium can be mobilized in the environment in various pathways. Each of the cycling pathways contributes to selenium contamination in the environment. Figure 1 presents an overview of selenium mobilization in the environment and the multiple channels by which it is transferred from the ecosystem to humans. The mobilization processes are discussed below:



**Figure 1.** Schematic illustration of selenium cycling in the environment and the human intake channels.

### 3.1. Selenium Speciation and Chemistry

In the environment, selenium exists predominantly in four oxidation states namely selenate [ $\text{SeO}_4^{2-}$ ,  $\text{Se(VI)}$ ], selenite [ $\text{SeO}_3^{2-}$ ,  $\text{Se(IV)}$ ], selenide [ $\text{Se}^{2-}$ ,  $\text{Se(-II)}$ ] and elemental selenium ( $\text{Se}^0$ ) [42]. It exists in both inorganic and organic forms; the most common inorganic species in aqueous medium are the soluble selenium (selenate and selenite) and the suspended particulates [18,43,44]. While the major organic forms exist as selenomethionine (SeMet) and selenocysteine (SeCys) [8]. Speciation of selenium in water is controlled by oxidation-reduction reactions, accessibility of adsorbing surfaces, pH, water chemistry and biological processes that take place in the receiving water [37]. These factors are of important consideration in designing selenium treatment techniques.

Figure 2 shows a selenium speciation diagram with different oxidation states of selenium in an aqueous phase at different pH and redox potential conditions (pE). As is observed from Figure 2, between pH 6 and 9, selenite, biselenite ion ( $\text{HSeO}_3^{-1}$ ), selenate, and  $\text{Se}^0$  are the primary selenium species that are found in water [18]. Selenate, which is the most oxidized form of selenium, is more dominant under strongly oxidizing conditions, while selenite is favored in moderate redox potential range and neutral pH environment [33,45]. Under acidic conditions, selenate can exist in solution as biselenate ( $\text{HSeO}_4^-$ ), and selenite can exist as a weak acid in the form of biselenite ( $\text{HSeO}_3^-$ ) and selenious acid ( $\text{H}_2\text{SeO}_3$ ) [37].

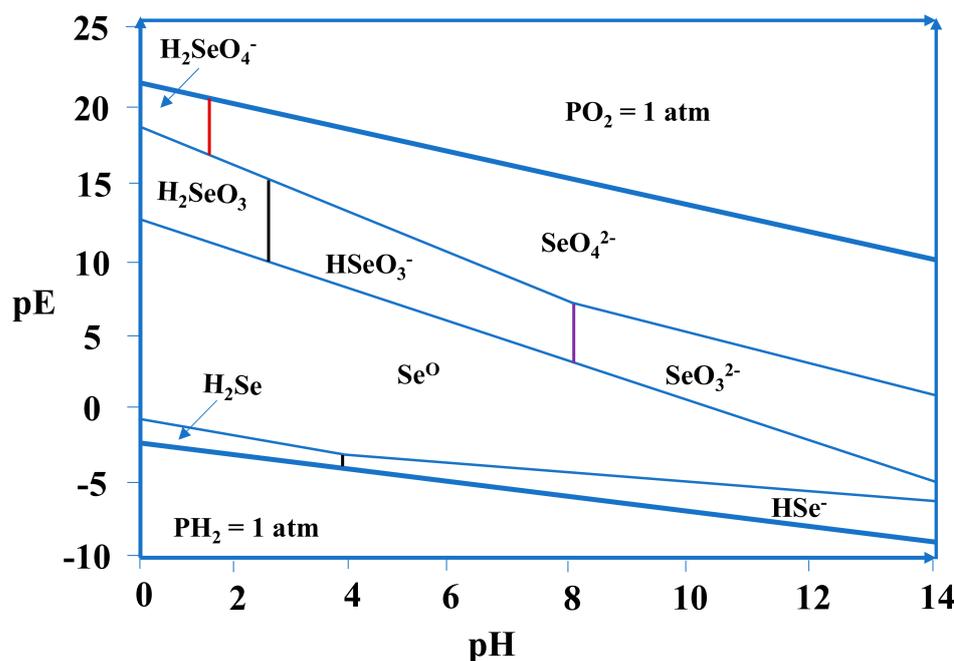


Figure 2. pE-pH phase diagram of selenium speciation adapted from [33,37].

### 3.2. Role of the Atmosphere in Selenium Deposition

The atmosphere is a major pathway for the distribution, cycling, and deposition of selenium in the environment. Selenium emissions in the atmosphere due to anthropogenic activities account for between 37–40% of selenium mobilization and accumulation in the environment [24]. Some recent estimations regarding selenium budget globally conclude that approximately 13,000–19,000 tons of selenium is cycled annually through the troposphere [46]. Several studies conclude that atmospheric deposition may be an important source of selenium contamination [47–50]. The release of selenium into the atmosphere occurs through a variety of natural and anthropogenic sources, with the former contributing up-to 50–65% of total emission on a global scale [46]. Natural sources of selenium release include (i) volcanic eruption and weathering, (ii) sea salt and evaporation from ocean surface. While the anthropogenic sources includes emissions from industrial processes involving combustion of coal, oil, wood, biomass, and nonferrous metals [46,50–52]. As may be applicable to air pollution in general, global industrialization may influence selenium anthropogenic emissions. As a result, it is necessary to evaluate the source and fate of selenium in the atmosphere. Among other sources, combustion of coal is the most dominant anthropogenic source contributing about 50% of the selenium in the atmosphere [46,50].

#### Atmospheric Selenium Pathways

Selenium emitted into the atmosphere undergoes various physical, chemical, and photochemical processes and interactions prior to deposition in the aquatic and terrestrial environment [50,53]. Typically, atmospheric selenium can be categorized into (a) volatile organic selenium comprising (dimethyl selenide, DMSe, dimethyl diselenide DMDSe), (b) volatile inorganic selenium ( $\text{Se}^0$ , hydrogen selenide  $\text{H}_2\text{Se}$ ,  $\text{SeO}_2$ ) and the particulate selenium [50].

The volatile inorganic form (elemental selenium and  $\text{SeO}_2$ ) can exist in the atmosphere; however, these species of selenium are unstable when present in the air and has a limited lifetime, with the tendency to transform to the particulate phase. Another form of gaseous selenium in the atmosphere is volatile organic selenium (DMSe and DMDSe). Both DMSe and DMDSe may be generated and volatilized under terrestrial biogenic conditions [50]. However, most of the organic selenium in the atmosphere is in the form of DMSe. DMDSe, on the other hand, is unstable and gets rapidly adsorbed onto the soil grains even prior to

wide-scale distribution in the atmosphere [50,53]. As a biogenically produced selenium, the rate of volatilization of DMSe is impacted by soil moisture content [54]. Temperature, pH, and oxidation-reduction reaction invariably control microbial activity in the soil; therefore, these factors affect the volatilization rate of DMSe [55]. The volatilization of methylated selenium at the air-sea interface is dependent on climate conditions, salinity, mineral composition of sea-water, temperature, and pH [50].

As important as the atmospheric selenium pathway is in understanding the physio-chemical reaction of selenium in the atmosphere, only a few studies have investigated the entire selenium behavior from atmospheric emission to re-deposition. Selenium and sulfur (S) share similarities in terms of physical and chemical properties. Therefore, the chemistry of selenium in the atmosphere is sometimes estimated using atmospheric sulfur chemistry [50].

### 3.3. Aquatic Selenium Pathways

In an aquatic environment such as lotic (flowing waters) and lentic (non-flowing waters) selenium can be cycled within the biota and be transferred from one trophic level (ecosystem) to another. Mainly, there are four pathways by which selenium can be mobilized in the aquatic environment. (a) absorption or ingestion by organisms, (b) mixed in particulate matters, (c) dissolved in solution and (d) volatilized from water to the atmosphere [56]. Organisms in aquatic environments are exposed to selenium accumulation primarily through their diet and water [33]. Because selenium is either absorbed directly or bound to particulate matters. Over time, by a means of deposition or sedimentation (settling of particulate), selenium can accumulate in the top layer of sediment or if dissolved, can remain in free solution. In the aquatic system, organisms are dynamic in nature and are constantly hunting for food in the sediment. Selenium can be mobilized and acquired from sediment into biota and be accumulated at a high concentration for a long period of time [56]. Even when the water input of selenium has ceased to exist or stopped, aquatic organisms can still have selenium accumulated (bioaccumulation of selenium).

### 3.4. Organoselenium (Seleno-Amino Acid)

Organoselenium (organic selenium) are compounds that possess selenium elements in addition to nitrogen, oxygen, carbon, or hydrogen in their molecular structure. The main form of organoselenium is selenoamino-acids and selenoprotein [56]. While SeMet and SeCys are the primary forms by which selenoamino-acids exist in the environment and are absorbed by both plants and aquatic organisms [57,58]. Organic selenium is categorized as an emerging contaminant; and can be present in the effluent of industrial wastewaters [59], mostly emanating from oil and gas refineries, coal-fired power plants and mining. It is known to have high level of bioavailability compared to the inorganic selenium species because it is readily absorbed; hence, it has a higher threshold for toxicity [60]. This is the reason why this species of selenium (SeMet) is often used for selenium toxicity assessments [59].

The primary concern of organoselenium includes the ability to bioaccumulate in aquatic organisms for long period of time, inevitably contaminating fish and wildlife diets [56]. In several lakes near Sudbury, Ontario, Canada, the presence of organic selenium has been reported to exist in a low concentration range of 122 to 330 ngSe/L [61]. However, the low concentration does not negate organic selenium propensity to bioaccumulate within the food-web; it is undoubtedly an environmental concern. Besides SeMet and SeCys, selenocyanate ( $\text{SeCN}^-$ ) is another organic selenium species that exist typically in oil and gas refinery effluent.

### 3.5. Selenium Toxicity

Acute and chronic selenium poisoning can result from exposure to high concentrations of selenium above the normal beneficial limit. Acute exposure often results in neurotox-

icity, while chronic exposure can affect endocrine functions such as synthesis of thyroid hormones [62,63]. The oxidation states and various chemical forms of selenium, to a large extent, determine the toxicological effects. In general, selenium tends to be toxic at a concentration above the homeostatic requirement and causes health challenges that are not limited to prostate carcinoma, hepatic cancer, nervous or dermal diseases, hair loss, defective skins and nails, and genotoxicity (mutilation of DNA) [26,37,64]. One of the toxicological concerns of selenium is the evaluation of the exact limits between toxicity and deficiency [21]. Previous research reported different concentration limits by different authors. However, according to Albert et al. [65] the micronutrient benefit of selenium for human physiological functions is between the concentration of 63–135 µg/L; above this limit, selenium is considered to be toxic [65]. Symptoms of selenium toxicity were noted to have occurred at a daily intake of more than 800 µg/day [66], while chronic toxicity results in selenosis. Typical dietary intake of selenium in the United States is between 80–120 µg/day but varies significantly across other world regions [58,67]. However, the National Academy of Sciences Institute of Medicine has set 400 µg/day of selenium as the tolerable upper safe limit [58].

In the environment, selenium toxicity is not limited to physico-chemical phenomena; the toxicity risk is affected by the mobility of selenium compounds, bioavailability [60] and magnification [12] in the food chain. Long-term exposure effects, as well as ingestion, are likely mechanisms by which toxicity can occur. The uptake of selenium by living creatures can either occur through a water pathway or assimilated via diet as explained in Figure 1. While fish may ingest soluble selenium through the water pathway, for humans and terrestrial animals selenium uptake is mainly through the dietary pathway [20]. For this reason, bioaccumulation and biotransformation are vital considerations for the evaluation of selenium toxicity [33], especially with organic selenium.

Chapman et al. 2010 [68] related selenium toxicity to selenium concentration that is bioaccumulated by sensitive biota (fish, waterfowl, benthic, etc.). The magnitude of bioaccumulation depends on many factors, such as selenium concentration and speciation [69] and the composition of biological entities in the receiving environment [70,71]. There are subjective opinions from different authors on the toxicity of inorganic and organic selenium. Much emphasis has been placed on the organic selenium being more toxic than the inorganic because of bioaccumulation [59,60,65]. However, the inorganic selenium species (Se (IV) and Se (VI)) are toxic at high concentrations [26,72].

### 3.6. Selenium Regulations

The United State Environmental Protection Agency (USEPA) in 2016, issued a new selenium regulation for aquatic life ambient water quality standard for selenium, which is based on fish tissue residue concentration. This regulation is mainly to protect against selenium toxic effects, hence, the following were recommended: (a) fish egg-ovary element (maximum selenium concentration of 15.1 mg/kg); (b) fish whole-body (maximum selenium concentration of 8.5 mg/kg) or muscle tissue of fish (maximum selenium concentration of 11.3 mg/kg); and (c) water column element (30-days average concentration of selenium in water should not exceed 3.1 µg/L in lotic (flowing) waters and 1.5 µg/L in lentic (non-flowing) waters more than once in three years.) [73].

Selenium may cause acute toxicity at high concentrations, however, the most adverse effect on aquatic organisms is due to its bioaccumulative tendency [73]. As discussed in Sections 3.4 and 3.5, organoselenium has both toxicity and bioaccumulation concerns in aquatic organisms [56,60]. The current understanding of selenium bioaccumulation promulgated the USEPA 2016 selenium regulation that set selenium thresholds based on fish tissue concentration as opposed to the traditional aqueous concentration limits [73]. For this reason, it is imperative to remove organoselenium from wastewater.

Other regulatory agencies and organizations such as World Health Organization (WHO) and Health Canada (HC), set guidelines to regulate selenium in water and the environment. For instance, WHO recommended the maximum selenium content in drinking

water to be 40 µg/L [10,74]. Health Canada suggested the maximum acceptable concentration for selenium in drinking water to be 50 µg/L [75]. USEPA—national primary drinking water standard, maximum contaminant level (MCL) for selenium is 50 µg/L [15]. These regulations articulate the importance of selenium remediation and the level of treatments that are necessary to remove selenium from wastewaters.

#### 4. Removal and Treatment Techniques

There is no specified universal method to remove selenium contaminants from wastewater [76]. Various methods and techniques to be considered are dependent on several factors such as selenium speciation, the nature of the receiving water, and the location and nature of the source of contamination [76]. Therefore cost-effective treatment technologies are essential for the removal of selenium contaminants from the aqueous environment [77]. From the basic wastewater treatment techniques to the advanced removal process for selenium contaminated waters, remediation technologies had advanced; hence, a comprehensive review that presents the current understanding is needed.

##### 4.1. Physical Operation—Membrane Filtration

Physical treatment methods used on an industrial scale for selenium removal include membrane filtration, media filtration, and ion exchange. These are conventional methods employed for industrial wastewater treatment and are relatively simple in operation. Membrane filtration utilizes a semi-permeable membrane to which a pressure gradient is applied, resulting in the contaminants being retained on the membrane (retentate). At the same time, the clean water is forced through the membrane permeate. Membrane filtration technology is further classified as (i) microfiltration, (ii) ultrafiltration, (iii) nanofiltration (NF), and (iv) reverse osmosis (RO) [78].

Nanofiltration and RO are the two types of membrane filtration applicable to selenium removal. Only selenate and selenite can be removed using NF and RO, this is as a result of the molecular size of these selenium species [18]. Removal will vary depending on the properties of the membrane used. NF has been reported to remove about 95% of selenium at a laboratory scale from agricultural drainage wastewater [79]. Selenium pollution from mining-impacted water has been effectively treated using RO techniques and the concentration was reduced to 5 µg/L [37]. A solar photovoltaic powered NF/RO device has been tested by Richard et al. [80] to investigate contaminant retention from groundwater; these contaminants include selenium at low concentrations (8 µg/L). Significantly, selenium retention was found to be pH-independent with more than 70% retention achieved. Generally, the advantage of membrane technology (NF and RO) is the capability to produce very high-quality permeate; and can remove selenium (selenite and selenate) from wastewater. Nevertheless, this technology is expensive and poses operational challenges, such as fouling and scaling of the membrane. Additionally, the presence of competing ions in water matrices such as nitrates, sulfates, and chlorides can be a limitation to selenium removal using this method.

##### 4.2. Ion Exchange

In the ion-exchange process, undesirable ions on a solid or gel surface present in water are adsorbed in exchange for the desirable ion. The solid surface can be a resin or polystyrene resin. However, this method has not demonstrated sufficient capacity to treat all selenium species [81]. The presence of sulfate usually hinders the removal of selenates and decreases the reaction rate, thereby making the techniques ineffective. An alternate solution is the application of a pre-treatment stage for sulfate ion followed by ion exchange [33]; however, this is rarely a preferred option because it can increase the cost of treatment significantly.

#### 4.3. Biological Processes

Selenium contaminants can be removed from an aqueous medium using a biological treatment process. Primarily it involves the ability of bacteria, fungi and algae to methylate selenium and convert it to gaseous form [37]. The biological process can use sulfate-reducing bacteria (SRB) species (*Desulformicrobium* sp.) for the treatment of selenium contaminated wastewater [33]. The advantages of using this method include low cost, in-situ removal, and minimal risk to the environment because harmful substances are not required. It is significant to note that selenium bioremediation aims to reduce toxic, mobile and soluble selenium oxyanion to  $\text{Se}^0$  via microbial actions. Several studies have demonstrated that microbial species can convert soluble selenium (selenite and selenate) to  $\text{Se}^0$  [82–85]. Lawson and Macy et al. [84] found that more than 95% of selenite (3690  $\mu\text{g}/\text{L}$ ) can be reduced to elemental selenium and be removed from oil refinery wastewater selenium by using an anoxic biological reactor. Selenate in San Joaquin agricultural drainage water was successfully treated by a similar system [86,87]. Soda et al. [88] removed the soluble selenium from refinery wastewater using microbial reduction and found that the selenium concentration dropped from 1500  $\mu\text{g}/\text{L}$  to 100  $\mu\text{g}/\text{L}$  after 15 days of operation in a up-flow anaerobic sludge bed (UASB) reactor. Lenz et al. [89] also investigated the removal of selenate (790  $\mu\text{g}/\text{L}$ ) in up-flow anaerobic sludge bed reactors (UASB) with sulfate-reducing bacteria and achieved high removal efficiency.

In the biological method of selenium removal, biofilms or communities of microorganisms play a crucial role in transforming selenium oxyanions into less toxic chemical forms [90]. Yan et al. [91] characterized selenium species (selenite and selenate) in multi-species biofilms injected from coal mining effluent. In their study, confocal laser scanning microscopy (CLSM) revealed a distinct biofilm morphology at increased oxyanion concentrations. X-ray absorption spectroscopy (XAS) was used to demonstrate biofilm biotransformation of selenium oxyanions, while extended X-ray absorption fine structure (EXAFS) analysis showed elemental selenium as a product. Detoxification reaction is another process of biological reduction of selenium. This process involves Se (IV) reduction, which can occur enzymatically and non-enzymatically [92]. Several studies have discussed selenium removal using this process [92–94].

Other biological removal processes discussed in the literature include the commercial GE ABMet (advanced biological metal removal) technology. This removal technique is based on bioreduction in active filters; essentially, it reduces selenium and other toxic metals. ABMet has previously been used to remediate selenium from water in metal recycling facilities, coal mining and power plants (flue gas desulfurization) [95].

Another exciting aspect of the biological method is the use of wetlands. It has been demonstrated as a passive biological treatment for selenium in the aqueous medium [18]. Specifically, wetlands are integrated water systems containing plants, and microorganisms in the environment, where contaminants can be removed via biological reduction, sorption to soil, plants, and volatilization [78]. Both Se (IV) and Se (VI) can be uptaken by various aquatic plants, reducing the total level of selenium concentration in the aqueous medium [96]. The advantages of using wetlands include low cost, operation and easy maintenance [97].

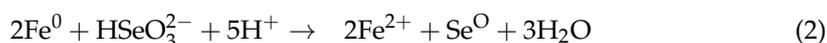
Typically, the biological process is the most commonly used method to remove selenium from industrial effluent. This method has compelling advantages, including being active, passive, and applicable under in situ conditions [19]. However, there are some challenges with the operational complexity and cost of bioreactors associated with this technique [98]. Volumes of selenium-containing sludge from the post-treatment can be a problem. Influence of environmental conditions such as temperature, and pH could be a concern; also eutrophic condition can exist downstream of the receiving waters if sludge is not adequately treated [18]. Studies have shown that inorganic selenium biological treatment can transform selenium to the organic form (selenomethionine) [59,82].

#### 4.4. Chemical Reduction Techniques

Chemical reduction techniques can remove soluble selenium from an aqueous medium by altering the physical or chemical properties. Nanoscale zerovalent iron (nZVI) is a commonly used nanoparticle for selenium remediation, both in groundwater, surface water and industrial effluent [99]. nZVI can be used as a reducing agent or as a catalyst for inorganic selenium treatment. The use of nZVI has increasingly gained attention in selenium remediation because of the competitive advantages, among other similar chemicals. It is readily available to source, inexpensive, easy to handle, environmentally friendly and can produce a relatively low reduction potential in aqueous solution [100–102].

Nano zerovalent iron has a core-shell structure; the core consists of metallic iron and the shell comprises a layer of mixed Fe(0)/Fe(II)/Fe(III) [103,104]. Selenium reduction by nZVI is made possible by a combination of adsorption and chemical reaction mechanisms [11,103]. The nZVI removal mechanism is characterized by a corrosion process that results in the formation of ferrous iron and other by-products such as green rust, magnetite (Fe<sub>3</sub>O<sub>4</sub>), lepidocrocite (γ-FeOOH), ferrihydrite (Fe(OH)<sub>3</sub>) and goethite (α-FeOOH) [11,105,106]. Se (IV) can be removed from wastewater via nZVI through a chemical reduction process to Se (II) and Se<sup>0</sup> as well as encapsulation in the nanoparticles [103]. Dissolved selenite has been reported to bind to the surface of nZVI, leading to the formation of inner-sphere surface complexes [107]. Due to the large surface area of nZVI and the presence of mixed-valence iron oxide on the shell, the removal rate is relatively fast [108].

To remove Se (VI) using nZVI has some peculiarity with the removal of Se (IV). It's a two-stage process that entails a change in oxidation state, Se (VI) is reduced to Se (IV) and further reduction produces Se<sup>0</sup>. The alternative process is the direct adsorption of the reduced Se (IV) by ferrihydrite or ferri-oxyhydroxide amorphous solids formed during the redox reaction with the nZVI [20]. The chemical Equations (1)–(2) describes nZVI removal process [104].



The use of nZVI to treat Se (VI) contaminant from mining-impacted waters with a concentration of 1000 µg/L under oxic conditions was evaluated by Das et al. [10]. They reported that 90% of Se (VI) removal was achieved within 4–8 h in the absence of sulfate and nitrate. In general, nZVI is an efficient technique for selenium treatment in an aqueous system. However, there are notable disadvantages in using nZVI technology, which include the effect of temperature and pH-dependent, associated cost of post-treatment sludge disposal, long hydraulic residence time, chemical scaling and suspended solids, and other metals redox reactions [18]. In the presence of dissolved oxygen (DO), nZVI can easily be oxidized to ferrous ions via aerobic corrosion. The ferrous ions can readily be oxidized to ferric ions and thereafter form loose ferric hydroxide in water at near-neutral pH [105]; the rapid oxidation process and passivation is undoubtedly a concern for nZVI. Agglomeration of particles is another hurdle that can reduce nZVI reactivity and application [106]. In order to overcome the aforementioned challenges of nZVI reactivity in the water, several studies have developed composites to improve nZVI performance for selenium removal [77,109].

#### 4.5. Coagulation and Flocculation Process

Coagulation by aluminum (Al) and iron (Fe) salts have been tested to remove selenium from drinking water. This technology has been widely applied in industrial effluent treatment but may not be sufficient for reaching low selenium limits (below 5 µg/L) [18].

Coagulation can be an effective method for Se (IV) removal but not effective for Se (VI) [108]. Pre-treated is required for Se (VI) to be effectively removed by the coagulation process. Hu et al. [110] investigated the removal of inorganic selenium from drinking water using FeCl<sub>3</sub> and AlCl<sub>3</sub> coagulants. More than 98% of selenite (250 µg/L) and around 40% of selenate (250 µg/L) were removed. It was found that the efficiency of selenium removal

by coagulation was dependent on selenium species, the type of coagulants, the dosage of coagulants, pH, and the water matrix. The study of Hu et al. [110] found Fe-based coagulants more efficient than Al-based coagulants in selenium treatment. Aluminum chloride ( $\text{AlCl}_3$ ) and polyaluminum chloride (PACl) are the most efficient Al-based coagulant for the removal of selenium contaminants. Both Fe-based and Al-based coagulants remove selenium more successfully in acidic pH conditions compared to high pH range.

In most coagulation based removal processes, some competing anions preferentially get removed before selenium; this can be a limitation of this process. The negative impact of competing anions on Se (IV) and Se (VI) removal occurs in the following sequence:  $\text{PO}_4^{3-} > \text{SiO}_3^{2-} > \text{CO}_3^{2-} > \text{SO}_4^{2-}$ . Overall, competing anions appear to have a more significant impact on Se (VI) removal compared to Se (IV) [109].

#### 4.6. Electrocoagulation Process

The electrocoagulation method of selenium treatment uses electrodes to removal selenium species from water. Insoluble precipitates are obtained electrochemically from selenium [81]. This technique involves the in-situ formation of coagulants using electrolytic oxidation process that involves a sacrificial electrode (dissolution of anode) to form flocs, after destabilization of contaminants and particulate [111]. Staicu et al. [112] investigated the removal potential of  $\text{Se}^0$  by the electrocoagulation process using Fe and Al electrodes. Fe electrode removed more than 92% of selenium compared to the Al electrode which had 54% removal efficiency [112]; this is because Al flocs were less compact in nature [25]. These results demonstrate that Fe electrodes (as a soluble anode) in the electrocoagulation removal process are a better option than Al electrodes for the electrochemical sedimentation of colloidal  $\text{Se}^0$ .

Mavrov et al. [81] demonstrated 98.7% removal of selenium using electrocoagulation in a continuous flow regime with a treatment time of 20 min and a current density of anode  $4.8 \text{ mA/cm}^2$ . The disadvantages of using this technique include the high costs associated with electrolyzer construction, electrode replacement and increased energy consumption. Hence, it is expensive from an economic point of view [113].

#### 4.7. Co-Precipitation Method

Ferrihydrite adsorption or iron co-precipitation is the technology recommended by USEPA [97] as the best demonstrated available technology (BDAT) for selenium treatment. Ferrihydrite adsorption involves the two-step physical process in which ferric salt (e.g., chloride or ferric sulfate) is introduced to a solution under proper conditions such that ferric hydroxide and ferrihydrite precipitate simultaneously adsorb selenium on iron surface; in other words, it is known as the iron co-precipitation method [18]. The technology requires pH adjustment and adequate mixing conditions to facilitate ferric oxyhydroxide flocs, which is the driving mechanism for selenium removal [76]; the optimum pH range is 4.0–6.0 [18].

Several studies used the co-precipitation method to immobilize inorganic selenium (Se (IV) and Se (VI)) from a contaminated solution using barite ( $\text{BaSO}_4$ ) [114,115]. Merrill et al. [116] explained the co-precipitation mechanism of removing selenium from the ash pond effluent of a coal power generation plant. A study by Haye et al. [117] found that Se (IV) co-precipitation onto ferrihydrite matrix is by adsorption to the inner sphere. While Se (VI) adsorb as an outer-sphere hydrated complex at the surface of the ferrihydrite matrix, it can be easily replaced by anions such as sulfate. This technology can remove selenium when it exists in the form of Se (IV) [18]. Most recently, Okonji et al. [76] investigated the application of co-precipitation technology supported by ferrous ion for selenium treatment. The study obtained an optimal dose of 0.5 g/L at pH 4.0 using ferric salt and observed that more than 99.9% of Se (VI) removal was achieved with an adsorbent dose of 1.5 g/L. Short treatment time, low cost, simplicity, and able to preserve substituent ions in crystal lattice for a long time are certainly some of the advantages of co-precipitation treatment technique.

#### 4.8. Removal by Precipitation

Under commonly encountered waste stream conditions (temperature, pH and ionic strength), soluble selenium (Se (IV) and Se (VI)) will not directly precipitate out of solution [18]. Some chemical reagents can be of great use in this process. Selenium removal by precipitation using dithionite ion and sodium sulfide has been investigated [118,119]. A weak sulfuric acid solution containing 300 µg/L of Se (IV) was used as the synthetic wastewater to stimulate typical industrial scenarios for zinc refinery acid effluents. It was observed that a significant amount of selenium was precipitated (almost complete removal achieved); the excellent performance (precipitation) was attributed to high initial selenium concentration. Selenium precipitate obtained from the dithionite ion solution was considered unstable [118]. On the other hand, selenium sulfide precipitate from the sodium sulfide was stable at neutral pH but partially dissolved at pH 3.0, 5.0 and 10.0 [119]. Research has shown that other reagents (e.g., sulfur dioxide (SO<sub>2</sub>)) can reduce selenious ions to Se<sup>0</sup> via precipitation; nevertheless, sodium dithionite has been highly favored in the industry [25]. However, if the concentration is lower and at ambient temperatures, as one may encounter in the zinc industry, the decrease of Se (IV) with SO<sub>2</sub> reagent becomes too slow to be of practical interest [25]. Overall, the precipitation method is not effective for Se (VI) removal, as it only achieves about 87% removal efficiency [120].

#### 4.9. Chemical Cementation

The catalyzed cementation removal technique involves the remediation of selenium from wastewater by reduction to elemental selenium followed by cementation onto an iron surface. Specifically, this process is improved by the addition of some catalysts, such as copper and nickel [18]. This technique was used to treat mining-impacted water with a selenium concentration of approximately 1000 µg/L and achieved about 100% removal efficiency [15]. Chemical cementation is a promising technology for treating mining-influenced wastewater. However, the full-scale application of this remediation method has not been demonstrated. There are apparent disadvantages of high costs related to chemicals and sludge management [15,18].

#### 4.10. Photocatalytic Reduction

Photocatalytic reduction of selenium oxyanion (Se (IV) and Se (VI)) to elemental selenium over UV-illuminated TiO<sub>2</sub> have been investigated [121]. This process entails using formic acid and methanol. However, formic showed the fastest rate of selenium ions photo-reduction to Se<sup>0</sup> with an optimum pH of 3.5 and 4.0 for Se (VI) and Se (IV), respectively [121]. The photocatalytic reduction of selenium species is based on their ability to form a reducing radical. This technique was explored in Nguyen et al. [111] study; UV-vis reflectance measurements showed that the selenium/TiO<sub>2</sub> particles demonstrated a red-shift compared to pure TiO<sub>2</sub> [111]. The use of toxic chemicals is not required in this technique; clearly, that is an advantage.

#### 4.11. Adsorption

Adsorption has been reported as the most widely used technology in terms of flexibility, low-cost of implementation, high efficiency, and easy operational design [122,123]. As shown in Table 1, it can be seen that the adsorption method has been widely used to remediate selenium from wastewaters. Adsorption is a promising technology for the industrial application of selenium removal [77]. That is not to say that this technique does not have some hurdles; some potential challenges certainly exist in the adsorption process. Temperature and pH dependence, the competitive effects of oxyanions and cations, and cost associated with the regeneration, management and disposal of exhausted adsorbents are some of the imminent concerns of using adsorption as a remediation strategy.

Research interest in adsorption and development of suitable adsorbents that could take-up selenium contaminants from aqueous medium while remaining eco-friendly has gained more attention. Conventional and alternative material has been explored as poten-

tial adsorbents for selenium in order to find a low-cost approach for water and wastewater treatment [37]. Essentially, the amounts of selenium adsorbed are dependent on some factors that are initiated in the experimental conditions, such as effects of initial concentrations, pH, ionic strength of the medium, adsorbent dosages, temperature, etc. Therefore, maximum adsorption capacity is not the only determining factor to evaluate an adsorbent potentiality, though it is a significant parameter. Other factors such as adsorption kinetics, solid-liquid separation, pH influence, adsorbent regeneration, post adsorption disposal and environmental conditions, are necessary points of considerations [37].

#### 4.11.1. Metal-Based Adsorbents

Selenium adsorption from aqueous media using iron oxides and aluminum oxides has been extensively studied [124–129]. These oxides have a large surface area making them suitable to adsorb selenium over a wide range of pH (4.0–8.0). The following studies were conducted to enhance selenium removal using iron-based adsorbent/oxides, such as  $\text{Fe}_3\text{O}_4$  [76,113,130,131], hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) [132], maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) [133], lepidocrocite ( $\gamma\text{-FeOOH}$ ), ferrihydrite ( $\text{Fe}(\text{OH})_3$ ) and goethite ( $\alpha\text{-FeOOH}$ ) [11,105,106]. Verbinnen et al. [134] investigated the concurrent removal of molybdenum (Mo), antimony (Sb) and selenium oxyanions from wastewater by adsorption onto zeolite-supported magnetite. According to the study, there was no significant competition with anions (sulfate and chloride), but considerable competition existed among metals which decreased in the following order:  $\text{Mo(VI)} > \text{Sb(V)} > \text{Se(VI)}$ .

One peculiarity among the aforementioned studies is the fact that Se (IV) adsorbs more actively than Se (VI) onto all iron-based adsorbent/oxides. Recently, Okonji et al. [76] studied the adsorption of Se (IV) and Se (VI) onto nZVI and magnetite and evaluated the kinetics. The author found that the adsorption mechanism of the adsorbents was similar for both selenium species and was driven by electrostatic attraction. With initial concentration of 5 mg/L, the removal efficiency of Se (IV) using 1.5 g/L of  $\text{Fe}_3\text{O}_4$  at pH 4.0 and 8.0 was reported as follow, at pH 4.0, 91.3% of Se (IV) was removed within 10 min and further reached steady-state removal of approximately 93% in 15 min. On the other hand, removal of Se (IV) was gradual for pH 8.0, as 76% removal was observed over a period of 5 h [76]. This demonstrated that inorganic selenium removal adsorption performance is pH-dependent and increases with a decrease in pH [76]; similar findings have been reported in literature [113,128,135].

Activated alumina (AA), mostly comprised of aluminum oxides ( $\text{Al}_2\text{O}_3$ ), is a widely recognized material for adsorption and catalysis application. AA has been used for selenium removal; while it appears ineffective for Se (VI), AA adsorption favors Se (IV) take-up considerably [136]. The performance is mostly dependent on pH influenced. To improve the adsorption of AA for Se (VI) removal, Yamani et al. [137] developed a composite of nanocrystalline aluminum oxide ( $n\text{-Al}_2\text{O}_3$ ) impregnated chitosan beads (AICB). The adsorption capacity of AICB to removes Se (IV) and Se (VI) simultaneously was more effective than chitosan or  $n\text{-Al}_2\text{O}_3$  alone [137]. For Se (IV) medium,  $n\text{-Al}_2\text{O}_3$  was the active adsorbent simply because chitosan had a low affinity for Se (IV); but in Se (VI) system, chitosan and AICB were active adsorbents [138].

Other useful oxides for selenium species adsorption include Titanium dioxides ( $\text{TiO}_2$ ), which adsorb via one of its polymorphs called anatase [138,139]. Se (IV) adsorption kinetics onto anatase has been described by a pseudo-second-order kinetic model [138–140]. From the studies, the rate constant was dependent on two factors: (a) pH and (b) adsorbate initial concentration [139]. Ionic strength did not influence the removal efficiency for Se (IV) [139]; however, increased ionic strength decreased Se (VI) adsorption significantly [140]. Additionally, some metal oxides reported in the literature for selenium species adsorption are manganese ( $\text{Mn}_3\text{O}_4$ ) [141,142], binary metal oxides Al (II)/ $\text{SiO}_2$  and Fe (III)/ $\text{SiO}_2$  synthesized to improve the adsorption of Silicon dioxide ( $\text{SiO}_2$ ) [143].

#### 4.11.2. Non-Metal Adsorbents

Activated carbon (AC) is the most frequently used adsorbent for water purification. Its adsorption capacity for removing organic compounds from water is undoubtedly recognized; however, it shows low adsorption for inorganic selenium species, mostly Se (VI). AC has a large surface area [144], which makes it a suitable adsorbent with good adsorption sites. Several studies have described that granular activated carbon (GAC) supported Fe composite (Fe-GAC) have a high surface area which enhances its ability to remove Se (VI) and Se (VI) oxyanions from wastewaters [77,109]. Okonji et al. [76] investigated the application of non-modified GAC to remove selenium species from water. With an initial concentration of 5 mg/L and GAC adsorbent ratio of 7 g/L, Se (VI) adsorption was pH controlled, with about 95 % removed at pH 4.0.

Most of the conventional adsorbents such as clay, silica gel and bio-sorbents (peanut shell and rice husk) have been used for Se (IV) adsorption but show weaker performance for Se (VI) removal [25,145–147]. Composites of the above materials have displayed a high potential to remove Se (VI) from water [125,129,147] Li et al. [148] found that double-layered hydroxide/chitosan nanocomposite beads can be used as an effective adsorbent for removing selenium oxyanions. Hasan and Ranjan [149] investigated the selection of potent bio-sorbent from three agro-industrial wastes (wheat bran, maize bran, and rice bran). Wheat bran demonstrated maximum uptake for both Se (IV) and Se (VI) ions. The study was further evaluated using a continuous up-flow fixed-bed column system [150]. The removal efficiency of bio-sorbent/natural adsorbent may not be too high, but it is certainly cost-effective and is environmentally friendly.

#### 4.12. Organic Selenium Removal

To date, inorganic selenium has been the main focus of selenium remediation from wastewater. Organic selenium (SeMet and SeCys) removal from wastewaters has limited studies. Manceau [151] investigated selenocyanate ( $\text{SeCN}^-$ ) removal from contaminated water emanating from sour crude production using reducing agents as precipitant. Among the precipitants tested, silver (I) nitrate, tin (II) chloride, and copper (II) chloride showed promise for  $\text{SeCN}^-$  removal, with more than 95% removal efficiency [151]. Meng et al. [105] investigated the removal of  $\text{SeCN}^-$  from refinery wastewater using elemental iron. About 94% of  $\text{SeCN}^-$  was removed from the wastewater in the form of  $\text{Se}^0$  after 8 h of mixing. Latva et al. [152] studied seleno-DL-methionine separation from inorganic selenium solution using magnesium-loaded activated charcoal. Okonji et al. [76] investigated the removal of SeMet by adsorption and compared the kinetics of the adsorbent candidates (GAC,  $\text{Fe}_3\text{O}_4$  and nZVI). Research on removal strategies for seleno-amino acids (SeMet and SeCys) is still evolving. One of the most recent studies conducted on the removal of organoselenium involved the efficacy of GAC and nZVI technologies to treat SeMet and SeCys contaminated wastewater [153]. The study revealed that SeMet is more refractory to partition onto the adsorbents and be removed from the solution compared to SeCys [153].

**Table 1.** Selected adsorption techniques used for the removal of organic and inorganic selenium.

Adsorbents	Selenium Species	C <sub>0</sub> (mg/L)	Dosage (g/L)	pH	q <sub>e</sub> (mg.g <sup>-1</sup> )	Assessment	Reference
<b>Iron based adsorbents</b>							
Magnetite	SeMet	5	0.5	7	-	Organic selenium adsorption by Fe <sub>3</sub> O <sub>4</sub> was significantly low (<10%). The batch experiment attained equilibrium in 1 h. Inorganic selenium (Se (IV) and Se (VI) achieved a higher removal compared to organoselenium. Greater than 84.5% of Se (IV) removal obtained in less than 1 h	[76]
	Se (VI)	5	2.5	7	2.19		
FeOOH	Se (IV)	5	1	4	4.36	Showed good adsorption capacity for Se (IV), can be applicable for Se (VI) reduction.	[154]
	Se (IV)	0.5–20	0.5	5	26.3		
FeCl <sub>3</sub>	Se (IV)	5	1	4	4.9	Two-step adsorption process - precipitation and concurrent adsorption of selenium on the surface of ferri-oxyhydroxide amorphous solid. More than 99.6% of Se (IV) removed in 30 mins.	[76]
NZVI/NanoFe	SeMet	5	0.5	7	-	This technology is both cost-effective and environmentally friendly. Organic selenium removal capacity achieved was less 7.5%. This method achieved a concentration of residual selenium of about 0.01 mg/L in 6 h, which is acceptable by water quality regulation—MCL. The removal efficiency of over 97% was recorded in 4 h. Faster adsorption process compared with Se (VI).	[15,76]
	Se (IV)	5	2.5	6	-		
Elemental iron Fe <sup>0</sup>	Se (IV)	5	2	4	2.75	Refinery wastewater and KSeCN solution were used. More than 98% of SeCN <sup>-</sup> was removed from KSeCN solution at pH 7 in 2 h. About 66% was removed from refinery wastewater. The slow kinetics observed with refinery wastewater can be attributed to the interference of coexisting organic and inorganic compounds with the chemical reactions between SeCN <sup>-</sup> and the adsorbent.	[105]
	SeCN <sup>-</sup>	5	15	6–7	-		
<b>Activated carbon-based</b>							
Fe-GAC	Se (IV)	2	0.3–2.8	5	2.58	Oxyanion competitive adsorption showed that sulfate (0.1–5 mM) barely affected selenite adsorption. However, phosphate mostly impacted selenite adsorption at high ionic strength.	[109]
GAC	SeMet	5	0.5	7	-	A promising candidate for organic selenium treatment, achieved about 50% removal efficiency, with fast kinetics. Overall, it can be a multifunctional adsorbent. The rate of adsorption was slow with not more than only 78% of equilibrium capacities achieved in 4 h.	[76]
	Se (VI)	5	2.5	7	0.91		
<b>Bio-sorbents</b>							
Sulfuric acid-treated peanut shell	Se(VI)	25–250	2	1.5	24–43	Temperature influenced the adsorption capacity (higher uptake occurred at elevated temperature). SEM and XRD studies revealed Se (IV) was reduced to elemental selenium. The technology is both eco-friendly and cost-effective.	[146,147]
Sulfuric acid-treated peanut rice husk	Se (IV)	25–250	2	1.5	26–41		

q<sub>e</sub>—adsorption capacity; C<sub>0</sub>—initial concentration.

## 5. Selenium Analytical Techniques

In recent years, there has been significant improvement in the analytical speciation techniques, fostering good separation and powerful detection limits [155]. However, quantitative evaluation of selenium in terms of speciation and total contaminant amount still presents some difficulties, mostly in reducing environments. Particularly, speciation analysis has two common challenges; both of which can be attributed to matrix interferences and the low concentration of contaminant species, i.e., below limit of quantification [37]. Table 2 presents various analytical methods used in selenium studies; this includes speciation and total concentration.

### 5.1. Spectrophotometric Methods

Spectrophotometric methods for Selenium analysis using—methylene blue and 2,3-diaminonaphthylene have been reported in literature [156–158]. However, studies have shown that some spectrophotometric methods lack sufficient sensitivity and selectivity for trace levels of selenium in environmental media [155]. In addition, some chemical reagents used in the spectrophotometric analysis are unstable and may impose toxicity risk [159].

Another spectrophotometric analysis technique reported in literature is the kinetic catalytic spectrophotometric method. This method was developed for the determination of selenium in water samples; the operation mechanism relies on the catalytic effect of selenium on the reaction of methylene blue with sodium sulfide [160]. Specifically, Chand and Prasad [161] used kinetic catalytic spectrophotometric method for Se (IV), Se (VI) and total inorganic selenium determination in water. Different authors have reported various detection limits. However, most studies on kinetic catalytic spectrophotometric methods gave a detection limit in the range of 0.3–15 µg/L [161–163]. Advantages of spectrophotometric methods encompass simplicity, easy to operate and cost-effectiveness.

### 5.2. Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) techniques have been extensively used for selenium analysis. There are three main configurations for this method [164]: (a) Electrothermal atomization absorption spectrometry (ETAAS) with direct sample injection in a graphite furnace, (b) hydride generation atomization absorption spectrometry (HG-AAS) with quartz tube atomization (HG-AAS) and (c) hydride generation atomization absorption spectrometry (HG-ETAAS), with in situ trapping in a graphite furnace. ETAAS can quantify selenium using an appropriate matrix modifier, such as nickel, with a low detection limit between 1–2 µg/L [155,165]. In comparison, HG-AAS and HG-ETAAS have the advantage of reduced chemical interferences but require more sample volumes than ETAAS. For studies involving Se (IV) reductant systems, HG-AAS has recently been applied to determine Se (IV) concentration. In general, the measurements were preceded by tests that show Se<sup>0</sup> was kinetically unable to develop hydrogen selenide by reaction with sodium borohydride [166,167].

### 5.3. Plasmic Spectrometric Methods

Plasmic spectrometric methods represent the latest instrumental techniques with more powerful excitation energy to detect and quantify selenium species. These methods involve the use of optical techniques which measure the results of the interaction between radiant energy and elements. Specifically, plasmic spectrometric methods comprises inductively coupled plasma—atomic emission spectrometry (ICP—AES), inductively coupled plasma—optical emission spectrometry (ICP—OES) and inductively coupled plasma—Mass spectrometry (ICP—MS) [37,155,168]. Figure 3 illustrates an overview of ICP—OES operating technique, as well as comparative advantages. Prominent among all is the sensitivity and low detection limit capacity of ICP, making it more suitable than ETAAS [37]. On the other hand, mass spectrometry takes advantage of sorting out charged gas molecules or ions based on their mass. The substance to be analyzed is vaporized and converted to

positive ions by bombardment with swift-moving electrons. ICP—MS has an excellent detection ability and can detect selenium concentration as low as 0.1 µg/L [155].

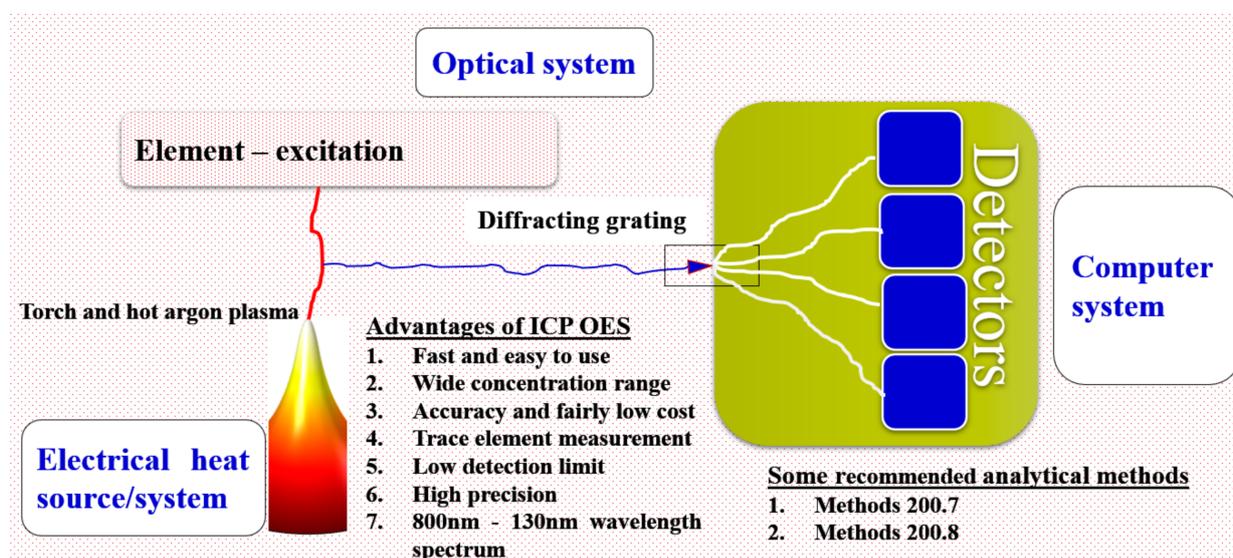


Figure 3. Schematic overview of ICP operation and the advantages for selenium analysis.

Several studies on selenium analysis have been based on ICP analytical techniques [76,169–172]. The compelling advantages of plasmic spectrometric methods include having more energy atomization sources, lower interelement interference, obtaining good spectra for many elements under the same excitation conditions and simultaneous detection [168]. However, the cost of experienced analysts and equipment, including maintenance, could be expensive.

#### 5.4. Chromatography Method of Analysis

In selenium speciation analysis, chromatography methods have been used extensively to separate selenium components in a mixture based on their relative affinity to partition between different phases. High-pressure liquid chromatography (HPLC) [172,173] and gas chromatography (GC) [174] are the most widely used techniques for identifying and determining various selenium species at a low level. HPLC is mostly used for non-volatile selenium species. Advance research on HPLC resulted in a new technology that uses sensitive and robust detectors such as HPLC coupled to ICP—MS instrument. Kolbl et al. [175] presented a review on the hyphenated technique HPLC—ICP—MS; this approach has been a good choice for selenium speciation analysis in many biological samples [37]. On the other hand, GC is a good fit for volatile organic selenium analysis, but some adaptation is required to use GC for inorganic selenium analysis [174].

#### 5.5. Other Methods

Some other techniques reported in the literature include the electroanalytical method. Trace amounts of Se (IV) can be effectively determined with electroanalytical techniques, but Se (VI) determination is only feasible after preliminary reduction to Se (IV) [176]. Compared to other instrumental methods discussed in the preceding sections, the advantage of this technique is the low cost of the equipment and selective analysis [37]. Atomic fluorescence spectroscopy (AFS) is another spectroscopic method that has been explored in the analysis of selenium species [164,177]. The high-performance capillary electrophoresis method of analysis has been used for organic and inorganic selenium compounds [65]. Others are neutron activation analysis (NAA) and fluorimetry techniques [155,178]. In general, there are some factors that may determine the preferred choice of analysis to be used. Some of these include low-cost, low detection capabilities, and multi-spectral detection.

**Table 2.** Examples of analytical techniques for selenium detection and quantification.

Analytical Techniques	Speciation	LOD ( $\mu\text{g/L}$ )	Samples Evaluated	Reference
Flow injection-electrothermal atomic absorption spectrometry (FI-ETAAS)	The total selenium concentration	-	Grape pomace	[179]
Vortex-assisted ionic liquid-based microextraction (VA-IL-DLLME)	The total selenium concentration	-	Food (ginger, wheat flour and garlic)	[180]
Inductively Coupled Plasma HPLC-ICP-MS	Se (IV)	0.3	Human waste	[172]
	Se (VI)	0.2		
	Organic Selenium	0.1		
Atomic Fluorescence Spectrometry Separation onto nano-sized $\text{TiO}_2$ colloid as sorbent; HG-AFS	Se (IV)	0.042	Environmental water	[181]
	Se (VI)	0.024		
HPLC-HG-AAS (anion-exchange column)	Se (IV)	2.4	Groundwater	[173]
	Se (VI)	18.6		
CE-HG-ICP-AES	Se (IV)	2.1	Tap and river water samples	[182]
	Se (VI)	2.3		
Ultrasound-assisted alkaline extraction and hydride generation atomic absorption spectrometry (HG AAS)	Se(IV)	-	Soil	[183]
Gas chromatography	Inorganic selenium	0.11	Environmental water	[174]
HPLC-ICP-MS	SeMet, SeCys, Se(IV), Se(VI)	-	Fish	[184]
High-resolution continuum source graphite tube atomic absorption spectrometry (HR-CS GF AAS)	The total selenium	-	Soil	[183]
	Se (IV)	0.05	Flue desulfurization residues (coal combustion)	[185]
HG-AFS	Se (VI)	0.06		
	Organic Selenium	0.06		

Limit of detection (LOD).

## 6. Selenium Resource Recovery

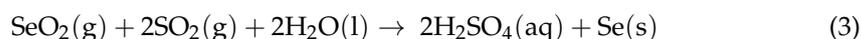
There are various known selenium-bearing minerals from which selenium is produced. However, selenium is a relatively rare and broadly dispersed element in nature and does not commonly exist alone. While some independent selenium minerals may be found, no deposits are ever extracted exclusively for selenium [186]. Globally, the average selenium content in the earth's crust is approximately 0.09 ppm [187,188]. It is obtained as a by-product of extraction of metals such as copper, iron, and lead; or captured from the sludge accumulated in factories of  $\text{H}_2\text{SO}_4$  [188–190]. Selenium recovery is primarily from the anode slimes of copper refineries. Bhappu [191] reported that the anode slimes from electrolytic copper refineries provide the source of most of the world selenium, and its production is centered at such refineries in the industrialized nations of the world.

There are various techniques for recovering selenium from minerals. Selenium recovery from ores that are rich in selenium is majorly through leaching and flotation techniques [192]. This process involves the use of cyanide and calcium oxychloride as a leaching agent. Selenium can be recovered from selenium-bearing minerals (eucairite:  $\text{CuAgSe}$ , clausthalite:  $\text{PbSe}$ ) by leaching techniques. This entails the use of calcium oxychloride to oxidize selenides to selenious acid, followed by the addition of sulfur dioxide as a reducing agent [192]. This method recovers approximately 95% of selenium from selenium minerals [192].

From copper anode slime, selenium can be recovered as a modification or combination of these fundamental methods: (i) smelting with soda ash, (ii) roasting with soda ash (iii) roasting with sulfuric acid [191]. These methods basically recover selenium from copper

refinery factories. Roasting is an industrial pyrometallurgical extraction and it includes oxidation, reduction, chlorination, sulphation, and pyrohydrolysis [192]. The choice of a roasting process used for selenium recovery is greatly influenced by the slime composition and its essential consideration for commercial selenium production. Recovery by roasting can be performed to produce selenite, selenate, and selenium dioxide. In this paper, sulphation roast recovery is discussed briefly.

In sulphation roasting recovery technology of selenium, sulfuric acid is used as an oxidant in the presence of oxygen to transform tetravalent oxides of selenium at roasting temperatures of 500–600 °C in a gas-fired furnace to remove selenium from slimes [193]. Selenium is volatilized as selenium dioxide and captured or collected in the scrubbers for recovery at the specified temperature. The scrubbing of the off-gases results in the complete recovery of the selenium from the gas stream [194]. Equation (3) below describes the process:



One advantage of this process is the reduction of selenious acid to elemental selenium by sulfur dioxide produced in the roasting process and regeneration of the sulphuric acid initially consumed in the roasting process [194]. One of the main challenges in selenium resource recovery is its dependence on refining electrolytic copper. The source of the by-product (selenium) is not sufficiently flexible to warrant a normal supply-demand balance [191]. Therefore, given the economic importance of selenium resources, advanced recovery techniques are needed for selenium production.

#### *Distribution of Selenium Resources*

Demographically, Canada, Japan, Belgium, and Germany are the largest production of selenium in the world [26]. Information reported in the US Bureau of Mines (USBM), the global selenium reserve is about  $1.3 \times 10^5$  tons, with approximately  $7.1 \times 10^4$  tons of proved reserves [194]. North America's reserves represent 52.7% of the total reserves while Asia, Africa, Europe, and Oceania account for 15.4%, 15.4%, 12.2%, and 4.4%, respectively [194,195]. Figure 4 shows selenium usage in some industries. This illustrates most of the applications of selenium resources.

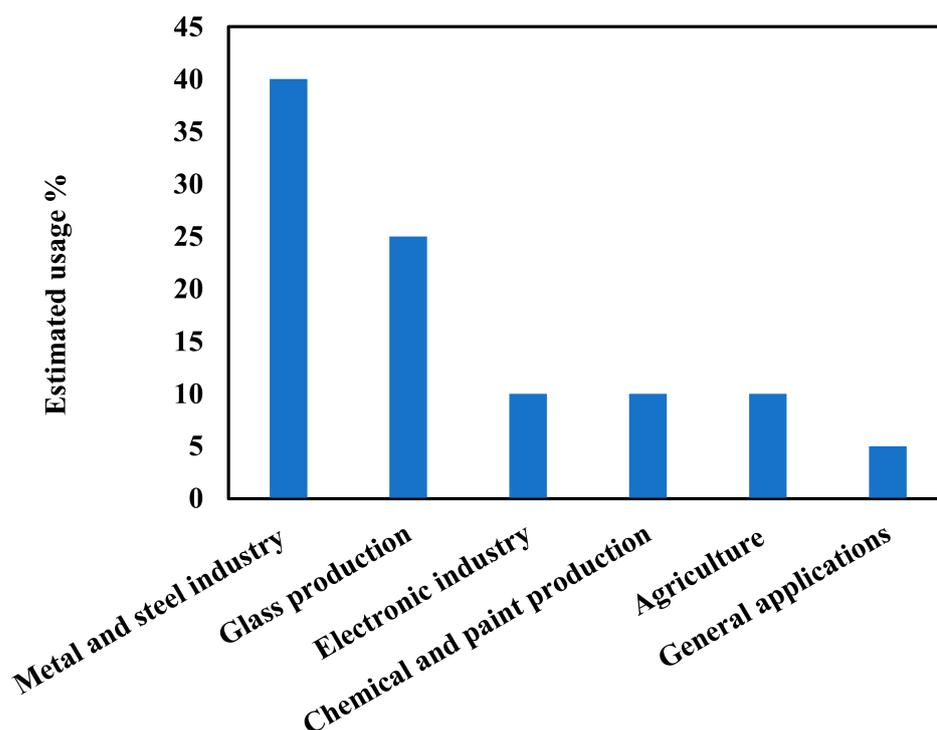


Figure 4. Selenium usages in some industries adapted from [26].

## 7. Knowledge Gaps and Conclusions

Key highlights of the main aspects that relate to selenium speciation in water, circulation in the environment, toxicity, analysis and remediation from wastewaters and industrial effluents were presented in this section. Selenium in low concentrations is a micronutrient, but prolonged exposure to higher concentrations can cause life-threatening diseases. The most effective option to keep humans health, animals and wildlife safe from selenium toxicity is the treatment of selenium to meet the acceptable limits. To achieve this objective various remediation strategies are being applied. Many of these methods are effective, but some are not cost-effective, others are yet to be developed into full-scale treatment technologies.

Among the techniques evaluated, adsorption and bioremediation are the most consistently used and most economical methods used for selenium treatment from an industrial perspective. Presented below are some of the knowledge gaps that need to be explored for further research in selenium treatment.

- i. pH effect is apparently a limiting factor that affects selenium treatment options; most of the studies evaluated showed that better adsorption performance occurs at acidic and slightly acidic conditions. Typical pH values for mining influenced and flue-gas-desulfurization wastewaters are acidic; hence pH is not a major adverse factor for adsorption technology in these wastewaters. For selenium contaminants in agricultural runoff (moderately alkaline), adsorption cannot be a suitable method without pretreatment and a promising adsorbent with a high affinity for adsorbate. pH adjustment can be costly, and hence should be carefully considered in the design of selenium adsorption process.
- ii. Ion exchange, coagulation, electrocoagulation, co-precipitation and chemical reduction techniques are widely-used selenium removal methods. These remediation techniques can reduce selenium significantly to a level below 5 µg/L in optimal conditions [149]. However, the cost involved in using these methods can affect their full-scale implementation to remediate selenium species from wastewaters.
- iii. Studies have recently demonstrated that biosorption and natural adsorbents can be applied to treat selenium species from wastewaters. Some of the benefits include low cost of raw material, good adsorption performance, and environmentally friendly. Therefore, it is a promising technique for selenium removal. However, most research related to selenium biosorption has primarily focused on laboratory batch equilibrium studies. There are two reasons for this, (a) unavailability of bulk quantity of biomass for full-scale application, and (b) batch operations at a laboratory scale can be easy to implement but difficult to implement in the field. Therefore, developing low-cost biosorbents for selenium treatment with high adsorption capacity is undoubtedly an area for further investigation.
- iv. Selenium contaminants coming from anthropogenic sources, especially mine-waters, generally contain elevated  $\text{SO}_4^{2-}$  concentrations derived from sulfide-mineral oxidation and high  $\text{NO}_3^-$  concentration from the blasting agent commonly used during mining activities. The influence of these ions and other competing oxyanions decreases adsorbent uptake capacity and impedes selenium removal efficiency. The practical application of adsorbents should be studied carefully on a case-specific basis to overcome the effects of oxyanion on selenium removal. Also, there are limited studies on the effects of competing cations on selenium removal compared to anions.
- v. Some selenium removal techniques have some limitations, such as the generation of a large volume of sludge. From an environmental perspective, the post-treatment sludges and by-products might be a further potential source for secondary selenium contamination. The use of toxic chemicals and the amount of sludge generated can further limit the application of selenium removal technology. Hence, research that can minimize selenium post-treatment sludge and maximize removal efficiency is desirable.

- vi. Organic selenium contaminants such as SeMet and SeCys can be a threat to public health and wildlife. This is because organoselenium tend to bioaccumulate within the food web. However, limited studies have been published on organic selenium removal strategies, analysis and sample prep work. It's essential to have more investigations of organic selenium removal from industrial effluents, to explore the effects of pH, initial adsorbate concentration, removal mechanisms, and kinetics. Studies with low adsorbate concentrations are recommended to mimic organic selenium concentrations in wastewaters.

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