Review article

Flue gas desulfurization effluents: An unexploited selenium resource

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ABSTRACT

With the advent of the Industrial Revolution, the natural cycle of selenium (Se) Se has been altered, thus leading to cases of severe environmental degradation. Nowadays, an important share of the global energy is generated by coal combustion. During this process, Se is concentrated in Flue Gas Desulfurization (FGD) wastewaters. FGD effluents can be treated by bioremediation, using bacterial metabolism to convert soluble and toxic forms of Se into elemental Se (nano)particles. Se and bacteria are intimately linked in a complex interplay since the element serves nutritional and metabolic energy generation functions, in addition to behaving as a powerful toxicant. In this article we explore the coupling of FGD treatment and resource recovery in the framework of circular economy. This approach reduces the burden of Se pollution for aquatic ecosystems, while also providing a way to recover a valuable resource, generating profit and offsetting the treatment costs.

1. Introduction

Industrial Revolution has interfered with the natural cycles of numerous chemical elements, including selenium (Se) [1]. A number of environmental incidents caused by Se pollution were documented in North America, the most severe ones leading to the virtual elimination of various ecological groups such as fish and aquatic birds [2]. The main toxicological mechanisms of selenium poisoning are related to sulfur substitution leading to dysfunctional biomolecules and to the production of reactive oxygen species such as hydroxyl radical ($\cdot$OH), hydrogen peroxide (H_2O_2), and superoxide radical ($\cdot O_2^-$) [3]. Selenium pollution is associated with industrial activities such as energy production based on fossil fuel combustion, metal and oil refining, and agricultural practices. Among them, coal-fired power generation is one of the major Se contributors to the environment.

Currently, coal is an important fuel used to generate energy worldwide [4]. The European Union (EU) generates a quarter of its power by burning coal (http://www.coalmap.eu/#/coal-fleet/30plus). In the EU, coal-fired power generation is unevenly distributed with countries using low amounts of coal (e.g. France), while others heavily relying on this fossil resource (e.g. Germany, ~40%, Poland, ~70%) (http://www.coalmap.eu/#/coal-fleet/30plus). Other big coal consumers for energy purposes are China (~62%), India (~57%), and South Africa (~70%) [4].

Coal-fired power plants are regarded as big polluters; pulverized coal combustion leads to the generation of coal combustion by-products, mostly ashes and gaseous pollutants. However, increased

pressure exerted by the public, various environmental protection groups and politicians has led to a gradual reduction of pollution incidence associated with coal combustion. Modern coal-fired stations contain a number of pollution control devices aiming at reducing the pollution load. Once coal is burned in the boiler to produce energy used to generate superheated steam, an important component of the power station is devoted to cleaning up the flue gas [5]. The coarser fraction of ashes, bottom ash or slag, is removed from the bottom of the boiler, whereas the finest particles, fly ashes, are separated using filter bags or electrostatic precipitators (ESP). Gaseous pollutants such as NO_x and SO_2 are removed using Selective Catalytic Reduction (SCR) and Flue Gas Desulfurization (FGD) systems, respectively (Fig. 1). The most popular FGD system is wet FGD using a slurry of lime/limestone that is sprayed in the flue gas, resulting in the production of solid and aqueous by-products [6]: gypsum slurry (aqueous phase + gypsum sludge), FGD-gypsum, and filtered water. Gypsum slurry is the total fraction of the slurries (solid + water), while the term aqueous phase of gypsum is employed for the water fraction of the total slurry. Gypsum sludge is referred to the solid fraction of gypsum slurry, and FGD-gypsum is the solid end-product after filtration process. Filtered water is the resulting water from gypsum slurry filtration [6–8].

Depending on the characteristics and properties of the by-products and the availability and resources of the power plant, the fate of FGD-gypsum and filtered water can be the disposal in landfills and water treatment or recycling, respectively [6,9]. FGD effluents have a complex matrix containing anions (e.g. sulfate, selenate, carbonate, chloride), major cations (e.g. Ca, Mg), and a wide spectrum of metals
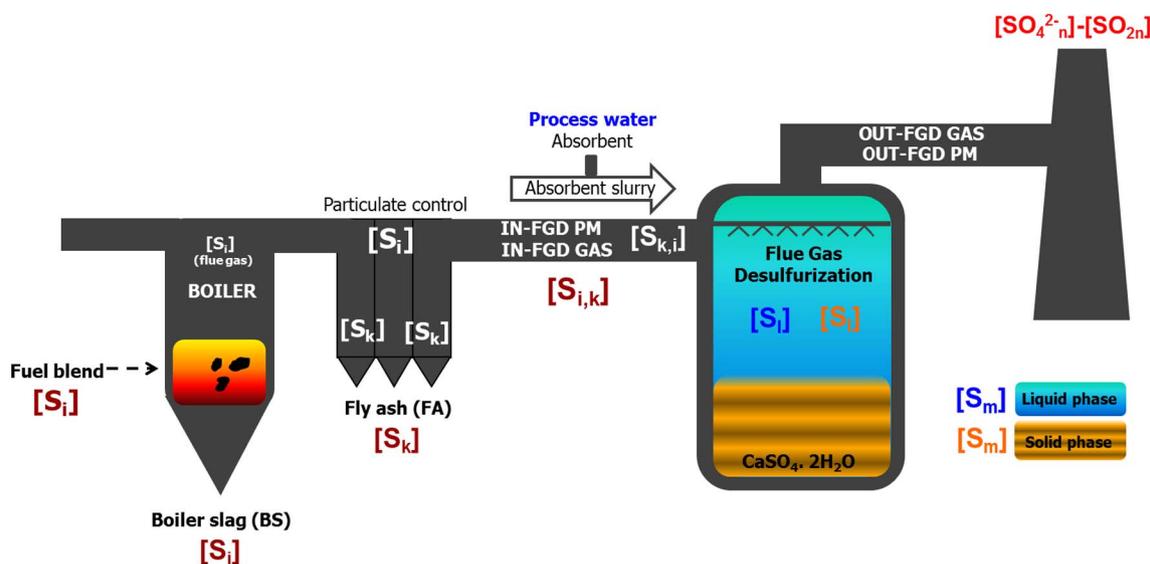
Fig. 1. Diagram of a coal-fired power plant equipped with a flue gas desulfurization (FGD) system. Legend: S_i to S_m refers to the partitioning of a given element in the *in* and *outgoing* streams during PCC-FGD process.

(e.g. Cd, Cr, Hg, Ni, V, Zn) [10–12]. It is worth mentioning that Se displays several valence states ($+VI$, $+IV$, 0, $-II$) with contrasting water solubility and toxicology profiles. FGD effluents contain Se mainly ($> 90\%$) in its most oxidized state (selenate, $+VI$, SeO_4^{2-}), which has high water solubility and is bioavailable [12,13]. FGD effluents are currently a big challenge for power industry because of the following characteristics: i) are generated in large volumes, ii) have a complex matrix, and iii) the discharge limits for Se are low and difficult to achieve using most treatment systems. For a detailed presentation of the main Se treatment strategies, the reader is referred to Tan et al. [10] and Staicu et al. [10–14].

An interesting treatment approach using microbial inocula (bioremediation) is gaining in popularity worldwide. A recent development of this approach seeks to couple wastewater treatment with resource recovery [15]. Bioremediation of Se-laden effluents is founded on the microbial conversion of Se oxyanions, selenate and selenite (Se, $+IV$, SeO_3^{2-}), into solid elemental Se, Se^0, which is less toxic owing to its limited bioavailability. Currently, Se^0 resulted from bioremediation is not considered as a potential resource, although it has high recovery potential and Se is a critical element with multiple industrial and domestic applications.

In this review article, we explore the production of FGD effluents containing high levels of Se and link the generation of these effluents with bioremediation in an attempt to achieve both waste treatment and resource recovery. Firstly, the current situation of coal combustion for energy production and the generation of FGD effluents are presented and discussed. Secondly, the fundamentals of the microbial conversion of Se and the biotechnological applications including bioremediation are reviewed. Finally, the last part unifies the FGD generation with the biological treatment, coupled with Se^0 recovery in the framework of the circular economy strategy.

2. Power generation from coal

2.1. Status of coal power generation

Coal plays an essential role in our global energy scheme for power generation. However, coal is currently a target to comply with the Paris climate agreement for both countries and companies. In 2016, world coal production fell by 6.2% (231 million tonnes of oil equivalent (mtoe)), the largest decline on record. US production fell by 19% or 85 mtoe, while China's production fell by 7.9% or 140 mtoe [4].

In 2016, coal's share of global primary energy consumption also fell to 28%, the lowest share since 2004 [4]. The largest declines in coal consumption were seen in the US (-8.8% fall). Chinese coal consumption also declined (-1.6%) for the third consecutive year, which led China to resuming its position as the world's largest importer of coal [4]. In the UK, global coal prices were amplified by the increase in the UK's Carbon Price Floor in 2015, which resulted in the UK's last three underground coal mines closing, consumption falling back to where it was roughly 200 years ago around the time of the Industrial Revolution [4].

However, coal is the world's most abundant energy resource. There are 1,139,331 million tonnes of proven coal reserves worldwide, sufficient to meet 153 years of global production. Total proven coal reserves are shown for anthracite and bituminous (including brown coal) and sub-bituminous and lignite. In comparison, proven oil and natural gas reserves are equivalent to around 50 and 53 years, respectively, at 2016 production levels [16]. Therefore, despite the decline in coal production and consumption, coal is and will be a reliable source for power generation.

2.2. Coal combustion

Pulverized coal combustion (PCC) is the most widely used technology for coal power generation. In this process, coal is milled, pulverized, and injected in the boiler with air to allow combustion. Combustion takes place at temperatures from 1300 to 1700 °C, depending largely on coal rank [17]. The heat generated is used to produce a steam of high pressure (25–30 bars) and temperature to power high and medium turbines that are connected to a generator which produces electric energy (Fig. 1).

Pulverized coal combustion leads to the generation of coal combustion by-products, mostly ashes. The coarser fraction of ashes, bottom ash or slag, is removed from the bottom of the boiler, whereas the finest particles, or fly ashes, are retained from the flue gas stream by the particulate controls, usually Electrostatic Precipitators (ESP) or Fabric Filters (FF). Despite the high efficiency of the ESPs and FFs ($> 99\%$) [18,19], a small fraction of fly ashes escapes from the controls and reaches the FGD system (Fig. 1).

The conventional process of coal combustion can be modified to improve the energetic efficiency of the process and reduce the environmental impacts. The *Fluidized Bed Combustion* (FBC) allows a better use of the fuel and a better transference of the heat for power

generation. The basis for a FBC system and the main difference with respect to the conventional PCC is the formation of a bed of an inert material, such as sand or limestone, through which air is blown from below at sufficient velocity to suspend particles. The melting of the bed is not reached by limiting combustion temperature to 850–950 °C. Due to the lower temperatures and the longer residence time with respect to PCC, the FBC produces less NO_x emissions and reduces the SO_2 emissions when limestone is added to coal or to the fluidized bed [18]. There are three different types of FBC available: the *Circulating FBC* (CFBC)**,** the *Bubbling FBC* (BFBC), and *Pressurized FBC* (PFBC) [23].

Another option for coal power generation is *co-combustion* or *co-firing* which entails the simultaneous combustion of two or more fuels in the same power plant in order to produce one or more energy carriers [20]. The worldwide electricity demand and the environmental regulations led to a market increase of the use of the co-combustion matters such as petroleum coke, sewage sludge, and biomass in coal power generation.

Oxy-fuel combustion is a promising technology that may greatly contribute to the reduction of carbon dioxide (CO_2) emissions from power plants. The principle of oxy-fuel combustion is to increase the partial pressure of CO_2 in the flue gas in order to make its sequestration and compression easier and more cost effective [21]. This can be achieved by burning a fuel with pure oxygen instead of air as a primary oxidant, which results in higher flame temperatures. For this reason, the mixture is diluted with a portion of the resulting flue gas composed primarily of CO_2. Fundamentally, due to the variation in the oxidant, and consequently in the in-furnace gas environment (as compared to conventional air-fired combustion), oxy-fuel combustion affects the combustion process of pulverized coal as well as related processes such as heat transfer [22]. As a result, most studies and research projects have focused on fundamental scientific and engineering issues (e.g. ignition, flame stability, heat transfer, recycled flue gas ratio, and combustion characteristics).

3. Coal-fired emissions and abatement technologies: SO_2, PM, NOx, and CO_2

Coal-fired power plants are one of the most significant sources of air pollutants (SOx, NOx, Particulate Matter (PM), and trace pollutants). Emissions from large industrial facilities are currently regulated by the TEC directives, such as the Integrated Pollution Prevention and Control (IPPC, 1996/61/EC) later replaced by 2008/1/EC, and Large Combustion Plants Directives (LCP, 2001/80/EC), which implement Emission Limit Values (ELVs) for SOx, NOx, and PM (among other pollutants) from large combustion plants (> 50 MW).

Most widespread strategies for controlling SOx emissions are based on the *(1)* use of low sulfur (S) fuel, *(2)* reduction or removal of S from the feed fuel, *(3)* use of appropriate combustion technologies, and *(4)* emissions control technologies based on FGD technologies [23,24].

3.1. Flue gas desulfurization (FGD) systems

The term flue gas desulfurization (FGD) system has traditionally referred to wet scrubbers that remove SO_2 emissions from large electric utility boilers. The FGD systems emerged in the industrial field of the coal-fired power plants and on some industrial processes in the early 1970s in US and Japan and expanded rapidly in the 1980s [25] in Europe. In the FGD process, the flue gas interacts with an absorbent medium in either an absorber or a scrubber vessel to produce high solid S slurry.

US EPA [26] classifies FGD systems as non-regenerable and regenerable processes based on whether the S compounds are separated from the absorbent as a by-product or discarded along with the absorbent as a waste product; whereas the Clarke and Sloss (1992) [28] classifies the FGD systems as regenerable and non-regenerable and subdivides the non-regenerable category into wet scrubber and spray dry systems. Other authors [27] propose the following four categories for the FGD systems: wet scrubbers, spray dry scrubbers, sorbent injection, and regenerable processes; and each major category is divided into several subcategories depending on the specific chemical reactions and flow conditions. Independently of the classification, most of specialized literature [19,28–30] agrees on the fact that the wet limestone FGD system is the FGD process most widely used because of its high desulfurization performance and low operating cost.

3.1.1. Wet FGD systems

The wet scrubbers produce a wet product that might be regenerable or non-regenerable. In the regenerable processes [28] the sorbent reagent follows a regeneration step which gives rise to SO_2, H_2SO_4, or S^0, and produces a sludge that may be sold to partially offset the cost of operating the FGD system; whereas in the non-regenerable processes S permanently bounds with the sorbent to form a new product that must be disposed of properly or used in specific applications.

Commercial power generation wet FGD system uses limestone ($CaCO_3$), slaked lime ($Ca(OH)_2$), or a mixture of slaked lime and alkaline (FA) sorbents, which react with SO_2 to form a Ca-S compound [31].

3.1.1.1. Wet limestone FGD system. The wet limestone FGD process (non-regenerable) is based on complex acid-base reactions that take place under forced or natural oxidation conditions. According to the reactions of the desulfurization process, two regions can be differentiated in most of the scrubbers: the gas-to-liquid contact zone and the reaction tank. In forced oxidation, the following overall reaction in the gas-to-liquid contact zone with a pH range from 5 to 6 is as follows:

$$CaCO_{3(s)} + SO_{2(g)} + 2H_2O_{(aq)} \rightarrow CaSO_3. 2H_2O_{(aq)} + CO_{2(g)} \qquad (R1)$$

Reactions initiated in the gas-to-liquid contact zone are completed in the reaction tank. The reaction tank provides an adequate residence time for the complete oxidation of the SO_3^{2-} to SO_4^{2-}.

At a lower pH range (4.5–5.5), the chemical reaction is different [32]. The primary product of the neutralization by limestone is Ca$(HSO_3)_2$:

$$CaCO_{3(s)} + 2SO_{2(g)} + H_2 O \leftrightarrow Ca(HSO_3)_{2(aq)} + CO_{2(aq)} + H_2O \qquad (R2)$$

Also in the reaction tank, the partly spent slurry is mixed with fresh limestone slurry to replace the consumed $CaCO_3$ and the acidic slurry is neutralized in the reaction tank. The reaction tank provides an adequate residence time for the complete oxidation of the SO_3^{2-} to SO_4^{2-}. As shown below, CO_2 is produced which is later desorbed [32]:

$$CaCO_{3(s)} + H_2SO_{4(aq)} + H_2 O \rightarrow CaSO_4. 2H_2O_{(s)} + CO_{2(g)} \qquad (R3)$$

Depending on the SO_2 concentrations and the excess air in the flue gas, as well as on the pH of limestone slurry, some systems may be operated in the natural oxidation mode. However, for most applications it is beneficial to control oxidation [23]. In natural oxidation mode, the main product is a mixture 50–60% of $CaSO_3.\frac{1}{2} H_2O$ and $CaSO_4.2H_2O$ in a sludge form which is difficult to dewater, whereas in forced oxidation mode, the final end-product is 90% $CaSO_4.2H_2O$ [23].

4. Partitioning of selenium in PCC-FGD

The world average Se content in hard coals is 1.6 ± 0.1 ppm, while Se content in brown coals is 1.0 ± 0.15 ppm [33]. On ash basis, however, these contents are greatly increased to 9.9 ± 0.7 ppm for hard coals and to 7.6 ± 0.6 ppm for brown coals. Besides, there are two genetic types of the Se-accumulations in coal: "reducing" and "oxidizing". In reducing accumulations, Se is enriched in high sulfur coals, concentrating in sulfide phases. These accumulations are syngenetic (formed contemporaneously with the parent rock and enclosed by it) and they may be epigenetic (formed later than the enclosing rocks) only if there are abundant hydrothermal sulfides of Fe, Cu, As, Pb. In

"oxidizing" accumulations, Se is enriched in the bed oxidation zones where coals are (or were) located in the areas with arid climate and enhanced Se content in water. Selenium concentrates in coal as a reduction or sorption geochemical barrier, probably, mostly as Se^0 in oxidized organic matter and partly pyrite. These Se accumulations are mostly epigenetic [33]. It is noteworthy to mention that the first documented case of Se deleterious impact on an aquatic ecosystem occurred as a results of coal ash deposition in the vicinity of Lake Belews (North Carolina). The gradual leaching of Se from this waste resulted in the collapse of the ecosystem, 19 out of 20 local fish species being eliminated [34].

4.1. Behavior and partition of selenium in PCC

During coal combustion, Se is volatilized to elemental Se^0 and SeO_2. In the boiler, gaseous SeO_2 can be chemisorbed on the FA surface and/or remain in the gas phase. The quantity of Se retained or captured in fly ashes may vary from coal to coal, depending on the characteristics of the ashes and process conditions. The chemisorption of SeO_2 on FAs depends on the temperature and gas composition as well as on the FA chemistry [20]. It has been observed that Se might react with Ca and form stable compound such as calcium selenite ($CaSeO_3$) during post combustion environment.

FAs are generally captured in particulate control devices with a very high efficiency. However, a small fraction may escape from the control and reach the FGD system [7–9]. In addition, the occurrence of harmful acidic gases during PCC other than SO_2, such as HCl may play a significant role in the partitioning, speciation, and fate of Se. During combustion, coal chlorine (Cl) is released primarily as HCl in the high temperature zone of a boiler [35]. As the combustion gases cool (430–475 °C), a proportion of HCl can partially be oxidized to Cl_2 in the presence of O_2 and H_2O, but the presence of SO_2 can inhibit the formation of Cl_2 by the production of HCl $_{(g)}$. Although SeO_2 is released in a lower concentration compared to that of SO_2 during coal combustion, SeO_2 can also inhibit the formation of Cl_2 in a similar manner as $SO_{2(g)}$:

$$Cl_{2(g)} + SeO_{2(g)} + H_2O_{(g)} \leftrightarrow 2HCl_{(g)} + SeO_{3(g)} \tag{R4}$$
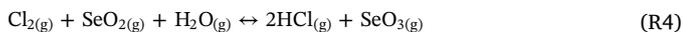
Gaseous SeO_3 may then be chemisorbed on FA or it can also remain in gas phase in the incoming flue gas to the FGD.

4.2. Behavior and partition of selenium in wet limestone FGD

4.2.1. Selenium chemistry in wet limestone FGDs

Once in the FGD, Se chemisorbed in FAs (e.g. as SeO_3^{2-}) may be dissolved in the aqueous phase of the slurry to form an array of Se-aqueous complexes and/or solid species or retained in the gypsum sludge [5] (Fig. 2). However, if SeO_2 remains in the gas phase, which

will depend on the flue gas temperature, a proportion of gaseous SeO_2 can either react with moisture in flue gas to form H_2SeO_3 and subsequently condense in the scrubber as the flue gas undergoes a rapid quench to a temperature between 50 and 60 °C [35], or diffuse through the gas to the aqueous phase as SeO_2 where it will dissolve to form selenous acid (H_2SeO_3) [5]. In wet limestone FGDs, with oxidation-reduction potential (ORP) values $\leq 300\,mV$, Se will predominantly exist as selenite, SeO_3^{2-}. In contrast, with ORP values $\geq 300\,mV$, Se can be oxidized to SeO_4^{2-} [22,36]. In 2011, Petrov et al. [37] found 13 different Se species in FGD waters and conclusively identified only two of them: selenocyanate ($SeCN^-$) and selenosulfate ($SeSO_3^{2-}$). This fact indicates that Se chemistry in FGD waters is more than the interconversion between SeO_3^{2-} and SeO_4^{2}.

Besides SeO_3^{2-} and SeO_4^{2-}, Se can form a complex array of chemical aqueous complexes whose formation also depends on the oxidation air rate contribution to the ORP conditions, as well as the presence and concentration of redox-active species in FGD scrubbers (Fig. 2). High ORP conditions, often favoured to maintain SO_2 removal performance of FGD scrubbers, promote the formation of dithionate ($S_2O_6^{2-}$), peroxydisulfate ($S_2O_8^{2-}$), peroxymonosulfate (HSO_5^-), and/or hypochlorite (OCl^-) which tend to interfere with most Se removal technologies [38]. These species are considered potential oxidizing agents involved in most mechanisms of SeO_3^{2-} oxidation in FGDs (Fig. 2).

Akiho et al. [39] in a study on the effect of oxidizing agents (H_2O_2, $S_2O_8^{2-}$, ClO^-) on SeO_4^{2-} formation in a wet FGD indicated that the sulfate ion radical (SO_4^-) which resulted from decomposition of $S_2O_8^{2-}$ ion is the predominant oxidizing agent that oxidises SeO_3^{2-} to SeO_4^{2-}. However, with Mn^{2+} addition, $S_2O_8^{2-}$ oxidises Mn^{2+} to MnO_2, which captures some dissolved SeO_3^{2-}. In an earlier study (Akiho et al., 2010), authors found that with no additives, the concentration of $S_2O_8^{2-}$ decreased progressively irrespective of the Se oxidation reaction.

An extensive study by the Electric Power Research Institute (EPRI) [38] on the Se speciation and management in wet FGD systems indicated that solid-phase manganese [Mn(IV)] catalytically oxidises SeO_3^{2-} to SeO_4^{2-} under moderate to high ORP conditions. These results are in agreement with those reported by Searcy et al. [40]. These authors indicated that conditions that produce solid phase Mn also promote SeO_3^{2-} oxidation to SeO_4^{2-}, but conditions that favour dissolved Mn (excluding Mn species in high oxidation states) do not favour SeO_4^{2-} formation.

It has also been found that Se may form a number of analogous compounds to those of sulfur, as well as interact with polyoxosulfur anions to form Se-S aqueous complexes [5] because of the similar chemistries between Se and S. Sulfite (SO_3^{2-}), trithionate (($SO_3)_2^{2-}$) and thiosulfate (($S_2O_3)_2^{2-}$) tend to form Se complex ions such as selenosulfate ($SeSO_3^{2-}$), selenotrithionate ($Se(SO_3)_2^{2-}$) and

$$H_2SeO_{3(aq)} + 4S_2O_3^{2-}{}_{(aq)} + 4H^+ \leftrightarrow Se(S_2O_3)_2^{2-}{}_{(aq)} + S_4O_6^{2-}{}_{(aq)} + 3H_2O$$
$$HSeO_3^-{}_{(aq)} + 3HSO_3^-{}_{(aq)} \leftrightarrow Se(SO_3)_2^{2-}{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H_2O$$

Polyoxosulfur donors

$$SeO_3^{2-}{}_{(aq)} + 2SO_4^-{}_{(aq)} + H_2O \leftrightarrow SeO_4^{2-}{}_{(aq)} + 2SO_4^-{}_{(aq)} + 2H^+$$
$$SeO_3^{2-}{}_{(aq)} + OCl^-{}_{(aq)} \leftrightarrow SeO_4^{2-}{}_{(aq)} + Cl^-{}_{(aq)}$$

Oxidizing agents

ORP values $\geq 300\,mV$

$$SeO_{2(g)} + 2HCN_{(g)} \leftrightarrow SeCN_2 + H_2O$$
$$SeCN_2 + (S_2O_3)_2^{2-}{}_{(aq)} \leftrightarrow 2SeCN^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

HCN/sulfur donors
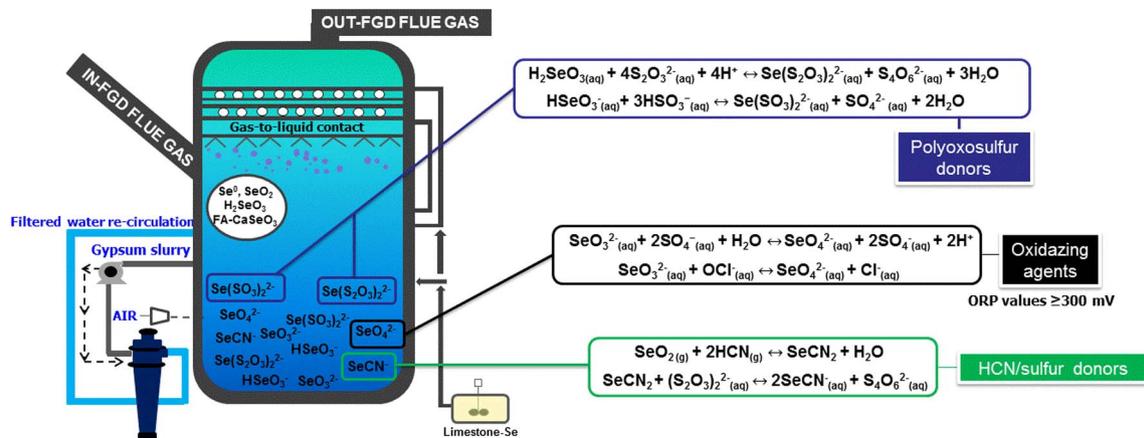
Fig. 2. Selenium chemistry in wet limestone FGD systems.

selenopentathionate $(Se(S_2O_3)_2^{2-})$ increasing the concentration of dissolved Se in untreated FGD waters (Fig. 2). While the formation of selenosulfate can be considered the result of the dissolution and reaction of elemental selenium with sulfite [41] in the aqueous phase of the FGD slurry, the substitution of sulfur by Se in selenotrithionate and selenopentathionate anions may give rise to array of Se-S stable compounds and/or isomers whose identification can be a challenge because of their complex structures.

Selenocyanate $(SeCN^-)$ has also been identified in FGD waters. The formation of selenocyanate $(SeCN^-)$ could be the result of the reaction between Se^0 and free cyanide (CN^-), as is observed in other types of industrial process waters, e.g., in gold mining operations, but there are no conclusive results. Analytical results reported by Petrov et al. [37] indicated that a fraction of the initially produced HCN reacts with Se species (possibly Se^0), either in the flue gas or in the scrubber, to form selenocyanate by currently unknown mechanisms. Córdoba (2017) [5] proposed two mechanisms on the formation of $SeCN^-$ aqueous complexes by gas- and aqueous-phase reactions. In the first mechanism, the HCN formed as an intermediate product in coal combustion would react with $SeO_{2(g)}$ to give $(SeCN)_2$ in FGDs. In the FGD, $(SeCN)_2$ may then oxidize thiosulfate ion $(S_2O_3^{2-})$ to tetrathionate ion $(S_4O_6^{2-})$ in the FGD scrubber giving $2SeCN^-$:

$$(SeCN)_{2(aq)} + S_2O_{3(aq)}^{2-} \leftrightarrow 2SeCN_{(aq)}^- + S_4O_{6(aq)}^{2-} \qquad (R5)$$
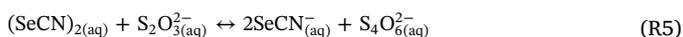
A second mechanism for $SeCN^-$ formation in the FGD scrubber could occur as a consequence of the reaction between H_2SeO_3 and thiocyanic acid (HSCN) to give selenium dithiocynate $(Se(SCN)_2)$. The oxidation of thiocyanic acid by H_2SeO_3 has been shown to take place in an analogous way as that found for H_2SeO_3 oxidation of most thiols and thiolates generating the corresponding selenotrisulfide and disulfide products [42]. Solid selenium dithiocyanate contains isolated Se(SCN), molecules with S-bonding to Se and a cis arrangement of the CN groups. $Se(SCN)_2$ may then decompose to give $SeCN^-$.

4.3. Partitioning of selenium in the FGD effluents

4.3.1. FGD effluents

The FGD process at coal-fired power plants entails the production of solid and aqueous by-products, FGD-gypsum and filtered water (effluent) from gypsum slurry filtration, respectively [6]. Depending on the characteristics and properties of the by-products and the availability and resources of the power plant, the fate of FGD-gypsum and filtered water can be the disposal in landfills and water treatment or recycling, respectively [6,9].

Filtered water, the effluent produced as a result of the gypsum slurry filtration, may act as retention sinks for some metals as a result of partial or total dissolution processes, the efficiency of which largely depends on chemical properties such as the pH and temperature of the solvent and/or the solubility constant of the specific element, among other parameters [9]. In the FGD systems, under operational conditions of water re-circulation, inorganic trace pollutants initially in sub-saturation in FGD waters may reach equilibrium and a subsequent saturation in the water stream after a number of water re-circulations in the scrubber. The gradual increase in the concentration of inorganic trace pollutants from the sub-saturation to equilibrium and/or saturation because of continuous water re-circulation in the scrubber, accounts for enriched inorganic trace pollutants in the re-circulated water [6]. This process may increase the concentration of trace pollutants in re-circulated waters up to very high levels compared with that of the original input water, which could result in environmental and/or technical problems, especially if the re-circulation of the water streams is interrupted and/or a water treatment is necessary for hypothetical and eventual discharges to the environment.

FGD-gypsum is a synthetic solid by-product obtained by the absorption of SO_2 in the absorbent slurry [43]. The properties of FGD-gypsum should be at least comparable to that of natural gypsum, since stringent specifications on the properties of the gypsum used for building purposes are required. In order to obtain high-quality FGD-gypsum from flue gas desulfurization, the FGD process must attain *(1)* a high efficiency of particulate controls; *(2)* causing a low Cl^- and F^- in FGD-gypsum; *(3)* a high efficiency of the forced oxidation process to oxidize the $CaSO_3.2H_2O$ and/or $Ca(HSO_3)_2$ to $CaSO_4.2H_2O$; *(4)* using a high-purity limestone to reduce FGD-gypsum impurities; and *(5)* obtaining a high $CaCO_3$ to $CaSO_4.2H_2O$ conversion efficiency [23].

According to new Smithers Apex study [44], the world output of by-product gypsum has now topped 30 million tonnes annually. This represents 8.5% of a global market at 350 million tonnes in 2016, with an overall value of $2.1 billion. The study demonstrates how worldwide demand for all gypsum grades will grow at 9.6% year-on-year for 2016–2026, to yield a total demand of 531 million tonnes in 2026.

In this regard, China already dominates the world gypsum supply market with a network of mines and strong local demand from the construction and other industries. In 2014, raw production in China stood at around 132,000 tonnes – or 53.6% of global output and the annual gypsum production is predicted to reach 90 million tonnes in 2020 [44], resulting in large potential profits through the responsible reutilization of this material. Additionally, in the coming years, the Chinese air quality improvement programme features the installation of 300 FGD units, which will allow China to overtake the US in terms of installed FGD capacity. Therefore, large amounts of FGD effluents have been and will be generated.

4.3.2. Partitioning of selenium in the FGD effluents

Most of specialized literature [7–8,29,46] reports that most of Se in FGD systems is removed in the aqueous effluent (filtered water) and FGD-gypsum and only a fraction of Se remains in the flue gas.

The high concentration of major, minor, and trace elements in the aqueous phase of the gypsum slurries and filtered waters from two coal-fired power plants, prompted a detailed study of the enrichment of inorganic trace pollutants in re-circulated water streams [6]. According to this study, the enrichment of inorganic trace pollutants, such as Se, because of continuous water re-circulation in the scrubber was promoted by the operational conditions affecting the wet limestone FGD-system. Results demonstrated that the emission of Se particles and droplets from gypsum slurry by the OUT-FGD gas was the most important consequence of the high enrichment of inorganic trace pollutants in the re-circulated waters [6,9]. Álvarez-Ayuso [46] in a study at a coal-fired power plant equipped with a wet limestone FGD indicated that Se was mostly partitioned in the FGD-gypsum with values comprised in the range 90–99%. Cheng et al. [47] reported removal efficiencies by a wet FGD system only 30% of Se. Approximately 30% of Se removed by the FGD was associated with FGD-gypsum; and less than 5% of Se was emitted into the atmosphere.

As mentioned above, Se forms a complex array of chemical aqueous complexes in FGD wastewaters whose formation depends on the oxidation air rate contribution to the ORP conditions as well as the presence and concentration of redox-active species in FGD scrubbers. In addition, Se may form a number of analogous compounds to those of sulfur [48] as well as interact with polyoxosulfur anions to form Se-S aqueous complexes [5] because of the similar chemistries between Se and S. Some of the Se-S aqueous complexes may give rise to array of Se-S stable compounds and/or isomers whose identification can be a challenge because of their complex structures. The retention of Se in FGD-gypsum, on the other hand, has been attributed to the similar structures of gypsum and calcium selenate di-hydrate $(CaSeO_4.2H_2O)$. These solid species are iso-morphous and their lattice constant are very similar [48,49] showing that SeO_4^{2-} can substitute for SO_4^{2-} in the gypsum structure the retention of Se in FGD-gypsum [50,51]. Since FGD effluents, filtered water and FGD-gypsum contain relatively high amounts of Se, these by-products from coal power generation may be considered as valuable resource of Se to be exploited. It is noteworthy

to mention that Se is commonly present in minerals as a trace element [52]. Currently, Se is produced industrially as a by-product of copper and lead refining. Apart from FGD effluents which typically contain Se in the low mg L^{-1} levels, seleniferous soils (> 0.5 mg Se kg^{-1}) are the only potential source of this element of comparable abundance [53]. However, the recovery of Se from soils is a challenging task, the only feasible method of extraction being the biofortification of various food crops or phytoremediation [54].

5. Biological treatment of FGD effluents

5.1. Microbial production of Se^0

Over the course of evolution, bacteria have developed an intricate scheme of recycling and reusing chemical elements as they provide a wide array of basic functions for homeostasis [55]. Bacteria contribute significantly to the natural cycling of Se and almost all valence state transformations undergone by this element were shown to be catalyzed by bacterial metabolism [56]. Furthermore, Se and bacteria are intimately linked as the element serves both nutritional and energy generation functions. A common denominator in the cycle of Se is Se^0 that is generated through dissimilatory (cellular energy generation) and detoxification processes [57,58].

Se respiration in bacteria has been documented for the first time at the end of 1980's in *Thaurea selenatis*, a gram-negative betaproteo-bacterium [59]. *T. selenatis* generates energy in the form of ATP by coupling the reduction of selenate to selenite with the oxidation of acetate to CO_2 and intracellular polyhydroxybutyrate (PHB) (R6). Later on, the first selenate reductase, *SerABC*, was isolated from *T. selenatis* and fully characterized [60]. Apart from *T. selenatis*, other Se respirers and a handful of selenate reductases have been described [56]. Fig. 3(a) presents the anaerobic respiration of Se in gram-negative bacteria. After entering the cell, selenate is enzymatically converted to selenite by a specialized selenate-reductase. Then, selenite is converted to Se^0 by a non-specific reductase such as nitrite reductase. To date, no high-affinity selenite reductase has been identified. These reactions occur in the periplasmic compartment of the cell. Biogenic Se^0 is then exported to the extracellular milieu by an unknown mechanism. The possibility of Se^0 release following cell lysis has also been considered since Se^0 particles can reach up to 300 nm in diameter during stationary phase. This size makes the existence of a transport system unlikely.

$$C_2H_3O_2^- + 4SeO_4^{2-} + H^+ \rightarrow 4SeO_3^{2-} + 2CO_2 + 2H_2O$$
$$\Delta G_f^\circ = -556 \text{ kJ mol}^{-1} \text{ acetate } (C_2H_3O_2^-) \tag{R6}$$
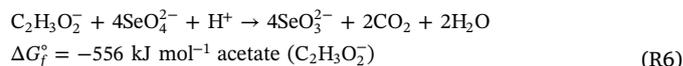
On the other hand, Se can behave as a toxicant and bacteria have developed a broad array of mechanisms to counteract it [61]. A model of Se detoxification in anaerobic bacteria such as *T. selenatis* has been proposed by Butler et al. [62]. This model (Fig. 3(b)) assumes that selenite, after being produced in the periplasmic space, enters in the cytoplasm where it is reduced to Se^0 by glutathione (GSH). GSH is a common detoxification molecule used by both prokaryotic and eukaryotic cells. From the cytoplasm, Se^0 is exported to extracellular environment or remains inside the cell. An interesting question can be raised with regards to the function of Se^0 particles in bacteria. Since Se^0 has no known ecological function such as the magnetite particles in magnetotactic bacteria or any nutritional function such as PHB and S^0 in various bacterial groups, it appears likely that Se^0 is a byproduct of either Se respiration or detoxification.

5.2. Bioremediation of FGD effluents

Biological treatment of Se-laden industrial effluents has emerged upon the understanding of the microbial metabolism of Se. Although the conversion of Se by way of assimilation and detoxification may take place simultaneously with the cellular respiration of Se oxyanions, it is the latter that accounts for the overall process in bioremediation [58]. Interestingly, although numerous fundamental studies have focused on pure (axenic) bacterial cultures that transform Se, bioremediation employs exclusively mixed microbial cultures. The reason behind this choice is the non-sterile nature of the industrial effluents and their complex matrix, requiring microorganisms with diverse metabolic repertoires to achieve efficient treatment.

Various bioreactor types have been tested for the treatment of Se-laden wastewaters. Granular sludge bioreactors (e.g. upflow anaerobic sludge blanket, UASB), used primarily to treat organic-rich wastewaters, were later adapted for Se treatment. A schematic of an UASB set-up is presented in Fig. 4. UASB operates by pumping the wastewater containing selenate or selenite upwards through a sludge blanket composed of self-aggregated microorganisms (sludge granules).
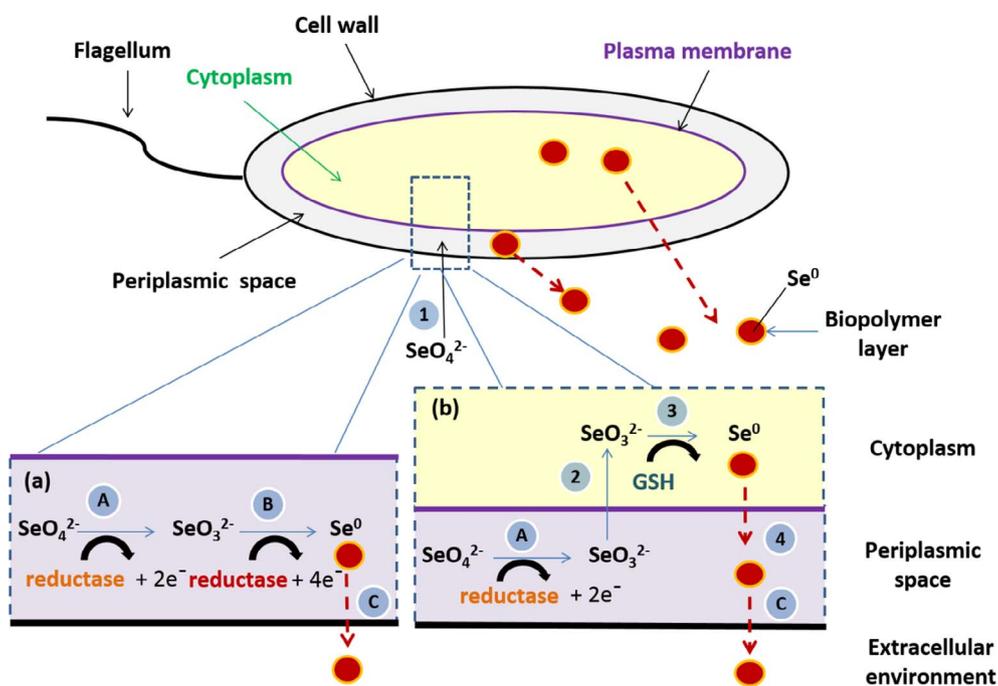

Fig. 3. Dissimilatory reduction and detoxification of selenium in gram-negative anaerobic bacteria. (a) Selenate respiration: 1. SeO_4^{2-} entering the periplasmic compartment, A. SeO_4^{2-} enzymatic reduction, B. SeO_3^{2-} enzymatic reduction, C. Se^0 export past the cell wall; (b) Detoxification of selenite: 2. SeO_3^{2-} passing through the plasma membrane; 3. SeO_3^{2-} reduction by GSH, 4. Se^0 export past the plasma membrane (modified from Staicu and Barton, 2017 [56]).
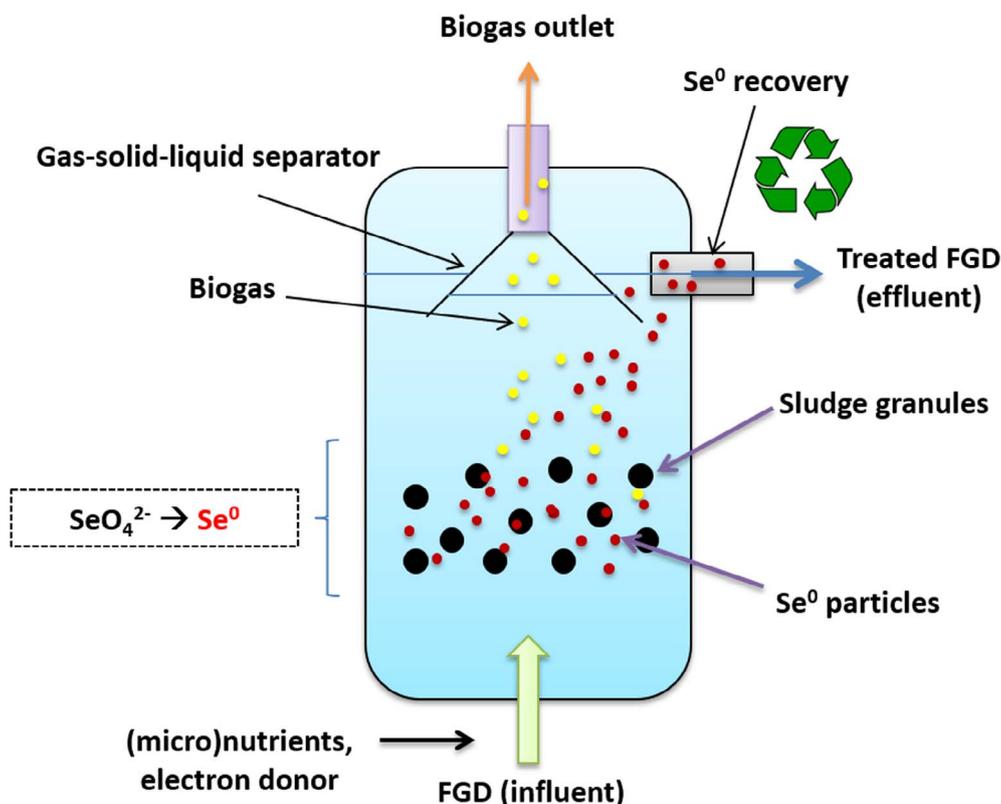
Fig. 4. Bioremediation of selenium-containing industrial effluents using an UASB system.

Specialized microorganisms from these granules are involved in the respiration of Se oxyanions into red Se^0 particles. Owing to its solid state, Se^0 can be recovered from solution and extracted from the system. This bioreactor type has an extra feature allowing the collection of biogas produced by methanogenic consortia co-present in the sludge granules that converts the organic load of the wastewater. Apart from self-aggregating granular sludge, other types of inocula exist and are characteristic of certain bioreactors: biofilm formed on added substrate/carrier material (e.g. sand, granular carbon) and biofilm formed on flat surfaces (e.g. hollow fiber membranes). Other reactor types such as fluidized-bed bioreactor (FBBR), packed-bed bioreactor, hydrogen-based hollow fiber membrane biofilm reactor (MBfR), and electro-bio-chemical reactor (EBR) were later developed and some are commercially available. For a fuller description of each bioreactor type the reader is referred to Nancharaiah and Lens [58] and Staicu et al. [14].

All reactors have an input and an output. The input (influent) contains the wastewater to be treated, alongside a feedstock that provides an organic carbon source, an electron donor and essential trace metals. Organic carbon is added when the wastewater is carbon-deficient. Typically, this is the case for Se-laden wastewaters, including FGD. Apart from organic carbon, an exogenous electron source should commonly be provided. For organotrophic microbial communities an organic electron donor such as ethanol, methanol, or lactate is required, whereas for lithotrophic communities H_2 is used (e.g. MBfR system). A particular type of electron donor is the electric current that is conveyed to microorganisms via a graphite electrode (e.g. EBR system). Sometimes, one reagent provides both organic carbon and electrons (e.g. ethanol). Essential trace elements including cobalt, molybdenum, nickel, iron, tungsten, and zinc are key components of various enzymes involved in anaerobic respiration. Usually, trace elements are provided as a cocktail and their scarcity was associated with severe bioreactor underperformance [63a]. Since FGD effluents contain trace metals (e.g. Co, Fe, Ni, Zn), this characteristic could be an extra benefit for bioremediation, since these metals act as cofactors for the enzymatic systems at play in anaerobic respiration. Conversely, the co-presence of Cr,

Hg or V in FGD systems could have a negative impact on the proper microbial metabolism. To date, no study reported the potential adverse effect of FGD matrix for the microbial metabolism of mixed communities such as those of granular sludge. FGD effluents typically a have circumneutral pH (~ 7) and a positive ORP ($+100$–500 mV) [12]. This pH is ideal for neutrophilic microbial communities, which is the case for Se respiration. The optimal ORP for Se anaerobic respiration occurs at negative values, -100 to -200 mV, and this range is used to selectively reduce Se oxyanions over nitrate (0 to -50 mV) and sulfate (< -200 mV) [63b]. In addition, due to the presence of carbonate, these effluents also display good buffering capacity. This means the microbial activity in the bioreactor does not lead to a significant pH change, thus reducing the need for additional pH correction.

The output (effluent) is the treated wastewater, alongside Se^0 particles (Fig. 5) and, in some cases, biogas. The treatment efficiency
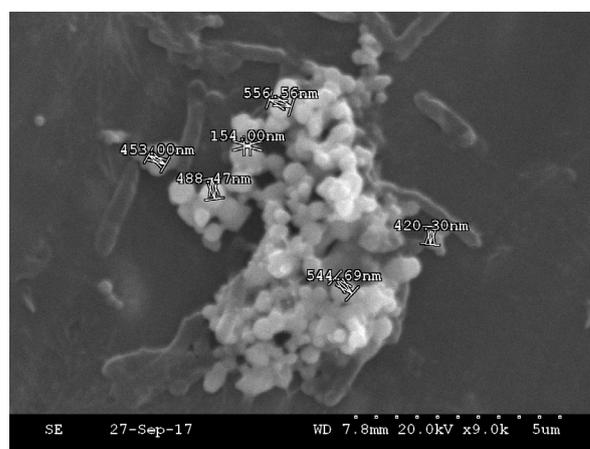

Fig. 5. SEM micrograph of Se^0 nanoparticles produced by *Sulfospirillum sp.* under anaerobic conditions (courtesy of Dr. Gavin Collins and Simon Mills, NUI Galway, Ireland).

depends on many variables such as wastewater make-up, bioreactor type, optimal working parameters (e.g. pH; temperature; ORP; hydraulic retention time, HRT) and inoculum type. Se^0 particles could potentially be recovered and reused (see next section). The advantage of the biological treatment is the high selectivity of Se-respiring bacteria for Se oxyanions over sulfate, nitrate and other constituents typically present in real wastewaters. In the case of physical-chemical processes, such as ion exchange, the capacity to preferentially separate Se from the complex FGD matrix cannot be achieved due to excess sulfate and carbonate [64]. The biogas, provided the methane content is high (> 60%), could be used to generate energy and thus offset the treatment costs [65].

6. Biogenic Se^0 recovery

Biogenic Se^0 particles have a negative surface charge in the range of -20 to -30 mV [70]. The negative charge is induced by a biopolymer coating (Fig. 3) composed of proteins, DNA and extracellular polymeric substances (EPS) [66]. It is unclear whether this coating attaches to Se^0 during intracellular nucleation of the particles or is acquired during transport, in the spent (extracellular) medium. Ni et al. [67] identified bare Se^0 particles inside a *Pseudomonas* strain, indicating the acquisition of the biopolymers during transport or outside the cell. However, certain bacteria are capable of extracellular reduction of metals and metalloids and were shown to produce Se^0 outside the cell, thus excluding the intracellular origin of the biopolymer [68,69]. Several coal-fired power units currently use ABMet technology (a type of packed-bed reactor) to treat FGD effluents, but the treatment is not coupled with biogenic Se^0 recovery [14].

Because of the biopolymer layer, Se^0 displays colloidal properties [70]. This means the Se^0 particles will not settle easily under the force of gravitation, making it an advantage when performing recovery. As such, biogenic Se^0 can be recovered by filtration or centrifugation from the treated effluent exiting the bioreactor (Fig. 4). The magnetic separation often used to separate magnetic particles cannot be applied for Se^0 since it does not display magnetic properties. Interestingly, the magnetotactic bacterium *Magnetospirillum magneticum* was shown to mineralize Se^0 in the presence of selenite, independent of the magnetite chain that is usually produced by this species [71]. In addition, Se^0 granules did not interfere with the magnetite synthesis. This opens the possibility for a mixed synthesis of these particles with the potential of further magnetic recovery of the cells harboring both Se^0 and Fe_3O_4 particles.

Size separation of biogenic Se^0 could be achieved by a number of techniques tested for other nanoparticles of both biogenic and chemogenic origin [72]. These include i) centrifugation in various media such as density gradients, ii) electrophoresis, iii) chromatography, iv) selective precipitation, and v) membrane filtration. Of these, density gradient centrifugation appears suitable when the suspension contains polydisperse Se^0 particles of various diameters, which is often the case. Interestingly, Se^0 particles have been shown to exhibit markedly different optical properties (UV–visible absorption and Raman spectra) in relation to their size and shape when produced by three different bacterial Se respirers [72].

Pure selenium powder sells at a high price (~ 81 euros for 5 g) (http://www.sigmaaldrich.com). Typical FGD effluents contain around $1 \, mg \, L^{-1}$ Se [11]. Assuming stoichiometric conversion of Se oxyanions into Se^0 by way of biological reduction, 5 m^3 of Se-laden effluent would be required to produce 5 g of Se. However, under non-ideal conditions, the volume of wastewater needed to obtain this amount of Se is expected to be higher. Nevertheless, extracting a valuable resource from a wastewater needing treatment could be considered a bonus that can help offset the treatment costs in addition to providing a service to the environment [73].

Circular economy (CE) is a paradigm shift proposing "a regenerative system in which resource input and waste, emission, and energy

leakage are minimized by slowing, closing, and narrowing material and energy loops" [74]. From a post-production perspective, CE attempts to recover and reuse part of the raw materials and energy employed in the production cycles, unlike its Linear Economy counterpart which is based on the obsolete mode of production that disposes of the waste generated at the end of the cycle. This new approach attempts to transform the industrial system to a sustainable basis, thus considering the waste as an unexploited resource/secondary material [75]. In the case of treating Se-laden industrial effluents using the bioremediation approach, the waste is biogenic Se^0 that is currently disposed of after exiting the bioreactor system (Fig. 4). Bioremediation, therefore, benefits both the environment which receives a cleaner effluent, but also the economy, by coupling the water treatment with resource recovery. Other alternative approaches such as biomining and phyto(agro)mining are currently considered as a sustainable way to extract/recover metals from naturally metalliferous soils, low grade ores or industrially polluted areas, in a likely scenario of a future resource-depleted environment [76].

7. Conclusions

While Se is transferred through the environment by natural processes, the advent of the Industrial Revolution resulted in the disruption of its natural cycle. Power plant facilities based on coal combustion are a major source of Se emissions mainly as FGD effluents. The bioremediation of this wastewater generates colloidal Se^0 that can be further recovered and reused since it has numerous industrial and domestic applications. Viewed from a circular economy perspective, FGD wastewaters are an unexploited (re)source of Se and their biological treatment could meet the expectations of sustainability, operating on a more efficient and environmental-friendly basis.

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