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REVIEW ARTICLE

Allotropy of selenium nanoparticles: Colourful transition, synthesis, and biotechnological applications

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Abstract

Elemental selenium (Se^0) nanomaterials undergo allotropic transition from thermodynamically-unstable to more stable phases. This process is significantly different when Se^0 nanoparticles (NPs) are produced via physico-chemical and biological pathways. While the allotropic transition of physico-chemically synthesized Se^0 is fast (minutes to hours), the biogenic Se^0 takes months to complete. The biopolymer layer covering biogenic Se^0 NPs might be the main factor controlling this retardation, but this still remains an open question. Phylogenetically-diverse bacteria reduce selenium oxyanions to red amorphous Se^0 allotrope, which has low market value. Then, red Se^0 undergoes allotropic transition to trigonal (metallic grey) allotrope, the end product having important industrial applications (e.g. semiconductors, alloys). Is it not yet clear whether biogenic Se^0 presents any biological function, or it is mainly a detoxification and respiratory by-product. The better understanding of this transition would benefit the recovery of Se^0 NPs from secondary resources and its targeted utilization with respect to each allotropic stage. This review article presents and critically discusses the main physico-chemical methods and biosynthetic pathways of Se^0 (bio)mineralization. In addition, the article proposes a conceptual model for the resource recovery potential of trigonal selenium nanomaterials in the context of circular economy.

INTRODUCTION

The formation of solid, elemental selenium, Se^0, via physico-chemical and biological pathways is still a poorly understood process (Ruiz-Fresneda et al., 2020). Se^0 is a key component of the biogeochemical cycle of selenium (Se) in nature and in industrial settings (Staicu & Barton, 2021). This is particularly relevant since its solid state and poor water solubility make it non bioavailable and thus unavailable to biota. In addition, Se finds multiple uses in industry and commercial applications, therefore understanding the synthesis route leading to Se^0 (nano)particles is important for its recovery from aqueous solutions as a solid product. Based on the agent controlling the synthesis of Se^0, we distinguish between biogenic (resulting from the metabolic activity of a biological system) and chemogenic (produced as a results of physico-chemical methods). While the physico-chemical methods rely mainly on the reduction of tetravalent selenite, SeO_3^{2-}/Se^{IV}, the biological systems can reduce both selenite and hexavalent selenate, SeO_4^{2-}/Se^{VI}, oxyanions to Se^0. The formation of Se^0 by biological systems is considered a biomineralization process, mainly leading to an amorphous mineral phase (Staicu et al., 2022). Interestingly, elemental selenium has several different allotropes: two

amorphous (red and black), three crystalline monoclinic (deep red), crystalline trigonal (or rhombohedral) selenium (metallic grey), orthorhombic selenium and three allotropes of crystalline cubic Se^0 (Fernández-Martínez & Charlet, 2009). The phase transition between these allotropes (i.e. allotropic transition) is relevant from a biological and technological perspective. Biologically, the formation of crystalline Se^0 with needle-like structures is detrimental for the cellular integrity and homeostasis (in contrast, the amorphous allotrope is regularly globular in shape). Technologically, the transition to trigonal (metallic grey) Se^0 is desirable since this allotrope is a semiconductor, making it useful in photocells (trigonal Se^0 is a photoconductor, which means it has the ability to change electromagnetic energy into electrical energy).

This review article presents and discusses the up-to-date physico-chemical and biosynthetic (biomineralization) methods and pathways of Se^0 nanomaterials synthesis and proposes a conceptual model for the resource recovery potential of Se^0 in the context of circular economy.

PHYSICO-CHEMICAL SYNTHESIS OF SE^0

Nowadays, there is a huge demand for the large-scale production of SeNPs due to their enormous usefulness in many industrial and medical applications (Ojeda et al., 2020). Physico-chemical methods have been the most widely used so far for their fabrication. Although these procedures have several disadvantages over biosynthesis, they provide a quick and reproducible way to produce large amounts of NPs.

The chemical route is based on the use of chemical compounds that initiate the synthesis reaction under controlled conditions. The most common and simplest method employed is chemical reduction, which involves the use of reducing agents (e.g., ascorbic acid, glutathione, sulfur dioxide, glucose, cysteine, sodium dodecyl sulfate, etc.) of Se salts precursors (sodium selenite, sodium selenate, selenious acid, thiosulfuric acid, sodium selenosulfate, etc.) (Table 1). This experimental setup is fast and has therefore been used to a greater extent than physical methods. However, the process is commonly based on the use of toxic and expensive compounds. Many chemical reducing agents have been reported in the literature for the formation of SeNPs of different sizes and morphology. Ascorbic acid is one of the most employed agents due to its lower toxicity and higher biocompatibility (Gangadoo et al., 2017; Sun et al., 2009). Gangadoo et al. (2017) showed a quick and replicable methodology to synthesize amorphous nanospheres of Se using this compound. They demonstrated that the concentration of ascorbic acid affects NP size, forming smaller Se spheres (<70 nm) with increasing concentrations. Other acids are also useful as effective reducing agents. For instance, Dwivedi et al. (2011) developed a simple chemical method to produce amorphous SeNPs ranging from 35 to 70 nm based on different organic acids (acetic acid, oxalic acid, and gallic acid) reactions in aqueous medium with sodium selenosulphate as Se source. In many cases, chemical reduction is accompanied by other chemical reactions such as precipitation and acid decomposition. Panahi-Kalamuei et al. (2015) mixed $SeCl_4$ with CTAB (cetrimonium bromide) before reduction with different compounds (hydrazine, TGA, or borohydride) for co-precipitation of SeNPs. A wide variety of shapes and sizes were observed with SEM (Scanning Electron Microscopy) depending on the precipitant: Se nanorods (nm scale in diameter and μm scale in length) were produced with hydrazine, spherical SeNPs (20 nm) with TGA, and big Se aggregates with borohydride. Decomposition with non-oxidative acids (HCl, H_3PO_4, etc.) prior to reduction has also been employed to produce SeNPs. For example, Stroyuk et al. (2008) proposed an indirect reduction method based on the reduction of bulk Se crystals with sodium sulphite to obtain sodium selenosulfate (Na_2SeSO_3), which was decomposed and converted to SeNPs with HCl in aqueous solution of a surfactant or polymer.

SeNPs can be also synthesized through several physical methods including ultraviolet (UV) radiation, laser ablation, gamma irradiation, microwaves, hydrothermal techniques, sonochemical methods, etc (Table 1). Although these methodologies can be dangerous, they have some advantages over chemical methods, including the absence of contaminants and toxic compounds, shorter reactions, and low-cost equipment (Shahbazi et al., 2015). Most procedures are based on the application of physical phenomena, mainly radiation and temperature variation, to selenium sources in liquid solvents. Liquid laser ablation is being deeply explored for its advantages such as being a non-toxic, low-cost, and homogeneous method in comparison with conventional chemical procedures. Amorphous SeNPs of around 20–100 nm were produced with this method in water by using pulsed copper vapour laser (wavelengths 510.6 and 578.2 nm; pulse duration 15 ns; and pulse repetition rate 15 kHz) over polycrystalline Se as target (Kuzmin et al., 2012). Microwave irradiation can assist Se salts interaction with liquid solvents to synthesize SeNPs. Ahmad (2016) reported on a method for trigonal Se nanosphere production on a silicon surface by applying microwave radiation combined with high pressures (60 bar) and temperature (160°C) to selenium powder in hydrofluoric acid. Another type of radiation that could be involved in SeNP synthesis is the Gamma rays. Pereira et al. (2022) were able to produce amorphous Se nanospheres (100–220 nm) through Gamma irradiation (25 kGy dose) over sodium selenite as precursor in YPG (Yeast-Peptone-Galactose) broth.

TABLE 1 Physico-chemical methodologies for the synthesis of selenium nanoparticles.

Chemical method	Reagent	Se precursor	Se product	Allotropic form and morphology	Size (nm)	Reference
Chemical reduction	Ascorbic acid	Selenium tetrachloride ($SeCl_4$)	Se^0 NPs	Amorphous nanospheres	<100	Gangadoo et al. (2017)
Chemical reduction	Acetic acid Oxalic acid Gallic acid	Sodium selenosulphate (Na_2SeSO_3)	SeNPs	Amorphous nanospheres	40–100	Dwivedi et al. (2011)
Chemical reduction	L-cysteine	Sodium selenite (Na_2SeO_3)	Se^0 NPs	Amorphous nanospheres	~100	Li et al. (2010)
Chemical reduction	Glutathione (GSH)	Sodium selenite (Na_2SeO_3)	SeNPs	Rods	~178 (by DLS) ~75 (by SEM)	Verma and Maheshwari (2018)
Chemical reduction	Glucose	Sodium selenite (Na_2SeO_3)	SeNPs	Amorphous nanospheres	280–295	Nie et al. (2016)
Acidic Decomposition	HCl	Sodium selenosulfate (Na_2SeSO_3)	SeNPs	Amorphous nanospheres	25–200	Stroyuk et al. (2008)
Chemical precipitation	Hydrazine	$SeCl_4$	SeNPs	Hexagonal microrods	-	Panahi-Kalamuei et al. (2015)
Chemical precipitation	TGA	$SeCl_4$	SeNPs	Hexagonal nanospheres	20	Panahi-Kalamuei et al. (2015)
Physical method	**Reagent**	**Se precursor**	**Se product**	**Structure and morphology**	**Size**	**Reference**
Liquid laser ablation	Purified water	Polycrystalline Se	Se^0 NPs	Amorphous spheres	20–100	Kuzmin et al. (2012)
Liquid laser ablation	Deionized water	Selenium pellet (99.99% purity)	SeNPs	Amorphous spheres	~115	Guisbiers et al. (2016)
Microwaves	Hydrofluoric acid	Se powder (99.99% purity)	Se^0 NPs	Trigonal spheres	30 nm-50 μm	Ahmad (2016)
Microwaves	Oleic acid and diophenyl ether	Cycloocteno-1,2,3-selenadiazol	Se^0 NPs	Amorphous, monoclinic, and trigonal Nanospheres and plates-like shape	1–100 (nanospheres) 300 nm- 1 μm (plates)	Jadhav and Khanna (2015)
Gamma radiation (25 kGy dose)	YPG broth	Sodium selenite (Na_2SeO_3)	Se^0 NPs	Amorphous nanospheres	100–220	Pereira et al. (2022)
Gamma radiation (25 kGy dose)	Dextran	Selenium dioxide (SeO_2)	Se^0 NPs	Nanospheres	~74	Hien et al. (2018)
Photocatalysis (UV radiation)	TiO_2	Sodium selenite (Na_2SeO_3) Sodium selenate (Na_2SeO_4)	Se^0 NPs	Amorphous aggregates	-	Nu Hoai Nguyen et al. (2005)
Hydrothermal (150°C)	L-cysteine	Selenium dioxide (SeO_2)	Se^0 NPs	Trigonal microrods	600–650	Mondal et al. (2008)
Hydrothermal (130°C)	Glucose and CTAB	Sodium selenite (Na_2SeO_3)	SeNPs	Trigonal nanorods	200–300	Cao et al. (2011)

Although it is a promising method, the high danger of gamma rays is well known. Photocatalytic processes involve the activation of semiconductor catalysts with different light sources. Titanium dioxide (TiO_2)-based photocatalysis with UV radiation has been extensively used as an economic strategy for Se^{VI} and Se^{IV} reduction and production of SeNPs. Following this method, Nu Hoai Nguyen et al. (2005) showed the formation of amorphous Se^0 and their transformation to crystalline Se after drying and ageing process for 2 weeks. In a recent study, Holmes et al. (2022) investigated the reduction of Se^{VI} in a mine-impacted wastewater, revealing the ability of photocatalytic reduction of TiO_2 to selectively reduce selenate from >500 $\mu g\,L^{-1}$ to <2 $\mu g\,L^{-1}$. The reduction yield was unaffected by the presence of the more energetically favourable electron acceptor, nitrate (250× molar concentration of selenate) or the high concentrations of sulfate (1940× molar concentration of selenate).

Physically-based methods are frequently combined with chemically-based methods to improve the quality of the NPs (in terms of size, stability, crystallinity, purity, and other physico-chemical properties). High temperatures influence the allotropic transition from unstable amorphous to trigonal crystalline Se, the most thermodynamically stable phase (Properzi et al., 2013). For this reason, hydrothermal-based methods are being employed to increase the crystallinity of chemically-formed SeNPs for the production of trigonal Se crystals (Chen et al., 2010; Dwivedi et al., 2011), which exhibit different properties and applications compared to amorphous Se materials, such as high photoconductivity and piezoelectricity (Lei et al., 2020; Mayers et al., 2003). Several authors have employed this methodology as an emerging tool for the synthesis of crystalline Se nanomaterials using autoclaving conditions (120–150°C) for 12–24 h on different Se sources (Cao et al., 2011; Mondal et al., 2008). Temperatures oscillating from 80 to 100°C are generally sufficient to obtain crystalline SeNPs as reported in the literature (Chen et al., 2010; Lortie et al., 1992; Stroyuk et al., 2008). However, in the recent years several processes using lower temperatures for crystallization have been proposed. Vieira et al. (2017) reported a facile synthesis way to produce trigonal crystalline SeNPs using D-fructose as reducing agent and sodium selenite as Se source, respectively, at 45°C. Similarly, Hageman et al. (2017) employed a 50°C temperature to gradually transform red amorphous nanospheres to grey hexagonal Se crystals, providing a simpler and more economical way for large-scale production.

These traditional methods involving the use of physico-chemical procedures are usually costly, dangerous, and in many cases require the use of high temperatures, acidic pHs, or hazardous chemicals, which may make NPs unsafe for biomedical application (Iranifam et al., 2013). However, inorganic SeNPs are currently being investigating in the field of nanomedicine due to their low toxicity and safe purification protocols. Indeed, many examples of physico-chemically synthesized SeNPs have been proved to trigger cellular apoptosis in tumoral cell lines (Cui et al., 2018; Geoffrion et al., 2020; Zou et al., 2019). In addition, green chemistry is gaining attention as a hybrid and safe method based on the use of environmentally benign solvents and non-toxic reducing agents. For instance, silver NPs have been synthesized using several green solvents such as water, polyethylene glycol (PEG) and β-D-glucose as reducing agent (Shameli et al., 2012; Shanan Abed et al., 2019). Despite all the advances that have been made with regards to physico-chemically methods, the biosynthesis of Se^0 by non-pathogenic microorganisms is gaining attention in the last years as an eco-friendly, non-toxic, and cheaper procedure to safely produce nanoparticles (Salunke et al., 2014; Wadhwani et al., 2016).

BIOLOGICAL SYNTHESIS OF SE^0

Bacteria

As mentioned in the previous section, production of nanoparticles though biological procedures is one of the most promising methods today as an eco-friendly and safe technology. The use of living organisms and their derivates (plant and bacterial extracts) to produce NPs of interest would avoid the use of hazardous and toxic chemicals, harmful radiation, high temperatures, and other technologies that are expensive and dangerous to human health. Thus, biosynthesized NPs could be safely used for biomedical applications. However, like the physico-chemical methods, biosynthesis of nanoparticles also presents some disadvantages. For example, industrial-scale production could be a problem with living organisms. In this regard, one of the main concerns is the longer reaction times required for biologic synthesis compared to physico-chemical methods. An added difficulty is that the biomaterial (plant, bacteria, etc.) is often abundant in exclusive habitats and/or during certain times of the year (Ying et al., 2022). Another limitation is the quality of the nanoparticles. Biological formation of SeNPs by microorganism exhibit variation over size and shape due to the wide diversity of mechanisms and enzymes involved during the synthesis process. For instance, Oremland et al. (2004) characterized the structural and spectral features of the biogenic Se^0 from three phylogenetically-diverse Se-respiring bacteria (*Sulfurospirillum barnesii*, *Bacillus selenitireducens* and *Selenihalanaerobacter shriftii*). The study observed large differences in the optical properties (UV–visible absorption and Raman spectra) of biogenic Se^0 produced by the three different bacterial

species. These properties also differed substantially from those of amorphous Se^0 formed by chemical synthesis, probably reflecting the diversity of Se-respiring enzymes. However, many efforts are being made to overcome these limitations and shortcomings to put biological synthesis of NPs into practical use.

A great number of studies have reported the biogenic synthesis of SeNPs mediated by different living organisms including bacteria, plant, fungi, and archaea (Table 2). From all of them, bacteria have been by far the most studied for SeNPs synthesis probably due to their ease of handling. Many bacterial species including both Gram-negative and Gram-positive exhibit the ability to enzymatically reduce toxic Se oxyanions, Se^{VI} and Se^{IV}, to non-toxic Se^0 in the form of nanoparticles with a wide variety of shapes, sizes, and structures (Eswayah et al., 2019; Fischer et al., 2020; Pinel-Cabello et al., 2021). Most bacteria produce amorphous spherical NPs variable in size located both extracellularly and intracellularly. In the case of extracellular anaerobic respiration, Se^0 particles are disposed outside the cells (Figure 1A), thus overcoming the challenge of managing such bulky products inside the cell. In other cases, such as detoxification reactions, Se^0 is synthesized inside the cell (Figure 1B) most probably because the reducing agent (e.g. glutathione) is present in the cytoplasm.

For instance, a broad spectrum of bacterial species belonging to genera such as *Bacillus subtilis, Bacillus cereus, Stenotrophomonas maltophilia, Stenotrophomonas bentonitica, Thauera selenatis, Ralstonia metallidurans* or *Geobacter sulfurreducens*, have been reported to produce amorphous nanospheres ranging from 50 to 200 nm (Butler et al., 2012; Jia et al., 2022; Kora, 2018; Lampis et al., 2017; Pearce et al., 2009; Roux et al., 2001; Ruiz-Fresneda et al., 2023). Less frequently, some bacteria have been reported to form crystalline NPs (monoclinic, trigonal allotropes) with different shapes (polygonal, nanorods, nanowires, hexagons, etc.). Interestingly, some microorganisms are able to crystallize NPs under mesophilic conditions without using any chemical agent or physical method. For instance, the bacterial species *Bacillus subtilis* and *Stenotrophomonas bentonitica* have been reported to reduce Se^{IV} to Se^0 amorphous nanospheres, which were transformed by the cells into crystalline nanostructures at room temperature. This is a huge advance over physico-chemical methods and provides a promising option for the eco-friendly formation of crystalline SeNPs.

Plants

The use of plant extracts also represents a good alternative to physico-chemical methods for the synthesis of SeNPs. In addition, they offer a cost reduction compared to microbial-based methods, which requires a final purification step to remove the cellular content. Plant extracts contain biomolecules (e.g., flavonoids, amino acids, proteins, polysaccharides, polyphenols, minerals, etc.) that can act as biodegradable and easily accessible reducing agents of Se to produce NPs. The general experimental setup is simple and inexpensive, mainly consisting of extracting the chosen part of the plant (fruit, leave, seed, peel, etc.), washing and drying, to finally crushing it vigorously. Subsequently, the plant extract is soaked in the solution with the Se feedstock. Leaf extracts from *Withania somnifera* (Fam. *Solanaceae*) produced amorphous and spherical SeNPs within the diameter range of 45–90 nm after exposure to seleniuos acid (H_2SeO_3) at room temperature (Alagesan & Venugopal, 2019). The leaf extract exhibited huge quantities of phytoconstituents (flavonoids, phenolics, tannins, and alkaloids) with reducing functional groups which may play a crucial role in NPs synthesis. Some of these compounds could act as natural stabilizers of the produced NPs due to their electron-donating capability and capping properties, making them more attractive as antibacterial agents. Indeed, SeNPs (55–100 nm in size) synthesized following a similar method (H_2SeO_3 as Se source, room temperature, etc.) by leaf extract from *Enicostema axillare* (Fam. *Gentianaceae*) exhibited efficient antibacterial properties against a broad range of bacteria including *B. subtilis, S. aureus, E. coli, Klebsiella pneumoniae* (Perumal et al., 2021). Bacteria have also been reported to produce polysaccharides and protein-capped SeNPs with potential medical purposes. The cells of *Lactobacillus casei* 393 form protein-associated SeNPs with excellent antioxidative properties in intestinal epithelial cells and cytotoxic activity against HepG2 (liver hepatocellular carcinoma) cells (Xu et al., 2018). These findings propose capped-SeNPs from *L. casei* 393 as a potential antioxidant and drug for hepatocellular carcinoma.

Fungi

In contrast to bacteria and plant extracts, a lower number of fungi were shown to synthesize SeNPs, mainly because they have low tolerance against selenium. However, a broad range of fungal species including filamentous fungi (*Trichoderma, Aspergillus*, etc.) and yeasts (*Saccharomyces, Candida*, etc.) have been reported in the last years to efficiently reduce Se oxyanions (Faramarzi et al., 2020; Herrero & Wellinger, 2015; Hussein et al., 2022; Liang et al., 2019). The molecular mechanisms proposed to be involved in the metabolic reduction pathway of inorganic Se to Se^0 are very similar to those reported for bacteria (Herrero & Wellinger, 2015; Lampis & Vallini, 2021). Interestingly, rhizosphere fungi isolated from Se-resistant plants in polluted sites are not inhibited in the presence of this element (Shoeibi et al., 2017). This tolerance could be related to long-term adaptation to the Se present in the habitat (Shoeibi

TABLE 2 Comparative analysis of the different biological procedures for the synthesis of selenium nanoparticles by living organisms.

Living micro/ macroorganisms	Taxonomic affiliation	Se precursor	Interaction mechanism	Se product	Allotropic form and morphology	Size (nm)	Location	Reference
Bacteria								
Rhodococcus aethirovorans	Actinobacteria Gram positive	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres Nanorods	53–97 (nanospheres) 444–555 (nanorods)	Bacterial surface Extracellular	Presentato et al. (2018)
Azospirillum brasilense	Alphaproteobacteria Gram negative	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres	25–84	Extracellular	Tugarova et al. (2020)
Azospirillum thiophilum	Alphaproteobacteria Gram negative	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres	50–90	Extracellular	Tugarova et al. (2018)
Bacillus subtilis	Bacilli Gram positive	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres	135–165	Extracellular	Zhu et al. (2021)
Bacillus cereus	Bacilli Gram positive	Se^{VI} Se^{IV}	Reduction Volatilization	Se^{0} NPs DMDSe DMDSes	Amorphous nanospheres Trigonal nanorods	50–150	Intracellular Extracellular	Che et al. (2019)
Herbaspirillum sp.	Betaproteobacteria Gram negative	Se^{VI}	Reduction Volatilization	Se^{0} NPs	Amorphous nanospheres Se flowers	≥200	Cellular surface Extracellular	Xu et al. (2020)
Thauera selenatis	Betaproteobacteria Gram negative	Se^{VI} Se^{IV}	Reduction	Se^{0} NPs	Nanospheres	~150	Intracellular Extracellular	Butler et al. (2012)
Spirullina platensis	Cyanobacteria	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres Monoclinic and trigonal structures	70–80	Extracellular	Zhang et al. (2020)
Geobacter sulfurreducens	Deltaproteobacteria Gram negative	Se^{IV}	Reduction Volatilization	Se^{0} NPs Se^{-II}	Amorphous nanospheres	100–250	Intracellular Bacterial surface Extracellular	Pearce et al. (2009)
Stenotrophomonas bentonitica	Gammaproteobacteria Gram negative	Se^{VI} Se^{IV}	Reduction Volatilization	Se^{0} NPs DMDSe DMSeS	Amorphous nanospheres Trigonal and monoclinic nanorods	50–200	Intracellular Extracellular	Ruiz-Fresneda et al. (2018, 2019, 2020)
Stenotrophomonas maltophilia	Gammaprotebacteria Gram negative	Se^{VI} Se^{IV}	Reduction Volatilization	Se^{0} NPs Se^{-II}	Amorphous nanospheres Crystalline nanorods	118±36 (nanospheres) 324±89 (nanorods)	Intracellular Extracellular	Piacenza et al. (2018)
Acinetobacter sp.	Gammaproteobacteria Gram negative	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres Crystalline nanorods	≥100	Extracellular	Wadhwani et al. (2017)
Pseudomonas putida	Gammaproteobacteria Gram negative	Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres	100–500	Bacterial surface Extracellular	Avendaño et al. (2016)
Escherichia coli	Gammaproteobacteria Gram negative	Se^{VI} Se^{IV}	Reduction	Se^{0} NPs	Amorphous nanospheres	100–220	Cellular surface Extracellular	Kora and Rastogi (2017)
Fungi								
Trichoderma atroviride	Fungi Sordariomycetes	Se^{IV}	Reduction	Se^{0} NPs	Crystalline nanospheres	60–123	Intracellular	Joshi et al. (2019)

TABLE 2 (Continued).

Living micro/ macroorganisms	Taxonomic affiliation	Se precursor	Interaction mechanism	Se product	Allotropic form and morphology	Size (nm)	Location	Reference
Alternaria alternata	Fungi Dothideomycetes	Se^{IV}	Reduction	Se^0 NPs	Amorphous nanospheres	30–150	Extracellular	Shoeibi et al. (2017)
Aspergillus terreus	Fungi Trichomaceae	Se^{IV}	Reduction	Se^0 NPs	Amorphous nanospheres	≥100	Extracellular	Shoeibi et al. (2017)
Saccharomyces cerevisiae	Fungi Saccharomycetes	Se^{IV}	Reduction	Se^0 NPs	Crystalline (nanocomposite)	30–150	Intracellular	Shoeibi et al. (2017)
Archaea								
Halococcus salidofinae BK8	Haloarchaeae	Se^{IV}	Reduction	Se^0 NPs	Nanospheres Nanorods with hexagonal phase	~9 (nanospheres) ~129 (nanorods)	Intracellular Extracellular	Srivastava et al. (2014)
Haloferax alexandrines	Haloarchaeae	Se^{IV}	Reduction	Se^0 NPs	Pentagonal nanoparticles with hexagonal structure	15 diagonal length	Intracellular Extracellular	Alvares and Furtado (2022)
Halorubrum xinjiangense	Halobacterium	Se^{IV}	Reduction	Se^0 NPs	Amorphous nanospheres	-	Intracellular Extracellular	Güven et al. (2013)
Halogeometricum sp.	Halobacterium	Se^{IV}	Reduction	Se^0 NPs	Hexagonal nanospheres	~30	Extracellular	Abdollahnia et al. (2020)
Plants								
Saussurea costus (roots extract)	Magnoliopsida	Se^{IV}	Reduction	Se^0 NPs	Spherical nanospheres	3–9	Extracellular	Al-Saggaf et al. (2020)
Vitis vinifera (dried extract of raisin)	Magnoliopsida	H_2SeO_3	Reduction	Se^0 NPs	Amorphous nanospheres	3–18	Extracellular	Husen and Siddiqi (2014)
Therminalia arjuna (leaf extract)	Magnoliopsida	Se^{IV}	Reduction	Se^0 NPs	Crystalline nanospheres	10–80	Extracellular	Prasad and Selvaraj (2014)
Catharanthus roseus (flower extract)	Magnoliopsida	Se^{VI}	Reduction	Se^0 NPs	Crystalline nanospheres	17–34	Extracellular	Deepa and Ganesan (2015)
Withania somnifera (leaf extract)	Eudicotyledoneae	H_2SeO_3	Reduction	Se^0 NPs	Amorphous and trigonal agglomerated nanospheres	40–90	Extracellular	Alagesan and Venugopal (2019)
Enicostema axillare (leaf extract)	Magnoliopsida	H_2SeO_3	Reduction	Se^0 NPs	Spherical nanoparticles	56–98	Extracellular	Perumal et al. (2021)

Abbreviations: DMDSe, dimethyl diselenide; DMSe, dimethyl selenide.

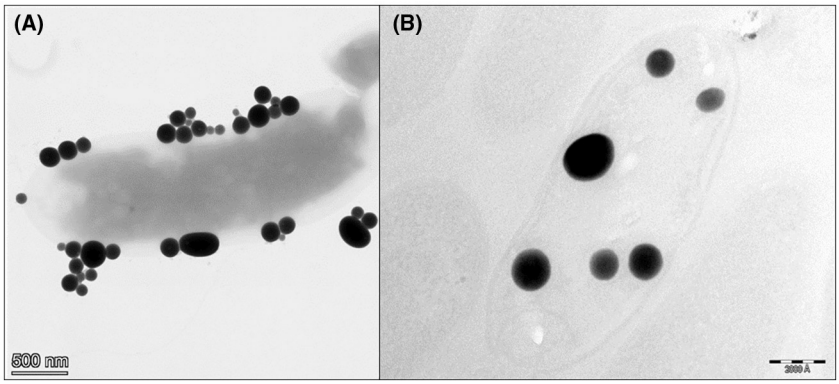

FIGURE 1 Biogenic Se^0 particles: (A) Extracellular Se^0 produced by a strain of *Shewanella* (related to *Shewanella baltica*) via extracellular respiration (personal archive of Dr Staicu; growth conditions detailed in Staicu et al. (2022)); (B) intracellular Se^0 nanoparticles produced by the bacterial species *Stenotrophomonas bentonitica* (personal archive of Dr Merroun; growth conditions detailed in Ruiz-Fresneda et al. [2018]).

et al., 2017). *Mariannaea* sp. HJ, *Trichoderma atroviride*, *Aspergillus oryzae*, *Aspergillus terreus*, and *Lentinula edodes* are among the few known fungal species capable of reducing Se^{IV} to Se^0 particles. Se^{VI} can be reduced as well by several fungal species. Rosenfeld et al. (2017) reported six different Ascomycete fungi (*Pyrenochaeta* sp. DS3sAY3a; *Acremonium strictum* DS1bioAY4a; *Plectosphaerella cucumerina* sp. DS2psM2A2; *Stagonospora* sp. SRC1lmsM3a; *Alternaria alternat* asp. SRC1lrK2f; and *Paraconiothyrium sporulosum*) capable of removing dissolved Se^{VI} and Se^{IV} from solution and producing Se^0 biominerals. In spite of the limited number of Se-reducing fungi, they exhibit exceptional protein secretion which may result in an increased production of NP in comparison to bacteria and other microorganisms (Joshi et al., 2019). Overall, spherical Se^0 NPs were formed in all cases, most of them being crystalline in structure. This differs from other living organisms such as bacteria and plants, where most of the Se nanospheres produced are amorphous. One of the potential applications of fungal SeNPs that is being investigated is related to agricultural industry. The SeNPs produced by *Trichoderma atroviride* are a promising plant-defensive strategy against fungal phytopathogens and provide an economic and eco-friendly alternative to chemical fertilizers. They have been demonstrated to efficiently inhibit *Pyricularia grisea*, *Colletotrichum capsici*, *Alternaria solani*, which cause blast and early blight diseases, among other pathologies (Joshi et al., 2019). The results described here show that the number of Se-reducing fungal species discovered is increasing significantly in recent years, whereas a few years ago not many species had been described.

Archaea

In comparison to bacteria, a limited number of reports have been published on the synthesis of SeNPs by Archaea. Specifically, most of archaea involved in Se reduction and SeNPs production belong to the salt-resistant class haloarchaea, such as *Halococcus salifodinae* BK18, *Halogeometricum* sp., *Halorubrum xinjiangense*, or *Halobacterium* sp. SP1 (Abdollahnia et al., 2020; Güven et al., 2013; Naik et al., 2017; Srivastava et al., 2014). Halophilic Archaea are considered potential candidates for Se and other toxic substances tolerance because of their ability to survive under high stressful concentration of anions and cations. The Se reduction products derived from *Halorubrum xinjiangense* consist of intracellular spherical deposits with an amorphous nature. In contrast, the cells of *Halococcus salifodinae* BK18 and *Halogeometricum* sp. produced crystalline Se with hexagonal phase of different morphologies: nanorods and nanospheres for *H. salifodinae* BK18 and spherical shape for *Halogeometricum* sp. Although, from an industrial point of view, the synthesis process of SeNPs by archaea would require more complex conditions (high salt concentrations, temperatures, etc.), they provide an efficient option for bioremediation in extreme environments such as hypersaline habitats or marine sites, where few microorganisms can survive.

ALLOTROPIC TRANSITION

Most commonly, bacterially-synthesized Se^0 has an amorphous structure. Because this mineralogical phase is thermodynamically unstable, it undergoes a phase transition towards a more crystalline and thermodynamically-stable state (Fernández-Martínez & Charlet, 2009). This process is known as allotropic transition, and it shows a stark contrast between biogenic and chemogenic Se^0. In the absence of a capping agent (e.g., Bovine Serum Albumin/BSA), chemogenic Se^0 undergoes a quick transition

towards crystalline states ranging from minutes to hours (Johnson et al., 2008). In contrast, biogenic Se^0 exhibits a very slow allotropic transition (Figure 2). Fellowes et al. (2011) determined by XRD analysis that biogenic Se^0 retained its amorphous structure after 58 days. This retardation may be associated with the biopolymer layer covering biogenic Se^0 particles but a mechanistic explanation underlying this process was not proposed as yet. The biopolymer was shown to contain mainly proteins (Pearce et al., 2009; Staicu et al., 2015) and Extracellular Polymeric Substances (Jain et al., 2015). Bulgarini et al. (2021) performed an in-depth study involving five phylogenetically-diverse bacterial strains (*Bacillus mycoides* SeITE01, *Stenotrophomonas maltophilia* SeITE02, and three strains closely related to *Achromobacter* sp., *Ensifer* sp., and *Lysinibacillus* sp.) with the aim of characterizing the chemical composition of the biopolymer layer covering biogenic Se^0 particles. The study identified carbohydrates, proteins and lipids present in the capping layer of biogenic Se^0 with distinct, strain-specific concentrations.

From a biological perspective, the allotropic transition of biogenic Se^0 is an intriguing process. Amorphous Se^0, irrespective of its diameter, is commonly round (globular), thus making it safe for the delicate cellular components, especially the plasma membrane. The transition to crystalline Se^0 states entails the formation of structurally-harmful nanorods (needle-like structures). This might explain the stabilization of Se^0 in its globular shape for a longer time frame than the growth cycle of the bacterial cell (e.g., months vs days). The formation of biogenic Se^0 is a puzzling process in itself since this biomineralization product does not seem to have a biological function (discussed in Staicu & Barton, 2021). Thus, Se^0 might be a byproduct of a detoxification mechanism (Ni et al., 2015) or of a respiratory process (Se oxyanions act as electron acceptors in anaerobic respiration, being reduced to Se^0) (Staicu & Barton, 2021). Both detoxification and anaerobic respiration commonly lead to intracellular Se^0, however, certain bacteria are capable of extracellular respiration (Gralnick & Newman, 2007), discarding the biomineralization byproducts in the vicinity or in the extracellular milieu (Staicu et al., 2022). From a more speculative perspective, biogenic Se^0 might have an unknown biological function such as a density agent for anaerobic granules in upflow bioreactors or act as an electron donor/acceptor, analogous to S^0 (Cosmidis & Benzerara, 2022; Staicu & Barton, 2021).

TOWARDS CIRCULAR ECONOMY: APPLICATIONS OF THE DIFFERENT SE ALLOTROPES

Treatment and decontamination of soils and wastewaters containing toxic Se and its recovery in form of non-hazardous NPs has a huge potential within the concept of circular economy. The development of an efficient model for the recovery of Se and its use for the benefit of society would be of crucial importance. The authors propose herein a resource recovery framework of this element that could be of interest for the community (Figure 3).

It is well established that Se causes severe damage to biota and to human health depending on its chemical form, which deeply affects its toxicity. Specifically, Se oxidized forms (+VI and + IV) have been documented to be toxic due to their high solubility and bioavailability, while elemental Se^0 is considered the least toxic due to the opposite, its solid state and low solubility. Se toxicity is due to its ability to substitute for sulfur (leading

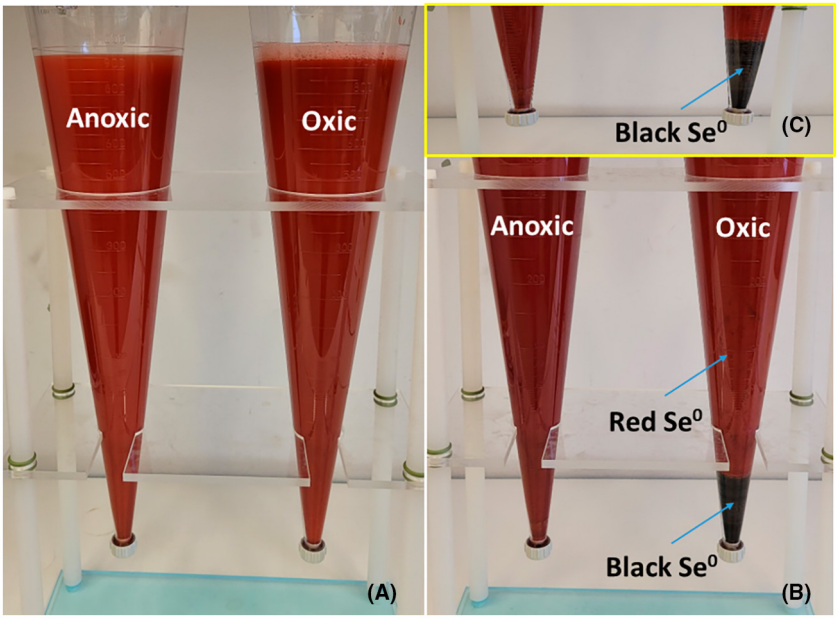

FIGURE 2 Allotropic transition of biogenic red Se^0 produced by *Shewanella* sp. O23S under anoxic (left cone) and oxic (right cone) conditions. Oxically-sourced Se^0 undergoes allotropic transition to black at the bottom of the cone, while the anoxic counterpart shows allotropic stability. (A) Day 1; (B) 6 months; (C) inset (panel B) of the cone tips after 6 months (personal archive of Dr Staicu). The incubation conditions are detailed in Staicu et al. (2022).

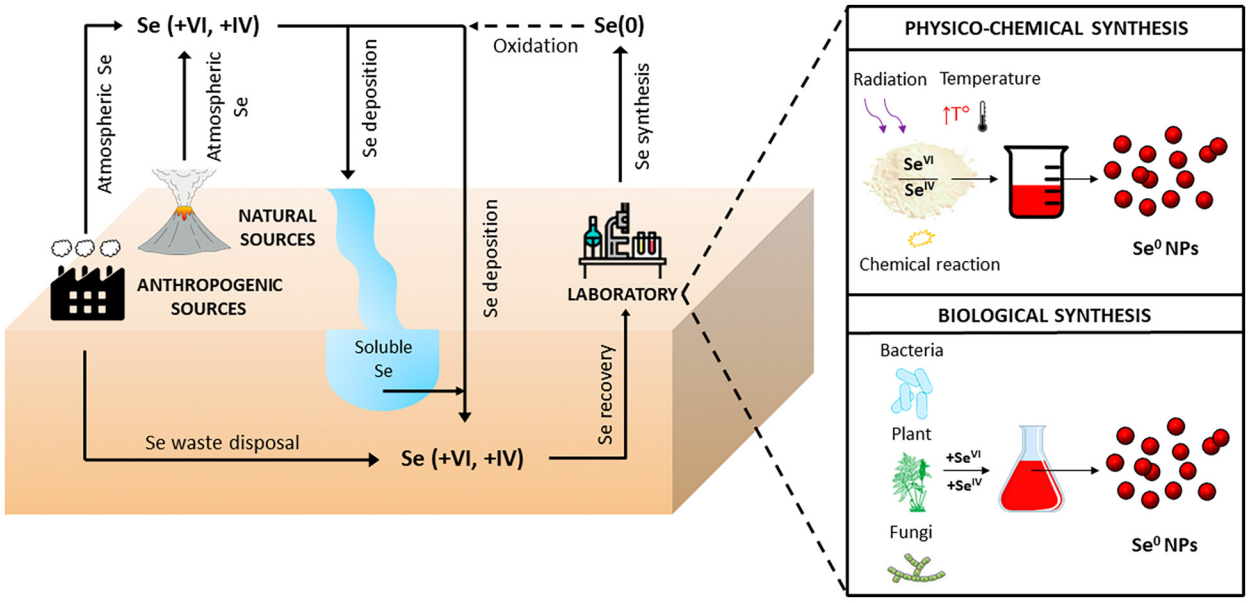

FIGURE 3 Se^0 recovery and synthesis model from anthropogenic and natural sources of toxic Se (Se^{VI} and Se^{IV}).

to dysfunctional macromolecules) and to the production on reactive oxygen species (ROS) (Ohlendorf et al., 2020). Selenium contamination of different environmental compartments (atmosphere, geosphere, hydrosphere) can originate from both anthropogenic and natural activities including mining, agricultural drainage water, fertilization, radioactive waste from power plants, petroleum refining, fossil fuel residues, or volcanic activities (Floor et al., 2013; Staicu et al., 2017; Wang et al., 2022) (Figure 3). Se oxyanions (+IV and + VI) are usually present at relatively low concentrations in nature (He et al., 2018; Wang et al., 2022). Concentrations ranging from 0.15 to 4.73 $\mu g L^{-1}$ Se^{IV} have been detected, for example, in ground waters from Chandigarh (India) (Bajaj et al., 2011). Higher amounts (around 341 $\mu g L^{-}1$) were found, however, in ground waters from Jaipur (India), and in industrial wastewater from Japan, with a maximum level of 0.1 $mg L^{-1}$ (Bajaj et al., 2011; Soda et al., 2011). However, release of Se and other contaminants into the environment is steadily increasing in the past years. For instance, Gerson et al. (2022) identified multiple anthropogenic sources of selenium release from coal wastes, mining activities being an important source of Se reaching the environment (Figure 3).

By transporting samples from contaminated environments or waste to laboratories and industrial facilities, chemical or biological processes can be employed for both bioremediation and NPs synthesis (Figure 3). As mentioned in the previous sections, Se^{IV} and Se^{VI} can be biologically and chemically transformed into insoluble and less toxic Se^0, forming useful and applicable NPs. Both amorphous and crystalline SeNPs are widely used nowadays in many applications. They have been intensively investigated firstly for early applications in xerography (Li & Regensburger, 1963; Tang et al., 2006) to the current use in X-ray imaging, photocells, rectifiers, solar cells, photographic exposure meters, pigment and glass production, etc. (Abbaszadeh & Huang, 2020; Ho et al., 2021; Panahi-Kalamuei et al., 2015). One of the most promising research lines about SeNPs use is focused on their potential role as anti-tumoral agents in several tumour types including lung, prostate, colorectal, cervical, and breast cancer (Cui et al., 2018; Hu et al., 2019; Liao et al., 2020; Xia et al., 2018). Although the specific molecular mechanisms are not fully understood, numerous studies reported that SeNPs can induce apoptosis of cancer cells inhibiting malignant tumours in different ways, with minimal effects on normal cells (Liao et al., 2020; Skalickova et al., 2017; Steinbrenner & Sies, 2009). Specifically, some proteins have been found to regulate crucial apoptotic pathways. Cruz et al. (2019) demonstrated the involvement of SeNPs in the caspase-3 enzyme activation, ultimately leading to the blockage of cancer cell proliferation and their apoptosis in lung cancerous cell lines. SeNPs have been identified as well to exhibit cytotoxic activity against prostate tumour cells (Liao et al., 2020). The findings of Liao et al. (2020) suggested that SeNPs treatment in prostate tumours increased apoptosis rates by upregulating microRNA miR-16 expression. Another important pathway to control cancer cell proliferation is related to the role of ROS. Chemically-synthesized Glu-SeNPs (glucose as reducing agent) with an amorphous nature quickly triggered intracellular ROS overproduction and mitochondria dysfunction leading to cellular death of hepatocellular carcinoma cells HepG2 (Nie et al., 2016). All these investigations on SeNPs provide new

promising alternative therapies against a disease as harmful as cancer.

Although both crystalline and amorphous NPs are of interest, recent studies indicate that crystalline t-Se NPs have different optical, thermodynamical, and electrical properties, which could make them more attractive in many fields. However, the unique properties of the most thermodynamically-stable phase of Se (t-Se), a layered Van der Waals solid, have not been deeply studied. For instance, crystalline Se capping topological insulators (TI) showed improved capability to preserve the intrinsic transport properties of TI in comparison with amorphous Se (Lin et al., 2018). In addition, Barman et al. (2022) recently observed high optical absorption coefficient and favourable transport properties of t-Se ultrathin films, which make t-Se attractive for the fabrication of photosensitive detector devices. Not only industrially, but also from an environmental point of view, crystalline Se has been described to be highly settleable and therefore more prone for separation/recovery than a-Se (Lenz et al., 2009). This fact makes Se crystals more attractive for bioremediation purposes since they would entail easier recovery. To sum up, the structure of SeNPs (amorphous or crystalline) can considerably affect their application due to their different properties. Notably, the new potential contributions and applications of crystalline properties are being investigated in the last years. However, this is the first review in the literature reporting and comparing the most recent advances in crystalline and amorphous Se applications separately.

After experimental treatment in laboratories and industries, SeNPs must be extracted and purified, and subsequently "cleaned" soils and wastewaters could be returned to their original location (Figure 3). The current problem is that a fully effective method for SeNPs production and extraction, that can be applied in the environment, has not yet been proposed and validated. As cited in the present study, many investigations are trying to elucidate an effective methodology, whether biological, physical, or chemical, with the aim of solving this environmental problem and making profit at the same time. The proposed model recognizes the importance of the circular economy concept in addressing environmental challenges such as global pollution.

CONCLUSIONS AND FUTURE DIRECTIONS

This review provides an updated bibliographical survey on the physicochemical and biological methods used for the reduction of Se oxyanions and the production of SeNPs with different shape, size, and allotropy. In addition, the Se^0 allotropic transition from amorphous to thermodynamically stable trigonal Se by different microbial strains was reviewed. This section is focused on underlying the gaps and perspectives both on Se reduction, Se allotropic biotransformation mechanisms and biotechnological applications of Se reduction products in the field of bioremediation, nanotechnology, and food industry.

An open question awaiting further investigation pertains to the origin of macromolecules capping biogenic SeNPs macromolecules. Some of them would have been involved in the biosynthesis of biogenic Se^0, while others may have been acquired later from the internal or from the spent microbial media due to electrostatic interactions. A future study using transposon mutagenesis could identify the macromolecules involved in the biomineralization process by creating mutants lacking or having impaired capacity to produce Se^0. In addition, further characterization of the molecular mechanisms of transport of biogenic SeNPs from the cytoplasm to extracellular space is needed to shed light on the microbial adaptation mechanisms to Se stress and the recovery of the intracellular and extracellular SeNPs for their industrial uses. Identification and characterization of proteins (e.g., flagella like proteins) involved in the transition of amorphous to trigonal Se could mimic cell properties and contribute to the fabrication of trigonal Se NPs without the use of microbial cells should be further investigated.

Immobilization of Se-reducing microbial strains on different inorganic matrices through technologies like sol gel will be useful for the design of efficient and sustainable bioremediation approaches of Se contaminated waters. These immobilization approaches promote cell viability, mechanical stability, enhancing the Se elimination potential of the biomaterial. A controlled and up-scalable route for the Se reduction using immobilized cells needs to be optimized. The bioremediation of Se through the immobilized Se reducing cells or their proteins would contribute to the recovery of Se as SeNPs with trigonal structure from wastes, and their reuse in different industrial fields within the concept of circular economy.

In addition to their potential use in bioremediation and nanotechnology, Se reducing microbes are very attractive in the food industry to meet the demand of Se supplementation for humans in Se-deficient regions. However, this field is in its infancy and further research should be addressed. For instance, understanding the mechanisms of microbial fabrication of organic Se through the Se reducing ability of Se-enriched lactic acid bacteria (LAB) deserve more attention. Specifically, targeting the fabrication of low toxic and high nutritional value Se compounds (e.g. selenocysteine, selenomethionine) needs to be further explored.

AUTHOR CONTRIBUTIONS

Miguel Angel Ruiz-Fresneda: Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); software (equal); supervision (equal); validation (equal); visualization (equal); writing – original draft (equal);

writing – review and editing (equal). **Lucian C. Staicu:** Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); supervision (equal); validation (equal); visualization (equal); writing – original draft (equal); writing – review and editing (equal). **Guillermo Lazuén-López:** Data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); software (equal); visualization (equal); writing – review and editing (equal). **Mohamed Larbi Merroun:** Conceptualization (equal); formal analysis (equal); funding acquisition (lead); investigation (equal); project administration (lead); resources (lead); supervision (lead); validation (equal); visualization (equal); writing – original draft (equal); writing – review and editing (equal).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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REFERENCES

Abbaszadeh, S. & Huang, H. (2020) Recent developments of amorphous selenium-based X-ray detectors: a review. *IEEE Sensors Journal*, 20, 1694–1704. Available from: https://doi.org/10.1109/JSEN.2019.2950319

Abdollahnia, M., Makhdoumi, A., Mashreghi, M. & Eshghi, H. (2020) Exploring the potentials of halophilic prokaryotes from a solar saltern for synthesizing nanoparticles: the case of silver and selenium. *PLoS One*, 15, e0229886. Available from: https://doi.org/10.1371/journal.pone.0229886

Ahmad, M. (2016) Solvothermal synthesis of selenium nano and microspheres deposited on silicon surface by microwave-assisted method. *MRX*, 3, 105–9031. Available from: https://doi.org/10.1088/2053-1591/3/10/105031

Alagesan, V. & Venugopal, S. (2019) Green synthesis of selenium nanoparticle using leaves extract of *Withania somnifera* and its biological applications and photocatalytic activities. *BNSC*, 9, 105–116. Available from: https://doi.org/10.1007/s12668-018-0566-8

Al-Saggaf, M.S., Tayel, A.A., Ghobashy, M.O., Alotaibi, M.A., Alghuthaymi, M.A. & Moussa, S.H. (2020) Phytosynthesis of selenium nanoparticles using the costus extract for bactericidal application against foodborne pathogens. *Green Processing and Synthesis*, 9, 477–487.

Alvares, J.J. & Furtado, I.J. (2022) Conversion of selenite by *Haloferax alexandrinus* GUSF-1 (KF796625) to pentagonal selenium nanoforms which in vitro modulates the formation of calcium oxalate crystals. *Journal of Applied Microbiology*, 132, 1900–1913. Available from: https://doi.org/10.1111/jam.15309

Avendaño, R., Chaves, N., Fuentes, P., Sánchez, E., Jiménez, J.I. & Chavarría, M. (2016) Production of selenium nanoparticles in *pseudomonas putida* KT2440. *Scientific Reports*, 6, 1–9. Available from: https://doi.org/10.1038/srep37155

Bajaj, M., Eiche, E., Neumann, T., Winter, J. & Gallert, C. (2011) Hazardous concentrations of selenium in soil and groundwater in north-West India. *Journal of Hazardous Materials*, 189, 640–646. Available from: https://doi.org/10.1016/j.jhazmat.2011.01.086

Barman, S.K., Huda, M.N., Asaadi, J., Gramellini, E. & Nygren, D. (2022) Surface and optoelectronic properties of ultrathin trigonal selenium: a density functional theory study with van der Waals correction. *Langmuir*, 38, 8485–8494. Available from: https://doi.org/10.1021/acs.langmuir.1c02935

Bulgarini, A., Lampis, S., Turner, R.J. & Vallini, G. (2021) Biomolecular composition of capping layer and stability of biogenic selenium nanoparticles synthesized by five bacterial species. *Microbial Biotechnology*, 14, 198–212. Available from: https://doi.org/10.1111/1751-7915.13666

Butler, C.S., Debieux, C.M., Dridge, E.J., Splatt, P. & Wright, M. (2012) Biomineralization of selenium by the selenate-respiring bacterium *Thauera selenatis*. *Biochemical Society Transactions*, 40, 1239–1243. Available from: https://doi.org/10.1042/bst20120087

Cao, G.S., Zhang, X.J., Su, L. & Ruan, Y.Y. (2011) Hydrothermal synthesis of selenium and tellurium nanorods. *Journal of Experimental Nanoscience*, 6, 121–126. Available from: https://doi.org/10.1080/17458081003774677

Che, L., Xu, W., Zhan, J., Zhang, L., Liu, L. & Zhou, H. (2019) Complete genome sequence of *Bacillus cereus* CC-1, a novel marine selenate/selenite reducing bacterium producing metallic selenides nanomaterials. *Current Microbiology*, 76, 78–85. Available from: https://doi.org/10.1007/s00284-018-1587-9

Chen, H., Shin, D.W., Nam, J.G., Kwon, K.W. & Yoo, J.B. (2010) Selenium nanowires and nanotubes synthesized via a facile template-free solution method. *Materials Research Bulletin*, 45, 699–704. Available from: https://doi.org/10.1016/j.materresbull.2010.02.016

Cosmidis, J. & Benzerara, K. (2022) Why do microbes make minerals? *Comptes Rendus Geoscience*, 354, 1–39. Available from: https://doi.org/10.5802/crgeos.107

Cruz, L.Y., Wang, D. & Liu, J. (2019) Biosynthesis of selenium nanoparticles, characterization and X-ray induced radiotherapy for the treatment of lung cancer with interstitial lung disease. *Journal of Photochemistry and Photobiology B: Biology*, 191, 123–127. Available from: https://doi.org/10.1016/j.jphotobiol.2018.12.008

Cui, D., Yan, C., Miao, J., Zhang, X., Chen, J., Sun, L. et al. (2018) Synthesis, characterization and antitumor properties of selenium nanoparticles coupling with ferulic acid. *Materials Science and Engineering*, 90, 104–112. Available from: https://doi.org/10.1016/j.msec.2018.04.048

Deepa, B. & Ganesan, V. (2015) Bioinspired synthesis of selenium nanoparticles using flowers of *Catharanthus roseus* (L.) G. Don. And *Peltophorum pterocarpum* (DC.) backer ex Heyne–a comparison. *International Journal of ChemTech Research*, 7, 725–733.

Dwivedi, C., Shah, C.P., Singh, K., Kumar, M. & Bajaj, P.N. (2011) An organic acid-induced synthesis and characterization of selenium nanoparticles. *Journal of Nanotechnology*, 2011, 651–971. Available from: https://doi.org/10.1155/2011/651971

Eswayah, A.S., Hondow, N., Scheinost, A.C., Merroun, M.L., Romero-Gonzalez, M., Smith, T.J. et al. (2019) Methyl selenol as precursor in selenite reduction to Se/S species by methane-oxidizing bacteria. *Applied and Environmental Microbiology*, 85(22), e01379–e01319. Available from: https://doi.org/10.1128/AEM.01379-19

Faramarzi, S., Anzabi, Y. & Jafarizadeh-Malmiri, H. (2020) Nanobiotechnology approach in intracellular selenium nanoparticle synthesis using *Saccharomyces cerevisiae*—fabrication and characterization. *Archives of Microbiology*, 202, 1203–1209. Available from: https://doi.org/10.1007/s00203-020-01831-0

Fellowes, J.W., Pattrick, R.A., Green, D.I., Dent, A., Lloyd, J.R. & Pearce, C.I. (2011) Use of biogenic and abiotic elemental selenium nanospheres to sequester elemental mercury released from mercury contaminated museum specimens. *Journal of Hazardous Materials*, 189, 660–669. Available from: https://doi.org/10.1016/j.jhazmat.2011.01.079

Fernández-Martínez, A. & Charlet, L. (2009) Selenium environmental cycling and bioavailability: a structural chemist point of view. *Reviews in Environmental Science and Biotechnology*, 8, 81–110.

Fischer, S., Krause, T., Lederer, F., Merroun, M.L., Shevchenko, A., Hübner, R. et al. (2020) *Bacillus safensis* JG-B5T affects the fate of selenium by extracellular production of colloidally less stable nanoparticles. *Journal of Hazardous Materials*, 384, 121146. Available from: https://doi.org/10.1016/j.jhazmat.2019.121146

Floor, G.H., Marguí, E., Hidalgo, M., Queralt, I., Kregsamer, P., Streli, C. et al. (2013) Study of selenium sorption processes in volcanic ash using Total reflection X-ray fluorescence (TXRF). *Chemical Geology*, 352, 19–26.

Gangadoo, S., Stanley, D., Hughes, R.J., Moore, R.J. & Chapman, J. (2017) The synthesis and characterisation of highly stable and reproducible selenium nanoparticles. *Inorganic and Nano-Metal Chemistry*, 47, 1568–1576. Available from: https://doi.org/10.1080/24701556.2017.1357611

Geoffrion, L.D., Hesabizadeh, T., Medina-Cruz, D., Kusper, M., Taylor, P., Vernet-Crua, A. et al. (2020) Naked selenium nanoparticles for antibacterial and anticancer treatments. *ACS Omega*, 5, 2660–2669. Available from: https://doi.org/10.1021/acsomega.9b03172

Gerson, A.R., Fan, R., Qian, G., Schumann, R.C., Olin, P., Howard, D.L. et al. (2022) Examination of multiple sources of selenium release from coal wastes and strategies for remediation. *Journal of Hazardous Materials*, 422, 126924. Available from: https://doi.org/10.1016/j.jhazmat.2021.126924

Gralnick, J.A. & Newman, D.K. (2007) Extracellular respiration. *Molecular Microbiology*, 65, 1–11. Available from: https://doi.org/10.1111/j.1365-2958.2007.05778

Guisbiers, G., Wang, Q., Khachatryan, E., Mimun, L.C., Mendoza-Cruz, R., Larese-Casanova, P. et al. (2016) Inhibition of *E. Coli* and *S. aureus* with selenium nanoparticles synthesized by pulsed laser ablation in deionized water. *International Journal of Nanomedicine*, 11, 3731–3736. Available from: https://doi.org/10.2147/IJN.S106289

Güven, K., Mutlu, M.B., Çirpan, C. & Kutlu, H.M. (2013) Isolation and identification of selenite reducing archaea from Tuz (salt) Lake In Turkey. *Journal of General Microbiology*, 53, 397–401. Available from: https://doi.org/10.1002/jobm.201200008

Hageman, S.P.W., van der Weijden, R.D., Stams, A.J.M. & Buisman, C.J.N. (2017) Bio-production of selenium nanoparticles with diverse physical properties for recovery from water. *International Journal of Mineral Processing*, 169, 7–15. Available from: https://doi.org/10.1016/j.minpro.2017.09.018

He, Y., Xiang, Y., Zhou, Y., Yang, Y., Zhang, J., Huang, H. et al. (2018) Selenium contamination, consequences and remediation techniques in water and soils: a review. *Environmental Research*, 164, 288–301. Available from: https://doi.org/10.1016/j.envres.2018.02.037

Herrero, E. & Wellinger, R.E. (2015) Yeast as a model system to study metabolic impact of selenium compounds. *Microbial Cell*, 2, 139–149. Available from: https://doi.org/10.15698/mic2015.05.200

Hien, N.Q., Tuan, P.D., van Phu, D., Quoc, L.A., Lan, N.T.K., Duy, N.N. et al. (2018) Gamma Co-60 ray irradiation synthesis of dextran stabilized selenium nanoparticles and their antioxidant activity. *Materials Chemistry and Physics*, 205, 29–34. Available from: https://doi.org/10.1016/j.matchemphys.2017.11.003

Ho, C.T., Nguyen, T.H., Lam, T.T., Le, D.Q., Nguyen, C.X., Lee, J. et al. (2021) Biogenic synthesis of selenium nanoparticles by *Shewanella* sp. HN-41 using a modified bioelectrochemical system. *Electronic Journal of Biotechnology*, 54, 1–7. Available from: https://doi.org/10.1016/j.ejbt.2021.07.004

Holmes, A.B., Ngan, A., Ye, J. & Gu, F. (2022) Selective photocatalytic reduction of selenate over TiO_2 in the presence of nitrate and sulfate in mine-impacted water. *Chemosphere*, 287, 131–951. Available from: https://doi.org/10.1016/j.chemosphere.2021.131951

Hu, Y., Liu, T., Li, J., Mai, F., Li, J., Chen, Y. et al. (2019) Selenium nanoparticles as new strategy to potentiate γδ T cell anti-tumor cytotoxicity through upregulation of tubulin-α acetylation. *Biomaterials*, 222, 119–397. Available from: https://doi.org/10.1016/j.biomaterials.2019.119397

Husen, A. & Siddiqi, K.S. (2014) Plants and microbes assisted selenium nanoparticles: characterization and application. *Journal of Nanobiotechnology*, 12, 1–10. Available from: https://doi.org/10.1186/s12951-014-0028-6

Hussein, H.G., El-Sayed, E.S.R., Younis, N.A., Hamdy, A.E.H.A. & Easa, S.M. (2022) Harnessing endophytic fungi for biosynthesis of selenium nanoparticles and exploring their bioactivities. *AMB Express*, 12, 68. Available from: https://doi.org/10.1186/s13568-022-01408-8

Iranifam, M., Fathinia, M., Sadeghi Rad, T., Hanifehpour, Y., Khataee, A.R. & Joo, S.W. (2013) A novel selenium nanoparticles-enhanced chemiluminescence system for determination of dinitrobutylphenol. *Talanta*, 107, 263–269. Available from: https://doi.org/10.1016/j.talanta.2012.12.043

Jadhav, A.A. & Khanna, P.K. (2015) Impact of microwave irradiation on cyclo-octeno-1,2,3-selenadiazole: formation of selenium nanoparticles and their polymorphs. *RSC Advances*, 5, 44756–44763. Available from: https://doi.org/10.1039/c5ra05701a

Jain, R., Jordan, N., Weiss, S., Foerstendorf, H., Heim, K., Kacker, R. et al. (2015) Extracellular polymeric substances govern the surface charge of biogenic elemental selenium nanoparticles. *Environmental Science & Technology*, 49, 1713–1720. Available from: https://doi.org/10.1021/es5043063

Jia, H., Huang, S., Cheng, S., Zhang, X., Chen, X., Zhang, Y. et al. (2022) Novel mechanisms of selenite reduction in *Bacillus subtilis* 168:Confirmation of multiple-pathway mediated remediation based on transcriptome analysis. *Journal of Hazardous Materials*, 433, 128–834. Available from: https://doi.org/10.1016/j.jhazmat.2022.128834

Johnson, N.C., Manchester, S., Sarin, L., Gao, Y., Kulaots, I. & Hurt, R.H. (2008) Mercury vapor release from broken compact fluorescent lamps and in situ capture by new nanomaterial sorbents. *Environmental Science & Technology*, 42, 5772–5778. Available from: https://doi.org/10.1021/es8004392

Joshi, S.M., De Britto, S., Jogaiah, S. & Ito, S.I. (2019) Mycogenic selenium nanoparticles as potential new generation broad spectrum antifungal molecules. *Biomolecules*, 9, 419. Available from: https://doi.org/10.3390/biom9090419

Kora, A.J. (2018) *Bacillus cereus*, selenite-reducing bacterium from contaminated lake of an industrial area: a renewable nanofactory for the synthesis of selenium nanoparticles. *Bioresources and Bioprocessing*, 5, 1–12. Available from: https://doi.org/10.1186/s40643-018-0217-5

Kora, A.J. & Rastogi, L. (2017) Bacteriogenic synthesis of selenium nanoparticles by *Escherichia coli* ATCC 35218 and its structural characterisation. *IET Nanobiotechnology*, 11, 179–184. Available from: https://doi.org/10.1049/iet-nbt.2016.0011

Kuzmin, P.G., Shafeev, G.A., Voronov, V.V., Raspopov, R.V., Arianova, E.A., Trushina, E.N. et al. (2012) Bioavailable nanoparticles obtained in laser ablation of a selenium target in water. *Quantum Electronics*, 42, 1042–1044. Available from: https://doi.org/10.1070/qe2012v042n11abeh014754

Lampis, S. & Vallini, G. (2021) Microbial reduction of selenium oxyanions: energy-yielding and detoxification reactions. In: Lens, P. & Pakshriajan, K. (Eds.) *Environmental technologies to treat selenium pollution: principles and engineering*. London: IWA Publishing, pp. 101–143. Available from: https://doi.org/10.2166/9781789061055_0101

Lampis, S., Zonaro, E., Bertolini, C., Cecconi, D., Monti, F., Micaroni, M. et al. (2017) Selenite biotransformation and detoxification by *Stenotrophomonas maltophilia* SeITE02: novel clues on the route to bacterial biogenesis of selenium nanoparticles. *Journal of Hazardous Materials*, 324, 3–14. Available from: https://doi.org/10.1016/j.jhazmat.2016.02.035

Lei, W.B., Xu, W.Q., Qi, R.J. & Huang, R. (2020) Facile synthesis and growth mechanism of trigonal selenium nanowries. *CHL*, 17, 615–621. Available from: https://doi.org/10.1016/j.matlet.2012.05.063

Lenz, M., Van Aelst, A.C., Smit, M., Corvini, P.F.X. & Lens, P.N.L. (2009) Biological production of selenium nanoparticles from waste waters. *Advanced Materials Research*, 71, 721–724. Available from: https://doi.org/10.4028/www.scientific.net/AMR.71-73.721

Li, H.T. & Regensburger, P.J. (1963) Photoinduced discharge characteristics of amorphous selenium plates. *Journal of Applied Physics*, 34, 1730–1735. Available from: https://doi.org/10.1063/1.1702669

Li, Q., Chen, T., Yang, F., Liu, J. & Zheng, W. (2010) Facile and controllable one-step fabrication of selenium nanoparticles assisted by l-cysteine. *Materials Letters*, 64, 614–617. Available from: https://doi.org/10.1016/j.matlet.2009.12.019

Liang, X., Perez, M.A.M.J., Nwoko, K.C., Egbers, P., Feldmann, J., Csetenyi, L. et al. (2019) Fungal formation of selenium and tellurium nanoparticles. *Applied Microbiology and Biotechnology*, 103, 7241–7259. Available from: https://doi.org/10.1007/s00253-019-09995-6

Liao, G., Tang, J., Wang, D., Zuo, H., Zhang, Q., Liu, Y. et al. (2020) Selenium nanoparticles (SeNPs) have potent antitumor activity against prostate cancer cells through the upregulation of miR-16. *World Journal of Surgical Oncology*, 18, 1–11. Available from: https://doi.org/10.1186/s12957-020-01850-7

Lin, H.Y., Cheng, C.K., Chen, K.H.M., Tseng, C.C., Huang, S.W., Chang, M.T. et al. (2018) A new stable, crystalline capping material for topological insulators. *APL Materials*, 6, 066108. Available from: https://doi.org/10.1063/1.5029706

Lortie, L., Gould, W.D., Rajan, S., McCready, R.G.L. & Cheng, K.J. (1992) Reduction of Selenate and selenite to elemental selenium by a *pseudomonas stutzeri* isolate. *AEM*, 58, 4042–4044. Available from: https://doi.org/10.1128/aem.58.12.4042-4044.1992

Mayers, B.T., Liu, K., Sunderland, D. & Xia, Y. (2003) Sonochemical synthesis of trigonal selenium nanowires. *Chemistry of Materials*, 15, 3852–3858. Available from: https://doi.org/10.1021/cm034193b

Mondal, K., Roy, P. & Srivastava, S.K. (2008) Facile biomolecule-assisted hydrothermal synthesis of trigonal selenium microrods. *Crystal Growth & Design*, 8, 1580–1584. Available from: https://doi.org/10.1021/cg7008557

Naik, M.M., Bagayat, A. & Charya, L.S. (2017) Extreme halophilic *archaea halobacterium* SP. SP1 in bioremediation of hypersaline water polluted with metal, metalloid, organometal and aromatic compound. *IJAM*, 20, 42–54.

Ni, T.W., Staicu, L.C., Nemeth, R., Schwartz, C., Crawford, D., Seligman, J.D. et al. (2015) Progress toward clonable inorganic nanoparticles. *Nanoscale*, 7, 17320–17327. Available from: https://doi.org/10.1039/c5nr04097c

Nie, T., Wu, H., Wong, K.H. & Chen, T. (2016) Facile synthesis of highly uniform selenium nanoparticles using glucose as the reductant and surface decorator to induce cancer cell apoptosis. *JMCBDV*, 4, 2351–2358. Available from: https://doi.org/10.1039/c5tb02710a

Nu Hoai Nguyen, V., Amal, R. & Beydoun, D. (2005) Photocatalytic reduction of selenium ions using different TiO2 photocatalysts. *Chemical Engineering Science*, 60, 5759–5769. Available from: https://doi.org/10.1016/j.ces.2005.04.085

Ohlendorf, H.M., Santolo, G.M., Byron, E.R. & Eisert, M.A. (2020) Kesterson reservoir: 30 years of selenium risk assessment and management. *Environmental Management*, 16, 257–268. Available from: https://doi.org/10.1002/ieam.4222

Ojeda, J.J., Merroun, M.L., Tugarova, A.V., Lampis, S., Kamnev, A.A. & Gardiner, P.H.E. (2020) Developments in the study and applications of microbial transformations of selenium species. *Critical Reviews in Biotechnology*, 40, 1250–1264. Available from: https://doi.org/10.1080/07388551.2020.1811199

Oremland, R.S., Herbel, M.J., Blum, J.S., Langley, S., Beveridge, T.J., Ajayan, P.M. et al. (2004) Structural and spectral features of selenium nanospheres produced by Se-respiring bacteria. *Applied and Environmental Microbiology*, 70, 52–60. Available from: https://doi.org/10.1128/AEM.70.1.52-60.2004

Panahi-Kalamuei, M., Salavati-Niasari, M., Zarghami, Z., Mousavi-Kamazani, M., Taqriri, H. & Mohsenikia, A. (2015) Synthesis and characterization of Se nanostructures via co-precipitation, hydrothermal, microwave and sonochemical routes using novel starting reagents for solar cells. *Journal of Materials Science: Materials in Electronics*, 26, 2851–2860. Available from: https://doi.org/10.1007/s10854-015-2768

Pearce, C.I., Pattrick, R.A.D., Law, N., Charnock, J.M., Coker, V.S., Fellowes, J.W. et al. (2009) Investigating different mechanisms for biogenic selenite transformations: *Geobacter sulfurreducens*, *Shewanella oneidensis* and *Veillonella atypica*. *Environmental Technology*, 30, 1313–1326. Available from: https://doi.org/10.1080/09593330902984751

Pereira, A.G., Gerolis, L.G.L., Gonçalves, L.S., Moreira, L.M.C., Gastelois, P.L. & Neves, M.J. (2022) Radiolytic synthesis and characterization of selenium nanoparticles: comparative biosafety evaluation with selenite and ionizing radiation. *World Journal of Microbiology and Biotechnology*, 38, 1–13. Available from: https://doi.org/10.1007/s11274-021-03218-9

Perumal, S., Gopal Samy, M.V. & Subramanian, D. (2021) Selenium nanoparticle synthesis from endangered medicinal herb (*Enicostema axillare*). *Bioprocess and Biosystems Engineering*, 44, 1853–1863. Available from: https://doi.org/10.1007/s00449-021-02565-z

Piacenza, E., Presentato, A., Ambrosi, E., Speghini, A., Turner, R.J., Vallini, G. et al. (2018) Physical–chemical properties of biogenic selenium nanostructures produced by *Stenotrophomonas maltophilia* SeITE02 and *Ochrobactrum* sp. MPV1. *Frontiers in Microbiology*, 9, 3178. Available from: https://doi.org/10.3389/fmicb.2018.03178

Pinel-Cabello, M., Chapon, V., Ruiz-Fresneda, M.A., Alpha-Bazin, B., Berthomieu, C., Armengaud, J. et al. (2021) Delineation of cellular stages and identification of key proteins for reduction

and biotransformation of Se(IV) in *Stenotrophomonas bentonitica* BII-R7. *Journal of Hazardous Materials*, 418, 126150. Available from: https://doi.org/10.1016/j.jhazmat.2021.126150

Prasad, K.S. & Selvaraj, K. (2014) Biogenic synthesis of selenium nanoparticles and their effect on As (III)-induced toxicity on human lymphocytes. *Biological Trace Element Research*, 157, 275–283. Available from: https://doi.org/10.1007/s12011-014-9891-0

Presentato, A., Piacenza, E., Anikovskiy, M., Cappelletti, M., Zannoni, D. & Turner, R.J. (2018) Biosynthesis of selenium-nanoparticles and-nanorods as a product of selenite bioconversion by the aerobic bacterium *Rhodococcus aetherivorans* BCP1. *New Biotechnology*, 41, 1–8. Available from: https://doi.org/10.1016/j.nbt.2017.11.002

Properzi, L., Polian, A., Munsch, P. & Di Cicco, A. (2013) Investigation of the phase diagram of selenium by means of Raman spectroscopy. *High Pressure Research*, 33, 35–39. Available from: https://doi.org/10.1080/08957959.2013.769048

Rosenfeld, C.E., Kenyon, J.A., James, B.R. & Santelli, C.M. (2017) Selenium (IV,VI) reduction and tolerance by fungi in an oxic environment. *Geobiology*, 15, 441–452. Available from: https://doi.org/10.1111/gbi.12224

Roux, M., Sarret, G., Pignot-Paintrand, I., Fontecave, M. & Coves, J. (2001) Mobilization of selenite by *Ralstonia metallidurans* CH34. *AEM*, 6, 769–773. Available from: 10.1128/AEM.67.2.769-773.2001

Ruiz-Fresneda, M.A., Martín, J.D., Bolívar, J.G., Cantos, M.V.F., Bosch-Estévez, G., Moreno, M.F.M. et al. (2018) Green synthesis and biotransformation of amorphous Se nanospheres to trigonal 1D Se nanostructures: impact on Se mobility within the concept of radioactive waste disposal. *Environmental Science. Nano*, 5, 2103–2116. Available from: https://doi.org/10.1039/C8EN00221E

Ruiz-Fresneda, M.A., Gomez-Bolivar, J., Delgado-Martin, J., Abad-Ortega, M.D.M., Guerra-Tschuschke, I. & Merroun, M.L. (2019) The bioreduction of selenite under anaerobic and alkaline conditions analogous to those expected for a deep geological repository system. *Molecules*, 24, 3868. Available from: https://doi.org/10.3390/molecules24213868

Ruiz-Fresneda, M.A., Eswayah, A.S., Romero-González, M., Gardiner, P.H.E., Solari, P.L. & Merroun, M.L. (2020) Chemical and structural characterization of SeIV biotransformations by *Stenotrophomonas bentonitica* into Se0 nanostructures and volatiles Se species. *Environmental Science. Nano*, 7, 2140–2155. Available from: https://doi.org/10.1039/D0EN00507J

Ruiz-Fresneda, M.A., Fernández-Cantos, M.V., Gómez-Bolívar, J., Eswayah, A.S., Gardiner, P.H.E., Pinel-Cabello, M. et al. (2023) Combined bioreduction and volatilization of Se(VI) by *Stenotrophomonas bentonitica*: formation of trigonal selenium nanorods and methylated species. *Science of the Total Environment*, 858, 160030. Available from: https://doi.org/10.1016/j.scitotenv.2022.160030

Salunke, G.R., Ghosh, S., Santosh Kumar, R.J., Khade, S., Vashisth, P., Kale, T. et al. (2014) Rapid efficient synthesis and characterization of silver, gold, and bimetallic nanoparticles from the medicinal plant *Plumbago zeylanica* and their application in biofilm control. *International Journal of Nanomedicine*, 9, 2635–2653. Available from: https://doi.org/10.2147/IJN.S59834

Shahbazi, B., Taghipour, M., Rahmani, H., Sadrjavadi, K. & Fattahi, A. (2015) Preparation and characterization of silk fibroin/oligochitosan nanoparticles for siRNA delivery. *Colloids and Surfaces, B: Biointerfaces*, 36, 867–877. Available from: https://doi.org/10.1016/j.colsurfb.2015.10.044

Shameli, K., Ahmad, M.B., Jazayeri, S.D., Sedaghat, S., Shabanzadeh, P., Jahangirian, H. et al. (2012) Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method. *International Journal of Molecular Sciences*, 13, 6639–6650. Available from: https://doi.org/10.3390/ijms13066639

Shanan Abed, M., Abed, A.S. & Mohammad Othman, F. (2019) Green synthesis of silver nanoparticles from natural compounds: glucose, eugenol and thymol. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 60, 95–111.

Shoeibi, S., Mozdziak, P. & Golkar-Narenji, A. (2017) Biogenesis of selenium nanoparticles using Green chemistry. *Topics in Current Chemistry*, 375, 1–21. Available from: https://doi.org/10.1007/s41061-017-0176-x

Skalickova, S., Milosavljevic, V., Cihalova, K., Horky, P., Richtera, L. & Adam, V. (2017) Selenium nanoparticles as a nutritional supplement. *Frontiers in Nutrition*, 33, 83–90. Available from: https://doi.org/10.1016/j.nut.2016.05.001

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

Srivastava, P., Braganca, J.M. & Kowshik, M. (2014) In vivo synthesis of selenium nanoparticles by *Halococcus salifodinae* BK18 and their anti-proliferative properties against HeLa cell line. *Biotechnology Progress*, 30, 1480–1487. Available from: https://doi.org/10.1002/btpr.1992

Staicu, L.C. & Barton, L.L. (2021) Selenium respiration in anaerobic bacteria: does energy generation pay off? *Journal of Inorganic Biochemistry*, 222, 111509. Available from: https://doi.org/10.1016/j.jinorgbio.2021.111509

Staicu, L.C., van Hullebusch, E.D., Oturan, M.A., Ackerson, C.J. & Lens, P.N.L. (2015) Removal of colloidal biogenic selenium from wastewater. *Chemosphere*, 125, 130–138. Available from: https://doi.org/10.1016/j.chemosphere.2014.12.018

Staicu, L.C., van Hullebusch, E.D. & Lens, P.N.L. (2017) Industrial selenium pollution. Wastewaterand physical-chemical treatment technologies. In: van Hullebusch, E.D. (Ed.) *Bioremediation of selenium contaminated wastewaters*. Cham: Springer, pp. 75–101.

Staicu, L.C., Wojtowicz, P.J., Molnár, Z., Ruiz-Agudo, E., Gallego, J.L.R., Baragaño, D. et al. (2022) Interplay between arsenic and selenium biomineralization in *Shewanella* sp. O23S. *Environmental Pollution*, 306, 119451. Available from: https://doi.org/10.1016/j.envpol.2022.119451

Steinbrenner, H. & Sies, H. (2009) Protection against reactive oxygen species by selenoproteins. *Bbva-gen Subjects*, 1790, 1478–1485. Available from: https://doi.org/10.1016/j.bbagen.2009.02.014

Stroyuk, A.L., Raevskaya, A.E., Kuchmiy, S.Y., Dzhagan, V.M., Zahn, D.R.T. & Schulze, S. (2008) Structural and optical characterization of colloidal Se nanoparticles prepared via the acidic decomposition of sodium selenosulfate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 320, 169–174. Available from: https://doi.org/10.1016/j.colsurfa.2008.01.055

Sun, K., Qiu, J., Liu, J. & Miao, Y. (2009) Preparation and characterization of gold nanoparticles using ascorbic acid as reducing agent in reverse micelles. *Journal of Materials Science: Materials in Electronics*, 44, 754–758. Available from: https://doi.org/10.1007/s10853-008-3162-4

Tang, K., Yu, D., Wang, F. & Wang, Z. (2006) Controlled growth of hexagonal trigonal selenium microtubes. *Crystal Growth & Design*, 6, 2159–2162. Available from: https://doi.org/10.1021/cg050653x

Tugarova, A.V., Mamchenkova, P.V., Datlova, Y.A. & Kamnev, A.A. (2018) FTIR and Raman spectroscopic studies of selenium nanoparticles synthesised by the bacterium *Azospirillum thiophilum*. *SAA*, 192, 458–463. Available from: https://doi.org/10.1016/j.saa.2017.11.050

Tugarova, A.V., Mamchenkova, P.V., Khanadeev, V.A. & Kamnev, A.A. (2020) Selenite reduction by the rhizobacterium *Azospirillum brasilense*, synthesis of extracellular selenium nanoparticles

and their characterisation. *New Biotechnology*, 58, 17–24. Available from: https://doi.org/10.1016/j.nbt.2020.02.003

Verma, P. & Maheshwari, S.K. (2018) Preparation of sliver and selenium nanoparticles and its characterization by dynamic light scattering and scanning electron microscopy. *J Microsc Ultrastruct*, 6, 182–187. Available from: https://doi.org/10.4103/JMAU.JMAU_3_18

Vieira, A.P., Stein, E.M., Andreguetti, D.X., Cebrián-Torrejón, G., Doménech-Carbó, A., Colepicolo, P. et al. (2017) "Sweet chemistry": a Green way for obtaining selenium nanoparticles active against cancer cells. *Journal of the Brazilian Chemical Society*, 28, 2021–2027. Available from: https://doi.org/10.21577/0103-5053.20170025

Wadhwani, S.A., Shedbalkar, U.U., Singh, R. & Chopade, B.A. (2016) Biogenic selenium nanoparticles: current status and future prospects. *Applied Microbiology and Biotechnology*, 100, 2555–2566. Available from: https://doi.org/10.1007/s00253-016-7300-7

Wadhwani, S.A., Gorain, M., Banerjee, P., Shedbalkar, U.U., Singh, R., Kundu, G. et al. (2017) Green synthesis of selenium nanoparticles using *Acinetobacter* sp. SW30: optimization, characterization and its anticancer activity in breast cancer cells. *International Journal of Nanomedicine*, 12, 6841–6855. Available from: https://doi.org/10.2147/IJN.S139212

Wang, Z., Wang, Y., Gomes, R.L. & Gomes, H.I. (2022) Selenium (Se) recovery for technological applications from environmental matrices based on biotic and abiotic mechanisms. *Journal of Hazardous Materials*, 427, 128122. Available from: https://doi.org/10.1016/j.jhazmat.2021.128122

Xia, Y., Chen, Y., Hua, L., Zhao, M., Xu, T., Wang, C. et al. (2018) Functionalized selenium nanoparticles for targeted delivery of doxorubicin to improve non-small-cell lung cancer therapy. *International Journal of Nanomedicine*, 13, 6929–6939. Available from: https://doi.org/10.2147/IJN.S174909

Xu, C., Guo, Y., Qiao, L., Ma, L., Cheng, Y. & Roman, A. (2018) Biogenic synthesis of novel functionalized selenium nanoparticles by *Lactobacillus casei* ATCC 393 and its protective effects on intestinal barrier dysfunction caused by enterotoxigenic *Escherichia coli* K88. *Frontiers in Microbiology*, 9, 1129. Available from: https://doi.org/10.3389/fmicb.2018.01129

Xu, X., Cheng, W., Liu, X., You, H., Wu, G., Ding, K. et al. (2020) Selenate reduction and selenium enrichment of tea by the endophytic *Herbaspirillum* sp. strain WT00C. *Current Microbiology*, 77, 588–601. Available from: https://doi.org/10.1007/s00284-019-01682-z

Ying, S., Guan, Z., Ofoegbu, P.C., Clubb, P., Rico, C., He, F. et al. (2022) Green synthesis of nanoparticles: current developments and limitations. *Environmental Technology and Innovation*, 10, 23–36. Available from: https://doi.org/10.1016/j.eti.2022.102336

Zhang, X., Yan, H., Ma, L., Zhang, H. & Ren, D.F. (2020) Preparation and characterization of selenium nanoparticles decorated by *Spirulina platensis* polysaccharide. *Journal of Food Biochemistry*, 44, 13–63. Available from: https://doi.org/10.1111/jfbc.13363

Zhu, Y., Kong, X., Wu, E., Zhu, N., Liang, D., Lou, M. et al. (2021) Biosynthesis of spherical selenium nanoparticles with halophilic *Bacillus subtilis* subspecies stercoris strain XP for inhibition of strawberry pathogens. *Chinese Journal of Biotechnology*, 37, 2825–2835. Available from: https://doi.org/10.13345/j.cjb.200581

Zou, J., Su, S., Chen, Z., Liang, F., Zeng, Y., Cen, W. et al. (2019) Hyaluronic acid-modified selenium nanoparticles for enhancing the therapeutic efficacy of paclitaxel in lung cancer therapy. *Artificial Cells, Nanomedicine, and Biotechnology*, 47(1), 3456–3464. Available from: https://doi.org/10.1080/21691401.2019.1626863

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