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REVIEW

Selenium and nano-selenium in agroecosystems

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Abstract Selenium (Se) is an essential health element becoming rare in food as a result of intensive plant production. Indeed, several enzymes contain selenium in the form of the unusual selenocysteine amino acid. Selenium was found an essential nutrient in the late 1950s, when selenium was found to replace vitamin E in the diets of rats and chicks for the prevention of vascular, muscular, and hepatic lesions. At that time, selenium was considered solely as a toxic element in the northern Great Plains of the USA, because selenium was associated with the 'alkali disease' of grazing livestock. The major source of Se in soils is the weathering of Se-containing rocks. Secondary sources are volcanic activities, dusts such as in the vicinity of coal burning, Se-containing fertilizers, and some waters. Se cycles through the food system; Se is first removed from soils by plants and soil microorganisms, which can take up Se into their proteins and produce volatile forms such as dimethylselenide. Dimethylselenide enters the atmosphere to be brought down with precipitation and airborne particulates. Here, we review Se in agroecosystems. We focus on the production, biological effects, and use of nano-selenium particles.

Keywords Selenium · Agroecosystem · Nano-selenium · Elemental selenium · Nanotechnology · Nanoparticles

Introduction

Selenium (Se), the essential poison, is a contradictory nutrient, because too much selenium in the diet can be toxic, whereas too little can result in chronic, and sometimes fatal, deficiency. Selenium is a key player in cellular metabolism, an essential component of enzymes that protect the body against oxidative damage and has important

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roles in metabolism of thyroid, human fertility, and many other vital functions (Reilly 2006). It is isolated and chemically characterized by Jöns Jakob Berzelius (1817). This scientist also discovered, or isolated for the first time, some new elements, including cerium (Ce), silicon (Si), thorium (Th), vanadium (V), and zirconium (Zr) (Hurd and Kipling 1964), as reviewed by Reilly (2006).

Selenium is playing an important role in human and animal health and is essential to all other organisms including bacteria and algae, whereas there is no evidence for selenium in higher plants (Novoselov et al. 2002; Zhang and Gladyshev 2010; El Mehdawi et al. 2011a). Although Se is not an essential nutrient for higher plants, it should be added to soil to ensure that both feed and food products contain the adequate amounts for the dietary needs. Therefore, it should be emphasized that the safety margin of Se concentrations is rather narrow (Kabata-Pendias 2011). Because of its similarity to sulfur (S), which leads to non-specific replacement of S by Se in proteins (El Mehdawi et al. 2011a), Se is toxic to most organisms at elevated concentrations (Stadtman 1990). In general, most plants contain rather low foliar Se (around 25 $\mu g\ kg^{-1}$) and rarely exceed 100 $\mu g\ kg^{-1}$ (Kabata-Pendias 2011). However, some plants have a great capability to accumulate Se (may be up to 100 $mg\ kg^{-1}$ in seleniferous soils (Beath et al. 1939)). Some plants can grow in such seleniferous soils and hyperaccumulate Se levels up to 15,000 $mg\ kg^{-1}$ dry weight (Galeas et al. 2007) as reviewed by El Mehdawi et al. (2011b).

Although Se concentration in most soils is low, it is particularly abundant in seleniferous soils, which typically contains from 1 to 10 mg Se kg^{-1} and may reach 100 mg Se kg^{-1} (Beath et al. 1939). The main bioavailable Se forms in different oxidizing and reducing environments are selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), respectively (White et al. 2007). Therefore, Se uptake by plants dependents on Se concentration and speciation, the concentration of competing anions (like SO_4^{2-}), rhizosphere pH, and redox conditions (Mikkelsen et al. 1989). In general, roots take up selenate (SeO_4^{2-}) faster than selenite (SeO_3^{2-}) at the same concentration (de Souza et al. 1998; Zhao et al. 2005). It is well known that translocation of Se from the roots to the shoots is highly dependent on the supplied Se form, where SeO_4^{-2} is transported more readily than SeO_3^{-2} or organic Se compounds (de Filippis 2010). Furthermore, both selenate and selenite can be reduced to selenide (Se^{2-}) and assimilated into amino acids including selenocysteine (SeCys) and selenomethionine (SeMet) via the S assimilation pathway (Terry et al. 2000). Both of these amino acids (SeCys and SeMet) can be incorporated into proteins (El Mehdawi and Pilon-Smits 2012).

In general, nanoparticles must traverse the cell wall before entering the intact plant cell protoplast, as reviewed by Dietz and Herth (2011). They also reported that the maximum pore size of plant cell walls is usually in the range of a few nanometers (nm): for example, 3.5–3.8 nm in case of root hairs and 4.5–5.2 nm in palisade parenchyma cells. Therefore, the specific objectives of this review are mainly to follow the distribution and occurence of Se in the different agricultural environments from soils, water, air, and plants to humans and animals. The nano-selenium, from agricultural nanotechnology and sustainable development, nanotechnology in agriculture and food, recent developments, risks and regulation of nanotechnology, and finally synthesis methods of nanoparticles will be also highlighted.

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Selenium characterization

Selenium is one of the rarest elements in the earth's crust (0.05 $mg\ kg^{-1}$), whereas it is 69th in abundance among the 88 elements (Shriver and Atkins 1999). Se is called the *two-faced element* (like the moon, where its name is originated); therefore, it has both a dark and a bright side (Table 1; Reilly 2006). It is also known as the "*essential poison or double-edged sword element*" for its dual toxic and beneficial character to health (Charlet et al. 2011). It is reported that the duality for Se came from how to reconcile its apparently contradictory properties and roles. Nevertheless, these gaps in our understanding of Se are rapidly being filled by great efforts of an extraordinary array of researchers, working in a range of disciplines, aided by powerful new research techniques and tools (Reilly 2006).

It is well known that Se has an atomic weight of 78.96 and its atomic number is 34. It is chemically related to other members of the chalcogen group (Group 16/VIA), which includes oxygen (O), sulfur (S), tellurium (Te), and polonium (Po). Therefore, it is classified as a half metal or metalloid, but elemental Se has several different allotropes (Chapman et al. 2010). This places Se in an important group of half metals or metalloids, elements that are neither fully metals nor non-metals, but share chemical and physical properties of both (Reilly 2006). This location accounts for many of its biological interactions with some important elements including sulfur, as well as with arsenic and its neighbor phosphorus (Frost 1972). About the outer electronic configuration of this element, it is $3d^{10}4s^24p^4$, with three completely filled inner shells.

Selenium has four valence states: −2 state, which predominates in organic Se compounds beside 2, 4, 6 states. There are around 50 Se minerals. The most important and relatively common ones include: clausthalite (PbSe),

Table 1 Discovery and origin for selected properties of Se comparing with some micronutrients and beneficial mineral elements (from Shehata and El-Ramady 2012)

	Discovery (year)	Name origin	Ran. no.	Concentration in ocean (ppm)	Elec. neg.	Most important minerals
B	Gay-Lussac and Thénard (1808)	Arabic word بورق *buraq* or Persian *burah* (name of borax)	37	4.44	2.04	Borax, tincal $Na_2B4O_7 \times 10H_2O$ Colemanite $Ca_2B_6O_{11} \times 5H_2O$ Kernite $Na_2B_4O_7 \times 4H_2O$ Ulexite $NaCaB_5O_9 \times 8H_2O$
Cl	C. W. Scheele (1774)	From the Greek word *khlôros* (green)	19	1.94×10^4	3.16	Halite, rock salt NaCl Sylvite, sylvine KCl Sylvinite NaCl (KCl)
Co	Georg Brandt (1735)	German word *kobalt* or *kobold,* evil spirit	30	2×10^{-5}	1.88	Skutterudite (Ni, Co)As_3 Cobaltite (CoAsS) Linnaeite $(Co, Ni)_3S_4$
Cu	Known 5000 BC	Latin *Cuprum*	26	2.5×10^{-4}	1.90	Chalcopyrite $CuFeS_2$ Malachite $Cu_2(OH)_2(CO_3)$ Cuprite Cu_2O
Fe	Known ancient times	From the Latin word *ferrum* (iron)	4	0.002	1.83	Hematite Fe_2O_3 Magnetite Fe_3O_4 Siderite $FeCO_3$
Mn	J. Gahn (1774)	From *Latin word mangnes,* magnet	12	2×10^{-4}	1.55	Pyrolusite MnO_2 manganite MnO(OH)
Mo	P. Hjelm (1781)	From Gr. word *molubdos* (lead)	58–59	0.01	2.16	Molybdenite (MoS_2) Molibdite (MoO_3)
Ni	Alex F. Cronstedt (1751)	From Ger. word *kupfernickel* (false copper)	23	5.6×10^{-4}	1.91	Pentlandite $(Ni,Fe)_9S_8$ Gersdorffite NiAsS Garnierite $(Ni,Mg)_6(OH)_8Si_4O_{10}$
Se	Berzelius (1817)	From Gr. word *Selēnē* (Moon)	69	2×10^{-4}	2.55	Berzelianite Cu_2Se Ferroselenite $FeSe_2$
Si	J. J. Berzelius (1824)	From the Latin word *silex* (flint)	2	2.2	1.90	Quartz, SiO_2 Kaolinite $Al_2(OH)_4Si_2O_5$ Serpentine $Mg_3(OH)_4Si_2O_5$
Zn	Marggraf (1746)	German word *zin* (meaning tin)	24	0.0049	1.65	Sphalerite, zinc blende (Zn, Fe)S Smithsonite $ZnCO_3$

Ran. no. = ranking in order of abundance in earth crust

Elec. neg. = electronegativity is a chemical property that describes the tendency of an atom or a functional group to attract electrons (or electron density) toward itself (Pauling 1932)

Conc. in ocean = mean content in oceans in ppm or g ton^{-1} (data from Enghag 2004)

Name origin from http://www.chemicalelements.com/index.html

klockmanite (CuSe), tiemannite (HgSe), berzelianite ($Cu_{2-x}Se$), crookesite $(Cu, Tl, Ag)_2Se$, and ferroselenite ($FeSe_2$) (Kabata-Pendias 2011). Therefore, the association of this element with host minerals, such as chalcopyrite, pyrite, and sphalerite, is relatively common. On the other hand, this element has a great affinity to different organic substances resulted in a large number of organic compounds that are analogous to those of S-organic compounds and are easily accumulated in some biolithes (Kabata-Pendias 2011). As mentioned before, the average content of Se in the Earth's crust is estimated as 0.05 mg kg^{-1}; however, a higher value (up to 0.5 mg kg^{-1}) is also given. This element is slightly more concentrated in mafic rocks (rarely exceeds 0.1 mg kg^{-1}), whereas Se is associated with clay fractions, and thus, its abundance in argillaceous sediments ranged from 0.3 to 0.6 mg kg^{-1} in sedimentary rocks. This concentration is higher than in sandstones and limestones (0.01–0.1 mg kg^{-1}), as shown in Table 2 (Kabata-Pendias 2011).

On the other hand, Se is a quite unique trace element, because it is a component of some amino acids (SeCys and

Table 2 Abundance of selenium in different environments comparing with some micronutrients and beneficial mineral elements

Element	Earth crust	Igneous rock, acid	Sedimentary rocks			Soils (mg kg^{-1})	Water (g l^{-1})[a]	Air[b] (ng m^{-3})
			Argi.	Sandstone	Calcareous			
	Concentration (mg kg^{-1}) in different environmental compartments							
B	10	10–30	120–130	30–35	20–30	15–35	10–100	–
Cl	145	300–850	500–800	50–270	50–350	300	50–2,700	1–7
Co	10–12	1–15	14–20	0.3–10	0.1–3.0	8.0	0.15	0.05
Cu	26	5–30	40–60	5–30	2–10	20	0.27–3.5	150–1,600
Mn	950	350–1,200	400–850	100–500	200–1,000	50–2,000	0.2–130	2.8–4.5
Mo	1.2	1–2	2–2.5	0.2–0.8	0.2–0.4	1.8	0.1	<0.2
Ni	20	5–20	40–90	5–20	5–20	19–22	0.8	0.9
Se	0.05	0.01–0.05	0.3–0.6	0.01–0.08	0.03–0.10	0.44	0.07	0.2
Zn	52–80	40–100	80–120	15–30	10–25	63	3.5–10.3	18–41
	Concentration (%) in different environmental compartments							
Fe	5.6	1.4–2.7	3.3–4.7	10–30	0.4–1.0	3.5	66	166–171
Si	26–29	31–34	25–28	30–40	5–30	54	1.3	20–100

Source: Compiled from Kabata-Pendias and Mukherjee (2007) and Kabata-Pendias (2011)

Argi. argillaceous; [a] water of river; [b] greenland

SeMet) and therefore involved in very specific biological roles. These main roles include protection against oxidative damages, defenses against infection, and modulation of growth and development. Therefore, the main exposure to Se occurs through food chain, and its distribution in natural environments has a marked effect on its content in soils, crops, and the human body (Marmiroli and Maestri 2008). In agriculture sector, Se is used mainly as sodium selenite (Na_2SeO_3) as an addition to fertilizers, insecticides, and foliar sprays. In small doses, Se is widely used in vitamins, other dietary supplements, and some livestock feeds (as a fortified element). Furthermore, it is a relatively common component of various medications and cosmetics, as a therapeutic agent (e.g., in cardiology as an antioxidant), as reported by Kabata-Pendias (2011).

Production, sources, and uses of selenium

Globally, there are no mines that specifically extract Se; instead, it is a by-product of the production of other metals such as refining of Pb and Cu, or recovered from the sludge accumulated in H_2SO_4 factories (Johnson et al. 2010). The supply of Se is directly affected by the supply of the materials from which it is a by-product—Cu, and to a lesser extent, Ni. Estimated domestic Se production was slightly higher in 2012 compared with that of 2011 owing to a slight increase in Cu production (1,980 and 2,000 metric tons in 2011 and 2012, respectively; USGS 2013). Most of the world's selenium is produced in the Japan, USA, and Canada, with smaller amounts coming from Finland, Australia, Peru, Zambia, Belgium, Russia, China, and other countries with a Cu-refining industry. Many compounds of Se are commercially available, including ferro- and nickel selenide, cadmium sulfoselenide, selenium dioxide, and selenium diethyldithiocarbamate, as well as sodium selenate and selenite, as reported by Reilly (2006).

At the global scale, Se is constantly recycled in the environment via the marine, atmospheric, and terrestrial systems. Estimates of Se flux indicate that anthropogenic activity (76,000–88,000 ton per year) is a major source of Se release in the cycle, whereas the marine system (38,250 ton per year) constitutes the main natural pathway (Haygarth 1994). Se cycling through the atmosphere (15,300 ton per year) is significant because of the rapidity of transport, but the terrestrial system (15,380 ton per year) is most important in terms of human and animal health because of the direct links with food chain and the agricultural activities. Although Se is derived from both natural and man-made sources, an understanding of the links between environmental geochemistry and health is particularly very important for Se as rocks are the primary source of this element in agroecosystems (Table 3; Fordyce 2013).

There are a number of important agricultural and horticultural applications for Se. These applications include the use of sodium selenate and selenite as additives and dietary supplements in animal feeds. It could be corrected

Table 3 Main sources of selenium in different environments (adapted from Fordyce 2013)

Main sources	Comments
Natural sources	
Volcanic activity	Important source
Weathering of rocks	Important source
Sea spray	Concentrations in ocean water are only an order of magnitude lower than those in rocks
Atmospheric flux	From the ocean surface to the atmosphere
Volatilization and recycling from biota	For example, in the UK annual selenium deposition = 2.2–6.5 g ha^{-1}
Aerial deposition	
Man-made sources	
Selenium-based industries	
Metal-processing industries	Important source
Burning of fossil fuels	Important source
Disposal of sewage sludge to land	Typical selenium contents 1–17 mg kg^{-1}
Agricultural use of pesticides	Potassium ammonium sulfide ($[K(NH_4)S]_5Se$)
Agricultural use of lime	Typical selenium contents 0.08 mg kg^{-1}
Agricultural use of manure	Typical selenium contents 2.4 mg kg^{-1}
Agricultural use of phosphate fertilizers	Typical selenium contents 0.08–25 mg kg^{-1}

soil deficiencies by adding Se compounds to fertilizers and top dressings. On the other hand, it could be noticed potassium ammonium sulfoselenide used as a pesticidal substrate and was one of the first systemic insecticides to be marketed in the 1930s. This compound is still in use, but is restricted to non-food crops because of its toxicity. In commercial greenhouses growing flowers for cutting, sodium selenate (Na_2SeO_4) has also been used for a similar purpose. This selenate (Na_2SeO_4) could be added to irrigation water, and the plant roots can take it up. Then, it is converted in the leaves into volatile selenide (Se^{2-}), which is released by the plant to aphids, repel red spiders, and similar pests (Reilly 2006).

Occurrence of selenium in terrestrial environments

Naturally, Se occurrence is rarely recovered in a free state, and it can be existed in different oxidation states including 6 (VI), 4 (IV), 0 (Se^0), and −2 (II). The oxidized water-soluble forms including selenate Se(VI) and selenite Se(IV) are recovered in both of natural water and in soil solution (Kabata-Pendias 2011). It is reported that the highly stable elemental selenium (Se^0) is also recovered in soils, but not in water solution because it is insoluble (Di Gregorio 2008). This elemental selenium (Se^0) could be existed in different allotropic forms including rhombohedral Se (containing Se_6 molecules), three deep-red monoclinic forms, α-, β-, and γ-Se (containing Se_8 molecules), trigonal gray Se (containing Se_n helical chain polymers), amorphous red Se, and black vitreous Se. The gray (trigonal) Se is the most thermodynamically stable form, which contains countless helical chains of Se atoms, and it is the only allotropic form that conducts electricity (Di Gregorio 2008). The most likely amorphous allotropes forms that are occurring in soils include both of red and black. Furthermore, red amorphous Se can gradually revert to the black amorphous form at temperature greater than 30 °C. This black form can then slowly transform into the much more stable gray hexagonal allotrope or it will be re-oxidized depending on pH and redox conditions of soil (Di Gregorio 2008).

Selenium is distributed in different environments by several processes, such as volcanic activities and hot springs, combustion of fossil fuels, soils and rocks weathering, soil leaching, sea salt spray, forest wildfires, groundwater movements, chemical and biological redox reactions, and mineral formation, as well as incineration of municipal waste, Pb and Zn smelting, Cu/Ni production, Fe and steel production, crop growth and irrigation practices, and plant and animal uptake and release (Nriagu 1989; Di Gregorio 2008). As a general rule, Se concentration in soils or ground and fresh waters depends upon the parent material, topography, age of the soil, climate, and agricultural or industrial utilization. Elemental Se and selenides (Se^{2-}) are the predominant species under acidic, reducing conditions in soils that may be waterlogged and rich in organic matter (McNeal and Balistrieri 1989; Di Gregorio 2008).

Selenium in soils

It is well known that Se content in soils is inherited from parent material and its distribution strongly reflects soil-forming processes and atmospheric deposition. Sandy soils, which developed under humid climate, particularly in podzols, have the lowest amounts of Se, whereas the highest contents occurring most often in organic and calcareous soils (Tables 2, 4; Kabata-Pendias 2011). In general, the concentrations of Se ranged from 0.05 to 1.5 mg kg^{-1} Se in worldwide soils, with a calculated average value 0.44 mg kg^{-1}. It could be observed higher contents of Se in surface layer of volcanic soils, forest soils, organic rich soils, and calcareous soils. In general, the main factors controlling Se forms and behavior in soils are Eh or redox potential and pH; however, several other parameters such as organic ligands, clay content, and hydroxides also play very significant roles (Table 4; Kabata-Pendias 2011). It is reported that about different inorganic species of Se, which associated with defined soil parameters, reveal variable properties as follows: (1) selenates (mobile in inorganic forms in neutral and alkaline soils but not absorbed on hydrous sesquioxides in particular $Fe_2O_3{\cdot}H_2O$), (2) selenites (slightly mobile in neutral and acid soils of humid temperate regions and are easily absorbed on hydrous sesquioxides and organic matter), and (3) selenides (rather immobile in acid soils due to the formation of stable mineral and organic compounds) (Lakin and Dawidson 1967; Combs and Combs 1986; Frankenberger and Engberg 1998; Kabata-Pendias 2011).

The most important forms and concentrations of Se in soil solution are governed by various physicoal, chemical, and biological factors, and common inorganic anions include $HSeO_3^-$, SeO_3^{2-}, $H_2SeO_4^-$, SeO_4^{2-}, and $HSeO_4^-$ (Kabata-Pendias and Sadurski 2004). Selenate anions (SeO_4^{2-}) are the favored form under oxidizing conditions, whereas in mild reducing conditions, SeO_3^{2-} is likely to dominate (Kabata-Pendias 2011). SeO_3^{2-} is strongly sorbed on oxides and precipitates such as $Fe(SeO_3)_3$, whereas SeO_4^{2-} anion is very weakly sorbed, especially at high pH. Therefore, mobile and easily phyto available (available to plants) Se occurs in well-aerated alkaline soils, which are common in arid and semi-arid regions. On the other hand, organic matter has a strong tendency to form organometallic complexes which remove Se from soil solution (Kabata-Pendias and Mukherjee 2007).

It is reported that the phyto-availability of different Se species in soils decreases in the following order: selenate>selenomethionine>selenocysteine>selenite>elemental selenium > selenide (Kabata-Pendias and Mukherjee 2007). It is also observed a close relationship between Se and organic carbon in most soils. Microbial processes play a crucial role in Se cycling in both the formation and mineralization of organic Se such as selenomethionine and selenocysteine and especially in its volatilization from Se-contaminated soils (Martens and Suarez 1998). These processes are important for the reduction of Se, principally through the reduction of selenate and selenite. Insoluble selenide compounds are likely to accumulate in case of poorly drained soils. Se may volatilize in the form of $(CH_3)_2Se$, as well as in forms of several other methane and sulfide Se compounds, due to methylation processes under anaerobic conditions (Kabata-Pendias and Mukherjee 2007). A number of microorganisms such as bacteria and fungi species are involved in volatilization processes of Se. It is reported that organic amendments may significantly increase the rate of Se volatilization from soils (Frankenberger and Karlson 1994; Kabata-Pendias and Mukherjee 2007).

Table 4 Soil factors affecting the mobility of selenium and impact of soil pH–Eh system on the formation of soluble Se species

Soil factors	Se form	Mobility
Soil acidity (pH)		
High (alkaline)	Selenates (Se^6)	High
Medium (neutral)	Selenites (Se^4)	Moderate
Low (acid)	Selenides (Se^{2-})	Low
Redox potential (Eh)		
High (high oxidation, >400 mv)	Selenates (SeO_4^{2-})	High
Moderate (200–400 mv)	Selenites (SeO_3^{2-})	Medium
Low (low oxidation, <200 mv)	Selenides (HSe^-)	Low
Hydroxides (Fe, Mn)		
High content	Absorbed all forms of Se	Low
Low content	Slight absorption	High
Organic matter[a]		
Undecayed	Absorbed	Low
Decayed (e.g., peat)	Complexed	High
Enhanced biomethylation	Volatilized	High
Clays[b]		
High content	Absorbed all Se forms	Low
Low content	Not fixed or soluble all Se forms	High
Interaction with		
S, P and N	Antagonistic effects	Rather low

Source: Compiled from Kabata-Pendias and Mukherjee (2007) and Kabata-Pendias (2011)

[a] Variable impact of organic matter depends on its kind

[b] Absorption by clay minerals decreases with increasing pH values and, at pH 8, is almost negligible

Selenium in waters

In aquatic environments and under most pH and redox conditions, the two oxyanions (Se^4 and Se^6) are dominant with several forms of selenide (Se^{2-}) also being present, as in soils (Cutter and Bruland 1984). A high biological activity and a locally oxidative environment may occur in contaminated aquifers. Therefore, these environmental conditions oxidize and then solubilize the reduced Se forms that enter into food web, and Se levels in biota can remain high for years after inputs have ceased (Lemly 1997; Di Gregorio 2008). Usually, natural waters contain Se < 1 $\mu g\ l^{-1}$, whereas these concentrations in seawater commonly range between 0.1 and 0.35 $\mu g\ l^{-1}$. The average global Se in river waters is about 0.07 $\mu g\ l^{-1}$, with a range of 0.02–0.5 $\mu g\ l^{-1}$ (Gaillardet et al. 2003). However, it is also reported by ATSDR (2002) in case of some rivers (e.g., Colorado River) contain Se in the range of 1–4 $\mu g\ l^{-1}$, although much higher values, up to 400 $\mu g\ l^{-1}$ (Kabata-Pendias and Mukherjee 2007).

Although ground waters usually contain more Se than surface waters, in groundwater and surface water, Se concentrations range from 0.06 μg l^{-1} to about 400 μg l^{-1} in general (Lindberg 1968), whereas it may approach 6,000 μg l^{-1} in groundwater in some areas (Cannon 1964). Levels of selenium in tap water samples from public water supplies around the world are usually much less than 10 μg l^{-1} but may exceed 50 μg l^{-1} (Gore et al. 2010). It is reported that, in China and from high soil Se area content, drinking water ranged from 50 to 160 μg l^{-1} (WHO 2011).

Labile Se usually in most soils and the Se deposited atmospherically onto soils are rapidly leached into groundwater (Haygarth 1994). In Finland, it is reported that levels of Se in stream and river waters increased up to an average of 180 μg l^{-1} and in bottom sediments up to around 4 mg kg^{-1}, after the Se-fertilizing program (Wang et al. 1994). WHO has been established the threshold value for Se in drinking water as 10 μg l^{-1}, whereas in the USA, it ranges between 10 and 45 μg l^{-1}. The maximum critical level value for the Se concentration in waters of all states of the USA is 50 μg l^{-1}. The limit level for Se in water used for irrigation is 20 μg l^{-1} (ATSDR 2002). The maximum permissible Se concentration are as follows: for drinking water for humans 10 μg l^{-1}, drinking water for livestock 50 μg l^{-1}, and irrigation water 20 μg l^{-1} in most countries (Kabata-Pendias and Mukherjee 2007). There several physical and chemical factors govern concentrations and chemical forms of Se in soils or drainage water, including chemical and mineralogical composition, pH, adsorbing surface, and oxidation–reduction status (Dhillon and Dhillon 1999).

Selenium in air

It is reported that Se concentrations in the atmosphere are highly variable due to differentiated sources: (1) evaporation from ocean and sea surface, (2) volcanic eruption, and (3) industrial emissions (Kabata-Pendias and Mukherjee 2007). Concentration of Se in air above the South Pole is 0.06 ng m^{-3} with average value for worldwide air from remote regions is 0.2 ng m^{-3}, whereas the median is 4.0 ng m^{-3} for polluted areas (Reimann and de Caritat 1998). It is found that, due to the impact of Se volatilization from the surface of seawaters, Se levels increased in mosses >1 mg kg^{-1} and in peat >2 mg kg^{-1} in the marine regions (Steinnes 2003). It is worth to mention that Se is released into the atmosphere as hydrogen selenide, produced metabolically by plants, and as selenates, selenites, and elemental selenium in particulate form (WHO 2011). Se level in most urban air ranges from 0.1 to 10 ng m^{-3}, whereas higher levels may be found in certain areas like the vicinity of copper smelters (Zoller and Reamer 1976).

It is reported by the US Environmental Protection Agency that inhalation exposure limits for Se include 12,700 μg m^{-3} for hydrogen selenide, 400 μg m^{-3} for Se-hexafluoride, and 200 μg m^{-3} for other Se compounds (Fordyce 2005). Se concentration in air may vary from 160 to 1,000 μg m^{-3} (ATSDR 2002), whereas its recommended threshold limit is 200 μg m^{-3} in workplace in general, 50 μg m^{-3} in Germany, and 100 μg m^{-3} in Russia (Schrauzer 2004). During fossil fuel combustion, Se is released and its global emission is >6 kt $year^{-1}$, in both small particles and volatile compounds which make around 40 % of the total aerial abundance (Kabata-Pendias and Mukherjee 2007).

Selenium in plants

In general, it could be increased Se content in plants in different ways including foliar applications, hydroponics, or aeroponic cultivation in a nutrient solution containing Se and soaking seeds in Se solution before sowing (Germ et al. 2007). Therefore, the Se uptake by plants (mainly as SeO_4^{2-} or SeO_3^{2-}, when it is present in soluble forms) depends on several factors related to soils and plants characterization, although differences between these plants species are very pronounced (Kabata-Pendias 2011). Rayman et al. (2008) reported that there is no bioavailability data for either *Se*-methyl-selenocysteine or γ-glutamyl-*Se*-methyl-selenocysteine. Although Se has not yet been classified as an essential element for higher plants, its role has been considered to be beneficial for plants that are capable of uptake and then accumulating in large amounts (Shanker 2006). There are several naturally occurring organic Se species including selenocysteine, methylselenocysteine, selenomethionine, selenotaurine, seleniobetaine, selenicocholine, dimethylselenide, dimethyldiselenide, and trimethylselenonium (Pyrzynska 1995). Although the essentiality of these selenoproteins in higher plants has not been documented, syntheses of them in some plants such as sugar beet have been reported by Terry et al. (2000). Furthermore, several selenoamino acids including selenomethionine (SeMet), selenocysteine (SeCys), and selenomethylocysteine (SeMC) in association with glutathione peroxidases have been found in both bacteria and higher plants (Kabata-Pendias 2011).

The uptake and metabolism of Se totally differ due to growth stage, plant species, and plant organs. More Se accumulates in shoot and leaf than in root tissues in several plants, but there are some exceptions (Zayed et al. 1998). It is observed that Se concentrations in the upper leaves, roots, stolons, and tubers of potato increased with increasing Se supplementation (Turakainen 2007). Furthermore, the Se concentration declined during the growing period in the aerial parts, roots, and stolons of potato plants, whereas an intensive accumulation took place in immature and mature tubers (Turakainen 2007). In seleniferous soils, a great variation in plants' capability exists to uptake Se from these soils. It is worth to mention that most of the cultivated crop plants have a low tolerance to high Se levels and in general, they contain less than 25 μg Se g^{-1} DW and are considered to be non-accumulators like potato (White et al. 2004).

It is reported that the critical Se concentration in plant tissues, which decreased the yield in case of the following plants Indian mustard, maize, rice, and wheat (in μg g^{-1} DW), was 105, 77, 42, and 19, when Se rates (as selenite) were 5, 5, 4, and 10 μg Se g^{-1} soil, respectively (Rani et al. 2005). There are several physiological functions or roles of Se in higher plants (Tamaoki et al. 2008; Pilon-Smits and Colin 2010; Hasanuzzaman et al. 2010; Hajiboland 2012). Some of the beneficial effects of Se in plants subjected to stress conditions, which increase antioxidant activity. It is reported that treated plants with selenate induced higher increases in plant enzymes that detoxify H_2O_2, especially both of ascorbate peroxidase and glutathione peroxidase. It is indicated that selenate application at low rates can be used to promote the induction of plant antioxidant system, thereby improving stress resistance (Hasanuzzaman et al. 2010).

An excess of Se may decrease germination and growth rates of non-tolerant plant species and cause leaves chlorosis and black spots. It is found that the critical Se concentration in solid media for gain reed (*Arundo donax* L.) plant ranged from 20 to 50 mg kg^{-1} for the American and Hungarian ecotypes, respectively (El-Ramady et al. 2014b). In some plants, increased Se levels suppress their concentrations of N, S, and P, as well as several amino acids (Kabata-Pendias 2011). Inhibition uptake of some metals (mainly Cu, Cd, Mn, and Zn) may happen under high Se concentrations. Therefore, the application of N, S, and P is known to help in Se detoxifying, which may be a result either of depressing the Se uptake by roots or of establishing a beneficial ratio of Se to these previous elements (Kabata-Pendias 2011).

It is estimated Se range in cereals at the worldwide level to be 100–800 μg kg^{-1} FW (Fordyce 2005). This range of Se mean (in μg kg^{-1}) varies from 142 to 970 and from 14 to 90 for countries with high and low Se levels in grains, respectively (Kabata-Pendias and Mukherjee 2007). Using soil application of 10 g Se ha^{-1} rate, it is found that Se contents in grains of barley and oats (in μg kg^{-1}) ranged from 19 to 260 and from 32 to 440, respectively (Gupta and Gupta 2000), whereas using two foliar application rates of Se (10 and 20 g Se ha^{-1}) increased Se contents of winter wheat grains from 0.094 to 0.192 mg kg^{-1} and the first Se rate was sufficient for reaching the required content in wheat grains (Duscay et al. 2006). A number of feed and forage samples from China were analyzed by Ge and Yang (1993). They found that these samples were from the Se-deficient regions, which contain the following Se levels (in μg kg^{-1}): <20, 30–50, 60–90, and >100 for severe deficient, deficient, moderate deficiency, and adequate Se supply areas, respectively (Kabata-Pendias 2011). Thus, the agronomic biofortification with Se-supplemented fertilizers is a common practice in cereal crops to increase the Se content and nutritional quality of grains (Bañuelos et al. 2005). However, the transformation of Se by bacteria and the effect of these bacteria on the Se availability to plants still are poorly understood (Acuña et al. 2013).

Selenium in food systems

There are several articles and books concerning with the relationship between Se and both of human health and plant foods (Combs 2005; Hartikainen 2005; Finley 2005; Reilly 2006; Rayman et al. 2008; Fairweather-Tait et al. 2010, 2011; WHO 2011; Hatfield et al. 2012; Bañuelos et al. 2014). In general, people can obtain virtually all of their Se requirements from eating foods, whereas Se is found mostly bound to proteins in both plant and animal tissues (WHO 2011). Therefore, meats, seafood, and cereals are considered to be the most important food sources of Se, because they have high-protein contents (for meats and seafood 0.3–0.5 mg Se kg^{-1}), because of its consumption in large amounts (for cereals 0.1–10 mg Se kg^{-1}). Vegetables and fruits (relatively low-protein-level foods) tend to have relatively low Se contents (<0.01 mg Se kg^{-1}). In general, Se content in different food systems depends on and at the same time reflects the soil available Se to produce those food systems (WHO 2011).

It is reported that the global Se intakes (in μg day^{-1}) vary significantly among different countries, whereas its average intakes were relatively low (10–20), moderate (40–90), and (85–150) in parts of China, Europe, and North America, respectively (FAO/WHO 1998; WHO 2011). In more details, it reported that dietary Se intake ranges from 7 to 4,990 μg per day, with mean values of 40 μg per day in Europe and 93 to 134 μg per day for women and men in the USA, respectively (Rayman 2012). Finally, it is recommended that the average Se intake is 60 and 53 μg per day for men and women, respectively (Rayman 2004). In UK, it is reported that the main food groups providing Se in the diet or contribution of each food group to total population dietary exposure include eggs (4 %), vegetables and fruits (7 %), fish (10 %), milk/dairy products (21 %), bread and cereals (26 %), and meat (26 %). On the other hand, some Brazil nuts are a rich source with Se concentrations ranging from ~0.03 to 512 mg kg^{-1} fresh weight (Rayman et al. 2008).

It is found that Se concentrations in heart, liver, and kidney of beef tissues were 0.55, 0.93, 4.5, and mg kg^{-1}, respectively, whereas muscle tissue was in the region of 0.2 mg kg^{-1}. Juniper et al. (2008) reported that supplementation of cattle with Se-enriched yeast increased muscle Se concentration up to ~0.6 mg kg^{-1}, whereas the average Se content in chicken was ~0.2 mg kg^{-1} and beef ~0.25–0.3 mg kg^{-1} in the USA (Fairweather-Tait et al. 2011). Total Se content in fish ranged between 0.1 and ~5.0 mg kg^{-1} (Fairweather-Tait et al. 2010), where the Se content in some marine fish is considered relatively high for cod, shark, and canned tuna (~1.5, 2.0, and 5.6 mg kg^{-1}, respectively; Reyes et al. 2009). It is worth to mention that the main Se species in fish include selenite/selenate (12–45 %) and selenomethionine (29–70 %) depending on both of fish species and the total Se content (Rayman et al. 2008; Fairweather-Tait et al. 2010).

Lipiec et al. (2010) reported that hens' eggs contain from 3 to 25 mg Se per whole egg, whereas Se supplementation in hen's diet may increase Se content of eggs up to 0.34–0.58 mg kg^{-1}. Se-enriched eggs are widely produced around the world (Fisinin et al. 2009). The main Se species in eggs include selenomethionine, selenocysteine, and possibly selenite, where the predominant species (>50 %) involve selenomethionine and selenocysteine in egg white and egg yolk, respectively (Lipiec et al. 2010). The predominant Se species in cows' milk include both of selenite and selenocysteine; furthermore, the supplementation program of dairy cows with Se-enriched yeast is already used, and after using this supplementation, the main species include selenite, selenocysteine, and selenomethionine (Muniz-Naveiro et al. 2007).

It is well known that both fruit and vegetables contain relatively small Se amounts. In case of un-enriched vegetables with low Se levels, the main species include selenate (4 %), Se-methyl-selenocysteine (12 %), γ-glutamyl-Se-methyl-selenocysteine (31 %), and selenomethionine (53 %) in garlic with natural Se content of <0.5 mg kg^{-1} (Kotrebai et al. 2000). However, certain vegetables such as broccoli, onions, and garlic when grown on Se-rich soil can accumulate Se, resulting in Se-enrichment from <0.5 up to 140–300 mg kg^{-1}. The main Se species in Se-enriched food such as onions is γ-glutamyl-Se-methyl-selenocysteine (63 %), selenate (10 %), and selenomethionine (5 %) plus some other species (Hurst et al. 2010). It could be concluded that Se species profile in such vegetables, such as garlic, broccoli, and onions, is variable depending on the total Se level of enrichment, the forms of Se used for this enrichment, and the type of vegetable. The predominant species in Se-enriched vegetables include Se-methyl-selenocysteine or γ-glutamyl-Se-methyl-selenocysteine, whereas these forms of Se in plant foods have received attention due to purported protection against cancer in animal models when compared with other forms of this element (Fairweather-Tait et al. 2011).

Nano-selenium and the environment

It is reported that nano-materials exhibit novel properties, like a high surface activity, a great specific surface area, a lot of surface active centers, and a high catalytic efficiency (Gao and Hiroshi 2005). Due to both high surface reactivity and advantage of size effect, nanoparticle has been already used in pharmaceutical applications to increasing the bioavailability of drugs and targeting therapeutic agents to particular organs (Davda and Labhasetwar 2002). It has been reported that nanoparticles showed new characteristics of transport and uptake and exhibited higher absorption efficiencies (Zha et al. 2008; Liao et al. 2010). However, there is little data on intestinal absorption and Se retention of nano-Se (Hu et al. 2012).

Different Se forms including organic and some salts have been used in studying its biological effects several years ago, whereas recently, nanoparticles of elemental selenium (Se^0) have gained the attention as a possible source of this beneficial element (Zhang et al. 2001). It is worth to mention that nanoparticles of Se^0, which has a very low bioavailability (<5 %), could be formed from some bacterial strains within redox system of glutathione or ascorbate and selenite (Garbisu et al. 1996). Furthermore, red elemental Se, which formed from selenite reduction and glutathione or other reducing agents, could further aggregate into gray and black elemental Se (Fig. 1). Nano-Se, which is bright red, soluble, highly stable, and nano-defined size in the redox state of zero (Se^0), has been manufactured for use in both of the nutritional supplements and developed for applications in medical therapy (Gao et al. 2002). It is well documented that black and gray elemental Se are biologically inert, which may be due to their insolubility, whereas the red elemental particulate Se has promising uses in the environmental protection from the pollution of the excessive Se (Garbisu et al. 1995). The size of this red elemental Se depends on the amount of protein in the redox system (Zhang et al. 2001). It is reported that nano-Se at 20–60 nm had a similar bioavailability to sodium selenite (Ball and Garwin 1992). Huang et al. (2003) suggested that the biological activities of nano-Se may come from the special properties of these nanoparticles.

Zhang et al. (2005) demonstrated that nano-Se has comparable efficacy to selenite in up-regulating seleno-enzymes and Se levels in tissue, but is less toxic. These results challenged to confirm that elemental Se has biological activities and stimulated us to further compare nano-Se with selenomethionine, which has excellent bioavailability and lower toxicity among various Se forms (Zhang et al. 2008). It has been reported that nano-Se has a higher efficiency in up-regulating seleno-enzymes and seem to be less toxicity comparing with selenite. In other

Fig. 1 Different possible colors of nano-selenium suspension after using of the biological synthesis method, where MRS medium, sodium hydrogen selenite, and bacteria strain were used (photo by El-Ramady, Nano Food Lab, Debrecen Uni., Hungary)

words, comparing with selenomethionine, nano-Se has lower toxicity and possesses equal efficacy in increasing the activities of seleno-enzymes (Wang et al. 2007). These results indicated that nano-Se can serve as an antioxidant with reduced risk of Se toxicity (Zhang et al. 2008).

A variety of microorganisms including algae, yeast, fungi, and bacteria can adsorb and accumulate metals, but only a few groups can selectively reduce metal ions to produce nanoscale mineral phases (Oremland et al. 2004). These previous organisms can produce inorganic phases of constant chemical composition and size (Pearce et al. 2008). The majority of several studies on the biogenesis of nano-Se particles have focused on the anaerobic systems, which have certain limitations such as culture conditions and isolate characteristics that make optimization and scale up in bio-manufacturing processes challenging. However, Se-tolerant aerobic organisms provide the opportunity to overcome these limitations in the biosynthetic process. The isolate tolerates Se oxyanions and generates Se-nanoparticles, thus combining the detoxification of oxidized seleniferous environments with the biotechnological production of nano-materials (Prakash et al. 2010).

Elemental selenium (Se^0)

As mentioned before, Se^0 is usually formatted in natural environments through a biotic process involving the reduction of selenate (Zhang and Frankenberger 2005) or selenite (Di Gregorio et al. 2005) by bacteria, whereas possible transformations of Se^0 include its oxidation to Se(IV) or Se (VI) or its incorporation into iron sulfides (FeS) or selenides (Belzile et al. 2000). Because of its existence between the higher chemical valence of Se(IV) and Se(VI) from one side, and the lower valence of Se(−II) from the other side, Se^0 could be transformed to either direction depending on the environmental redox potential and/or the presence of biological activity (Chen et al. 2006). Some information of allotropic elemental Se is summarized in Table 5.

Elemental Se is occurring mostly in sedimentary rocks, although it is rare in the nature (White et al. 2004). From three allotropes of elemental Se, the gray and the black one are biologically inert, which may due to their insolubility (Huang et al. 2003). The red allotrope has been produced by many kinds of bacteria from selenite, such as Hunter and Manter (2008), Prokisch et al. (2008), and Prokisch and Zommara (2008). It is found that the red elemental Se particles in nano-size scale have good free radical scavenging effects on different free radicals in vitro (Huang et al. 2003).

Recent developments, risks, and regulation of nano-Se

Recently, there is an increased interest in the potential use of nanotechnology applications in food sector and agriculture (Chaudhry et al. 2008). In general, nanotechnology-enabled products could be defined as material products derived or issued from materials less than 100 nm, although

Table 5 Some mineralogical, physical, and chemical properties of elemental selenium (Se^0)

Allotropic form	Common name	Solubility	Density (g cm^{-3})
Crystalline, hexagonal	β-Se, or grey-Se or black-Se, or metallic Se	The most stable form. Soluble: ether, chloroform; CS_2: 2 mg 100 mL^{-1}	4.82
Crystalline, monoclinic red	Crystalline red two forms: α-monoclinic, β-monoclinic	Soluble in CS_2	α-monoclinic: 4.46 β-monoclinic: 4.50
Amorphous	May exist as black or red amorphous, or colloidal	Se Soluble in CS_2, CH_2I_2, benzene or quinoline	

Source: Chen et al. (2006)

no unified definition has been approved internationally (Gruère et al. 2011). In food sector and agriculture, several applications of nanotechnology are being developed and commercialized with different targets, ranging from improved food safety, processing, and nutrition to reduced agricultural inputs and enhanced packaging (Yada 2009), and the global potential to promote sustainable agriculture and deliver better foods (Gruère et al. 2011).

Because of the limited information on the risks of handling nano-materials (like nano-Se), these materials have created an intense interest in their health risks under ultra-small scale. Therefore, the potential risks of nanomaterials have surprised the public by taking a strong precautionary tone on safety and health risks (ETC 2005a, b). Furthermore, due to the information lack about the impacts of nanotechnology (like nano-Se) on food industry, public safety, and society, as well as the potential toxicity of nano-materials, until proven otherwise, it is probably wise to take a full precautionary to deliberate the possible regulatory control as a proactive approach (Chau et al. 2007). Further investigations should be done on the applications of nanotechnology in packaging, nanotoxicity, food processing, and risk/benefit analysis. These studies will include the following items: sustain the growth of nano-food industry, fill the knowledge gaps, and avoid any unpredictable health hazard (Chau et al. 2007).

In general, there are some regulation issued by the European Union to regulate nanotechnologies in the food industry include the following: EC Cosmetics Regulation (EC No 1223/2009), EC No. 1223/2009 (2009), EC No. 1272/2008 (2008), EC No. 1907/2006 (2006), EC No. 1935/2004 (2004), and EC No. 258/97 (1997). The regulation of nanotechnologies is within the scope of both horizontal and vertical legislation (Cushen et al. 2012). Due to using of nanoparticles, it is urgently required the following issues: risk assessment and management, as well as exposure assessment for existing products available on the world market. Furthermore, existing uncertainties for risk and exposure assessment of nano-materials arise, due to limited information on several aspects including behavior, bioaccumulation, and toxicity. These uncertainties also have implications for the effective regulation of the use of nano-materials (Cushen et al. 2012).

Synthesis methods of Se-nanoparticles

It is well documented that nanotechnology has different tools showing the capability of synthesizing nanoscale materials with specific opto-electronic, physical, and chemical properties. Furthermore, various physical and chemical methods have been designed for the synthesis of nanoparticles, whereas the different problems related to these methods enforced the researchers to search for alternative methods. It could be synthesized elemental nano-Se within the reduction of a Se-salt with a reducing agent, usually in the presence of a stabilizing agent to prevent the clusters of Se atoms from growing and to obtain stabilized nanoparticles in colloidal suspension (Zhang et al. 2004).

Concerning of the accurate determination of Se^0, it is a key step in order to understand any process whether it is biological, geological, or environmental. However, finding an appropriate method for identification and measurement of Se^0 in natural systems like sediments or soils is a difficult task due to its both matrix complexity and low concentration (Chen et al. 2006). It is known that the lack of appropriate standard reference materials (SRM) is one of the most difficult problems analysts who are facing in quantitative speciation of the environmental samples. Hence, it is particularly problematic for Se^0, due to the exact mineralogical and chemical properties of this species in nature are unknown (Chen et al. 2006). It should be kept in mind that the original work on identification or synthesizing those forms of Se is very difficult to find and often lacks of details (Chen et al. 2006).

There are three different methods can be used for selenium synthesis including the chemical, physical, and biological methods, whereas the chemical and biological methods are common use.

Chemical methods

In general, the most often used method for the chemical synthesis of nanoparticles is the chemical reduction method, which deals with the reduction of metal particles to nanoparticles using chemical reducing agents such as sodium borohydride or sodium citrate (Cao and Hu 2009). Other chemical agents utilized for Se synthesis include *N*,*N*-dimethyl formamide (DMF) (Pastoriza-Santos and Liz-Marzan 2000), poly(*N*-vinyl pyrrolidine) (PVP), ethyl alcohol (Kim 2007), tetra-n-tetrafluoroborate (TFATFB), L-ascorbic acid, and hexadecyltrimethylammonium bromide (CTAB) (Hanauer et al. 2007). Electrochemical synthesis method induces chemical reactions in an electrolyte solution with the use of an applied voltage. A wide variety of nano-materials could be synthesized using this method (Sau and Rogach 2010).

In the chemical method, researchers do not use any living/organic material, but they usually start from inorganic selenite and add a reducer agent, like ascorbic acid. This method includes reduction of sodium selenite with glutathione at room temperature in aqueous solution. Therefore, glutathione, having a thiol group, reacts with sodium selenite to form selenodiglutathione, which decomposes to produce Se molecules and diglutahtione. Then, finally Se molecules aggregate together to form Se nano-spheres (Gao et al. 2003). It is reported by Ministry of Hygiene in China (1998) that nano-Se at dose of 180 g Se daily was granted as health care food.

Biological methods

Researchers started recently to recognize the importance of the ability of certain microorganisms to produce nano-sized particles within their metabolism. In trace concentrations, several elements are essential for growth and reproduction of animals, plants, and microorganisms; however, these elements easily become toxic when their concentrations are higher than the physiological level. The complete understanding of the synthesis mechanism of nanoparticles using the biological agents has not been devised. In addition, the synthesis mechanism for both intra- and extracellular of nanoparticles is totally different in various biological agents, because these biological agents react differently with metal ions and also there are different biomolecules responsible for the synthesis of these nanoparticles (Rai et al. 2011).

Biological agents used for nanoparticles synthesis represent mainly microbes including bacteria, fungi, algae and yeast (Ingle et al. 2008; Birla et al. 2009), and plants (Song and Kim 2009). The biological methods used for nanoparticles synthesis include both extra- and intra-cellular methods (Rai et al. 2008; Shaligram et al. 2009). There several benefits makes microbes advantageous for nanoparticle production including their economic viability, large-scale secretion of extra-cellular enzymes, and ease in scale up in solid substrate fermentations (Gardea-Torresdey et al. 2002). As mentioned before, plants have also the ability to produce nanoparticles. It is reported that live plants can manage themself to fabric gold nanoparticles (Gardea-Torresdey et al. 2002). It is confirmed by using atomic resolution analysis that Au nanoparticles inside plants are in a crystalline state and pure gold (Eszenyi et al. 2011).

The nanoparticles synthesis using bacteria and actinomycetes usually involves the intra-cellular synthesis method, in which the bacterial cell filtrate is treated with metal salt solution and kept in a shaker in dark at ambient temperature and pressure conditions (Ahmad et al. 2003a, b). For the extra-cellular nanoparticles synthesis using bacteria, the bacterial culture is centrifuged at $8{,}000\times g$ and the supernatant is challenged with metal salt solution (Ogi et al. 2010). In case of fungi, nanoparticles also are intracellularly synthesized by treating the fungal mycelium with metal salt solution and further incubation for 24 h (Mukherjee et al. 2001). In algal nanoparticles synthetism, washed culture of algae is treated with metal salt solution (without existence of any medium) and kept in dark with controlled pH and temperature conditions (Thakkar et al. 2010). The nanoparticles synthesis using yeast involves two steps including firstly nanoparticles synthesis and next recovery of the synthesized nanoparticles (Kowshik et al. 2003). Yeast culture is challenged with metal salt solution and incubated in dark for 24 h within the synthesis process (Fig. 2; Rai et al. 2011).

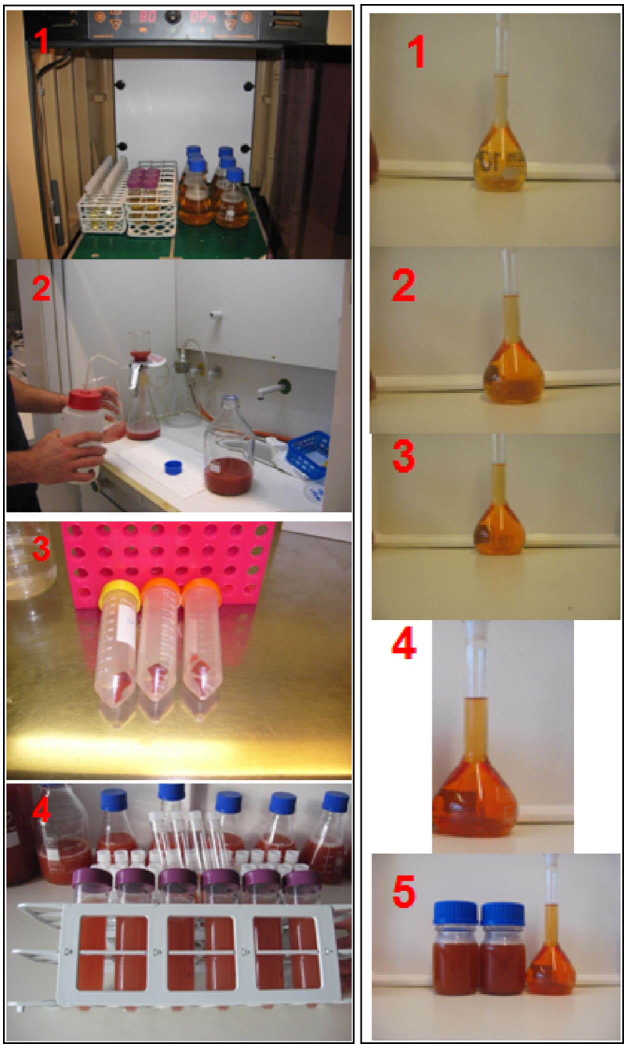

Fig. 2 The *left one* different steps of the biological synthesis of nano-Se using MRS broth. *1* The first step is the incubation at 37 °C for 48 h, the second is centrifuge, *2* then filter to separate the filtered bacteria. *3* Then, use concentrated hydrochloric acid for 3–4 days, *4* thus purifying nano-Se spheres, we get a solution or suspension called NanoSel, which is mainly for research. Photo 3 shows that nano-Se spheres consolidate to the bottom over time, but with a little shaking, we can get back the original state. The *right one* from *photo 1–4* represents how we can prepare nano-Se using chemical method. *Photo 5* represents the comparison between biological and chemical methods for nano-Se production. The right 100 measuring flask belongs to the chemical method, where it used vitamin C or ascorbic acid, and the other flasks belong to the biological method using MRS media and *Lactobacillus casei* as a bacteria strain (photo by El-Ramady, Nano Food Lab, Debrecen Uni., Hungary)

Conclusion

Selenium, the essential poison, is becoming more and more insufficient in food crops. It is biologically essential because it is an essential constituent of several enzymes. This essentiality of this nutrient was first recognized in the late 1950s. Since that time, Se has become a subject of several investigations in many parts all over the world. Furthermore, the main sources and behavior of Se in different terrestrial environments including soils, water, air, and plants are a very fertile field for investigation and research. The importance, production, and biological effects of this element and its use in the sustainable development were still an attractive issue. On the other hand, Se nanoparticles can be synthesized using different chemical, physical, and biological methods. The biological method is an environmental friendly method compared with other methods. There are certain open questions of research which need to be pointed out. These issues include different biological effects of Se and nano-Se on the terrestrial environments. A comparison between effects of both Se and nano-Se on soil microbial activities (including soils microbial enzymes and microbial counts) should be kept in mind.

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