Soil fertilizer based on selenium nanoparticles

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Abstract. The using laser ablation of massive selenium targets, aqueous colloids of selenium nanoparticles were obtained. The resulting nanoparticles are monodisperse in size and mass. The paper presents the optical properties of nanoparticles, morphology and composition. It has been shown that selenium nanoparticles do not significantly affect the development of plants under reference conditions, but effectively level the effects of hyperthermia. The most effective concentration of selenium nanoparticles in the soil is a concentration of 10 μg / kg.

1 Introduction

Selenium is a trace element necessary for the functioning of most living creatures and all mammals [1]. Selenium is present in soil, water, crops, and animal products [2]. Unfortunately, the soil in most European countries has a low Se content, while others, such as a number of countries in North and South America, are rich in this element [3]. The concentration of Se in mammals is highly dependent on its consumption [4]. The consumption rate of selenium is 55 and 70 mg per day for adult women and men, respectively [5]. Food is the main source of Se, respectively, the consumption of selenium depends on the content of selenium in food and the amount of food consumed [6]. Due to its variable distribution around the world, Se consumption may be relatively low in some

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countries or normal and even high in others [7]. In general, Se consumption is low among the population of the Old World [8].

In mammals, selenium is part of a number of proteins that have the common name selenoproteins [9]. Among the 25 known selenoproteins, at least 12 are antioxidant enzymes [10]. It should be noted that, along with other enzymes antioxidants, these proteins are largely involved in the redox homeostasis of the body [11,12]. The most famous are glutathione peroxidase (GSH-Pxs), thioredoxin-reductase (TrxRs) and selenoprotein P (SePP), the last protein of which contains up to 10 Se atoms [10]. Together, these proteins form a complex antioxidant defense that protects against the damaging effects of reactive oxygen species (ROS) and other harmful products of cellular metabolism [13,14]. The most studied enzymes are GSH-Pxs, they have a tetrameric form and contain one Se per subunit [15]. These enzymes decompose hydrogen peroxide and organic hydroperoxides, thereby protecting the tissue from oxidative damage [16]. TrxRs are involved in many important biological processes, including determining the redox potential of a cell and signaling. As for SePP, all its functions have not yet been studied, although it is already clear that SePP is an important extracellular antioxidant [17].

In most cases, the activity of selenoproteins is closely related to the concentration of Se in the tissues. Two approaches are used to normalize the balance of selenium. The production of food balanced in selenium content and the cultivation of agricultural production balanced in selenium content by introducing selenium with fertilizers into the soil [18]. From the point of view of toxicology and ecology, the approach to the manufacture of food balanced in selenium content is less attractive, although it can be easily solved. The approach with the creation of fertilizers for agriculture is certainly more complicated, but it allows to completely eliminate the problem of selenium imbalance in a single territory. The problem of the normalization of selenium concentration in soils has been tried to be solved for more than half a century [1]. At present, attempts have been made to use both organic (selenium-containing amino acids, chelates, etc.) and inorganic (oxides, salts and selenium minerals) selenium compounds as fertilizers. Attempts were successful, but the problem of both classes of fertilizers is that the introduced selenium remains in the upper fertile layer for one, or at best, several harvests. The fact is that inorganic selenium compounds are washed with rains into the infertile horizon, organic selenium compounds are not actively washed until they are destroyed, which happens rather quickly. Nanoscale selenium in the zero-valent state is of great interest as a concomitant additive to fertilizers. Firstly, nanoparticles are not washed for a long time in infertile horizons. Secondly, zero-valent selenium does not dissolve in water and aqueous solutions, therefore, its transition to plants occurs as a result of gradual oxidation of the surface of the nanoparticles and release as oxides. In this paper, a technology has been created for producing selenium nanoparticles in the zero-valent state and the question of the prospects for the use of such nanoparticles as fertilizers is investigated.

2 The Methods

2.1 Production and characterization of selenium nanoparticles

Selenium nanoparticles were obtained by laser ablation in water. Two types of laser sources were used for this purpose. The first one was fiber ytterbium laser with average power of 20 Watts, wavelength between 1060 and 1070 nm, pulse repetition rate of 20 kHz and pulse
duration of 80 ns. The second laser source was a copper vapour laser with wavelength of 510.6 and 578.2 nm with average power of 8 Watts. Laser irradiation of a solid Se target was performed in two experimental schemes. In the first scheme the target was exposed in a still water medium. In the second scheme flowing cell reactor was used. This approach allows reducing the screening action of already generated nanoparticles onto laser fluence on the target. As the result, the generation rate of Se nanoparticles was 0.8 mg/min in still water and 2.4 mg/min in flowing cell reactor [19]. The size of generated Se nanoparticles was determined using analytical measuring centrifuge DC24000 (CPS Instruments). The morphology of nanoparticles and partially their chemical composition was acquired with the help of Transmission Electron Microscope (TEM) Carl Zeiss 200FE with the spectroscopy of electron energy losses. Crystalline structure of obtained nanoparticles was characterized using X-ray diffractometer Bruker AXS P4.

2.2 Agricultural tests

The introduction of selenium nanoparticles into the soil was carried out in concentrations of 1.5 \times 10^3 and 25 μg / kg. To do this, the original colloidal solution of the nanoparticles of diluted water, so that for one kilogram of soil received 100 g of pure solution. After that, for uniform distribution of nanoparticles, there is a constant mechanical mixing. The experiments are carried out in a climate chamber according to two main methods. 1. Growing plants in soil with different breeding conditions under standard conditions (illumination 16 hours per day, temperature 22 ° C). 2. Growing plants in soil with different selection conditions under standard conditions (illumination 16 h / day, temperature 22 ° C) for 10 days, stress in plants using hyperthermia 40 ° C for 5 days, further cultivation under standard conditions. It is assumed that stressful plants may develop more slowly [20].

3 Results

Nanoparticles of Se obtained by ablation of a bulk Se target in water with powerful fiber laser have relatively large sizes, around 700 – 800 nm. This is due to the fact that Se is a brittle material, and the ablated particles are made of small entities in the course of “classical” ablation and particles that are detached from the target due thermal shock. The latters are large and should be used for tests. For the reduction of particles size the process of so called laser fragmentation has been applied. In this case individual particles are molten under the laser pulse, and their average size gradually decreases. Fig. 1, A shows the evolution of the mass distribution function of Se particles subjected to laser fragmentation. One can see that the main mass of particles is contained in particles with size about 800 nm in diameter. With gradual increase of laser fragmentation time the main mass shifts to smaller sizes arriving finally to size less than 100 nm. X-ray diffractograms of obtained Se particles. Fragmented Se nanoparticles are amorphous, which corresponds to previous observations. Relatively large Se particles preserve the crystallographic orientation of the initial target. So, small Se nanoparticles have no distinct crystalline structure. However, we believe that their structure will not affect their applications for other tests.

The effect of different concentrations of selenium nanoparticles on the development of a number of crops in climate chambers was studied. It has been shown that, under unchanged conditions, selenium nanoparticles have little effect on the development of plants up to 10 days. It can only be said with confidence that plants grown on soil in which
10 μg / kg of selenium nanoparticles are introduced look a bit large. For more accurate assessments, we used the Green Image software and found out the leaf area. The greatest differences were registered on the 30th day after landing. In this case, the leaf surface area the control plants is 30 ± 2 cm². In plants grown on soil with the addition of selenium nanoparticles at a concentration of 1 μg / kg, about 32 ± 3 cm². In plants grown on soil with the addition of selenium nanoparticles at a concentration of 5 μg / kg, about 37 ± 2 cm². In plants grown on soil with the addition of selenium nanoparticles at a concentration of 10 μg / kg, about 38 ± 3 cm². In plants grown on soil with the addition of selenium nanoparticles at a concentration of 25 μg / kg, about 28 ± 4 cm².

Fig. 1. A: Mass distribution function of Se particles as the function of laser fragmentation time. The time in minutes is indicated near each distribution. B: TEM view of Se nanoparticles after laser fragmentation. Scale bar corresponds to 200 nm.

The most illustrative results were obtained when growing radish plants after thermal stress (Fig. 2). Hyperthermia has been shown to inhibit the development of radish. So after 30 days the leaf surface area of the control plants is only 14 ± 3 cm². In stressed plants grown on soil with the addition of selenium nanoparticles at a concentration of 1 μg / kg, about 16 ± 4 cm²; 5 mcg / kg of the order of 27 ± 3 cm²; 10 μg / kg of the order of 29 ± 3 cm²; 25 μg / kg of the order of 15 ± 3 cm². That is, in stressed plants grown with the addition of selenium nanoparticles at a concentration of 5 and 10 μg / kg, the leaf area is almost 2 times larger compared to the stressed plants grown without the addition of selenium nanoparticles. It was established that such a pattern was observed when growing at least three radish generations on the cultivated soil. Further studies on the preservation of the effect of the addition of selenium to the soil are priorities for us. Since the effectiveness of the addition of selenium nanoparticles in concentrations of 5 and 10 μg / kg was not much different, we decided to use selenium nanoparticles of 10 μg / kg in additional experiments, since this could potentially increase the time for removal of selenium from the soil.
Fig. 2. Representative photographs of radish seedlings (Raphanus sativus var. Sativus) 20 days after planting. A - grown on intact soil; B - on the soil with the addition of selenium nanoparticles at a concentration of 1 μg / kg; C - at a concentration of 5 μg / kg; D - at a concentration of 10 μg / kg; E - at a concentration of 25 μg / kg.

It was shown that the development of plants after heat stress grown on intact soil and soil with the addition of selenium nanoparticles at a concentration of 10 μg / kg often proceeds in different ways. So the eggplant after exposure to hyperthermia had almost twice the area of leaflets. Similar results were obtained with tomato. The area of leaf plates in cucumber grown using selenium nanoparticles increased by almost 50% compared with the control. However, selenium nanoparticles practically did not affect the development of chilli peppers after hyperthermia. We also experimented with seedlings of barley (Hordeum vulgare) and cabbage (Brassica oleracea). The seedlings of both types did not survive hyperthermia. Cabbage grown in soil with the addition of selenium nanoparticles at a concentration of 10 μg / kg, also did not survive hyperthermia. The barley obtained selenium nanoparticles survived several plants (about 10% of the initial).

4 Conclusions

In this paper, a technology for producing selenium nanoparticles using laser ablation has been developed. The selenium nanoparticle preparation has one characteristic size and consists of nuvalent selenium. Selenium nanoparticles do not significantly affect the development of plants under reference conditions, but effectively level the effects of hyperthermia. The most effective concentration of selenium nanoparticles in soil is 10 μg / kg.

The results are in good agreement with the results of studies by other scientists [21-32]. This work was supported in part by RFBR research project No. 18-29-25071.

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