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Gamma Co-60 ray irradiation synthesis of dextran stabilized selenium nanoparticles and their antioxidant activity

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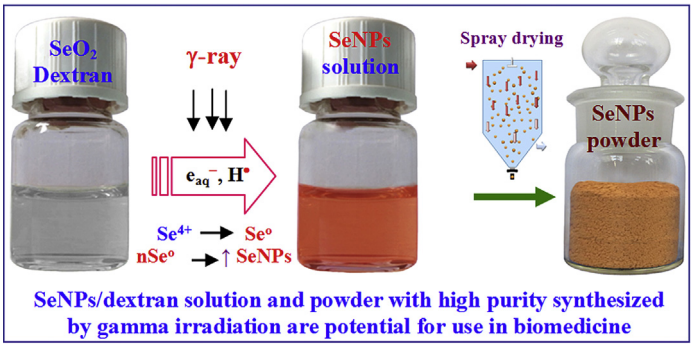
HIGHLIGHTS

- SeNPs were synthesized by γ-irradiation of 2.5 mM H_2SeO_3/1% dextran solution.
- pH 6 favored to obtain SeNPs ~74 nm with the narrow size distribution.
- SeNPs/dextran powder prepared by spray drying technique was high purity.
- SeNPs exhibited highly antioxidant activity.
- Radiation sterilization of SeNPs/dextran powder did not noticeable change in size.

GRAPHICAL ABSTRACT



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ABSTRACT

Selenium nanoparticles (SeNPs) with diameter of ~74 nm were synthesized by gamma Co-60 ray irradiation of H_2SeO_3/dextran solution. The SeNPs were characterized by UV–Vis spectroscopy spectrum and transmission electron microscope (TEM) images. The effect of pH of H_2SeO_3/dextran solutions before gamma irradiation on the size of SeNPs was investigated. The SeNPs/dextran powder was also prepared by spray drying technique and the purity was verified by energy dispersive X-ray (EDX) analysis. The $ATBS^{\bullet+}$ radical scavenging ability and reducing power of SeNPs were assessed. Results showed that SeNPs/dextran with concentration of 25–100 ppm exhibited high antioxidant activity. The as-prepared SeNPs/dextran powder with selenium content of ~2.51% (wt%) was of high purity. The influence of gamma Co-60 ray sterilization at dose of 25 kGy on the characteristics of SeNPs/dextran powder was also examined.

1. Introduction

Nanotechnology is multidisciplinary branch, being regarded as a new and emerging field of 21 century [1]. The properties of materials at the nanoscale level are radically transformed because of

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high surface area to volume ratio [2]. Among nanoparticle materials, selenium nanoparticles (SeNPs) have attracted wide spread attention due to their excellent bioavailability, high bioactivity and low toxicity compared to other ionic selenium compounds [3,4]. It was reported that SeNPs had much lower acute toxicity in mice with LD_{50} 91.2 mg Se kg^{-1} compared to about 14.6 mg Se kg^{-1} body weight of methylselenocystein [5]. Recently, Zhai et al. [6] also reported that LD_{50} of SeNPs for Kunming mice was of 258.2 mg kg^{-1} and belonged to a moderately toxic substance while H_2SeO_3 was highly toxic with LD_{50} of 22.0 mg kg^{-1}. Selenium is an essential trace dietary element for animal and human with variety of novel biological functions [3–5,7]. Due to low toxicity and comparable efficacy in increasing of activities of selenoenzymes [5], SeNPs overcome the dose gap between beneficial and potentially toxic levels of ionic selenium compounds [4,5,8,9]. Recently, it has been reported that SeNPs have excellent anticancer activity [10–14]. Sonkusre et al. [12] proved that SeNPs were highly efficacious and specific against prostate cancer. According to reference [10], oral administration of 0.2 mg Se kg^{-1} body weight of SeNPs with size of 50–80 nm induced chemoprevention of lung cancer for the experimented rats. Furthermore, Faghfuri et al. [13] reported that breast tumor volume in mice supplemented with a 200 μg day^{-1} dose of SeNPs for 60 days was smaller than the other groups including control group. Additionally, SeNPs also possess potential antioxidant activity [15–17]. For instance, SeNPs have potential size-dependent characteristics on scavenging the free radicals and furthermore, SeNPs with different sizes: small size (5–15 nm), medium size (20–60 nm), and large size (80–200 nm) also showed protective effects against the damaged oxidation of DNA [15]. Besides, the SeNPs antioxidant activity was also depended on dosage and its surface stabilizer. Chen et al. [18] reported that the scavenging ability of chitosan-stabilized SeNPs is higher than that of carboxymethyl chitosan-stabilized SeNPs. Selenium deficiency may result in a number of serious diseases such as cancer, cardiovascular and immune disorders [19,20].

Different methods have been used for synthesis of SeNPs from ionic selenium solutions such as chemical reduction using ascorbic acid [9,14,17,21], glutathione [4,5,8,15], hydrazine hydrate [22] as reductants; and biological synthesis using bacterial biomass as reductant agents [10–13,16]. In addition, γ-irradiation method has been also applied for synthesis of SeNPs using sodium dodecyl sulfate as a surfactant and ethanol as a scavenger for hydroxyl radicals [23]. Compared with other methods, gamma Co-60 ray irradiation has been considered as an effective method with several advantages as described by Hien et al. [24] and as a green route to noble metal nanoparticle synthesis [25].

Dextran polysaccharide composed of repeated monomeric glucose units with a predominance of 1,6-α-D-glucopyranosyl linkages with annual world production of about 500 metric tons [26]. Dextran is readily soluble in water and electrolytes with excellent stability and it has wide range of use in food, medical related areas and biological functions [27]. Dextran is also an agent commonly used in surgery to decrease vascular thrombosis. The antithrombotic effect of dextran is mediated through its binding of erythrocytes, platelets, and vascular endothelium, increasing their electronegativity and thus reducing erythrocyte aggregation and platelet adhesiveness.

In the present study, SeNPs were synthesized by gamma Co-60 ray irradiation method using dextran as both stabilizer and hydroxyl radical scavenger. The influence of pH of aqueous H_2SO_3/dextran solutions before irradiation on the size of SeNPs was studied. The SeNPs/dextran powder was prepared by spray drying of SeNPs/dextran solution and its antioxidant activity was investigated.

2. Experimental

2.1. Chemicals

Selenium dioxide (SeO_2) was of pure product of Merck, Germany. Dextran (MW 60,000–90,000 g mol^{-1}) purchased from Himedia, India. Ultra pure ABTS diammonium salt and potassium ferricyanide were products from Sigma-Aldrich. Other chemicals were of pure grade. Distilled water was used throughout the experiments.

2.2. Preparation of SeNPs/dextran by γ-irradiation

A required amount of SeO_2 was dissolved in 1% (w/v) dextran aqueous solution to prepare selenous acid (H_2SeO_3) solution (eq. (1)) with concentration of 2.5 mM. The pH of this solution was moderately acidic (pH ~4). In order to investigate the effect of pH, two other H_2SO_3/dextran solutions were adjusted to pH 6 and 8 by 5% NH_4OH solution.

$$SeO_2\,(s) + H_2O\,(l) \rightarrow H_2SeO_3\,(aq) \quad (1)$$

Irradiation of SeO_3^{2-}/dextran solutions to synthesize SeNPs was carried out on a Gamma Chamber 5000, BRIT (India) at the Nuclear Research Institute (Da Lat City) at dose of 20 kGy, with the dose rate of 2.5 kGy/h measured by a dichromate dosimetry system [28].

2.3. Characterization of SeNPs/dextran

The absorption spectra of dextran and the resulted SeNPs/dextran solutions were taken on an UV–Vis spectrophotometer model UV-2401PC (Shimadzu, Japan). The size and size distribution of the SeNPs were characterized by TEM images on transmission electron microscope (TEM), model JEM1010 (JEOL, Japan) and statistically calculated from about 300 particles [24]. The SeNPs/dextran powder was typically prepared by spray drying of 2.5 mM SeNPs/1% dextran solution (pH 6) with Spray dryer model ADL311 (Yamato, Japan). The content of selenium in SeNPs/dextran powder was assessed by energy dispersive X-ray (EDX) spectroscopy on a JEOL 6610 LA. The Fourier transform infrared (FTIR) spectra of dextran and SeNPs/dextran were also recorded on a Shimadzu FT-IR 8400S spectrophotometer using KBr pellets.

2.4. Antioxidant activity of SeNPs/dextran powder

2.4.1. $ABTS^{\bullet+}$ radical scavenging ability assay

The determination of $ABTS^{\bullet+}$ radical scavenging ability of samples was carried out as the method described by Zhai et al. [6] and Chen et al. [18] with slight modification. Briefly, 0.6 ml of samples (aqueous solution of dextran or SeNPs/dextran) was thoroughly mixed with 1 ml of $ABTS^{\bullet+}$ radical solution to obtain the desired concentrations. The $ABTS^{\bullet+}$ radical solution was prepared by mixing 7.4 mM ATBS and 2.6 mM $K_2S_2O_8$ in aqueous solution with the same volume and was kept in the dark for 16 h at room temperature, and then was diluted by water to reach the optical density of 1 ± 0.1 at the wavelength of 734 nm (OD_{734}) on a UV–Vis spectrophotometer before use. The 1 ml of ATBS solution without $K_2S_2O_8$ diluted with water was also added 0.6 ml sample with the same concentration for preparation of the blank samples. The OD_{734} was carried out in triplicate for each sample and the percentage of $ABTS^{\bullet+}$ radical scavenging ability was calculated as the following equation:

$$ABTS^{\bullet+}\text{ radical scavenging ability }(\%) = (Ac - As) \times 100/Ac \quad (2)$$