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Research article

Nutritional quality assessment of tomato fruits after exposure to uncoated and citric acid coated cerium oxide nanoparticles, bulk cerium oxide, cerium acetate and citric acid[☆]

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ABSTRACT

Little is known about the effects of surface modification on the interaction of nanoparticles (NPs) with plants. Tomato (*Solanum lycopersicum* L.) plants were cultivated in potting soil amended with bare and citric acid coated nanoceria ($nCeO_2$, $nCeO_2$+CA), cerium acetate (CeAc), bulk cerium oxide ($bCeO_2$) and citric acid (CA) at 0–500 mg kg^{-1}. Fruits were collected year-round until the harvesting time (210 days). Results showed that $nCeO_2$+CA at 62.5, 250 and 500 mg kg^{-1} reduced dry weight by 54, 57, and 64% and total sugar by 84, 78, and 81%. At 62.5, 125, and 500 mg kg^{-1} $nCeO_2$+CA decreased reducing sugar by 63, 75, and 52%, respectively and at 125 mg kg^{-1} reduced starch by 78%, compared to control. The $bCeO_2$ at 250 and 500 mg kg^{-1}, increased reducing sugar by 67 and 58%. In addition, when compared to controls, $nCeO_2$ at 500 mg kg^{-1} reduced B (28%), Fe (78%), Mn (33%), and Ca (59%). At 125 mg kg^{-1} decreased Al by 24%; while $nCeO_2$+CA at 125 and 500 mg kg^{-1} increased B by 33%. On the other hand, $bCeO_2$ at 62.5 mg kg^{-1} increased Ca (267%), but at 250 mg kg^{-1} reduced Cu (52%), Mn (33%), and Mg (58%). Fruit macromolecules were mainly affected by $nCeO_2$+CA, while nutritional elements by $nCeO_2$; however, all Ce treatments altered, in some way, the nutritional quality of tomato fruit. To our knowledge, this is the first study comparing effects of uncoated and coated nanoceria on tomato fruit quality.

1. Introduction

Lanthanides, also known as rare earth elements (REEs), are abundant in the Earth's crust; however, they tend to coexist, making single element acquisition quite challenging. In nature, they are present as oxide or phosphate complexes (Kabata-Pendias and Pendias, 1992). REEs are widely used in several applications, and their demand is estimated to increase around the world (EPA, 2012; Gonzalez et al., 2014). Cerium (Ce) and other REEs have found application in agriculture (Pang et al., 2001); however, the effects of these elements on plants are still not well understood. Even though Ce is nonessential to plants, previous studies have shown that it stimulates root growth and impacts other plant functions. According to Yuan et al. (2001), "Changle," a fertilizer composed mainly of Ce (50.2%), improved root growth in rice (*Oryza sativa*) seedlings. Similarly, Shyam and Aery (2012) reported that Ce, at low concentrations (0.713–17.841 μM), promoted chlorophyll content, dry matter production, and nitrate reductase activity in cowpea (*Vigna unguiculata*) plants. Liang et al. (2011) reported that Ce (20 mg L^{-1}) could alleviate ultraviolet-B-induced inhibition of photochemical reaction activity and photosynthetic pigments in soybean (*Glycine max*) seedlings. On the other hand, Diatloff et al. (2008) reported that Ce, at

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concentrations >5 μM, inhibited corn (*Zea mays*) or mungbean (*Vigna radiata*) root elongation. Hu et al. (2002) also reported that Ce (0.5–25 mg L^{-1}) reduced root elongation, shoot, and root dry weight and mineral content in wheat (*Triticum aestivum*). Another study by Thomas et al. (2014) showed that Ce (978 mg kg^{-1} soil) at low pH decreased germination in four crops, including tomato.

Oxides of some REEs and other metal elements, at nanoparticle level, have been found to reach crop plants through intentional exposure (Servin and White, 2016) or soil amended with engineered nanoparticle (ENP)-loaded biosolids (Rico et al., 2011; Miralles et al., 2012). Cerium oxide nanoparticles (NPs) or nanoceria ($nCeO_2$) are amongst the top 10 NPs produced worldwide (Piccino et al., 2012; Keller and Lazareva, 2014). One of the most common uses of $nCeO_2$ includes fuel additives and catalysts (Johnson and Park, 2012). This suggests a high probability of environmental dispersion and interaction of plants with $nCeO_2$.

Previous studies have shown controversial effects of $nCeO_2$ in crop plants (Gardea-Torresdey et al., 2014). However, findings by Lopez-Moreno et al. (2010) and Hernandez-Viezcas et al. (2013) seem to apply to all plants. Lopez-Moreno et al. (2010) reported that most of the $nCeO_2$ taken up by soybean (*Glycine max*) plants was stored without modification in the roots, while Hernandez-Viezcas et al. (2013) reported the translocation of $nCeO_2$ to soybean seeds. Other reports have shown that $nCeO_2$ affects crop production in several ways. Peralta-Videa et al. (2014) studied the alterations that $nCeO_2$ and ZnO NPs have on the nutritional value of soybean plants cultivated in farm soil. Rico et al. (2013a) reported that $nCeO_2$ at 500 mg kg^{-1} altered the grain quality in three varieties of rice and inhibited the grain formation in barley (Rico et al., 2015). Zhao et al. (2014) reported that $nCeO_2$ at 400 mg kg^{-1} increased starch, globulin, and nonreducing sugar, but at 800 mg kg^{-1} reduced phenolic content in cucumber fruits. Micronutrients were also affected in cucumber seeds (Zhao et al., 2014). Rico et al. (2014) also reported that $nCeO_2$ at 500 mg kg^{-1} improved wheat grain yield by 36.6% and modified S and Mn storage in grains. In a trans-generational tomato study, Wang et al. (2013a, b) reported that $nCeO_2$ (10 mg L^{-1}) treated second generation seedlings showed a reduction in biomass, water transpiration, and higher reactive oxygen species (ROS) content.

Next to potatoes, tomatoes are the most consumed vegetables in the United States. Mostly, tomatoes are eaten either fresh or canned (USDA, 2013) and are a primary source of sugars, proteins, carbohydrates, and many essential nutrients like: calcium, magnesium, iron, phosphorous, potassium, sodium, and zinc (https://ndb.nal.usda.gov/ndb/foods/show/3223?manu=&fgcd=). Tomatoes also have a high lycopene content, a carotenoid with antioxidant properties. Lycopene is present in chromoplasts during ripening (Hornero-Mendez and Britton, 2002). In humans, lycopene scavenges peroxy and singlet oxygen radicals and aids in the deactivation of agents that break DNA-chains (Stahl et al., 1997). The present study is a follow-up of a previous study where the effects of five different compounds: cerium oxide nanoparticles, citric acid coated cerium oxide nanoparticles, cerium oxide bulk, cerium acetate, and citric acid in soil grown tomato plants were reported (Barrios et al., 2016). The hypothesis of this work is that $nCeO_2 + CA$ affect in a different way than $nCeO_2$ the physiological and biochemical parameters of tomato fruits. In this manuscript, the changes in macro and micronutrient accumulation, carbohydrate (sugar and starch) content, and the lycopene content in tomato fruits of plants exposed to the Ce compounds mentioned above were studied. To the authors' knowledge, this is the first study comparing the effects of coated and uncoated cerium oxide NPs in the nutritional quality of tomato fruits.

2. Materials and methods

2.1. Nanoparticle suspensions and other treatments

The $nCeO_2$ (Meliorum Technologies, NY, USA) were obtained from the University of California Center for Environmental Implications of Nanotechnology (UC CEIN). According to Keller et al. (2010), these nanoparticles have a primary size of 8 ± 1 nm, particle size of 231 ± 16 nm in deionized water and a surface area of 93.8 m^2 g^{-1} and a ζ potential of 20.1 ± 1.2 mV (Trujillo-Reyes et al., 2013). Citric acid coated CeO_2 NPs ($nCeO_2 + CA$) on a 1:2 ratio were prepared and characterized by Trujillo-Reyes et al. (2013). Briefly, these NPs have an average primary size of 12.4 nm, particle size of 189 ± 2 nm in deionized water, and a ζ potential of −57 ± 0.6 mV. According to the manufacturer (Sigma-Aldrich), Cerium acetate (CeAc) and bulk cerium oxide ($bCeO_2$) have a size above 5 μm. The pH in soil of all suspensions was 6.12 ± 0.03 and the average temperature was 21.63 ± 0.06 °C. Citric acid (CA), CeAc, $nCeO_2$ and $nCeO_2 + CA$ solutions/suspensions were prepared with Millipore water (MPW) accordingly to have final concentrations of 0, 62.5, 125, 250 and 500 mg kg^{-1} of each compound. The concentrations were selected from previous studies by Rico et al. (2013b) and Barrios et al. (2016). The dispersed nanoparticle suspensions were sonicated in a water bath for 30 min at 20 °C with a sonication intensity of 180 W and immediately applied to the soil. Each compound had their individual set of MPW controls (no chemical added).

2.2. Experimental design and growth conditions

Roma tomato (*Solanum lycopersicum*) seeds were grown in Miracle-Gro® Organic potting mix and exposed to five different chemicals: $nCeO_2$, $nCeO_2 + CA$, $bCeO_2$, CeAc, and CA at the five concentrations mentioned above. Each treatment had four replicates, and each pot contained five seeds. After 60 days, the biggest plant per pot was selected and cultivated to full maturity. Plants were watered daily and kept in a greenhouse for 210 days. Tomato fruits were collected starting from 139 to 210 days after germination. Further details on the greenhouse conditions, soil composition, and experimental design are described in Barrios et al. (2016).

2.3. Nutrient content

After harvesting, tomato fruits were cut into halves. One-half was cryogenized in liquid nitrogen and stored at −20 °C for further analysis. The second half was oven dried for 72 h at 60 °C. Once dried, samples were ground to a powder with mortar and pestle, and 0.2 g were acid-digested with one mL of plasma pure nitric acid and four mL of 30% hydrogen peroxide in a microwave system (MarsX, CEM Corporation Mathews, NC, USA) as described by Packer et al. (2007). After digestion, tomato samples were diluted to 50 mL with MPW. Quantification of Ce, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, and Zn was conducted using inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 4300 DV, Shelton, CT). For quality assurance/quality control (QA/QC) purposes, blank and spikes containing Ce at 1 and 5 mg/L were read every 15 samples. Blanks, spikes, and standard reference materials NIST 1547 peach leaves, (Gaithersburg, MD) were used to validate the quantification.

2.4. Determination of total and reducing sugars

2.4.1. Total sugar

Total sugar was quantified following the method of Dubois et al. (1956). For sugar extraction, 100 mg of oven dried tomato samples were homogenized in 10 mL of 80% ethanol, boiled in a water bath