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# Green synthesis of sulfur nanoparticles using *Punica granatum* peels and the effects on the growth of tomato by foliar spray applications

Nidá M. Salem[a], Luma S. Albanna[a], Akl M. Awwad[b,*]

[a] Department of Plant Protection, Faculty of Agriculture, The University of Jordan, Amman, Jordan
[b] Nanotechnology Laboratory, Royal Scientific Society, Amman, Jordan

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ABSTRACT

Sulfur nanoparticles (SNPs) have been successfully prepared from sodium thiosulfate in the presence of *Punica granatum* peels aqueous extract at room temperature. The resulting sulfur nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Highly crystalline synthesized sulfur nanoparticles exhibiting high purity, spherical shape with average particle size of about 50 nm applied at a rate of 100 ppm, 200 ppm, and 300 ppm as foliar spray for tomato leaves. The obtained results revealed that the foliar spraying tomato leaves with 200 ppm sulfur nanoparticles are very beneficial to plant growth and produced healthy plant with greener leaves and high quality of tomato fruits compared with control.



## 1. Introduction

Sulfur is widely used as a fungi toxic agent in agricultural fields against a wide range of powdery mildews, certain smut and rust fungi and some other common fungal pathogens including *Cladosporium fulvum*, and *Fusarium* spp. Sulfur is enzymatically reduced in living cells to form hydrogen sulfide and this reduction proceeds by a single electron transfer from the donor in the cell to sulfur (Owens, 1963). Production of excess hydrogen sulfide within the fungal body spells enhanced toxicity and leads to the inhibition of fungal growth. Despite the antifungal efficacy of sulfur, its use is now restricted among farmers and agrochemical industries mainly for two reasons, firstly sulfur is required in bulk quantities for application in agricultural fields and secondly it is also likely to induce resistance in the target species. It is desirable to considerably reduce the amount, so that the cost is cut down and at the same time, the buildup of resistance in target pathogens is minimized. Intelligent bottom up nanoscience application is the most appropriate tool to resolve the aforesaid problems. Sulfur nanoparticles can be synthesized by different methods such as water-in-oil microemulsion technique (Guo et al., 2006), liquid phase chemical precipitation (Guo et al., 2005), from $H_2S$ gas, using novel biodegradable iron chelates in W/O microemulsion (Deshpande et al., 2008), and aqueous surfactant solutions (Chaudhuri and Paria, 2010). Among these methods, application of green synthesis technique is the simplest of all. The process can be carried out easily by using *Punica granatum* (pomegranate) peels at room temperature and with minimal facility. The effects of various nanomaterials on plants growth were studied. These nanomaterials include cerium (IV) oxide, $CeO_2$ and copper oxide, CuO (Hong et al., 2015), cerium dioxide and zinc oxide nanoparticles (Peralta-Videa et al., 2014), nano titanium oxide, $TiO_2$ (Gao et al., 2013), nano zinc oxide, ZnO, nano iron oxide, FeO and nano-ZnCuFe-oxide particles (Dhoke et al., 2013), iron oxide and titanium oxide nanoparticles (Burke et al., 2015), cobalt ferrite, $CoFe_2O_4$ (López-Moreno et al., 2016), silver nanoparticles, Ag (Larue et al., 2014), iron nanoparticles, Fe (Canivet et al., 2015), alumina, $Al_2O_3$ (Juhel et al., 2011), and magnesium nanoparticles, Mg (Indira and Tarafdar, 2015). These nanomaterials used to study their effects on plant growth contain toxic heavy metals such as Zn(II), Co(II), and Ag(I) ions to soil, plant, and humans, Sulfur is considered as safer element due to its ability to form organo-sulfur compounds in plant tissue, which are necessary to grow plants healthy and antifungal activity (Hawkesford, 2000; Kim et al., 2006; Bakry et al., 2015; Suleiman et al., 2015). As continuation of our previous work on sulfur nanoparticles synthesis and its effect on plant growth (Salem et al., 2016a,b), a new green and large-scale method using *Punica garantum* peels for synthesis sulfur nanoparticles (SNPs).

* Corresponding author.
*E-mail addresses:* akl.awwad@yahoo.com, akl.awwad@rss.jo (A.M. Awwad).

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The main objectives of this study is to synthesize sulfur nanoparticles by green method using *Punica granatum* peels extract and to investigate the impact of a foliar exposure to SNPs on tomato plant leaves.

## 2. Experimental

### 2.1. Materials

Sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}H_2O$, 99.5%), hydrochloric acid (32%, HCl) were obtained from Merck, Darmstadt, Germany. Fresh *Punica granatum* (Pomegranate) peels was obtained from local Jordan market. Double distilled and deionized water was utilized for the preparation of aqueous extracts.

### 2.2. Preparation of aqueous extract of Punica granatum *peels*

20 g of dried powder of *Punica granatum* peels were mixed with 500 ml distilled water and boiled for 20 min. The mixture was then cooled at room temperature, followed by filtration on filter paper Whatman No. 1 to remove solid particles. Then the extract centrifuged at 1200 rpm for 5 min to remove heavy biomaterials. The filtrate was stored at room temperature for further experimental work.

### 2.3. Synthesis of sulfur nanoparticles (SNPS)

Sulfur nanoparticles were synthesized as follows: 24.8 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) was dissolved in 500 ml of *Punica granatum* peel extract under mild stirring for 10 min at room temperature and then diluted with 500 ml deionized water. Afterwards 10% HCl was added drop by drop under stirring for allowing the sulfur precipitations uniformly. The suspended sulfur particles obtained were then centrifuged at 5000 rpm for 10 min at ambient temperature. The supernatant was discarded and the precipitate was repeatedly washed with distilled water and absolute ethanol to get rid any biological materials. The product was finally dried in a vacuum at 60 °C for 4 h. In *Punica granatum* peels extract and acidic solution, sodium thiosulfate ($Na_2S_2O_3$) undergoes through a disproportionation reaction to sulfur and sulfonic acid according to:

$$Na_2S_2O_3{\cdot}5H_2O + 2HCl \rightarrow 2NaCl + S\downarrow + SO_2 + 6H_2O$$

### 2.4. Foliar applications of SNPs

Tomato (*Solanum lycopersicum*) plants were cultivated in a greenhouse where the temperature was maintained at 26 ± 4 °C during day light and 20 ± 2 °C during night. Experiments were con-

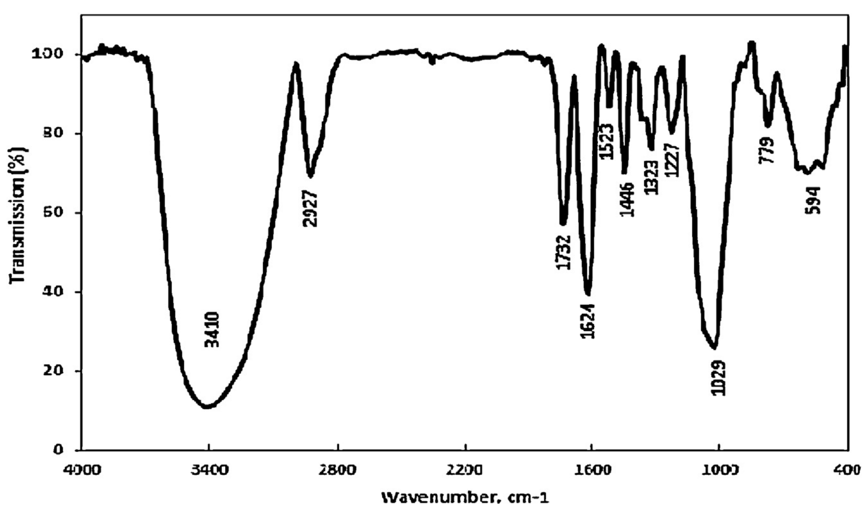


**Fig. 1.** FT-IR of *Punica granatum* peels aqueous extract.

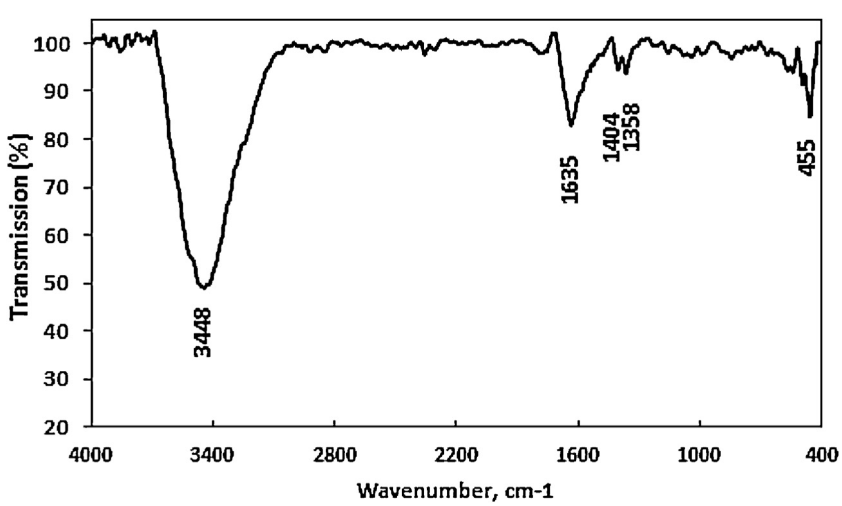


**Fig. 2.** FT-IR of the synthesized sulfur nanoparticles.