



A green and environmental sustainable approach to synthesis the Mn oxide nanomaterial from *Punica granatum* leaf extracts and its in vitro biological applications

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Abstract Pathogenic fungal infections in fruit cause economic losses and have deleterious effects on human health globally. Despite the low pH and high water contents of vegetables and fresh, ripened fruits, they are prone to fungal and bacterial diseases. The ever-increasing resistance of phytopathogens toward pesticides, fungicides and bactericides has resulted in substantial threats to plant growth and production in recent years. However, plant-mediated nanoparticles are useful tools for combating parasitic fungi and bacteria. Herein, we synthesized biogenic manganese oxide nanoparticles (MnONPs) from an extract of *Punica granatum* (*P. granatum*), and these nanoparticles showed significant antifungal and antibacterial activities. The production of MnONPs from plant extracts was confirmed by infrared spectroscopy (FTIR), X-ray diffraction (XRD) and UV visible spectroscopy (UV).

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The surface morphology and shape of the nanoparticles were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Using a detached fruit method, the MnONPs were shown to exhibit significant antimicrobial activities against two bacterial strains, *E. coli* and *S. aureus*, and against the fungal species *P. digitatum*. The results revealed that the MnONPs had a minimum antimicrobial activity at 25 µg/mL and a maximum antimicrobial activity at 100 µg/mL against bacterial strains in lemon (citrus). Furthermore, the MnONPs exhibited significant ROS scavenging activity. Finally, inconclusive results from the green-synthesized MnONPs magnified their significant synergetic effects on the shelf life of tomatoes (*Lycopersicon esculantum*) and indicated that they could be used to counteract the phytopathological effects of postharvest fungal diseases in fruits and vegetables. Overall, this method of MnONPs synthesis is inexpensive, rapid and ecofriendly. MnONPs can be used as potential antimicrobial agents against different microbial species.

Keywords Green nanoparticles · Antimicrobial activity · Antioxidant · Edible coating · Postharvest pathogen

Introduction

Different phytopathogens, such as fungi, bacteria and viruses, have harmful effects on crops and lead

to large economic losses (Al-Zubaidi et al., 2019) of the total food produced for human consumption in the world. This amounts to an approximate cost of \$680 billion in developed countries and approximately \$310 billion in developing countries (Sawicka, 2019). Generally, the postharvest loss of these perishables is estimated to be from 40 to 50%. Fungal infection is more devastating for fruit and vegetables than other phytopathogens because fungal spores spread through the air (Shah et al., 2022; Waithaka et al., 2017). Therefore, such fungal spores can also damage the postharvest quality of fruits. Thus, economic losses due to postharvest fungal attacks on fruit result in reductions in the quality of fresh fruit and vegetables. Currently, postharvest fungal diseases are an emerging problem for the fruit market. *Penicillium digitatum*, green mold, is one such phytopathogen; it is a wound pathogen that causes soft and wet rot diseases in citrus, banana and stored apples (Al-Dhabaan, 2018; Kwon et al., 2012). The conidia of this fungus quickly deteriorate the organoleptic characteristics of fruits. Synthetic fungicides are commonly used to overcome such fruit rot diseases (Perez et al., 2016). This destructive pathogen colonizes the fruit surface and causes massive economic losses during fruit storage and shipment (Wisniewski et al., 2016). However, the synthetic nonsystemic fungicide Prochloraz has been applied in packing lines to control anthracnose decay in different fruits (Shimshoni et al., 2020). Synthetic fungicides have been banned and are not permitted during the agricultural process due to several normative restrictions. They are considered unsafe for human health and for our environment. Therefore, there is an urgent need to develop natural, organic and safe measures to reduce fruit spoilage in stores.

Recent advances in the biofabrication of diverse nanomolecules of various sizes, shapes, and characteristics have established nanotechnology as an essential technology in a variety of disciplines. Thus, nanotechnology is prevalent in all of the life sciences fields and is used in many high-technology industries. Nanoparticles, in contrast with bulk materials, have greater specific exterior areas and high reactivity. Thus, they have been demonstrated to impact many living cells, including microbial cells (El-Nagagar et al., 2017). Moreover, at present, green nanotechnology is a promising tool to support sustainable

agriculture because of its unique properties (Souri et al., 2019). It has also gained additional attention due to its multiple applications in the field of agriculture, such as in soil remediation, plant nutrition, pest control, pathogen detection, remediation of disease severity and food packing (Kowsalya et al., 2019). Different metals, such as silver, copper, zinc, iron, magnesium, and gold, have unique physical and biological characteristics (Selvaraj et al., 2019). Among these, Mn nanoparticles are the cheapest, most stable, and nontoxic and can be employed in water treatment. They also act as image contrast agents because of their physicochemical properties (Jayandran et al., 2015; Souri et al., 2018; Zhang et al., 2017). In addition, manganese is an essential nutrient for plant growth and development. MnONPs have several forms, such as MnO and MnO₃, which are being used in different fields (Hoseinpour & Ghaemi, 2018). MnONPs have been prepared by several conventional methods (pulsed laser, ultrasonication, sol-gel, wet impregnation, microwave irradiation spray pyrolysis, laser vaporization routes, hydrothermal method, and deposition and a conventional coprecipitation method) (Iqbal et al., 2019; Lu et al., 2021; Munir et al., 2019). The chemical synthesis of nanoparticles is very expensive and toxic and has deleterious effects on the atmosphere (Negahdary et al., 2015; Ogunyemi et al., 2019). Therefore, to combat high residual toxicity, degradation, carcinogenic effects, and environmental pollution, a sustainable “green” approach, particularly based on plants, should be employed to eliminate the hazardous effects of chemically fabricated nanoparticles (Ciorîță et al., 2020; Khan & Lee, 2020; Khan et al., 2018). In addition, green-synthesized nanoparticles are more reliable and cost-effective (Nasiriboroumand et al., 2018). Moreover, phytochemical compounds present in plants, such as polyphenols, alkaloids, terpenoids and flavonoids, induce the reduction of metal ions and are used to stabilize metal NPs (Gharehyakheh et al., 2020). There are several reports of the green synthesis of Mn nanoparticles using plant extracts (Ahmad et al., 2022; Kumar et al., 2017; Souri et al., 2018). In this regard, we first encapsulated Mn with biomolecules present in the fruit peel and leaf extracts of *Punica granatum* using a green synthesis method. *Punica granatum* L. is commonly known as pomegranate and belongs to the family Lythraceae. It contains numerous secondary metabolites, such

as luteolin, alkaloids, glycolipids, flavonoids, tannis and an organic acid, which are important from a medical point of view (Kumar et al., 2018; Sarkar & Kotteeswaran, 2018). We hypothesized that the fruit peel and leaf extract have medical, antioxidant and antifungal activities, so they can be used as capping and reducing agents that could help us fabricate Mn nanoparticles (Joshi et al., 2018).

The main objective of this research is to create an environmentally friendly and cost-effective MnONPs for use as an antifungal and antibacterial agent. In this study, green-synthesized MnONPs were used against phytopathogens and provided full access to the antifungal and antibacterial properties of the synthesized NPs. These findings contribute a novel role for green MnONPs in phytopathogen integrative control and introduce techniques to research green nanopesticides and eliminate chemical pesticides from the environment. The biocompatible preparation of MnONPs can help us apply them for antimicrobial activities. In this study, for the first time, we used green-synthesized Mn nanoparticles against phytopathogens in vitro, providing a thorough understanding of the antimicrobial activities of green-synthesized NPs.

Materials and methods

Fruit collection

Fresh lemons (Citrus) and tomatoes (*Lycopersicon esculantum*) were collected from a local fruit market.

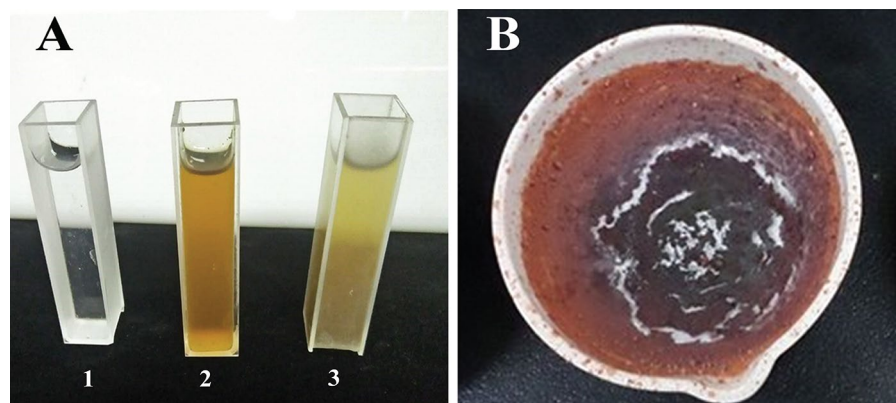
Collection of plant material and preparation of plant leaf extract

In this study, the leaves of the important medicinal plant pomegranate (*P. granatum*) were collected from District Bhakkar (Fig. 1) and further verified by a department professor of taxonomy at Quaid-i-Azam University, Pakistan. Surface sterilization of the leaves of *P. granatum* was performed with 75% ethanol for 3 min (min). The plant material was washed thoroughly three times in autoclaved distilled water, dried at room temperature for the removal of moisture and crushed to a powder. The plant materials were boiled in water, continuously stirred and left undisturbed overnight. The resultant filtrates were prepared by filtration through ply muslin cloth followed by fine filtration through Whatman filter paper (No. 4). The suspensions were further fine filtered with a Millipore filter (pore size 0.2 μm), and the filtrates were kept at 4 °C until further use.

Preparation of Mn nanoparticles using plant extracts and fruit peel

Biosynthesized MnONPs were successfully prepared by a previously established green protocol with slight changes (Shah et al., 2022). Next, 100 ml of filtered aqueous leaf extract was dissolved with 1 g of MnSO₄, heated at 80 °C, and continuously stirred at 500 rpm for 2 h with a magnetic stirrer. The resultant solution was left undisturbed for 30 min, and the yellow color of the extract solution changed to a reddish precipitate, which was the first indication of MnONPs formation. The obtained mixture was centrifuged at 12,000 rpm for 8 min, the pellet was retained, and the supernatant

Fig. 1 Formation of green MnONPs: a MnONPs were formed by the reduction of Mn ions by *P. granatum*. This figure illustrates the formation of MnONPs: **A** 1- solution of Mn sulfate, 2- pure plant extracts (pale yellow), 3- complete reduction, and **B** calcined MnONPs



was discarded in a Falcon tube. The pellet precipitate (containing potential MnONPs) was purified with autoclaved water to remove all unbound biological materials. Furthermore, the product was washed with ethanol and vacuum dried at 2 h. A reddish NP powder composed of MnO was finally collected in an airtight jar and stored at room temperature for further studies. Furthermore, the green-synthesized nanoparticles were calcined and analyzed by different microscopic and spectroscopic techniques, including UV, XRD, SEM and TEM.

Characterization of the synthesized MnO nanoparticles

The MnONPs were extensively characterized by FTIR, UV, SEM and TEM microscopy. The functional groups present in the plant extracts that were involved in the capping and stabilization of MnONPs were determined using Fourier transform infrared (FT-IR) spectroscopy (Schimadzu-Model FTIR, Kyoto, Japan). The MnONPs sample was ground according to a KBr pellet method to assess the biological constituents of the synthesized NPs, and scans were performed in the range of 400–4000 cm^{-1} (Subbaiya et al., 2017). The bioreduction of Mn ions to MnONPs was recorded by absorption spectral measurement of the reaction solution using a UV-4000 UV–Vis spectrophotometer (Abbasi et al., 2020). For spectral analysis, XRD was employed, for which a 3 ml reaction mixture was placed in a cuvette. The spectrum was obtained over a range of 200–800 nm. The MnONPs were centrifuged at 8000 rpm for 30 min and placed on a carbon film for XRD analysis (PANalytical XRD (Netherlands)). XRD analysis was performed to determine the crystal structural phases of the MnONPs using an X-ray diffractometer by the Debye-Scherrer equation.

$$(D = K\lambda/\beta\cos\theta)$$

The structure of the green-synthesized NPs particles was determined by (Shimadzu-Model Kyoto, Japan). The 2θ range was from 10° to 90° , and $\text{Cu}/\text{K}\alpha$ radiation was used (Khatami et al., 2016). The shape of the particles and morphology were investigated by SEM. A MnONPs solution was dropped carefully onto a carbon-coated copper grid. Next, the samples were air-dried before microscopic analysis (SEM JEOL JSM-5910), and an accelerating voltage of 10 kV was

used for four minutes with a gold coating. The photographs were taken with a camera installed on the instrument (Shiri et al., 2017; Ullah et al., 2019).

The average size of the particles observed by SEM was found to be below 50 nm, which is consistent with the XRD results in which sharp peaks showed the crystalline nature of the nanoparticles. To check the shape and size of the green MnONPs, TEM was performed, which provides a resolution 1000-fold higher than SEM. The TEM measurements were collected using an H7650 electron microscope with a CCD imaging system and an accelerating voltage of 200 kV. After evaporation of the water content, the MnONPs were dissolved in 1 ml of distilled water, dropped onto a copper grid and visualized.

Antimicrobial activity of biosynthesized MnONPs

The biocompatible and nontoxic nanoparticles that were synthesized through the green approach had an average size of approximately 20 nm. They were tested against a postharvest pathogenic fungal attack of *Penicillium digitatum* and of (*P. digitatum*) *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacterial strains.

Antibacterial activity

The antibacterial activity of the MnONPs was determined against two bacterial strains (*E. coli* and *S. aureus*) according to a previously established standard disc diffusion method (Iqbal et al., 2021). Before the interactions of MnONPs with bacterial strains were investigated, synthesized powders of the available cultures was added to nutrient broth media, and the flasks were incubated at 37°C for 24 h. Subsequently, an autoclaved agar medium was cooled to room temperature, and the medium was poured into Petri plates. After solidification, 40 μL of bacterial culture was spread onto the agar plates with sterilized cotton swabs. Four-millimeter filter discs were loaded with 20 μL of different concentrations of MnONPs, and dH_2O served as the control. The experiment was repeated three times, and the agar plates were placed in a laminar hood for 30 min. The plates were incubated at 37°C h, and the 24 h diameter of zone inhibitions on the coated discs was measured in millimeters (mm) (Chartarrayawadee et al., 2020).

Antifungal activity in vivo on fruit

The in vivo antifungal activity of fruit was assessed according to a previously established method with slight modifications (Madbouly, 2021). Then, *P. digitatum* fungus biomass was added to a medium by using a cork borer with a diameter of 2 mm. The medium was placed in an incubated shaker at 32 ± 2 °C for 24 h. Lemons that were fresh, healthy, free of injuries and equal in size were collected from a fruit market. The fruit was first sterilized with 70% sodium hypochlorite solution and rinsed with double distilled water. Prior to the application of NP treatments, the cuticle layer of each selected fruit was artificially damaged with a cork borer (2 mm in diameter and 4 mm deep). Different concentrations of green Mn nanoparticles (25–100 µg/mL) were applied as postharvest sprays onto the fruit, and sterilized water served as the control. After 2 h, 10 µl of a prepared spore suspension (106 conidia per mL) of fungus was inoculated into the lemons. Each fruit was covered with a sterilized wet muslin cloth to maintain humidity and avoid other fungal and bacterial infections. The disease severity was measured around the infected area in centimeters on each fruit after the 8th day postinoculation (Nikkhah et al., 2017; Xue et al., 2019).

Edible coatings

Fresh tomatoes of equal sizes were washed with dH₂O thrice and air-dried at room temperature for 2 h. The edible coating was analyzed for food preservation. Tomatoes were coated with biological MnONPs thrice with a cotton swab according to a previously reported protocol (Chandirika et al., 2018) and stored at room temperature for 12 days. Two replicates (coated and noncoated) were selected for each treatment, and weight loss was measured at different intervals. The mean \pm SD values obtained for the three replicates were analyzed by ANOVA, and significant differences were determined by using the Tukey–Kramer test at $p < 0.05$.

Antioxidant assay

The free-scavenging ability of the aqueous leaf extract of *P. granatum* and biosynthesized MnONPs were used to test the scavenging effect on 1,1-diphenyl-2-picryl

(DPPH) activity according to previously published methods (Muthuvel et al., 2020). For measurements of scavenging activity, various concentrations (25, 50, 75, 125 and 250 µg/ml) of the test sample were prepared, and an equivalent volume of 0.1 mM DPPH solution was added to the sample. The reaction mixture was left undisturbed for 30 min in the dark. The absorbance was measured at 517 nm using a spectrophotometer, and the results indicated the antioxidant activity. Ascorbic acid was used as a control to calibrate the resultant activity. Percent inhibition was calculated using a relevant formula (Das et al., 2013).

DNA cleavage assay

The DNA degradation activity of the MnONPs against *E. coli* plasmids was determined by a DNA cleavage assay using agarose gel electrophoresis (Jadhav et al., 2018). *E. coli* JM109 competent cells (Takara, Japan) were used to prepare synthesized compounds. A plasmid purification kit (TIANGEN) was used to obtain the maximum concentration of the *E. coli* plasmids. Plasmids treated with *P. granatum* plant extracts and MnONPs (25–100 µg/mL) were incubated at 37 °C for 1 h. After the incubation period, the plasmid DNA was mixed with a DNA loading buffer and loaded onto a 1% agarose gel containing 1 µl red nucleic acid. Finally, electrophoresis was carried out at 140 V for 25 min, and a UV illuminator was used to visualize the bands.

Results and discussion

Syntheses of green MnONPs

Several methods for the preparation of biosynthesized MnONPs exist. The plant extract-induced reduction and stabilization of manganese metal to produce MnONPs is a cost-effective, low-toxicity, biocompatible and ecofriendly approach in green chemistry (Ahmad et al., 2020; Jayandran et al., 2015). Green synthesis by plant extracts has advantages that include medical applicability, scalability and biocompatibility (Sharma et al., 2019). Most plant extracts are rich in functional molecules such as flavonoids and phenolic compounds, which are regarded to be powerful natural reducing and capping agents (Hassanien et al., 2018). In the present

study, we synthesized MnONPs using a *Punica granatum* plant extract, as it contains multiple biomolecules. The final product of the green-fabricated MnONPs was verified by a color change from yellowish to reddish, showing the reduction of Mn^{+} to MnO (NPs) (Fig. 1a-b) (Jayandran et al., 2015). The reaction conditions for the synthesis of NPs from green sources can be adjusted to control the size of the NPs (Souri et al., 2018). Previous studies have found that plant sources, microorganisms and low-temperature synthesis methods are appropriate processes for the production of ideal narrow size distributions and homogenous mixtures of NPs (Hoseinpour & Ghaemi, 2018).

Characterization of MnONPs

FTIR spectroscopy

FT-IR spectra were collected to estimate the role of phytochemical constituents in the aqueous *P. granatum* leaf extract. Plant sources that were rich in active secondary metabolites acted as capping and stabilizing agents, due to which the synthesized nanoparticles were reduced (Ifeanyichukwu et al., 2020). In our present work, the presence of different absorption peaks

and bands indicated that several functional groups of biomolecules were adsorbed onto the surface of MnONPs, which validated the synthesis of the reduced and stabilized MnONPs (Fig. 2). The strong and broad peak at 3408.41 cm^{-1} verified the O–H stretch of free hydroxyl groups, which implied that *P. granatum* leaf extracts contain polyphenols, flavonoids, and metabolites that have different functional groups with OH bonds, which is in strong agreement with previously published research (Ghidan et al., 2016). In our current findings, the presence of different carbonyl group C=O stretches of ketones, aldehydes, saturated aliphatics, and unsaturated esters was confirmed by pronounced peaks in the 1639.45 cm^{-1} range. Furthermore, the C–N stretch of aliphatic amines was represented by a strong peak at 1053 cm^{-1} . A smaller peak at 752 cm^{-1} , illustrated the N–H wag of primary and secondary amines, as well as the C–H out-of-plane bending of aromatics. The presence of the C–Br stretch of alkyl halides was shown by a peak at 659.92 cm^{-1} . R–CH was present in the plant extract, as seen by the peak at 610 cm^{-1} in Fig. 2 (Hoseinpour et al., 2018). The peak in the vicinity of 3000 cm^{-1} to 3500 was due to saturated C–H stretching vibrations (Ghidan et al., 2016; Kumar et al., 2017). The strong band at 1745 cm^{-1} indicated $\text{C}=\text{O}$ stretching. The FTIR spectrum of

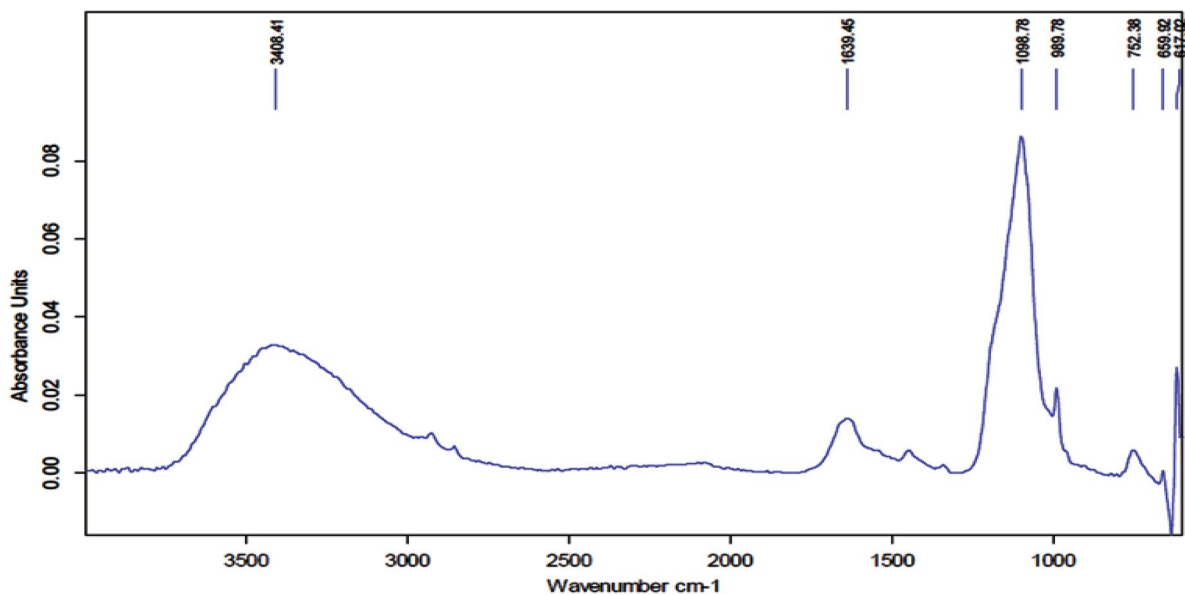


Fig. 2 Fourier transform infrared spectroscopy (FTIR): Different peaks in the spectra showing the presence of functional groups on the surface of green-synthesized MnONPs

green Mn NPs was used to identify possible functional groups. The data obtained in Fig. 2 displayed a peak that appeared in a broad wave region at approximately 3408.41 cm^{-1} , indicating free OH stretching, which has been identified in a previous study (Kumar et al., 2018). The band at 1645 cm^{-1} corresponded to the -C=C- stretching vibrations of alkanes. The band at 1324 cm^{-1} represented the -C-N- stretch. The band at 1228 cm^{-1} showed -C-O stretching. Some new peaks indicated the attraction of plant extracts to stable Mn particles. The positions of the bands in this study were very close to those reported in the cited literature, which suggests that biomolecules can function as capping and stabilization agents in green MnONPs (Nair Sreekala et al., 2019). New peaks appeared at 617 and 520 cm^{-1} , which were related to O-Mn-O stretching and bending and confirmed the formation of MnO_2 NPs (Hoseinpour et al., 2018).

UV-Vis and XRD spectroscopy

UV-Vis absorption spectroscopy was performed to analyze the optical properties of green MnONPs (Fig. 3a). The reduction of green Mn nanoparticles was optimized by UV spectroscopy at two different

pH values, 4 and 7, and an absorption spectrum was observed at 285 nm, which was reported in previous literature (Mahdavi et al., 2020). The SPR peak formed under acidic conditions was lower than that formed under neutral conditions. Acidic conditions were unsuitable for promoting the biosynthesis of MnONPs, while neutral conditions showed SPR peaks, indicating suitable nanoparticle formation. The higher SPR peak intensities under neutral conditions indicated an increase in the number of small MnONPs. Hence, the reducing and capping ability under acidic conditions was low due to the high degree of excitation of protons, and the nanoparticles formed were not completely stable. Therefore, a neutral pH is suitable for the reduction and stabilization of metal nanoparticles (Chitra & Annadurai, 2014; Velgosová et al., 2016).

The formation and average size of the MnONPs were evaluated from their XRD patterns by comparing corresponding peaks (Fig. 3b). MnONPs, which were synthesized from *P. granatum*, showed noticeable peaks at theta 18.19, 25.65, 28.60, 32.66, 36.49, 38.70, 44.58, 58.88, 60.64, 64.99 corresponding to the peak values for (101), (112), (200), (103), (004), (220), (321), (224) and (314). All peaks in the sample

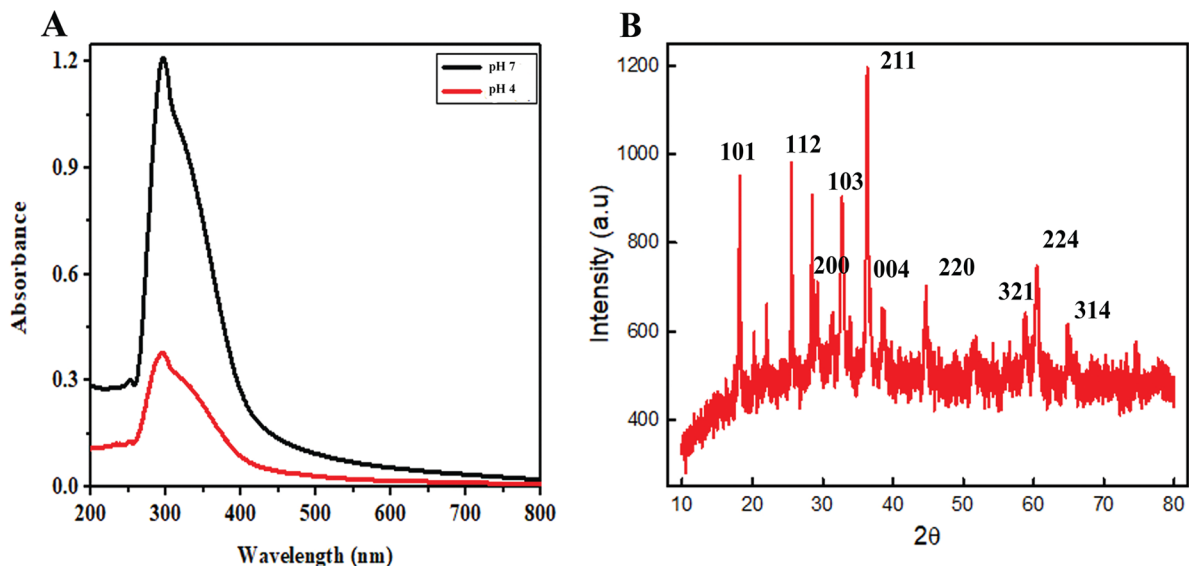


Fig. 3 Spectral analysis of green-synthesized MnONPs: **A** UV-Vis Spectroscopy of Green-Synthesized MnONPs: UV-Vis absorption maxima of Mn nanoparticles. The data are based on the presence of the absorbance peak of the MnONPs

solution in a wavelength range of 200–300 nm. The absorption maximum was found to be 285 nm. **B** XRD Spectra of Green MnONPs

synthesized with the *P. granatum* leaf extract showed characteristics of MnONPs. Some additional peaks were also noted in this sample. The planes of the XRD patterns were in good agreement with JCPDS 00–001–1127. The XRD diffraction pattern was recorded with a Siemens diffractometer using Cu K α ($\lambda=0.151418$ nm) radiation.

Structural analysis SEM and TEM microscopy

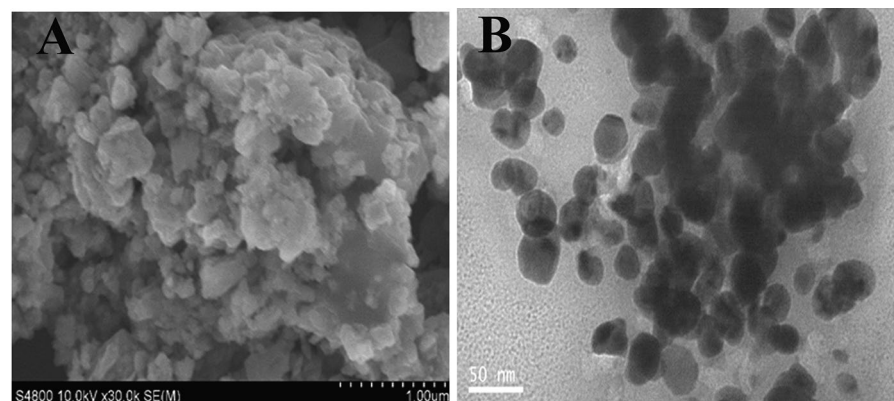
The surface morphology and phase structure of the MnONPs were examined using SEM. The nanoparticles observed in SEM images were below 40–80 nm, and some nanoparticles were in clusters and overlapped with each other. In Fig. 4a, our results were in good agreement with a previous report of synthesized MnONPs (Mahdavi et al., 2020). The physical overlap of particles was due to electrostatic attraction. Previous studies have reported that NPs can easily enter the cell walls of pathogens and are responsible for ROS generation, which leads to cell death (Pugazhendhi et al., 2018).

The TEM image in Fig. 4b provides the precise shape of the green nanoparticles, which were spherical, had 50 nm diameters, and were well dispersed (Devanesan et al., 2018). The findings of our work were in agreement with those of previous work (Souri et al., 2018). Generally, green synthesized nanoparticles have different forms, sizes, and shapes relative to those produced by conventional methods (Fernandes et al., 2018). Our study revealed that the sizes of the particles increased after biocapping, leading to larger particle sizes (Haneefa et al., 2017).

Antibacterial activity

The biosynthesized MnONPs were used to counteract multidrug-resistant pathogens due to their significant bactericidal activities. The bactericidal potentials of MnONPs were determined using two bacterial strains (*E. coli* ATCC 15,224, *S. aureus* ATCC 25,923) at three different concentrations (25–100 $\mu\text{g/mL}$). Figure 5 shows that the zone of inhibition against the bacterial strain produced by green MnONPs was higher at 100 $\mu\text{g/mL}$ relative to other treatments. The minimum zone of inhibition was observed at 25 $\mu\text{g/mL}$ (Fig. 5). The antibacterial graph shows a strong effect at a higher concentration of MnONPs. In previous reports, the use of stabilized MnONPs against the two gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* and against several gram-negative bacteria, such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus bacillus* and *Klebsiella pneumonia*, were evaluated (Cherian et al., 2016; Kunkalekar et al., 2013). NPs can penetrate pathogenic cell membranes through ion channels present in the bacterial membrane of gram-positive and gram-negative bacteria due to the biologically active molecules on the surface and may cause reactive oxygen species (ROS) production, ultimately resulting in cell growth inhibition and cell death (Boomi et al., 2019). MnONPs have been reported to have bactericidal effects toward Gram-positive rather than Gram-negative bacteria due to the structural and compositional variations between bacterial strains (Manjula et al., 2020).

Fig. 4 Structural analysis of MnONPs: (a) SEM analysis of green-synthesized MnONPs. Morphological images of synthesized MnONPs using SEM. This figure shows individual nanoparticles that are in clusters, are spherical or have irregular textures. (b) TEM analysis of MnONPs



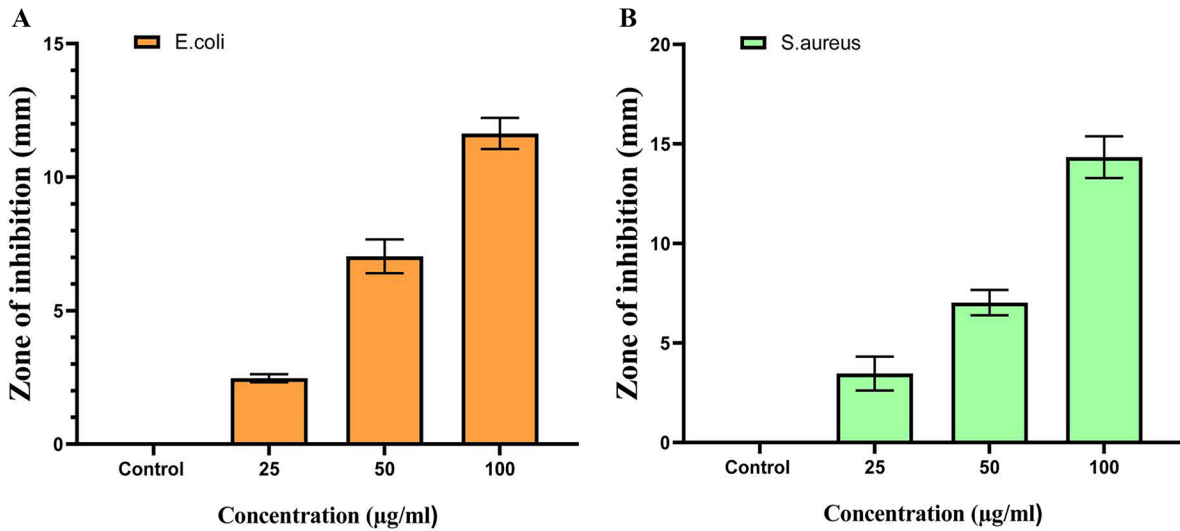


Fig. 5 Antibacterial Activity of MnONPs: **a** Sensitivity prototypes of Mn nanoparticles against the gram-negative bacteria *E. coli* and **b** the gram-positive bacteria *S. aureus* as microbial pathogens

Antifungal activity in vivo

The MnONPs were further used to evaluate their effectiveness in suppressing fruit rot disease caused by *Penecellium sp.* in citrus fruits. Fruit rot disease development in the wounds of fruits inoculated with phytopathogens was significantly decreased with increasing exposure to MnONPs (Figs. 6 and 7). At 8 days postinoculation with MnONPs, visible fungal growth was observed in the control group, with a

large infected area, but only minor wound decay was observed in the group treated with NPs. The infected areas of the treated and nontreated citrus fruits were measured in cm with a scale (Table 1). The group treated with a higher concentration of green MnONPs (100 µg/mL) showed less cuticle rot relative to the 25 µg/mL treatment group and the control group. After the inoculation sites of the citrus fruits were cut open, it was observed that the two groups, i.e., the citrus fruit control samples and the citrus samples

Fig. 6 In vitro antifungal activity of MnONPs evaluated at different concentrations: **a** Control, **b** 25 µg/mL **c** 50 µg/mL and **d** 100 µg/mL against the post-harvest fungal green mold disease that causes cuticle rot on lemons

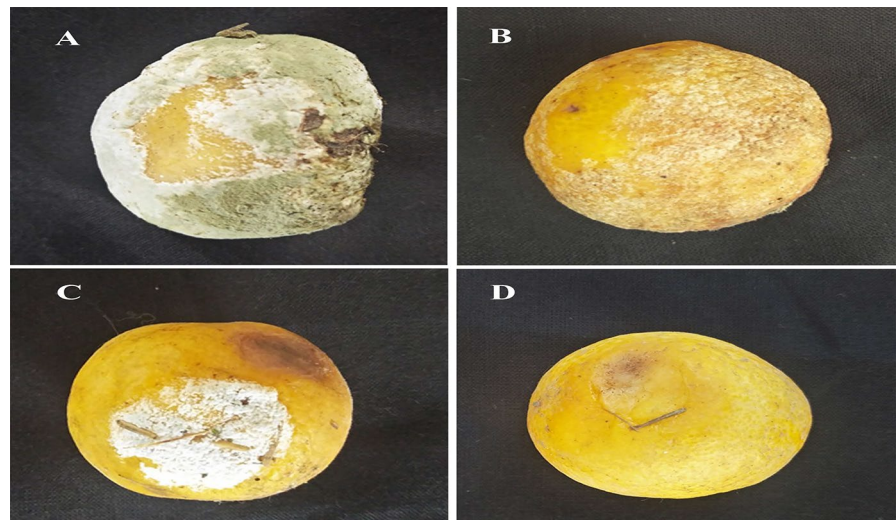
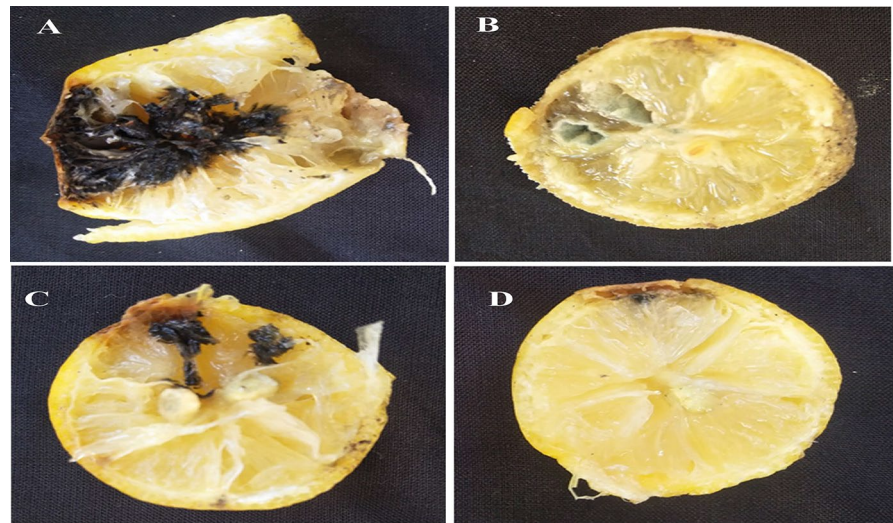


Fig. 7 In vitro Disease suppression of deep pulp rot by green MnONPs: Lemons assessed at different concentrations **a** Control, **b** 25 $\mu\text{g}/\text{mL}$ **c** 50 $\mu\text{g}/\text{mL}$ and **d** 100 $\mu\text{g}/\text{mL}$



inoculated with MnONPs, showed different infected areas due to rot disease in the pulp. MnONPs treatment at the 100 $\mu\text{g}/\text{mL}$ level did not allow for mycelial growth in the deep pulp (Fig. 7d). Clearly, 100 $\mu\text{g}/\text{mL}$ of the green MnONPs completely suppressed postharvest fungi attack on citrus fruits. Disease incidence in the control group was 97%, and in the treated group, the incidence was 68%, 40% and 21% for 25 $\mu\text{g}/\text{mL}$ to 100 $\mu\text{g}/\text{mL}$. The fungicidal activity of the NPs that led to a disruption in the fungal membrane was investigated (Wang et al., 2017). Nanoparticles can significantly permeate the cortex (Xue et al., 2019). Moreover, the disease control of fungal pathogens depends on the size and concentration of NPs because microbial cell walls are more permeable to particles of smaller sizes. Similarly, MnONPs possessed high fungicidal activity against *Candida albicans*, *Trichophyton simii*, *Aspergillus niger*, and *Curvularia lunata*, and their activity was compared with the antifungal drug fluconazole (Al-Zubaidi et al., 2019; Jayandran et al., 2015). Nanotechnology is an efficient tool and a promising option for extending the

shelf life of fresh fruits and vegetables (Chandirika et al., 2018).

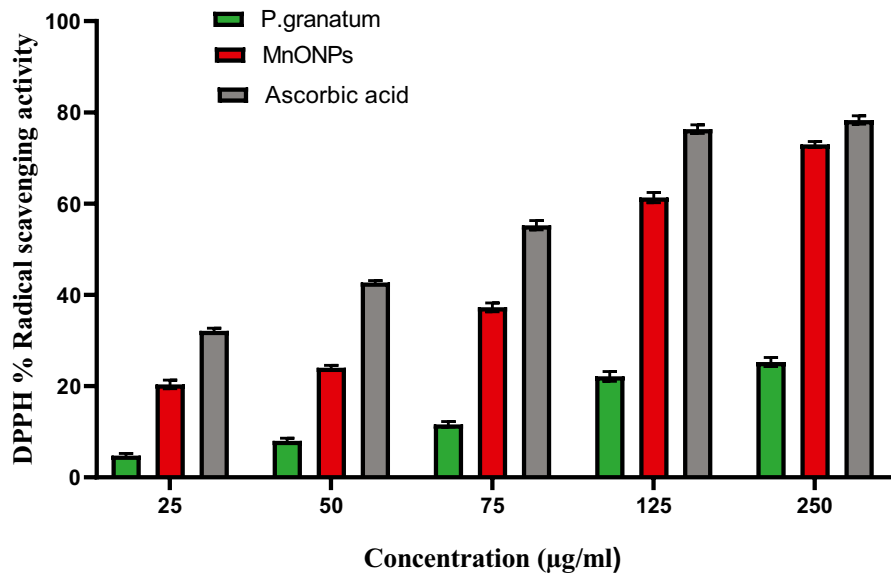
Antioxidant activity

A DPPH assay was performed to reveal the free radical scavenging activity of the prepared nanoparticles. Studies of the antioxidant activities of nanomaterials are important and essential to conduct in the field of nanotechnology (Dobrucka, 2018). Antioxidants have a large impact on the functions of all biomolecules. In biological systems, free radicals are produced as a result of interactions of biomolecules with molecular oxygen. The green MnONPs synthesized using plant extracts showed noteworthy radical scavenging activities relative to a *P. granatum* extract due to the presence of different secondary metabolites (flavonoids, glycosides, carbohydrates, saponins, phenolic compounds and tannins) in the plant extracts (Fig. 8). The free radical scavenging activity of nanoparticles increases with increasing sample concentration (Rehana et al., 2017). MnONPs, as simple and efficient antioxidants, have potential in

Table 1 Mean \pm SD In vitro antifungal activity of green synthesized MnONPs assessed at different concentrations (25, 50 and 100 $\mu\text{g}/\text{mL}$) against *Penicillium digitatum*

Disease Severity (cm) at different concentration of MnONPs					
S/N	Treatments	Experiment 1	Experiment 2	Experiment 3	Mean \pm SD
1	25 $\mu\text{g}/\text{mL}$	4.3	4.1	3.9	4.1 \pm 0.2
2	50 $\mu\text{g}/\text{mL}$	2.8	3.1	2.9	2.9 \pm 0.1
3	100 $\mu\text{g}/\text{mL}$	1.2	1.1	1.3	1.2 \pm 0.1
4	Control	6.3	5.9	6.4	6.2 \pm 0.2

Fig. 8 Antioxidant Activity of MnONPs: A DPPH assay was carried out at 25, 50, 75, 125 and 250 µg/mL concentrations of *P. granatum* extract. MnONPs and ascorbic acid were used as the standards



the biomedical treatment of diseases derived from ROS imbalances (Lu et al., 2021; Zhang et al., 2022). The redox potentials of biological compounds found in *P. granatum* assist in the neutralization of free radicals, in the quenching of singlet and triplet oxygen, and in the decomposition of free radicals. The antioxidant activity of MnONPs is assumed to be responsible for the capping of antioxidant material from the extract onto the surface of nanoparticles (Mahlangeni & Moodley, 2021; Sivanesan et al., 2017).

Edible coating

Edible coatings are composed of nontoxic, eco-friendly, readily available and biocompatible compounds that extend the shelf life of foods (Zambrano-Zaragoza et al., 2018). An edible coating was applied to the outer layer of fresh tomatoes. The results revealed that fruits coated with MnONPs showed longer shelf lives than noncoated fruits after 2 to 12 days at room temperature (Fig. 9). Fruit weight

Fig. 9 Edible coating of green-synthesized MnONPs to extend the shelf life of tomatoes: **a** after 2 days, **b** after 4 days, **c** after 8 days, and **d** after 12 days

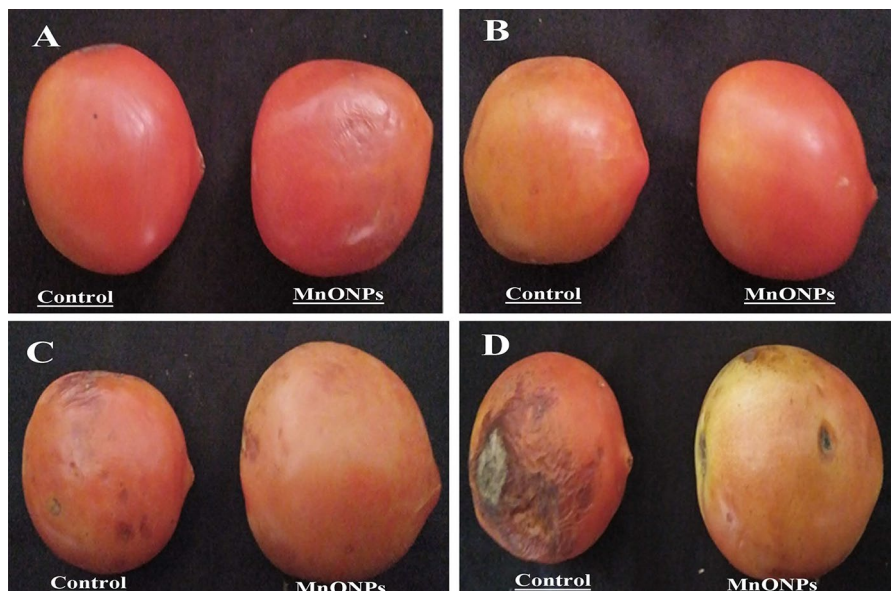
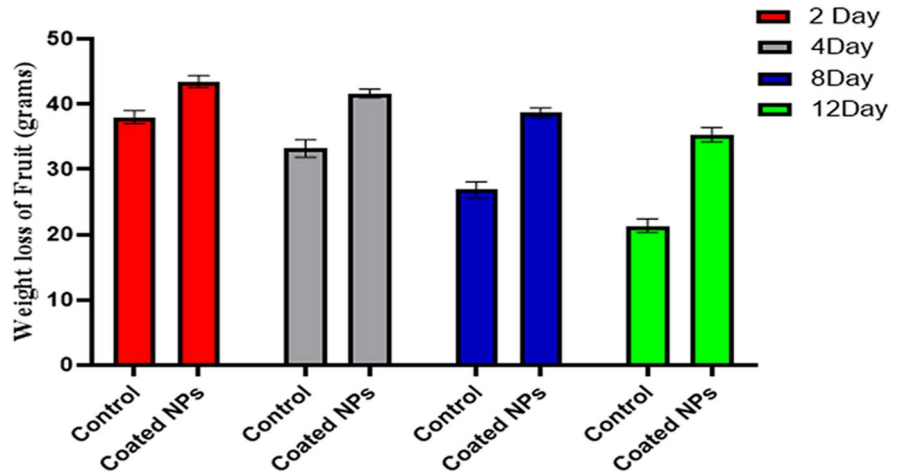


Fig. 10 Effect of green MnONPs on shelf-life extension: The graph shows reduced weight loss in tomatoes after 2, 4, 8 and 12 days



Edible Fruit Coating of MnONPs

loss was measured on a daily basis in grams. Fruits coated with MnONPs showed extended storage periods compared with noncoated fruits. Evaporation from vegetables and fruits causes weight loss, and the rate of evaporation depends on the thickness of the coating. Significant weight loss and color changes were observed in noncoated (control) fruit after 12 days (Fig. 10). An edible coating prevents oxygen penetration and aroma loss and inhibits moisture loss from plant tissues (Lustriane et al., 2018). Coatings improve the product aesthetics, reduce spoilage, and control gas exchange (oxygen, carbon dioxide, and ethylene) between food components and the surrounding atmosphere (Bakhy et al., 2018). Many studies have shown the potential use of metal nanoparticles in edible coatings for improving fruit and vegetable quality. Edible coatings provide nanocoating films and can provide a moisture barrier that reduces fruits evaporation rates, limiting weight loss and color changes and delaying ripening (Bakhy et al., 2018; Jafarzadeh et al., 2021; Zambrano-Zaragoza et al., 2018).

DNA cleavage assay

DNA cleavage activity was determined by gel electrophoresis. DNA cleavage by green-synthesized MnONPs was compared at different concentrations (Gulbagca et al., 2019). To investigate the effect of MnONPs on DNA stability, pBR322 DNA was used.

DNA plasmids were extracted from *E. coli*, and after treatment with DNase I, the plant extract and different concentrations of MnONPs were loaded, and the samples were run in agarose gel wells 1, 2, 3, 4 and 5. Line 1 indicated DNase I, Line 2 indicated the *P. granatum* leaf extract, and Lines 3–5 indicated different concentrations of MnONPs (25, 50 and 100 $\mu\text{g}/\text{mL}$) (Fig. 11). A clear smear was found in Line 5, which indicated that 100 $\mu\text{g}/\text{mL}$ MnONPs played a noticeable role in degrading plasmid DNA (Fig. 11), while no significant smearing was observed in Lines 2 and 3. However, Line 4 also showed some good

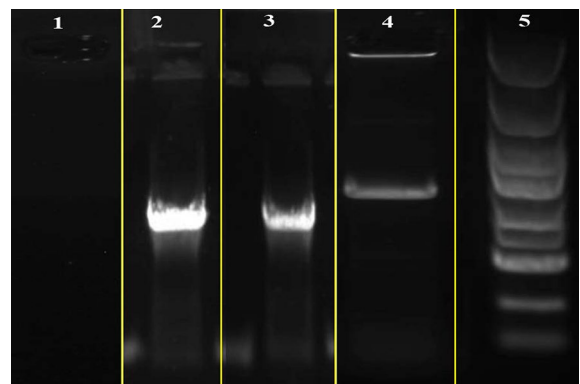


Fig. 11 DNA cleavage assay of MnONPs: Naked plasmid DNA after treatment with (1) DNase I (negative control), (2) *P. granatum* plant extract, (3) 25 $\mu\text{g}/\text{mL}$, (4) 50 $\mu\text{g}/\text{mL}$ and (5) 100 $\mu\text{g}/\text{mL}$ MnONPs

results (Fig. 11). These results indicated that there were no DNA degrading effects with the simple plant extract and with the lower concentrations of MnONPs. Hence, green-synthesized nanoparticles

can be efficient biological agents to counteract the effects of microorganisms and bacteria (Jadhav et al., 2018). Figure 12 shows that the proposed mechanism involved Mn ion release from the NPs, which could

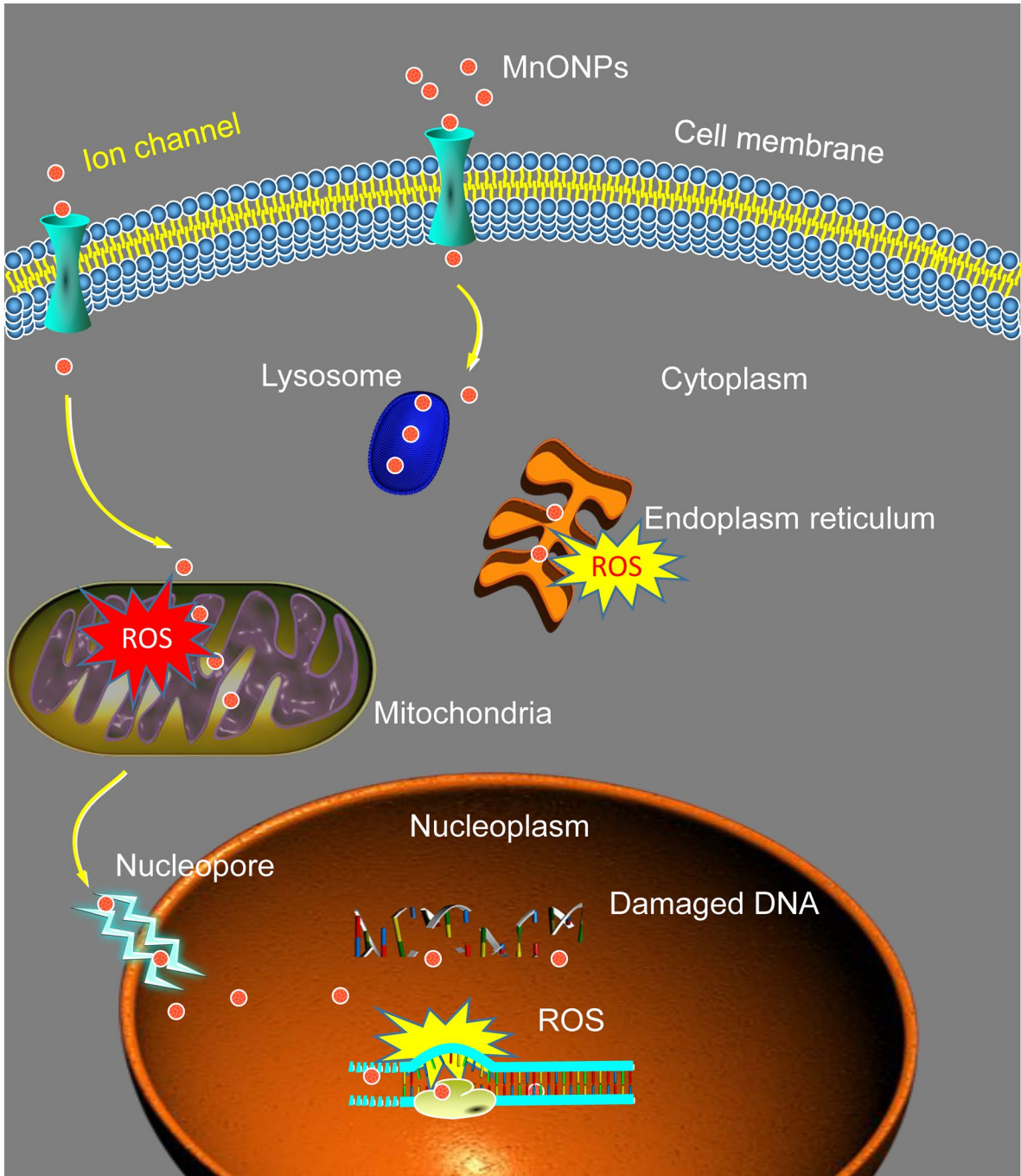


Fig. 12 Proposed mechanism of MnONPs action in pathogen cells

pass through the ion channels in the pathogen cell walls, leading to protein denaturation and cell death. Gram-negative bacteria (*E. coli*) may permit more Mn ions to reach the plasma membrane due to their negative surface charge. MnONPs are nanosized, so they easily enter bacterial pores and have the ability to penetrate the cell membrane and cause cell death in bacterial strains (Lu et al., 2021). Altogether, the results revealed that MnONPs are nontoxic and biocompatible and have considerable potential in biological applications.

Conclusion

The simple, eco-friendly green synthesis of MnONPs using *P. granatum* leaf extract as a capping and reducing agent is reported. The biosynthesized MnONPs produced by this novel technique are cost-effective, nontoxic and ecofriendly. The synthesized nanoparticles were found to be spherical in shape and were highly stable. The antibacterial activity of the MnONPs against gram-positive and gram-negative bacteria were studied, and the investigation revealed significant results at different concentrations. Furthermore, the MnONPs reduced disease severity on citrus fruits at the 100 µg/mL level. Moreover, the MnONPs displayed significant antioxidant activity. The MnONPs enhanced the quality and shelf life of citrus fruits destined for fruit markets, and they could be used in the future to reduce economic losses. Green MnONPs inhibited the growth of food-borne fungus and protected the fruit cuticle layer from spoilage. Finally, the MnONPs DNA cleavage properties were screened using the *E. coli* plasmid DNA pBR322 by gel electrophoresis. Overall, MnONPs have the potential to be externally applied as biological agents to counteract microorganisms and bacteria.

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Author contribution I H S conceptualization Formal analysis, Investigation, Methodology, Visualization, and Writing – original draft. M A M Conceptualization, Software. I A S Formal analysis, Investigation, MA Formal analysis, Visualization, Data correction. S G acquisition of data, analysis and/or interpretation of data. L C Conceptualization, Writing – review & editing. Yidong Zhang: Supervision, Project administration, Writing – review & editing.. All authors read and approved the final manuscript.

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Data availability and material Healthy equal size Fruit samples were purchased from fruit market. Nanoparticles were prepared in lab and their characterizations were performed in Shanghai Jiao tong University Analysis center with proper procedure. All nanomaterial procedure and applications data will be provided on reasonable request to Corresponding Author.

Declarations

Conflict of interest Authors declare that there is no conflict of interest.

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