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Manganese-doped Cerium Oxide (MnCeO₂) Nanoparticles Mitigate Manganese Deficiency and Improve Growth and Physiological Parameters in Barley (*Hordeum vulgare* L.)

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Abstract

Nanoparticles (NPs) hold promise for enhancing plant growth and productivity under stress and nutrient deficiency. Manganese (Mn) is an essential micronutrient, and its insufficiency results in stunted growth and diminished yield. In this study, we developed a novel NP, namely manganese-doped cerium oxide (MnCeO₂), to mitigate Mn deficiency in barley (*Hordeum vulgare* L.). The NPs were produced utilizing the sol-gel technique and characterized for their physical and morphological properties by using transmission electron microscopy (TEM), high-resolution-TEM (HR-TEM), scanning electron microscopy (SEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDX) analyses. The NPs (200 mg L⁻¹) were subjected to barley seedlings in a hydroponic culture under non-deficient (Mn0), 50% Mn-deficient (Mn50), and 100% Mn-deficient (Mn100) conditions. The physiological, morphological, and nutritional status of the seedlings were evaluated. Moreover, their possible cytotoxic and genotoxic impacts were assessed using confocal microscopy and random amplified polymorphic DNA - polymerase chain reaction (RAPD-PCR) methods, respectively. Results showed that MnCeO₂ NPs under Mn50 condition significantly ($P < 0.05$) improved germination rate (18%), pigmentation (chlorophyll-a and -b), photosynthetic parameters (ETR, Fv/Fm, and Y(II)), growth indices (shoot and leaf length), biomass (38.6–48.0%), and nutrient element content. This shows that MnCeO₂ NPs have a positive effect in eliminating Mn deficiency. In contrast, cytotoxic and genotoxic effects were observed under Mn100 conditions. These findings indicate that MnCeO₂ NPs effectively complemented Mn deficiency under 50% Mn-deficient conditions. However, they are insufficient to fully meet the Mn requirement of barley plants under severe Mn deficiency (Mn100). This is supported by elemental analyses of root and shoot tissues, which showed a substantial increase in Mn content under Mn deficiency conditions. Overall, this study demonstrates that MnCeO₂ NPs are a potential nanofertilizer for meeting the Mn needs in barley. However, it is insufficient to fully compensate for the Mn requirements under conditions of severe Mn deficiency. This study may serve as a model for addressing manganese deficiency using a novel Mn-containing nanoformulation.

Keywords Manganese · Cerium · Nanoparticles · Nutrient deficiency · Nanofertilizer · Barley

1 Introduction

Manganese (Mn) is an essential micronutrient for plants. It is involved in numerous vital physiological mechanisms, including photosynthesis, enzyme activation, lignin synthesis, antioxidant defense, and chlorophyll synthesis (Alejandro et al. 2020). Most plants generally require an Mn level of 10 to 50 mg kg⁻¹ (dry weight) in their tissue (Obeng et

al. 2024). Mn deficiency typically occurs when tissue levels fall below 20 mg kg⁻¹ (Rengel et al. 2022). When this happens, it leads to a range of symptoms, including chlorosis, reduced growth and stunted development, reduced fertility, and increased susceptibility to diseases (Husted et al. 2009). These effects cause to a reduction in food production, decreased nutrition quality, and economic losses. Severe conditions can reduce cereal yields by 30–60%. Globally,

Extended author information available on the last page of the article

nearly 10% of cultivated soils are Mn-deficient, resulting in millions of tons of lost grain production each year (Pahalvi et al. 2021). Manganese sulfate (MnSO_4) is a conventional Mn fertilizer that is frequently employed to address Mn deficiency. In bulk international markets, agricultural-grade Mn sulfate typically costs approximately US \$450 per ton, depending on the brand and region. In addition to the cost of Mn fertilizers, the economic consequences of failing to address Mn deficiency are significantly more severe due to substantial yield and quality losses (Husted et al. 2009).

By 2050, the necessity to nourish 9.7 billion individuals is projected to place considerable pressure on the agricultural sector, potentially leading to an increased dependence on fertilizers (United Nations 2022; Oluwole et al. 2023). Although synthetic fertilizers enhance crop yields, their improper application can result in eutrophication, algal blooms, the emission of greenhouse gases, and health hazards. Nanofertilizers containing micronutrients possess the ability to boost plant bioavailability and nutrient uptake efficiency under the most adverse conditions. The implementation of nano-fertilizers presents promising strategies to optimize nutrient utilization. Their adoption can support the achievement of future food security objectives while minimizing environmental impacts, thereby emphasizing the importance of sustainable practices to balance food production with environmental conservation (Wahab et al. 2023; Munir et al. 2024).

Previous studies have shown the effectiveness of Mn NPs in alleviating Mn deficiency in plants. For instance, the utilization of Mn-NPs augmented the growth and productivity in *Vigna radiata* (Pradhan et al. 2013). Compared to the control group, barley seedlings treated with Mn_xO_y NPs (0.05 mg L^{-1}) had a 68% increase in seedling length and a 50% increase in germination energy (Blinov et al. 2023). Kasote et al. (2021) found that the phenolic acid and phytohormone profiles of watermelon seedlings are strongly affected by Mn_2O_3 NPs ($\leq 40 \text{ mg L}^{-1}$), which resulted in higher crop yields. MnFe_2O_4 NPs at 250 mg L^{-1} was found to enhance the germination, growth and biomass of barley seedlings (Tombuloglu et al. 2018). Nawaz et al. (2023) found that 15 mg L^{-1} MnO NPs had a beneficial nutritional effect by increasing the formation of calluses in *Moringa oleifera*. Furthermore, Lu et al. (2020) emphasized the nanozyme function of Mn_3O_4 on the salinity stress tolerance of cucumber plants. Recently, Sharma et al. (2025) reviewed the Mn-based NPs and their applications by emphasizing their role in plant metabolism and physiology.

Cerium (Ce) is a non-essential element for plants; nonetheless, at lower quantities, it has demonstrated positive effects for maize (Liu et al. 2022) and peas

(Liu et al. 2020). However, Ayub et al. (2023) found that it became hazardous in maize at increasing quantities (500 mg kg^{-1}). It has a high capacity to scavenge reactive oxygen species (ROS) and enhance antioxidant defenses, which protect chloroplasts and cell walls from damage by increasing the activity of enzymes like peroxidase (POD) and superoxide dismutase (SOD) (Du et al. 2015; Lee et al. 2013; Liu et al. 2012). Numerous studies demonstrate the positive impact of CeO_2 NPs on the growth and development of various plants. CeO_2 NPs are recognized for their substantial impact on the agronomic characteristics and nutritional quality of plants (Rico et al. 2014). For instance, treatment of tomato (*Solanum lycopersicum* L.) by nano- CeO_2 at concentrations up to 500 mg kg^{-1} enhanced shoot growth, increased the production of photosynthetic pigments, and improved total yield (Barrios et al. 2016). Likewise, *Raphanus sativus* L. subjected to $1,000 \text{ mg kg}^{-1}$ of CeO_2 NPs generated increased root biomass without impacting chlorophyll levels in the plants (Zhang et al. 2017). Similarly, barley plants treated with CeO_2 NPs at dosages of 125, 250, and 500 mg kg^{-1} surpassed control plants in terms of growth indices, while productivity was negatively impacted by the 500 mg kg^{-1} dosage (Rico et al. 2015). The distinctive physiochemical and photoelectric properties of CeO_2 NPs may enhance plant photosynthesis by improving energy capture and other physiological parameters associated with gas exchange, such as stomatal conductance and transport rate (Giraldo et al. 2014; Wu et al. 2017; Abbas et al. 2020).

Despite existing studies, research on mitigating Mn deficiency with NPs in plants is still lacking in depth. We, therefore, hypothesized that the application of Mn through a novel Mn-containing nanoformulation would enhance the growth and yield of barley under Mn-deficient conditions. To test this, the present study was designed to develop a novel nanofertilizer, namely manganese-doped cerium oxide (MnCeO_2), by leveraging essential and beneficial properties of both Mn and Ce to alleviate Mn-deficiency in barley (*Hordeum vulgare* L.). Following synthesis and comprehensive characterization, the MnCeO_2 NPs were administered to barley plants during both germination and growth stages under three distinct conditions: Mn-sufficient, 50% Mn-deficient, and 100% Mn-deficient. The comprehensive analysis included several physiological indices and utilized scanning electron microscopy (SEM) and confocal microscopy to elucidate the associated morphological and cellular changes, respectively. Moreover, we assessed the nutritional status of roots and shoots, as well as the genotoxicity potential of the MnCeO_2 NPs, under both Mn-sufficient and Mn-deficient scenarios.

2 Materials and methods

2.1 Preparation and Characterization of Nanoparticles

Synthesis of MnCeO₂ NPs was carried out by the sol-gel technique. Initially, a specific amount of Mn(NO₃)₂ and a predetermined amount of Ce(NO₃)₃ were dissolved in 25 mL of methanol. After that, 2.5 mL of ammonium solution was added dropwise to produce a pink precipitate. The precipitate was filtered and washed multiple times with methanol, and then it was dried at a temperature of 80 °C overnight. In the final step, the powder was calcined at a temperature of 400 °C for four hours in an atmosphere at room temperature.

The structural information of MnCeO₂ NPs was investigated via an X-ray diffractometer (XRD) ($\lambda = 1.54059 \text{ \AA}$). The morphology was analyzed by using scanning electron microscope (SEM), transmission electron microscope (TEM), high-resolution-transmission electron microscope (HR-TEM), selected area electron diffraction (SAED) pattern, and energy-dispersive X-ray spectroscopy (EDX) analyses.

2.2 Growth Conditions and Treatment with Nanoparticles

Twenty barley (*H. vulgare*) seeds were germinated on damp tissue paper at 28 °C in the dark (four days). Seeds were accepted germinated when 65% of the control roots reached a minimum length of 0.5 cm (United States Environmental Protection Agency, 1996). After germination, ten evenly distributed seedlings were moved to a hydroponic system filled with modified Hoagland solution (Hoagland and Arnon 1950). To mimic the Mn-deficient conditions, three Hoagland solutions were prepared: (1) Mn0: Not deficient (contain 9 μM MnCl₂), (2) Mn50 (contain 4.5 μM MnCl₂): 50% Mn-deficient, and (3) Mn100: 100% Mn-deficient (contain 0 μM MnCl₂). Control samples contained Hoagland solution alone and were exempted from NPs supplementation. The NPs concentration was set at 200 mg L⁻¹. This research used this concentration because moderate concentrations of CeO₂ NPs (125–250 mg kg⁻¹) improved the physiological performance of barley seedlings (Rico et al. 2015). Nutrient solutions containing the NPs were subjected to a half-hour sonication in a sonic water bath (Powersonic 410, Hwashin Technology, Korea) to prevent or minimize NPs agglomeration. The seedlings were then kept at greenhouse conditions for three weeks at a temperature of 25 °C, 70% humidity, and a light/dark cycle of 16:8. The nutrient solution was changed every three days with

the same Mn and NPs concentrations. In the third week after the growth stage, the plants' fresh and dry weights, growth, chlorophyll content, photosynthetic parameters, relative water content (RWC), elemental analysis, and NPs' potential genotoxicity were assessed.

2.3 Determination of Photosynthetic Parameters and Pigments

The photosynthetic activity of the leaves was assessed using chlorophyll fluorescence measurements. For this experiment, we used separate leaves from three different plants ($n=3$). A PAM fluorometer (Walz® GmbH, Effeltrich, Germany) was utilized for this purpose. The seedlings were dark-adapted for thirty minutes prior to measurement. The leaf specimen was fastened to a clip holder. A 450 nm maximum emission actinic pulse laser was utilized for the measurements. The photosynthetic photon flux density (PPFD) was 1,500 $\mu\text{mol photon m}^{-2} \text{ s}^{-1}$. Electron transport rate (ETR), minimum fluorescence (Fo), maximum fluorescence (Fm), and effective photochemical quantum yield of photosystem II (Y(II)) were determined as photosynthetic parameters (WinControl-3.29 program, Wald® GmbH of Effeltrich, Germany). A PIN-photodiode was used to detect the fluorescence signal. Kitajima and Butler's (1975) formula was utilized to determine both Fv, the variable fluorescence, and Fv/Fm, the maximal quantum efficiency of PSII.

To find the pigment content, 50 mg of fresh leaf tissues ($n=5$) were homogenized in 4 mL of 80% acetone. Using a plate reader (Biotek, Synergy Neo 2), the absorbances of the supernatant that was obtained after centrifugation (4,000 rpm and 15 min), at 663 nm, 646 nm, and 470 nm were measured. The concentrations of pigments (carotenoids, chlorophyll a and b) were assessed following the protocols of Lichtenthaler and Wellburn (1983).

2.4 Leaf Relative Water Content Assay

The relative water content (RWC) of the leaves was calculated according to Nir Sade et al. (2015). The fresh weights (FW) of fully matured barley leaves were measured ($n=3$). Encased in airtight plastic containers, the previously removed leaf sections were left to soak for eight hours in a solution containing 5 mM calcium chloride (CaCl₂) to determine the turgid weight (TW). Then, the leaves were incubated at 60 °C for three days and the dry weights (DW) were noted. The RWC was calculated by plugging the values into the following formula:

$$RWC (\%) = \frac{FW - DW}{TW - DW} \times 100$$

2.5 DNA Extraction and Genotoxicity Assessment

Following three weeks, the roots of plants treated with NPs and those left untreated were harvested and promptly crushed with liquid nitrogen. The GeneJET plant genomic DNA purification micro kit (Thermo Scientific) was used to extract the genomic DNA. The gel electrophoresis examination and absorbance ratio measurements at 260/280 nm using a Thermo NanoDrop spectrophotometer confirmed the integrity and purity of the DNA template. A Nexus GSX1 thermocycler (Eppendorf, USA) was used to perform the random amplified polymorphic DNA - polymerase chain reaction (RAPD-PCR) assay. For the reaction, a 25 μ L reaction mixture containing 1 μ L of $MgCl_2$, 5 μ L of DNA template, 12.5 μ L of GeneAll[®] 2x master mix, and 5 μ L of OPA-8 primer was prepared. The reaction was initiated at 94 °C for three minutes, followed by 45 cycles of the following settings: one minute at 94 °C, one minute at 36 °C, and two minutes at 72 °C. The reaction was completed at 72 °C for five minutes. PCR products were separated by electrophoresis on a 2% agarose gel, after which the gels were stained with SuSafe DNA (Sugenomics, Türkiye) and run for 45 min in an electrophoresis unit. The standard DNA marker (100-1,000 bp, Thermo Sci.) was used as a molecular size indicator. Image Lab Software was used to examine the data acquired using a UV transilluminator (Gel Doc XR+ Imaging System, Biorad). ImageJ program was utilized to improve the gel image. Genomic template stability (GTS) was calculated based on the following equation:

$$GTS (\%) = \left(1 - \frac{a}{n}\right) \times 100$$

where:

- a is the number of polymorphic bands detected in the treated sample.
- n is the total number of bands detected in the untreated control sample.

2.6 The Status of Root Morphology

The scanning electron microscope (SEM) (Inspect S50; FEI) was used to evaluate the surface features and structure of the roots. Roots were first cut and rinsed in PBS (pH 7.4) before spending one night submerged in a glutaraldehyde solution (4% concentration). A gradient of ethanol concentrations, from 25% to 100%, was used

to dehydrate the specimens in stages. Scanning electron microscopy (20 kV) was applied after the specimens were carefully dried using a Leica EM CPD300. A Quorum Q150R ES was used for gold sputter coating.

2.7 Confocal Microscopy Analysis of Roots

To identify any potential membrane damage, the cells at the plant's root tips were stained with propidium iodide (PI). Cationic dyes, such as PI, can penetrate damaged cytoplasm but not undamaged cell membranes, which allows them to stain the nucleus. A sterile razor blade was used to file down the 10-millimeter root tips after immersing them in a diluted PI solution (1% P-4170, Sigma) for 4 min. The tissue was rinsed and any residual dye washed away with two one-minute soaks in distilled water. After the roots were fastened to the slides, a coverslip was put on top of them. Plant roots were studied using confocal laser field microscopy (LSM 900, Zeiss, Germany). The selected parameters incorporated the utilization of a red PI dye for excitation, with an excitation wavelength of 536 nm and a maximum emission wavelength of 617 nm.

2.8 Elemental Analysis

After being exposed to NPs for three weeks, the root and leaf samples were dried in a 70 °C oven for three days and then crushed with a ceramic mortar. The samples were digested following USEPA procedure 3051 A (USEPA 2007). Subsequently, the dry powder was treated with a mixture of 65% pure nitric acid (HNO_3) and 30% hydrogen peroxide (H_2O_2) in a 1:4 ratio. Teflon-1 microwave digesting containers (10 mL MARS Xpress Vessels, consisting of PFA material) from CEM were used for the digestion. ICP-OES was utilized to quantify macro and microelements. For element analysis, the Scott/Cross-Flow model, a PerkinElmer Avio[®] 500 ICP-OES apparatus was used.

2.9 Statistical Analysis

Three or more samples were collected in every study and all of them were employed in randomized sets. An unpaired *t*-test was utilized to assess the variation in the experimental data compared to the untreated control data. Statistically significant changes ($P < 0.05$, $P < 0.01$, and $P < 0.005$) were denoted by an asterisk when comparing the experimental value to the control or other treatment values.

3 Results

3.1 Morphological and Structural Analyses

The structural analysis of MnCeO₂ NPs, performed using X-ray diffraction (XRD) (Fig. 1), showed characteristic diffraction peaks corresponding to the cubic structure of CeO₂, which confirmed the absence of undesired phases. To further analyze the structural parameters, the XRD data were refined using Match! software with FullProf. This refinement yielded a lattice constant (*a*) of 5.4161 Å, a cell volume of 158.8784 Å³, and an average crystallite size of 11.9 nm, calculated from the most intense peak.

Microscopic and elemental analyses of the MnCeO₂ NPs are presented in Fig. 2, encompassing scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDX). The SEM image (Fig. 2a) revealed an agglomeration of microscopic particles. Magnified TEM imaging (Fig. 2b) further revealed a dense agglomeration of minuscule spherical particles. The cubic Ceria phase was verified by the HR-TEM images (Fig. 2c), which were used to calculate the d-spacing value using Gatan software.

Additionally, the SAED pattern (Fig. 2d) showed selected area electron diffraction rings. Analysis of this image using the ImageJ software indicated that the cubic structure of CeO₂ was preserved. Finally, EDX analysis (Fig. 2e) confirmed the presence of Ce, Mn, and O within the synthesized nanoparticles.

3.2 Physiological Effects of Nanoparticles on Barley Plants

3.2.1 Seed Germination and Plant Growth Indices

Barley seeds (*n* = 20) were germinated with NP treatment for four days under Mn0, Mn50, and Mn100 conditions. Apart from Mn0, NP treatment significantly improved the root and shoot lengths relative to the control group (*P* < 0.05; Fig. 3a–b). The most significant improvement was recorded under Mn50 conditions. In parallel, the germination ratio was significantly improved (*P* < 0.01) in the Mn50 group (65%) compared with the control group (55%), corresponding to an 18% increase (Fig. 3c). However, this improvement was not evident in the Mn0 group. This could be attributed to the compensation of Mn by MnCeO₂ NPs under Mn-deficient conditions.

Fig. 1 X-ray diffraction (XRD) pattern of Mn-doped CeO₂ nanoparticles (MnCeO₂ NPs)

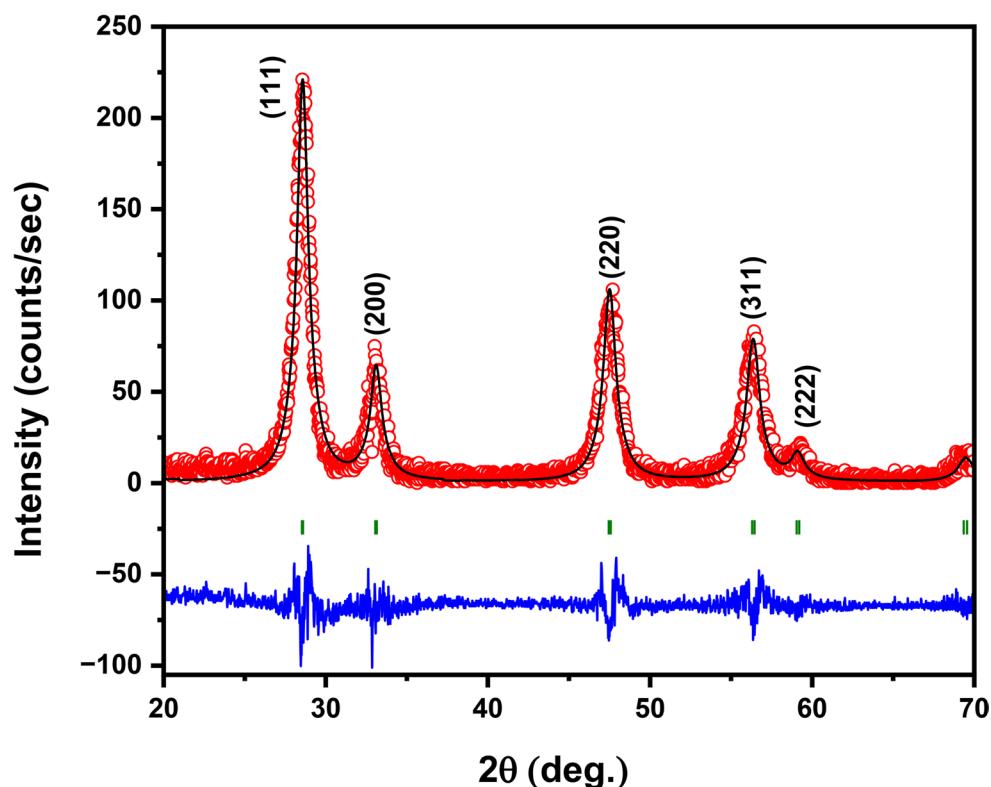
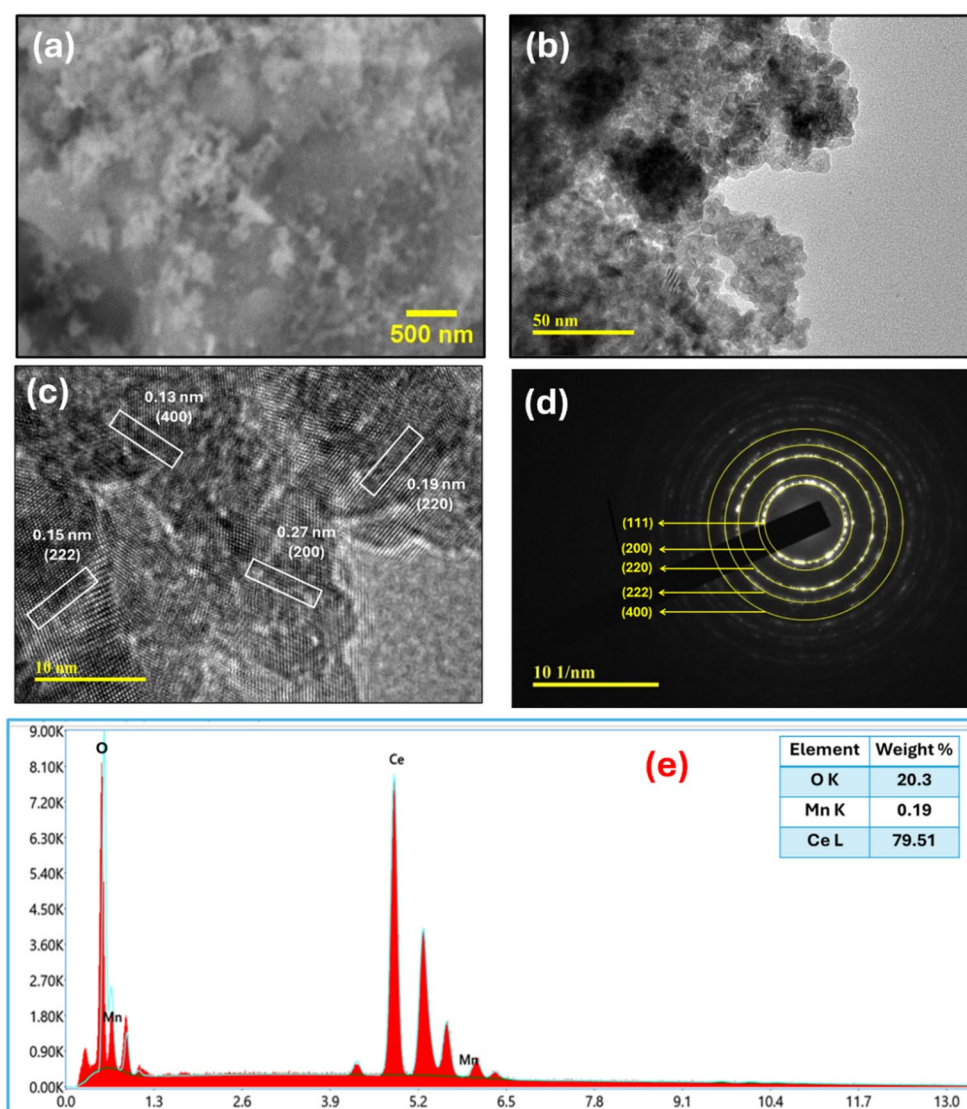


Fig. 2 Characterization of synthesized Mn-doped CeO_2 nanoparticles (NPs). **a** Scanning electron microscope (SEM) image, **b** transmission electron microscope (TEM) image, **c** high-resolution transmission electron microscope (HR-TEM) image, **d** selected area electron diffraction (SAED) pattern, and **(e)** energy-dispersive X-ray spectroscopy (EDX) analysis



Measurements were taken of the seedlings' root and leaf lengths after three weeks of treatment with NPs (Fig. 3d-e). Compared to that of the control group, the root and shoot length of Mn50 plants were considerably improved by 18.75%, and by 9.75% respectively. Additionally, NP treatment was deemed to have a beneficial effect on Mn100 seedlings. Conversely, NP treatment under Mn0 condition (no Mn deficiency) did not lead to an improvement in the growth indices. These findings indicate that MnCeO₂ NPs significantly influenced root and shoot growth throughout the germination (four days) and growth (three weeks) phases under Mn50 and Mn100 conditions. This implies NPs' contribution to the development of barley seedlings under Mn deficient conditions. In contrast, the NP treatment under Mn0 does not facilitate growth enhancement; rather, it induces growth suppression and possible harmful repercussions.

Furthermore, the biomass of the seedlings was assessed following three weeks of exposure. The fresh weight (FW) and dry weight (DW) of the seedlings ($n=8$) were quantified (Fig. 3g-h). Consistent with the previous findings, both FW and DW were considerably increased under Mn50 environment compared to the control group ($P<0.005$), rising by 38.6% and by 48.0%, respectively. Additionally, there was a notable increase when comparing Mn100 to the control groups ($P<0.01$; Fig. 3h). Like the tissue length results, FW and DW were found to be decreased in Mn0 seedlings.

Plant water status is mostly indicated by the relative water content (RWC). NPs can enhance water absorption by changing ion channels or membrane pores (Zhu et al. 2008). Hence, measuring RWC was critical for deducing how NPs aid plants in water efficiency. The results of treating barley leaves with NPs on RWC (%) are shown in Fig. 3i. The seedlings grown under Mn0 condition showed a significant

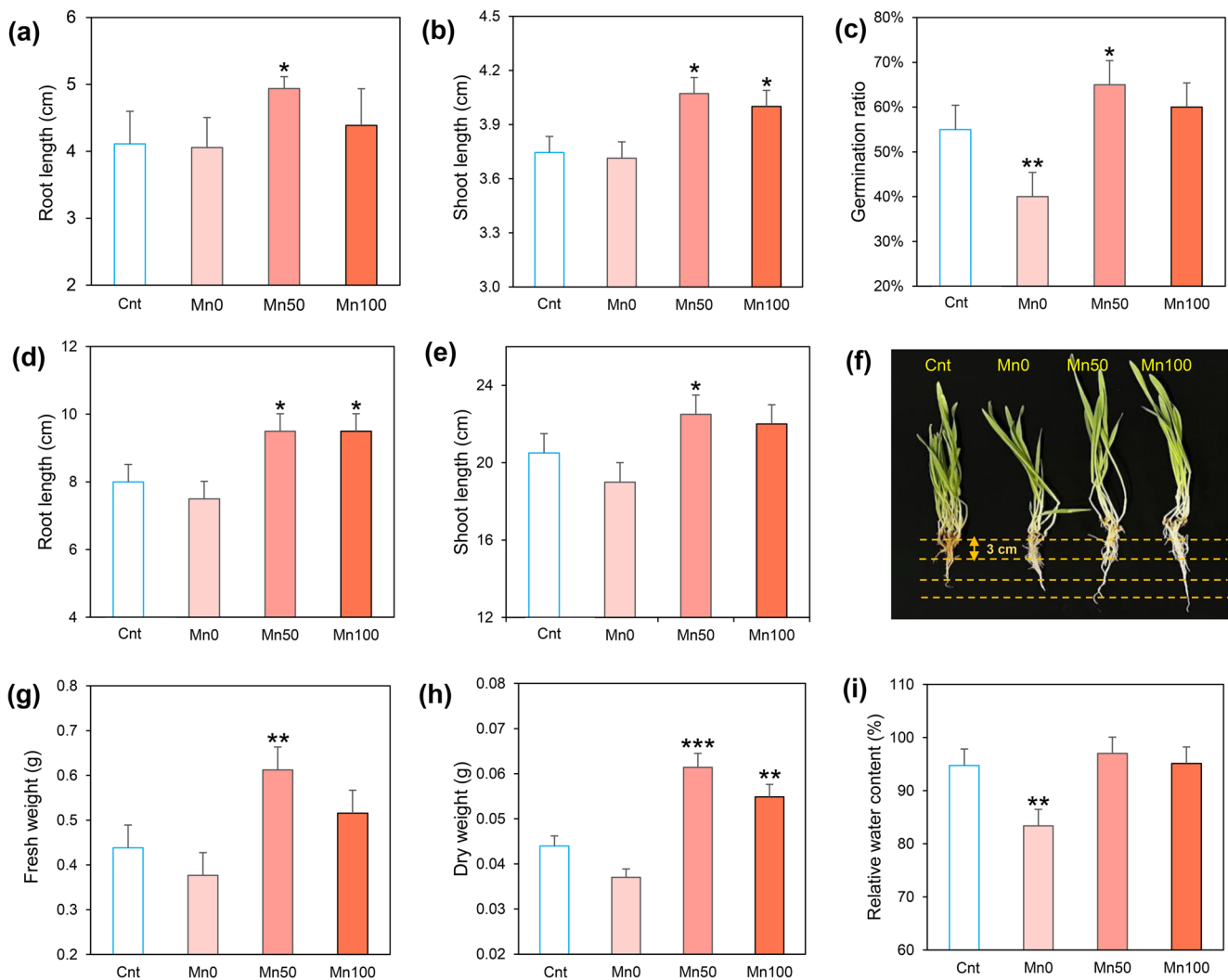


Fig. 3 Effect of Mn-doped CeO₂ nanoparticles (MnCeO₂ NPs) on barley seedling growth under varying manganese (Mn) concentrations (Mn0: non-deficient; Mn50: 50% Mn-deficient; and Mn100: 100% Mn-deficient). Control (Cnt) groups were grown without NPs application. **a** Root length (cm) and **(b)** shoot length (cm) after four days of germination. **c** Germination ratio (%). **d** Root length (cm) and **(e)** shoot

length (cm) after three weeks of NPs treatment. **f** Photograph of three-week-old seedlings. **g** Fresh weight (FW) and **(h)** dry weight (DW) of *H. vulgare* seedlings after three weeks (*n*=7). **i** Relative water content (RWC, %) of seedlings after three weeks of treatment. Error bars represent standard deviations. Statistical significance was determined using a t-test (**P* < 0.05, ***P* < 0.01, ****P* < 0.005)

reduction in RWC compared with the control (*P* < 0.01). However, Mn50 and Mn100 seedlings showed no considerable change in the RWC, revealing MnCeO₂ NPs' contribution in balancing the RWC under Mn-deficient conditions. This result showed barley seedlings had improved water use efficiency under Mn-deficient conditions (Mn50 and Mn100).

3.2.2 Effects of Nanoparticles on Pigmentation and Chlorophyll Fluorescence

We assessed the chlorophyll (*a* and *b*), total pigment, and carotenoid contents in leaves as a metric for the plant's photosynthetic efficacy (Fig. 4). Consistent with the growth

indices results (Fig. 3), pigment contents followed the same pattern. MnCeO₂ NPs significantly enhanced the chlorophyll-*a* and -*b* under Mn-deficient conditions (Mn50 and Mn100), but not in the Mn-sufficient condition (Mn0).

Aside from pigment analyses, the effect of MnCeO₂ NPs treatment under different Mn regimens (Mn0, Mn50, and Mn100) was assessed by measuring some key photosystem performance indicators, such as Fv/Fm, Y(II), and ETR (Fig. 5). Like the previous results, the chlorophyll fluorescence parameters exhibited a similar trend, where the MnCeO₂ NPs remarkably improved Fv/Fm, Y(II), and ETR values in the plants grown under 50% Mn-deficient condition (Mn50). Conversely, NPs treatment at non-deficient condition (Mn0) slightly decreased these parameters.

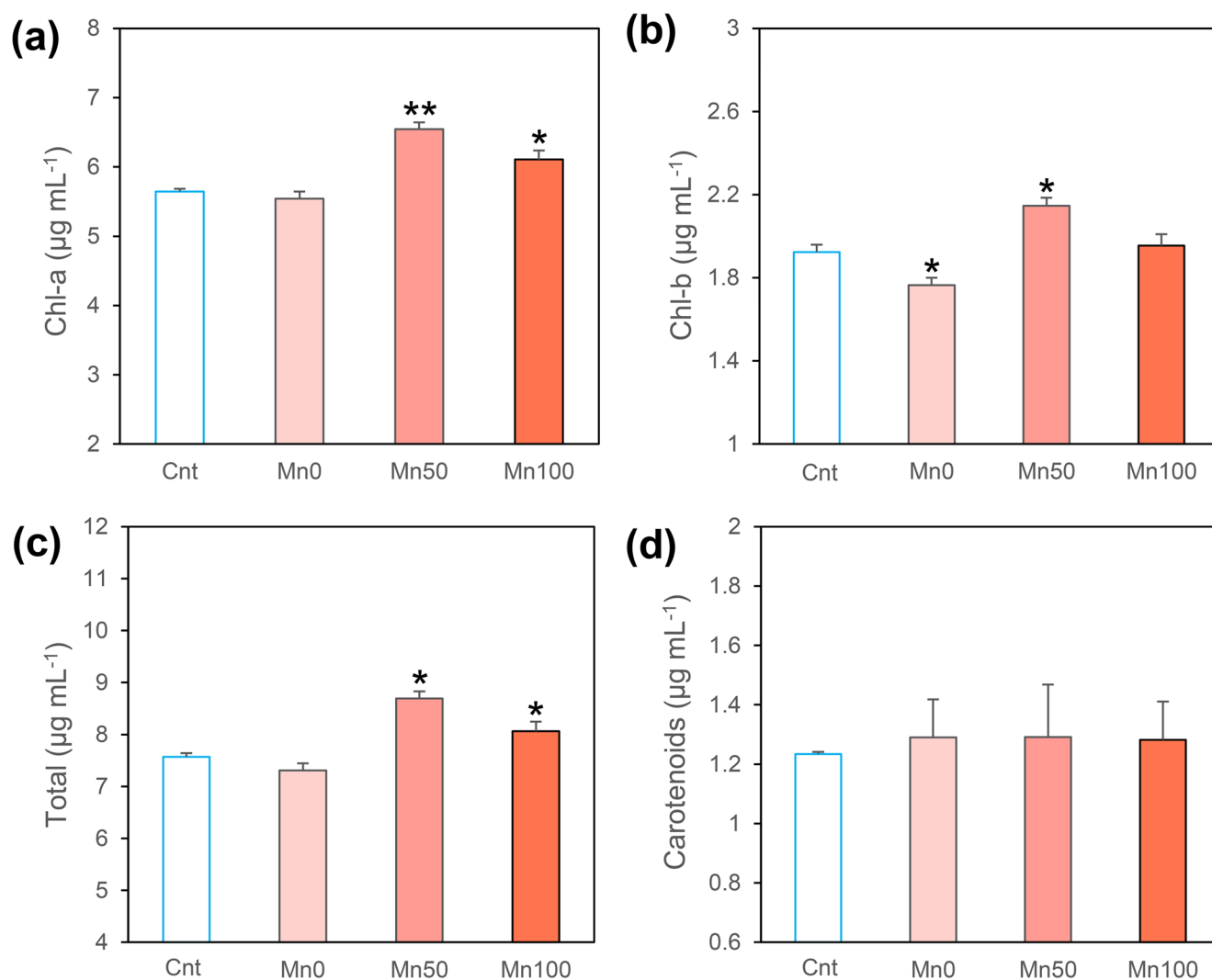


Fig. 4 Pigment content of barley upon three weeks of Mn-doped CeO_2 nanoparticles (MnCeO_2 NPs) treatments under varying manganese (Mn) concentrations (Mn0: non-deficient; Mn50: 50% Mn-deficient; and Mn100: 100% Mn-deficient). Control (Cnt) groups were grown without NPs application. **a** Chlorophyll-*a* (Chl-*a*), **b** chlorophyll-*b*

(Chl-*b*), **c** total (Chl-*a*+Chl-*b*), and **d** carotenoids pigments. Error bars show the standard deviation ($n=3$). Statistically significant differences from the control samples were denoted by an asterisk (* $P<0.05$, ** $P<0.001$)

3.3 Cytotoxicity Assessment

To ascertain any possible MnCeO_2 NPs-induced cell membrane damage and cytotoxicity, the roots were stained with propidium iodide, a cationic dye, and examined using confocal microscopy (Fig. 6). The presence of damaged cells was evidenced by red fluorescent specks, indicating PI staining of the cell nuclei due to compromised membranes. As expected, the control group exhibited a minimal number of injured cells. A similar result was evident in the Mn50 group, where no cell membrane injury was noted. However, the seedlings grown under Mn0 and Mn100 conditions demonstrated a notable rise in the quantity of injured cells. This finding can be attributed to increased cell membrane vulnerability resulting from reactive oxygen species (ROS)

production. As shown in the preceding sections, this finding aligns with the observed growth indices, photosynthesis, pigmentation, and morphological characteristics of the plants.

3.4 The Morphology of Roots Upon Nanoparticle Treatment

To evaluate potential harm to the morphology of the root surface, scanning electron microscopy (SEM) was used to examine the root tissue (Fig. 7). As expected, control roots showed no significant morphological abnormalities, exhibiting a clear, smooth, and intact surface. However, significant aberrations, fissures, fractured tissues, and bulging structures were observed on the surface of roots treated with

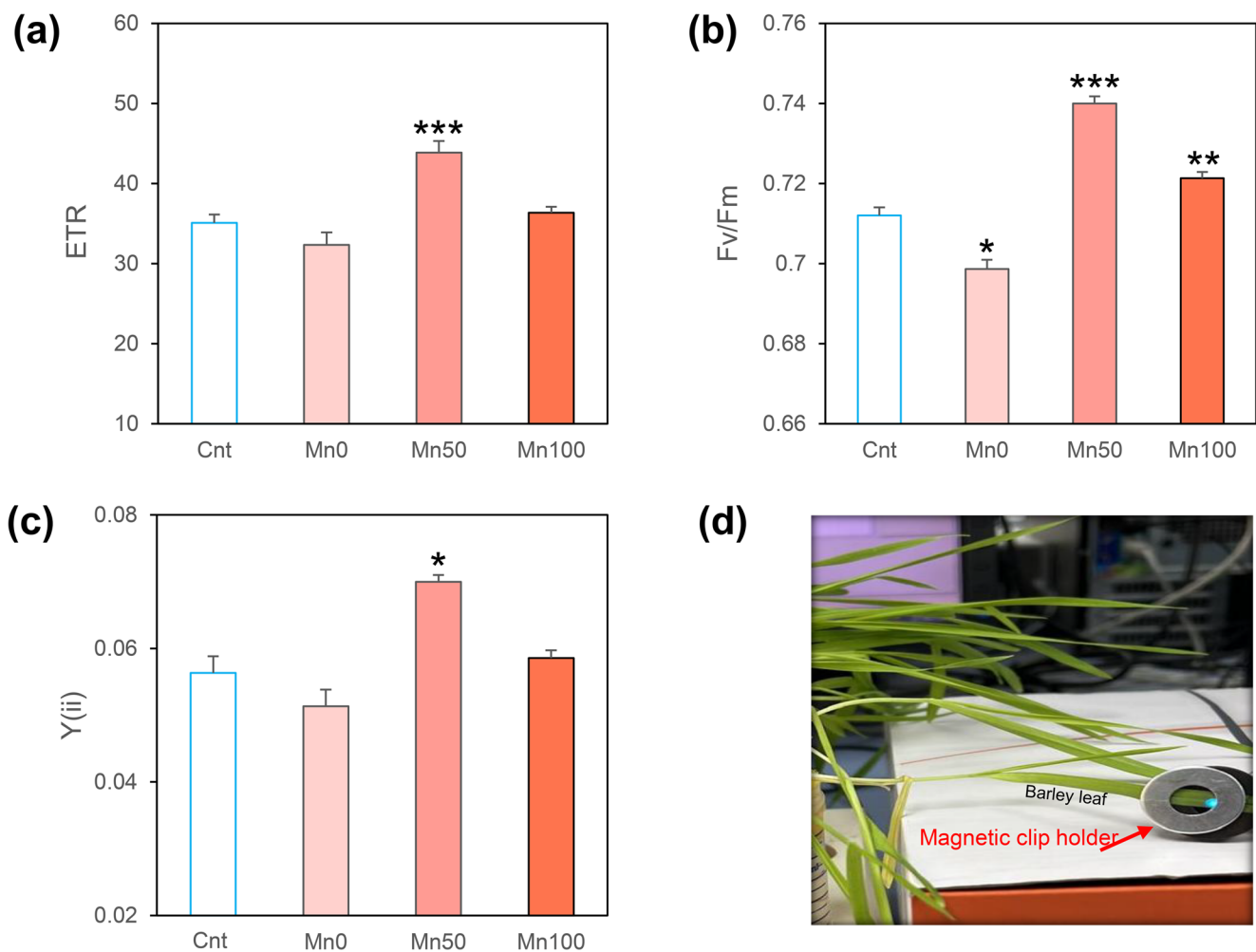


Fig. 5 Effects of Mn-doped CeO₂ nanoparticles (MnCeO₂ NPs) on chlorophyll fluorescence parameters: **a** Electron transport rate (ETR), **b** the maximal quantum efficiency of PSII (Fv/Fm), and **c** The effective photochemical quantum yield of photosystem IIY(II). **d** Measurements were conducted using a PAM fluorometer. Control (Cnt) groups

were grown without NPs application. Manganese (Mn) concentrations: Mn0 (non-deficient), Mn50 (50% Mn-deficient), and Mn100 (100% Mn-deficient). Asterisks indicate statistically significant differences from the control (* $P < 0.05$, ** $P < 0.01$, *** $P < 0.005$)

MnCeO₂ NPs under Mn0 and Mn100 conditions. Additionally, root cells appeared crumbled with ruptured surfaces.

3.5 Status of Plant Nutrition

The nutrients in the leaves and roots were measured using ICP-OES. The quantity of micro-elements (Mn, Zn, Fe, and Cu) and macro-elements (Ca, K, and Mg) are shown in Tables 1 and 2, respectively. In control roots, the Mn level was 118.2 mg kg⁻¹ DW, which increased to 148.1 mg kg⁻¹ DW after NP treatment, corresponding to a ~25% increase in root Mn levels. As expected, the Mn level in the Mn50 condition was lower (81.3 mg kg⁻¹ DW) than the control. However, NP supplementation did not fully compensate for the Mn deficiency in the root (15.5 mg kg⁻¹) and leaf (12.9 mg kg⁻¹) under Mn100 condition. This confirms that NPs contribute to plant Mn levels under moderate Mn-deficient

conditions, but are insufficient to meet the total Mn requirement in a 100% Mn-deficient environment.

NP treatment led to fluctuations in the abundance of other microelements. Notably, iron (Fe) content fluctuated in both root and leaf tissues. In the Mn50 environment, Fe levels were 517.2 mg kg⁻¹ in roots and 88.9 mg kg⁻¹ in leaves, representing approximately a 4.5-fold and 2.3-fold increase, respectively, compared to the control (115.2 mg kg⁻¹ in roots and 38.0 mg kg⁻¹ in leaves). Similarly, copper (Cu) content was significantly elevated upon NP treatment compared to the control. This improvement resulted in approximately a 13-fold increase in root Cu levels and a 2.5-fold increase in leaf Cu levels relative to the control.

Table 2 shows the quantity of macro-elements. Compared to the control, the Ca, K, and Mg contents in both NP-treated root and leaf tissue were significantly improved at Mn50 condition, which was 2.1, 1.5, and 0.5 times that of

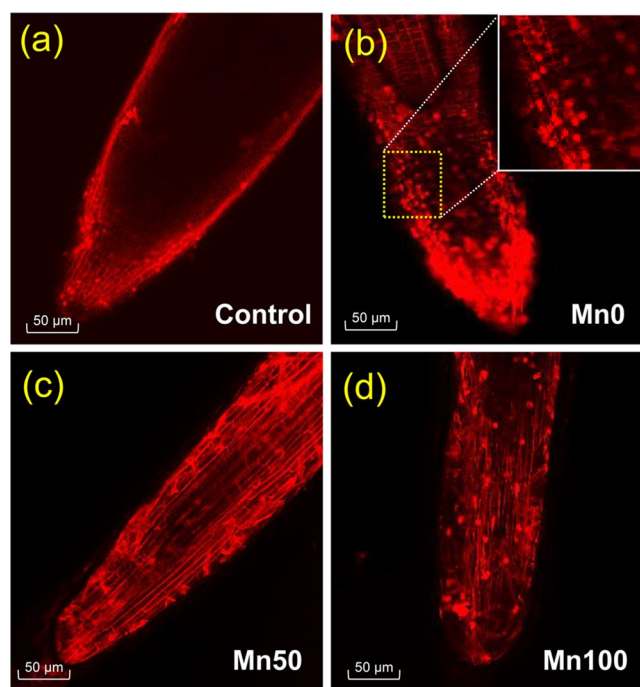


Fig. 6 Confocal microscopy analysis of the plant root tips (0.5 cm) upon Mn-doped CeO₂ nanoparticles (MnCeO₂ NPs) treatment. **a** Control, **b** Mn0 (non-deficient), **c** Mn50 (50% Mn-deficient), **d** Mn100 (100% Mn-deficient). Control (Cnt) groups were grown without NPs application. Roots were stained with propidium iodide (PI), a membrane-impermeable dye. The red dot represents PI uptake and nuclei staining, indicating cell membrane damage and cytotoxicity. The scale bar = 50 μ m

the control root ones, respectively. At the Mn100 environment, this increase was slightly reduced, however it was still remarkably above the control values. A similar improvement was also evident in the leaves, to the NP-induced enhancement in the nutrient uptake mechanism, particularly at the 50% Mn-deficient condition (Mn50).

3.6 Assessment of Genotoxicity

Plants can serve as bioindicators for nanotoxicity. Despite the observed improvements in plant germination and growth performance, it is essential to evaluate the potential genotoxic effects of MnCeO₂ NPs before widespread application. RAPD-PCR can detect diverse forms of DNA damage and mutations, enabling a rapid comparison of genomic DNA banding patterns between control and NP-exposed samples (Atienzar and Jha 2006). In this study, RAPD-PCR profiles of *H. vulgare* plants exposed to NPs were compared to those of unexposed controls. The analysis focused on variations in band intensity, including increases and decreases, as well as the presence or absence of bands (Fig. 8). The RAPD profiles revealed a significant difference between the treated and control groups, characterized by alterations in DNA band presence and absence. The GTS% was 58.3%, 33.3%,

and 100% for Mn0, Mn50, and Mn100, respectively. Under Mn0 conditions, only DNA band intensities were affected, with no observed band appearance or disappearance. A total of seven bands showed changes compared to the control, suggesting variations in amplification possibly resulting from DNA damage, mutations, epigenetic modifications, or DNA duplication. Under Mn50 conditions, these alterations were limited, with only four bands affected. However, under Mn100 conditions, a substantial number of bands disappeared, and a total of 12 bands showed alterations. This could be attributed to point mutations and the expression of genomic instabilities, including gene and chromosome rearrangements, deletions, and insertions (Atienzar and Jha 2006). These findings indicate that MnCeO₂ NPs may induce genotoxicity in barley seedlings, with the effect being more pronounced under 100% Mn-deficient condition. Conversely, the addition of MnCeO₂ NPs under moderately Mn-deficient conditions may mitigate this impact.

4 Discussions

This study designed and developed a novel NP (MnCeO₂ NP) to mitigate Mn-deficiency. After synthesis and characterizations (Figs. 1 and 2), barley seeds were exposed to MnCeO₂ NPs under moderate and severe Mn-deficient environments. Physiological analyses revealed that MnCeO₂ NPs enhanced barley germination rate, growth indices, and biomass in Mn-deficient environments (Mn50 and Mn100) compared to the untreated control plants (Fig. 3). Conversely, under non-deficient conditions (Mn0), MnCeO₂ NPs did not produce a similar positive effect and, but instead decreased most of the tested growth indices.

Several studies have reported growth enhancement induced by CeO₂ NPs. For example, 100 mg kg⁻¹ of CeO₂ NPs increased root and shoot elongation in rice seedlings by 35% and 38%, respectively (Zhang et al. 2021). Similarly, after 30 days of treatment, Gui et al. (2015) discovered that nCeO₂ can stimulate head lettuce growth at a moderate dose (100 mg kg⁻¹), while it has an inhibitory effect at a high concentration (1,000 mg kg⁻¹). However, other studies point to the toxic effect of CeO₂ NPs. For instance, a recent study found that the root growth of lettuce was suppressed by an aqueous suspension of 250 mg L⁻¹ nCeO₂ (~25 nm) (Andersen et al. 2016). Furthermore, a prior study conducted by Abbas et al. (2020) showed analogous alterations, demonstrating the positive impact of CeO₂ NPs at concentrations up to 500 mg L⁻¹, which enhanced wheat biomass. After being exposed to 2,000 mg L⁻¹ CeO₂ in a phosphate- and non-phosphate-containing nutrient solution, cucumbers (*Cucumis sativus*) showed no significant changes in root and shoot biomass production as compared to the control group

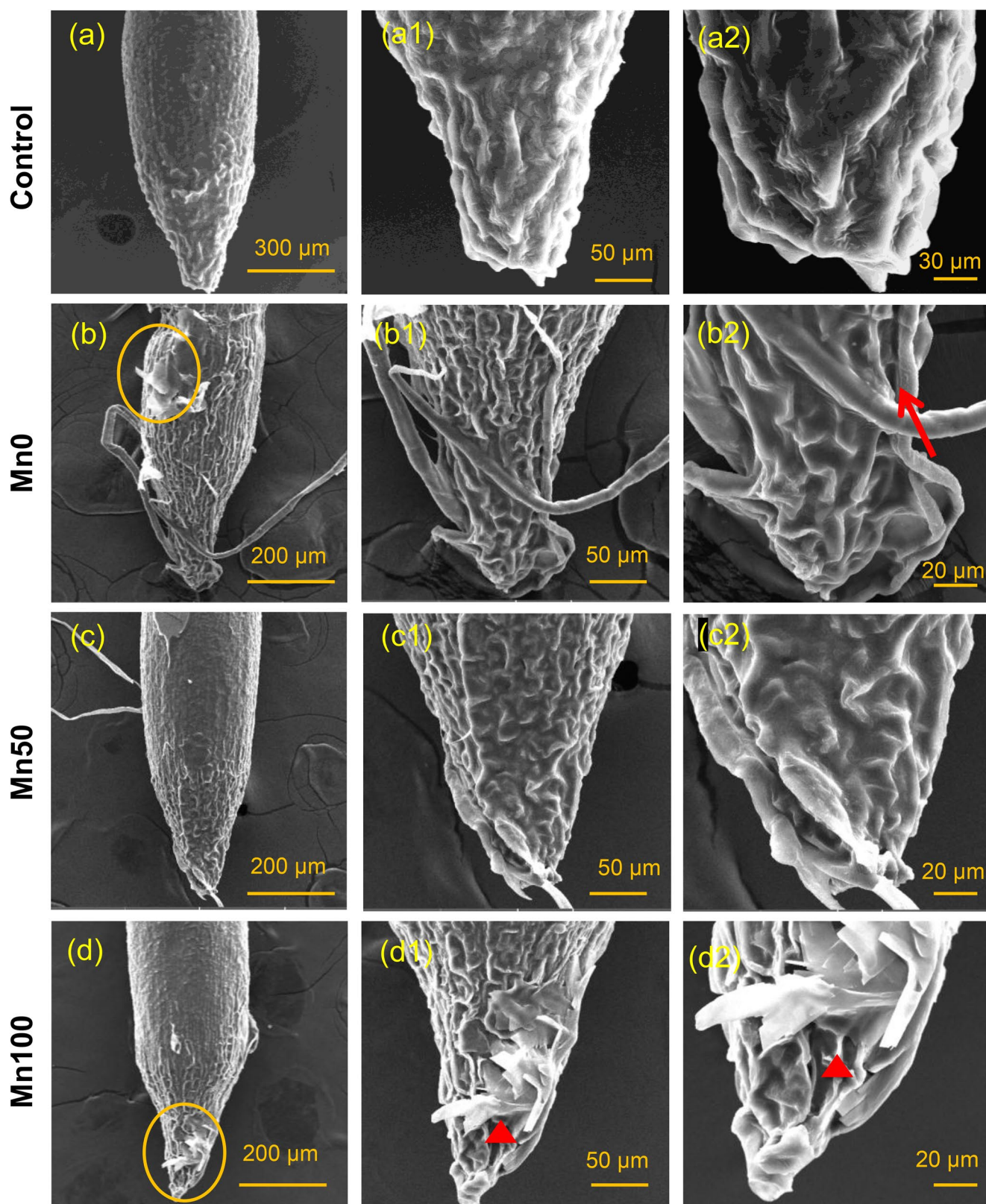


Fig. 7 Scanning electron microscope (SEM) examination of unexposed (control) and Mn-doped CeO_2 nanoparticles (MnCeO_2 NPs) exposed plant roots. **(a)** Control, **(b)** Mn0 (non-deficient), **(c)** Mn50 (50% Mn-deficient), **(d)** Mn100 (100% Mn-deficient). Control (Cnt)

groups were grown without NPs application. The images at three different magnifications were shown. Damaged structures on specimens as marked by red arrows. Cracks and disturbances are shown in orange circles

Table 1 Microelement concentration in the barley root and leaf tissues

Micro-elements (mg kg ⁻¹ DW)					
Tissue	Sample	Mn	Zn	Fe	Cu
Root	Control	118.2±0.1	15.4±0.2	115.2±1.6	3.7±0.2
	Mn0	148.1±0.2*	11.9±0.2*	86.4±1.9	8.3±0.1*
	Mn50	81.3±0.6*	16.0±0.2	517.2±11.7***	53.5±0.1***
	Mn100	15.5±0.3***	13.8±0.2	274.0±1.2**	38.6±1.2***
Leaf	Control	86.5±0.8	45.7±0.6	38.0±0.2	14.9±0.2
	Mn0	70.0±1.7*	35.5±0.9	35.3±1.7	12.2±0.1
	Mn50	77.6±1.2*	47.6±0.5	88.9±2.0***	37.9±0.6***
	Mn100	12.9±0.2***	45.4±0.1	62.9±0.7***	24.4±0.3**

* Contents of microelements (mg kg⁻¹ in DW) in the root and leaf tissues of untreated control and NPs-treated seedlings grown under non-deficient (Mn0), 50% Mn-deficient (Mn50), and 100% Mn-deficient (Mn100) conditions. The asterisk (*) symbol denotes a significant difference among treatment and control (**P*<0.05, ***P*<0.01, ****P*<0.005)

Table 2 Macro-elements concentration in the barley root and leaf tissues

Macro-elements (g kg ⁻¹ DW)				
Tissue	Sample	Ca	K	Mg
Root	Control	102.2±1.3	84.7±1.15	10.2±0.08
	Mn0	73.3±1.6 **	61.3±1.00 *	7.4±0.13*
	Mn50	211.3±1.7 ***	129.4±0.26 *	14.9±0.01 **
	Mn100	137.4±3.4 *	110.9±0.45 *	14.5±0.19 **
Leaf	Control	208.8±4.4	538.3±2.76	84.7±1.93
	Mn0	185.0±1.1	472.9±2.58	75.1±1.14 *
	Mn50	294.3±10.3 **	582.3±0.92	106.7±0.23 **
	Mn100	159.2±2.0 *	566.2±1.04	68.4±0.86 *

* Contents of macro-elements (g kg⁻¹ in DW) in the root and leaf tissues of untreated control and NPs-treated seedlings grown under non-deficient (Mn0), 50% Mn-deficient (Mn50), and 100% Mn-deficient (Mn100) conditions. The asterisk (*) symbol denotes a significant difference among treatment and control (**P*<0.05, ***P*<0.01, ****P*<0.005)

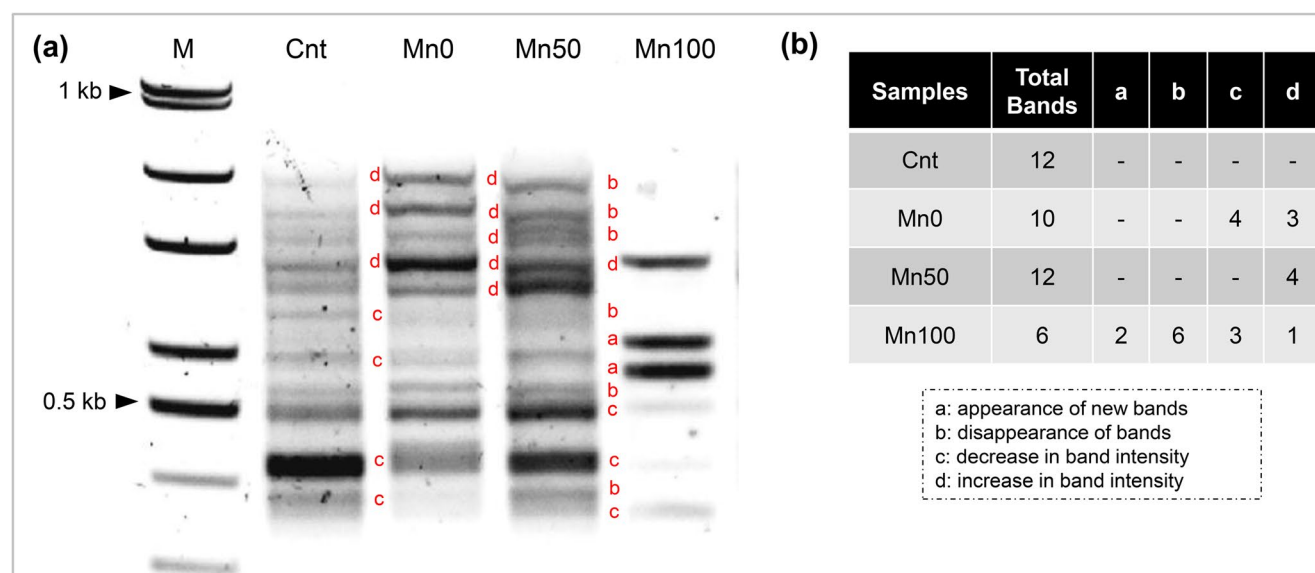


Fig. 8 Genotoxicity assessment of *H. vulgare* roots upon Mn-doped CeO₂ nanoparticles (MnCeO₂ NPs) treatment. **a** Randomly amplified polymorphic DNA-polymerase chain reaction (RAPD-PCR) profiles of 3% Mn-doped CeO₂ NPs-treated and untreated (control-Cnt) *H. vul-*

gare roots. **b** The number of total and polymorphic bands. a: indicates the appearance of new bands, b: disappearance of bands, c: decrease in band intensity, and d: increase in band intensity. M = 100 bp size marker

(Rui et al. 2015). In addition, earlier research indicated that 100 mg kg⁻¹ increased DW of rice roots by 22% and that 500 mg kg⁻¹ decreased DW of roots and shoots by 14% and 34%, respectively (Zhang et al. 2021). Zhang et al. (2017) reached the same conclusions on the use of CeO₂ NPs with concentrations from 0 to 500 mg kg⁻¹. While high doses of nCeO₂ (1,000–2,000 mg kg⁻¹) decreased FW and DW, no discernible effect of nCeO₂ on biomass production was observed. It should be noted that this comparison is shown primarily with nCeO₂. However, the synthesized MnCeO₂ NP may possess different structures and characteristics that affect plant responses differently than nCeO₂.

The improvement in pigmentation and chlorophyll fluorescence may be attributed to augmented water absorption, as shown in Fig. 3i and noted by Khan et al. (2020). Another plausible explanation is that MnCeO₂ NPs compensate for the lack of Mn, which is a vital micronutrient for plants. It involves many biochemical reactions, including the catalysis of water molecules that split within photosystem II (PSII). It forms a vital part of the oxygen-evolving complex (OEC), which is responsible for splitting water molecules. Thus, it primarily contributes to the photosynthetic and yield performance of plants. Mn-deficient conditions lead to reduced water splitting and consequently to impairment of photosystem reactions, decreased chlorophyll production, and impaired electron transport. At the physiological level, Mn-deficiency results in stunted growth and reduced yield (Alejandro et al. 2020). Herein, the pigment content of barley is improved by the MnCeO₂ NPs under Mn-deficient conditions. This result shows the NPs' potential in the alleviation of the Mn-deficiency problem. Incorporating MnCeO₂ NPs or their possible dissociation to elements might have contributed to metabolic mechanisms or components, such as chlorophyll and enzymes involved in photosynthetic activities.

In line with these findings, photosynthetic activity indicators were found to be improved (Fig. 5). For instance, the Fv/Fm ratio, a key indicator of leaf stress, was reduced ($P < 0.05$) in the Mn0 condition, indicating compromised PSII. This finding is consistent with earlier research that found a 17% decrease in Fv/Fm after treatment with 500 mg kg⁻¹ CeO₂ NPs (Zhang et al. 2021). In contrast, treatments with MnCeO₂ NPs under Mn50 conditions showed a significant increase in all chlorophyll fluorescence parameters ($P < 0.005$). These results suggest that MnCeO₂ NPs improved plant photosynthesis under Mn-deficient conditions while impairing the photosynthetic system once applied under non-deficient environments. These metrics are in agreement with the results for pigment contents and growth indices, as shown in Figs. 3 and 4. These findings point to the nanofertilizer potential of MnCeO₂ NPs in Mn-deficient conditions.

The cell membrane injuries (Fig. 6) as well as morphological disruptions on the root surface (Fig. 7) might have

affected nutrient uptake and, thus plant growth and physiology. These findings indicate that MnCeO₂ NPs under both Mn0 and Mn100 conditions induce disturbances in the root cells of barley, acting as a stressor, consistent with previous studies (Wang et al. 2016; Du et al. 2017). Conversely, no root injury was observed under 50% Mn-deficient conditions (Mn50), potentially enhancing nutrient absorption and promoting plant development. Lv et al. (2019) suggested that iron oxide NPs may enhance cell membrane permeability, resulting in increased water transport and nutrient absorption. When combined with our findings, this indicates that NPs may negatively impact adjacent cell membranes, alter water and nutrient transport, while also potentially improving nutrient absorption and plant development under suitable concentrations and conditions, specifically Mn50 in this study.

Under normal nutrient conditions (Mn0), NP treatment led to a reduction in several nutrient elements (Zn, Fe, Ca, K, Mg), likely due to nutritional imbalances caused by excess Mn concentration (Tables 1 and 2). This aligns with previous studies showing that while Mn is essential for plants, excessive Mn can be toxic, particularly in roots. For example, Zhao et al. (2024) demonstrated that Mn-based NPs inhibited the uptake of metallic minerals, including Cu, Fe, Mg, Zn, Na, and K. A potential explanation for the observed reduction in nutrient elements is NP aggregation, which could restrict elemental mobility within the root system. Studies indicate that nCeO₂ can inhibit the absorption of macronutrients. Research showed that nCeO₂ significantly reduces magnesium (Mg) uptake in wheat (Rico et al. 2017). Similarly, CeO₂ NPs at 500 mg kg⁻¹ negatively impacted barley kernel nutritional composition and yield, with reductions observed in potassium (K) and sulfur (S) content (Pošćić et al. 2016). In this study, in the moderate Mn-deficient condition (Mn50), a notable increase in root Fe, Cu, Ca, K, and Mg contents was determined. These findings suggest that MnCeO₂ NPs may help alleviate nutrient imbalances caused by Mn deficiency.

Beyond nutritional improvement, it is important to consider how MnCeO₂ NPs are taken up and translocated within the plant system. Despite the lack of direct mechanistic data in this study, previous research offers credible models for NP internalization. NPs can enter plant roots through the apoplastic pathway, which involves pores with a diameter of approximately 3.5–5 nm in plant cell walls (Lin et al. 2009), or through the symplastic pathway, which involves endocytosis. Once inside, they may move through the xylem to aerial tissues. Su et al. (2020) clarified the transit of silver NPs via the apoplastic pathway in citrus roots. In contrast, NPs can traverse via the symplastic pathway, which follows the conduits of the plasmodesmata (Scwab et al. 2016). In the case of NPs that are larger than the wall pores, endocytosis can facilitate internalization (Thwala et al. 2016).

For instance, the Ag NPs measuring 30 nm are more readily internalized than the larger Ag NPs measuring 85 nm and 110 nm, which can be internalized through endocytosis (Souza et al. 2021).

In this study, the average crystallite size of MnCeO₂ NPs is 11.9 nm, which is lower than the average size of plasmodesmata (40 nm) (Tilney et al. 1991). Thus, they can penetrate into the cell membrane and transport through the symplastic route. However, natural biobarriers, such as cell walls, cell membranes, sieve elements, and Casparian strips may limit the translocation of MnCeO₂ NPs. However, their uptake mechanism has still to be explored, and this necessitates further detailed investigations, such as transmission electron microscopy analysis.

5 Conclusion

High-quality manganese-doped cerium oxide nanoparticles (MnCeO₂ NPs) were produced and characterized using advanced analytical methods. To test its performance in mitigating manganese (Mn) deficiency, this study mimicked moderate and severe Mn-deficient conditions. The findings demonstrated the beneficial impact of MnCeO₂ NPs under moderately Mn-deficient conditions on nutrition, growth indices, and physiological characteristics of barley. These results highlight their potential as nano fertilizers for enhancing plant nutrition and productivity. In situations of severe deficiency, the nanoparticles were unable to compensate for the Mn need of barley, resulting in diminished growth indices, cell membrane damage, altered root shape, and significant genotoxicity. This study represents a preliminary finding on the contribution of MnCeO₂ NPs in nutrient media. Further studies should be conducted in soil with different characteristics, such as calcareous and high pH soils, organic soils, cool and wet soils, or sandy and leached soils, which are known to affect Mn uptake. Despite the potential of MnCeO₂ NPs to alleviate Mn deficiency, their environmental fate, potential accumulation in soil–plant systems, and implications for food safety must be assessed in future field-based studies prior to their widespread application.

Author Contributions MAA and HT conceptualized the study. FA, AB and MAA synthesized and characterized the nanoparticles. SA analysed the tissues with SEM. FA, MA and HT conducted physiological experiments. FA and GT conducted genotoxicity tests. CS and HT carried out nutrient analyses. FA, MAA, and HT wrote the manuscript.

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Data Availability The datasets produced and/or examined in this investigation are accessible from the corresponding author upon a reasonable request.

Declarations

Ethics Approval This manuscript has not been published elsewhere and is not under consideration by another journal. The Institutional Review Board (IRB) at Imam Abdulrahman bin Faisal University (IAU) sanctioned the study, assigned IRB number IRB-PGS-2024-10-511.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflict of interest The authors declare no conflict of interest associated with this work.

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