# Materials Advances



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View Journal | View Issue



Cite this: *Mater. Adv.*, 2025, **6**, 8011

Received 9th June 2025, Accepted 20th July 2025

DOI: 10.1039/d5ma00615e

rsc.li/materials-advances

# Sustainable synthesis of Nd<sub>2</sub>O<sub>3</sub> nanoparticles for photocatalytic degradation of tetracycline in aqueous media

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The great discrepancy in crystal size and incongruity in the crystal interface of catalysts lead to decreased catalytic performance, limiting their application for antibiotic removal. Herein, a regulation strategy via intrinsic ion interpenetration is proposed to engineer nanostructured  $Nd_2O_3$  photocatalyst for efficient photocatalytic degradation of tetracycline (TC). Mechanism studies indicate that  $Nd_2O_3$  NPs reduce metal ions into their elemental form, enabling oxygen atoms to adhere to the metal surfaces. Moreover, the degradation and mineralization rate of TC increased by 92% within 40 minutes by following first-order kinetics. Combining photocatalytic degradation with a first-order kinetics reaction could produce the oxygen-reactive species, which helps to enhance the degradation and mineralization rates of TC pollutants. Furthermore, the antibacterial efficiency of the as-synthesized  $Nd_2O_3$  NPs was assessed against Staphylococcus aureus and Staphylococcus and Staphylococcus aureus and Staphylococcus and Staphylococcus areus and Staphylococcus and Staphylococcus and Staphylococcus areus and Staphylococcus and Staphylococcus and Staphylococcus areus and Staphylococcus and S

#### 1. Introduction

The massive rise in global population raises the high demand for goods derived from agriculture and, at the same time, increases the global need for fresh water. Dyes, antibiotics, organic pollutants, pigments, pesticides, insecticides, and crop-based medicines also escalate the demand for fresh water. Pesticides and fungicides applied to crops during intense rainfall are immediately released into freshwater ponds, lakes, and rivers. The excess amount of antibiotics and their penetration into the water bodies provide a highly toxic environment. It takes billions of years to degrade and remove this contamination from these water basins. Tetracycline (TC), a widely used antibiotic, is another contaminant that has become an environmental concern due to its persistent nature. Serious drawbacks in water bodies remain due to their occurrence, which has led to

emerging antibiotic-resistant bacteria, potentially harmful to

Various techniques, such as advanced and chemical oxidation, adsorption, photocatalysis, coagulation, and filtration, are available for organic pollutants. Among these, photocatalysis is the most promising approach using a catalyst, breaking down the pollutants into less harmful substances.  $^{9,10}$  While various organic pollutants have been substituted for photocatalytic degradation, negligible work has been done on the photocatalytic degradation of TC. Among rare earth metal oxides, neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>) has recently attracted enormous interest due to its wonderful properties, such as high thermal stability, high value, and band

aquatic systems. The erroneous disposal and persistence of antibiotics like TC have led to a boom in antibiotic resistance in marine environments and paved the way for rising global health concerns. The presence of TC and other antibiotics poses a serious threat to environmental and human health. 4-6 The breakdown of these substances takes a long time, and great efforts are required to remove them, in terms of time, energy, and resources, stressing the need for effective and eternal solutions. Bacterial resistance to TC makes it difficult or impossible to treat against antibiotic-resistant bacteria.<sup>7</sup> Agricultural runoff is another serious threat resulting from the improper disposal of TC, worsening this problem. The entire health system of humans was found to be at increased risk due to the intake of water or food contaminated with antibiotic-resistant bacteria that were resistant to standard treatments, increasing the burden on healthcare costs and systems.8

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gap energy of approximately 4.6 eV.11 It has wide applications in catalysts, UV absorbents, luminescent materials, pro-coatings, and magnets.

Sol-gel, hydrogen plasma-metal reaction, precipitation, thermal breakdown, CVD, sputtering, green synthesis, and thermal combustion are a few ways to synthesize Nd<sub>2</sub>O<sub>3</sub> nanoparticles (NPs). 12-15 Some of these methods involve the emission of harmful byproducts and are costly, time-consuming, and subject to particle aggregations. Green synthesis has been regarded as a significant method for metal oxide NPs due to the use of fewer chemicals. It is known that very few metal oxide NPs (CuO, ZnO, TiO<sub>2</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>) are synthesized using green methods with a variety of plant extracts and have also unveiled their antibacterial efficacy against various bacterial cultures. 16-18 Caryota urens (C. urens), also known as fishtail palms, attract distinct interest in nanotechnology and biomedical sciences. This tropical plant has a rich phytochemical composition and is an eternal source of several bioactive compounds, such as flavonoids, steroidal saponins, tannins, polysaccharides, and phenolic acids.<sup>19</sup> These substances have diverse biological behaviors, such as antioxidant, anti-inflammatory, and antimicrobial properties. 19,20 A friendly alternative to conventional chemical methods is plant extract nanoparticle biosynthesis via green chemistry, which leverages the bioactive compounds in plants to enhance the stability and functionality of the synthesized nanostructures.<sup>21</sup> Specifically, zero-valent metal NPs were successfully biosynthesized using Jasminum grandiflorum, and unique properties obtained via the encapsulation of the plant's elements, facilitating the electron distribution in the interface of silicon and oxygen atoms.<sup>22</sup> The metal NPs via bioactive compounds in C. urens can play a crucial role as reducing agents and stabilizers, resulting in enhanced properties. Steroidal saponins were responsible for the stable and biocompatible coating over the NPs and served as capping agents. The uniformity and durability of the nanostructures were attained with flavonoids and phenolic acids, which further contribute to the reduction and stabilization processes.<sup>23</sup> A unique bio-organic interface resulting from the interaction between the metal NPs and the bioactive compounds in Caryota urens facilitates electron distribution between the metal atoms and lattice oxygen, stability, and functionality, making them suitable for diverse applications, particularly in biomedical and catalytic fields.<sup>24</sup> The novel aspect of this research lies in the fabrication of Nd2O3 NPs that have been utilized for the efficient environmental contaminant degradation of TC. Herein, the synthesized Nd<sub>2</sub>O<sub>3</sub> NPs were subjected to substantial testing against Staphylococcus aureus and Escherichia coli. The Nd<sub>2</sub>O<sub>3</sub> NPs using C. urens are unprecedented and represent a sustainable and eco-friendly method. The current focus of this study is to unveil the environmentally friendly biosynthesis procedure of Caryota urens extracts for the degradation of TC. The efficacy evaluation and the combat ability of Nd2O3 NPs against Staphylococcus aureus and Escherichia coli were investigated. The effectiveness of various photocatalysts and the reaction conditions were sufficient for efficient development of TC degradation and mitigated its environmental impact. This research emphasizes the development of nanotechnology and highlights the importance of sustainable practices in scientific innovation.

#### Materials and methods

#### 2.1. Reagents

Neodymium(III) nitrate hexahydrate (Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.9% AR-purity) and tetracycline (C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>, 99.9% AR-purity) were purchased from Sigma Aldrich. These chemicals were prepared using double-distilled water, with no additional substances involved in the synthesis process.

#### 2.2. Phytochemicals extraction

The leaf extract of Caryota urens was chosen as a reducer or stabilizer in the synthesis of Nd<sub>2</sub>O<sub>3</sub> NPs. Initially, the collected C. urens leaves were weighed at 10 g and washed with doubledistilled water to eliminate impurities. Following this, doubledistilled water was used to wash the leaf thoroughly. Then the leaves were cut into tiny pieces and added to a beaker containing 100 mL of deionized water. The solution was boiled for 15 min at 70 °C using a heating mantle. After incubation, the filtrate was collected by the filtration process with Whatman No. 1<sup>®</sup> filter paper and stored in a brown bottle for further production of Nd2O3 NPs.

#### 2.3. Green-mediated Nd<sub>2</sub>O<sub>3</sub> NPs

The neodymium nitrate salt (0.0487 g) was dissolved in 90 mL of double-distilled water and placed on a hot plate for stirring. The plant leaf extract, 10 mL, was mixed into the neodymium nitrate solution, and the suspension was stirred at temperature of 70 °C. The appearance of a greyish-dark blue color denotes the formation of Nd<sub>2</sub>O<sub>3</sub> NPs in the suspension. Furthermore, suspension was centrifuged at 8000 rpm for 8 min, and after that, the supernatant was removed, pellet was resuspended, and centrifugation was repeated 10 times (Fig. 1).

#### 2.4. Characterization of Nd<sub>2</sub>O<sub>3</sub> NPs

The crystalline structure and material stability were assessed using an X-ray diffractometer (PANalytical X'Pert) with Cu Ka radiation (1.5405 Å) at 30 kV and 40 mA. Optical properties were examined via UV-DRS (UV-2600 Shimadzu). FTIR spectroscopy (PerkinElmer) was employed to identify the functional groups of the Nd<sub>2</sub>O<sub>3</sub> NPs and plant extract, covering a range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Surface morphology and material composition were analyzed using FESEM (Carl Zeiss) and TEM (Titan) with EDX spectroscopy. The valence states and binding energies were investigated through X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe III, Physical Electronics, USA).

#### 2.5. Experimental design, photocatalytic tests, and kinetics

The prepared Nd<sub>2</sub>O<sub>3</sub> NPs were allowed to react with TC to confirm the degradation of antibiotics. Nd<sub>2</sub>O<sub>3</sub> NPs (0.01 g) were mixed with 10 mg of 100 mL TC solution for degradation. The absorbance was recorded in 30-minute intervals and UV-vis spectroscopy of the reaction mixture (Nd<sub>2</sub>O<sub>3</sub> NPs + TC) determined the degradation activity. The percentage of TC degradation is as



Fig. 1 Schematic illustration of the green-mediated formation of Nd<sub>2</sub>O<sub>3</sub> NPs using an extract from C. urens leaves.

follows,

Photocatalytic degradation = 
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (1)

$$r_{\rm p} = -\frac{\mathrm{d}C_{\rm p}}{\mathrm{d}t} = K_{n\,C_{\rm p}{}^{n}} \tag{2}$$

In eqn (2), n is denoted as the reaction order found in a range of  $0 \le n \le 2.25$ 

For n = 2. The integral form of eqn (2) is also known as a pseudo-first-order kinetic model and is expressed as follows:

$$C_{\rm p} = C_{\rm p,0} \exp(-K_1 t) \tag{3}$$

 $K_1$  is known as the first-order rate constant. Eqn (3) can be rewritten as

$$\ln \frac{C_{\rm p}}{C_{\rm p,0}} = -K_1 t \tag{4}$$

In eqn (4), the  $K_1t$  value is denoted as the slope of a straight line of  $In \frac{C_p}{C_{p,0}}$  vs. t.

#### 2.6. Antibacterial efficacy of Nd<sub>2</sub>O<sub>3</sub> NPs

The bacterial cultures of S. aureus (MTCC-902) and E. coli (MTCC-443) were procured from the Microbial Type Culture Collection (MTCC), Pakistan. Initially, a single bacterial culture of S. aureus and E. coli was inoculated into 100 mL of nutrient broth and incubated for 24 hours at 37 °C in a shaker. After 24 hours of incubation, bacterial cultures were separately swabbed on Muller-Hinton agar plates. Wells were made on the MHA plates using the gel puncture, and different concentrations of Nd<sub>2</sub>O<sub>3</sub> NPs (10, 20, 50, and 100 µg mL<sup>-1</sup>) were poured into the wells, and the plates were incubated for 24 h at 37 °C. The antibacterial efficacy of Nd<sub>2</sub>O<sub>3</sub> NPs was confirmed by measuring the zone of inhibition formed around well after the incubation period (24 hours). A streptomycin antibiotic disc was used as a control for this antibacterial study.

#### Results and discussion

#### 3.1. XRD analysis

The X-ray diffraction (XRD) analysis of bio-produced Nd<sub>2</sub>O<sub>3</sub> NPs, as shown in Fig. 2, reveals a distinctive hexagonal crystalline structure with pronounced peaks at the 27.7° (100), 28.7° (002),  $32.1^{\circ}$  (101),  $40.4^{\circ}$  (102),  $49.7^{\circ}$  (110),  $56.9^{\circ}$  (103),  $59.7^{\circ}$  (112),  $65.4^{\circ}$ (004),  $71.6^{\circ}$  (203), and  $78.7^{\circ}$  (211) planes. The pronounced peaks were matched to the JCPDS card number 43-1023, thus signifying the authenticity and credibility of the bio-produced Nd<sub>2</sub>O<sub>3</sub> nanoparticles. 26,27 These nanoparticles have great potential, further highlighted by their distinctive structural characteristics and their projected crystallite size of 24 nm using the Debye-Scherrer formula. Moreover, the Nd<sub>2</sub>O<sub>3</sub> NP production process involves adding plant extract to increase crystallinity. 11 Wherein, bulk Nd2O3 NPs show bigger crystallite sizes and smaller pore sizes. The enhanced electron stream mitigation, refined crystalline characteristics, and greater charge separations driven by lattice strain are its unique properties, which make it possibly a dependable material with enormous potential for use in energy, optics, and catalysis.<sup>28</sup>

#### 3.2. FTIR analysis

The functional groups present in the Nd<sub>2</sub>O<sub>3</sub> NPs were characterized with FTIR spectroscopy over the spectrum range of 400 to 4000 cm<sup>-1</sup>, as shown in Fig. 3. Great attention was paid

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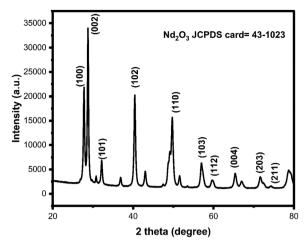


Fig. 2 XRD pattern of  $Nd_2O_3$  nanoparticles synthesized using green methods with a *Caryota urens* leaf extract.

to the wide Nd-OH vibration peak at 3335 cm<sup>-1</sup>, ascribed to water molecules absorbed on surface of the Nd<sub>2</sub>O<sub>3</sub> NPs, making it more reasonable for oxygen-hydrogen (O-H) bond stretching vibrations.<sup>29,30</sup> An intense signal appeared at 2452 cm<sup>-1</sup>, mainly due to the characteristic carbon atoms in the plant's bioactive compounds. The peaks showing at 1750 cm<sup>-1</sup> and 1409 cm<sup>-1</sup> were due to the surface chemistry and bonding configurations of Nd<sub>2</sub>O<sub>3</sub> NPs, unveiling the interactions of primary amine and carbon compounds found in plant biomolecules.<sup>31,32</sup> The detailed interactions between NPs and bioactive compounds from the plants reveal their surface characteristics and chemical interactions. The conversion of Nd3+ ions into O2- ions is prompted due to biochemical interaction with the Nd<sub>2</sub>O<sub>3</sub> NPs. The vibrational peak that appeared at 1059 cm<sup>-1</sup> is significant for nanomaterial formation and is known to be due to the asymmetric and bending vibrations of the Nd-O and Nd-O-Nd bonds.<sup>33</sup> The absorption band at 854 cm<sup>-1</sup> corresponds to the surface characteristics and functional groups of Nd<sub>2</sub>O<sub>3</sub> NPs.<sup>34</sup> A peak strongly depicted at 691 cm<sup>-1</sup> enables an intense understanding of

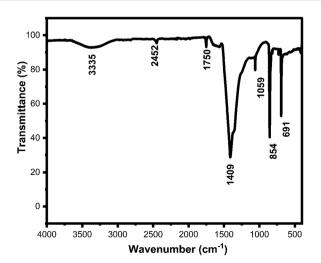


Fig. 3 FTIR spectrum of Nd<sub>2</sub>O<sub>3</sub> nanoparticles.

composition and structural features of NPs. No new peaks have appeared in the FTIR spectrum, confirming remarkable purity of synthesized Nd<sub>2</sub>O<sub>3</sub> NPs.<sup>35</sup>

#### 3.3. Optical properties of Nd<sub>2</sub>O<sub>3</sub> NPs

The optical properties of metal oxide constructions, specifically green-synthesized Nd2O3 NPs, were fully investigated using UV-DRS analysis, as shown in Fig. 4a, providing critical absorbance and bandgap spectrum information. The formation of these NPs, supported by a unique absorption edge around 210-280 nm in the UV-DRS spectra, involved reduction of Nd<sup>3+</sup> ions and stabilization of O<sup>2-</sup> ions. The absorption edge induced electron migration between energy bands, which resulted in significant color changes, with NPs exhibiting a pure milk-white color, confirming their effective synthesis. 36,37 For green-synthesized Nd<sub>2</sub>O<sub>3</sub> NPs, the defect analysis using Kubelka-Munk relationships, as shown in Fig. 4b, produced a bandgap value of about 3.5 eV. The large bandgap makes it easier for charge carriers to migrate and separate efficiently on NP surfaces and improves the ability of those particles to reduce and oxidize.38 The analysis provides insightful information about optical properties and defect features of NPs, potentially paving the way for their use in industries. To analyze the bandgap energy  $(E_g)$ , DRS was performed in a UV-Vis spectrophotometer with a wavelength ( $\lambda$ ) in the range of 200– 800 nm, and bandgap energy was determined using equation<sup>39</sup>

$$F(R) \to \frac{(1 - R_{\infty})2}{R_{\infty}} \tag{5}$$

$$hv = \frac{1240}{\lambda} \tag{6}$$

$$R = \frac{1}{A} \tag{7}$$

where F(R) is the Kubelka–Munk function,  $R_{\infty}$  is the reflectance (a.u.), hv is the incident photon energy (eV), and  $\lambda$  is the wavelength associated with maximum absorbance (nm).

#### 3.4. Chemical structure and morphology of Nd<sub>2</sub>O<sub>3</sub> NPs

The green synthesis of Nd<sub>2</sub>O<sub>3</sub> NPs is rigorously characterized in Fig. 5(a and b) and Fig. 6(a-c), revealing both structural properties using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) mapping, respectively. The particles stand out for having two main shapes: elongated-spherical and conjoint spherical, which suggests a variety of morphologies on their surfaces (as shown in Fig. 5(a and b)). The presence of plant phytochemicals during the green production process directly contributed to this unique combination of shapes. 40,41 With a focus on Nd and O, Fig. 6(a) shows weight percentages and energy spectrum of the components within the NPs. Nd dominates composition, making up a substantially higher percentage than oxygen. This is further shown in Fig. 6(b), which shows unequivocally that the concentration of Nd atoms in green-mediated Nd<sub>2</sub>O<sub>3</sub> NPs is three times higher than that of oxygen atoms. As shown in these NPs, the interaction of oxygen with metal components

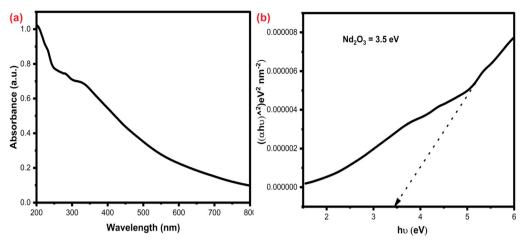


Fig. 4 UV-DRS (a) and bandgap (b) analysis of the Nd<sub>2</sub>O<sub>3</sub> nanoparticles.

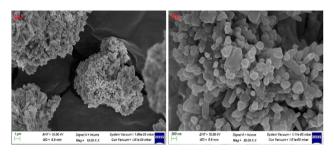


Fig. 5 FE-SEM images of the  $Nd_2O_3$  nanoparticles at different magnifications of 10.00kx (a) and 50.00kx (b).

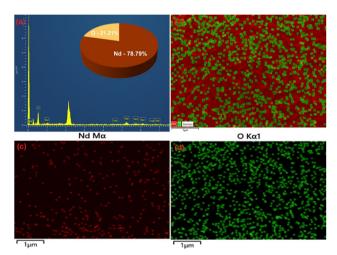


Fig. 6 EDX spectrum (c), elemental composition (d), and mapping of Nd<sub>2</sub>O<sub>3</sub> nanoparticles (e)-(g) synthesized using a leaf extract of Caryota urens.

has a significant effect. It successfully reduces agglomeration and ultimately improves the particles' general stability. The processes, such as bacterial inactivation and disintegration, multiply the efficacy of the NPs due to the oxygen enhancement in the green production process, retaining the electron trapping. The composition comprises large Nd atoms with oxygen atoms and quasi-spherical forms of the NPs resulting from Nd<sub>2</sub>O<sub>3</sub> NPs. The mapping results depicted in Fig. 6(a-c) confirm Nd and O distribution and spatial distribution of Nd and O enclosed in NPs is shown in Fig. 6a. Wherein, the neodymium and oxygen atoms hold one another and are scattered nearer and spectrum indicates the intriguing outcome of oxygen prevailing over neodymium in the NPs. This confirms the presence of a larger number of oxygen atoms than neodymium atoms in biosynthesized Nd<sub>2</sub>O<sub>3</sub> NPs. Understanding the NPs' structural features and characteristics is important in knowing the physical distribution of neodymium and oxygen.

#### 3.5. TEM analysis

TEM images of green-synthesized Nd2O3 NPs are shown in Fig. 7(a and b), unveiling morphological characteristics and particle size of synthesized Nd<sub>2</sub>O<sub>3</sub> NPs in C. urens leaf extract. The TEM images show elongated and conjoint spherical morphology. The elongated spherical shape at a magnification of 100 nm resulted in evenly distributed polydisperse NPs. The obtained particles in range of 50 nm magnification level view show that particles are agglomerated in an elongated spherical shape. These agglomerations are formed in Nd<sub>2</sub>O<sub>3</sub> NPs due to

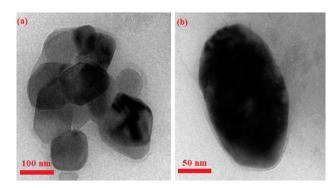


Fig. 7 TEM images of Caryota urens leaf extract-synthesized Nd<sub>2</sub>O<sub>3</sub> nanoparticles.

biochemicals present in plants.  $^{42,43}$  The X-ray diffraction (XRD) results are consistent with TEM results, wherein size of the NPs was found to be 25 nm. The broad bandgap associated with  $\mathrm{Nd_2O_3}$  NPs can be used to explain the polydisperse character of these biologically generated  $\mathrm{Nd_2O_3}$  NPs. The potential of these NPs for various applications, particularly in the context of materials science and advanced technologies, is highlighted by this thorough analysis of their morphology, size, and distribution. Therefore,  $\mathrm{Nd_2O_3}$  NPs in different mass proportions were confirmed by correlating the results of characterization techniques (XRD, FTIR, and SEM-EDX). The  $\mathrm{Nd_2O_3}$  NPs sample was used for photocatalytic heterogeneous application in pharmaceutical pollutants due to the narrow  $E_\mathrm{g}$  (3.5 eV) and increased light absorption during the heterogeneous photocatalysis process.

## 4. Evaluation of photocatalytic activity

Fig. 8(a-d) shows the photocatalytic breakdown of TC caused by visible light using green-synthesized  $Nd_2O_3$  NPs. Pharmaceutical pollutants can be more efficiently degraded by metal oxide-based photocatalysts. TC is prone to rapid degradation due to its interaction with high intensity light. The two powerful benzene rings that make up the molecular structure of TC are essential for its ability to bind and form bonds with other

chemical substances. Fig. 8 absorbance spectra, taken at 10minute intervals, show that light gradually dissociates the binding of TC as it passes through the TC solution and Nd<sub>2</sub>O<sub>3</sub> NPs. The Nd<sub>2</sub>O<sub>3</sub> NPs made via green synthesis demonstrated good catalytic activity, degrading TC by 92% in under 40 minutes. This effectiveness could be due to the Nd<sub>2</sub>O<sub>3</sub> NPs' broad bandgap, and capping effect of chemicals produced from plants, which regulate recombination processes and provide more host electrons that improve catalytic degradation. The photon energy is used for electrons' excitation in the valence band (VB) transition to the conduction band (CB). Defects are created in the VB during redox reactions. With breakdown of TC structure caused by this activity, superoxide (O<sup>2-</sup>), and hydroxyl radicals (OH<sup>-</sup>) are created. The increased surface area and active spots of Nd<sub>2</sub>O<sub>3</sub> NPs also prevent TC molecules from attaching to them. TC is broken down into harmless CO2 and H2O molecules thanks to the produced free radicals and Nd<sub>2</sub>O<sub>3</sub> NPs.

#### 4.1. Possible photocatalytic mechanism

During the photocatalysis, following reactions take place: Creation of electron–hole pairs upon visible light absorption by  $Nd_2O_3$ :

$$Nd_2O_3 + h\nu(visible) \rightarrow e^- + h^+$$
 (8)

TC molecules attach to the surfaces of Nd<sub>2</sub>O<sub>3</sub> NPs.

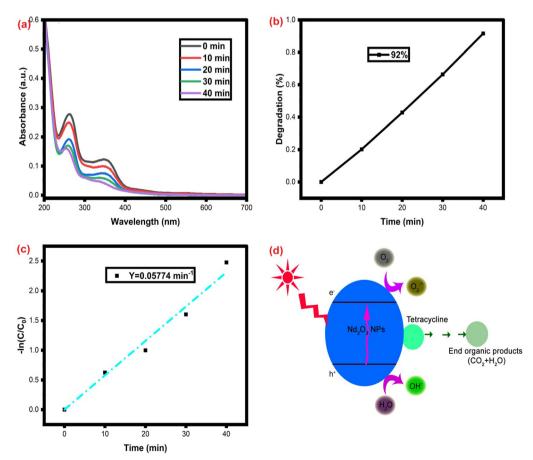


Fig. 8 Photocatalytic experiment of the Nd<sub>2</sub>O<sub>3</sub> nanoparticles against tetracycline.

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 Table 1
 Photocatalytic comparison table of different NPs with various antibiotics

Samples	Antibiotics	Molecular formula		Light	Time (min)	Degradation (%)	Ref.
$\mathrm{WO_3/g\text{-}C_3N_4/h\text{-}BN}$	TC	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH NH <sub>2</sub> OC OH OH Tetracycline	Visible light	60	81.4	44
CuO-Cu <sub>2</sub> O/GO	TC	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH NH <sub>2</sub> OC OH OH Tetracycline	Visible light	120	90	45
Fe₂O₃@PNH	TC	$C_{22}H_{24}N_{2}O_{8}$	H <sub>3</sub> C OH OH NH <sub>2</sub> OC OH OH Tetracycline	Visible light	120	90	46
$\mathrm{BiVO}_4$	Oxytetracycline	$C_{22}H_{24}N_2O_9$	OH OH OH OH OH	Visible	240	55	47
$\mathrm{BiVO}_4$	Oxytetracycline	$C_{22}H_{24}N_2O_9$	OH OH OH OH	Solar	240	83	48
${\rm AgCl/BiVO_4}$	Oxytetracycline	$C_{22}H_{24}N_2O_9$	OH OH OH OH	Visible	120	77	49
$\mathrm{BiVO}_4$	TC	$C_{22}H_{24}N_{2}O_{8}$	H <sub>3</sub> C OH OH OH NH <sub>2</sub> OC OH	Solar	240	72	50
${\rm Ti/BiVO_4}$	TC	$C_{22}H_{24}N_{2}O_{8}$	H <sub>3</sub> C OH OH NH <sub>2</sub> OC OH OH Tetracycline	Visible	180	60	51
g- $C_3N_4/BiVO_4$	TC	$C_{22}H_{24}N_{2}O_{8}$	H <sub>3</sub> C OH OH OH NH <sub>2</sub> OC OH	Visible	60	60	52
H <sub>2</sub> -BiVO <sub>4</sub>	TC	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH NH <sub>2</sub> OC OH OH Tetracycline	Visible	240	75	53

Table 1 (continued)

Samples	Antibiotics	Molecular formula		Light	Time (n	nin) Degrada	tion (%) Ref.
BiVO <sub>4</sub> /rGH-3	TC	$C_{22}H_{24}N_{2}O_{8}$	H <sub>3</sub> C OH OH OH OH OH OH Tetracycline	Visible	120	73	54
CuO/BiVO <sub>4</sub>	тс	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH OH NH <sub>2</sub> OC OH Tetracycline	Visible	50	28	55
${\rm BiVO_4/TiO_2}$	тс	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH OH NH <sub>2</sub> OC OH Tetracycline	Visible	60	73	56
$\mathrm{Nd}_2\mathrm{O}_3$	тс	$\mathrm{C}_{22}\mathrm{H}_{24}\mathrm{N}_2\mathrm{O}_8$	H <sub>3</sub> C OH OH OH NH <sub>2</sub> OC OH Tetracycline	Visible	40	92	[Present work]

$$TC + Nd_2O_3 \rightarrow TC-Nd_2O_3$$
 (9)

Electrons move from the CB of Nd<sub>2</sub>O<sub>3</sub> to the TC molecules that are adsorbed on its surface.

$$e^{-}(Nd_2O_3) \rightarrow TC-Nd_2O_3$$
 (10)

The TC molecules adsorbed on Nd<sub>2</sub>O<sub>3</sub> interact with the VB holes, and as a result, superoxide radicals formed.

$$h^{+}(Nd_{2}O_{3}) + TC-Nd_{2}O_{3} \rightarrow TC + Nd_{2}O_{3} + h^{+}$$
 (11)

$$O_2 + e^-(Nd_2O_3) \to O_2^{\bullet -}$$
 (12)

$$O_2^{\bullet -} + h^+(Nd_2O_3) \rightarrow HO_2^{\bullet}$$
 (13)

Continuous generation of superoxide and hydroxyl radicals through reactions with water molecules leads to the degradation of TC.

$$O_2 + e^-(Nd_2O_3) \to O_2^{\bullet-}$$
 (14)

$$O_2^{\bullet -} \rightarrow HO_2 \rightarrow HO_2^{\bullet} + OH^-$$
 (15)

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{16}$$

$$TC^{\bullet} + OH^{-} \rightarrow TC(H_2O + CO_2)$$
 (17)

Under visible light irradiation, photocatalytic degradation of TC by  $Nd_2O_3$  NPs involves several key steps: the generation of electron-hole pairs, adsorption of TC molecules onto the NP surfaces, transfer of electrons to these adsorbed molecules, and subsequent production of superoxide  $(O_2^{\bullet-})$  and hydroxyl radicals  $(OH^-)$  through reactions with holes and water molecules. These reactive radicals ultimately lead to breakdown of

TC into harmless byproducts. The degradation efficiency of Nd<sub>2</sub>O<sub>3</sub> NPs, synthesized through environmentally friendly methods, was evaluated using pseudo-first-order kinetics. The graphical representation in Fig. 8 illustrates degradation rate constant, showcasing the photocatalytic performance and durability of these green-synthesized NPs in TC degradation. Table 1 compares photocatalytic efficiency of various antibiotic drugs using different NPs and light sources. Each entry in Table 1 presents a specific nanoparticle composition, targeted antibiotic, type of light employed, duration of exposure, and the resultant degradation efficiency. Prominent compositions include WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/h-BN, CuO-Cu<sub>2</sub>O/GO, and Fe<sub>2</sub>O<sub>3</sub>@PNH, each showcasing high degradation percentages of TC under visible light within 60 to 120 minutes. Moreover, different variants of BiVO<sub>4</sub> composites exhibited varying efficiencies, with pure BiVO4 showing improved degradation under solar light compared to visible light. Conspicuously, the present work featuring Nd2O3 NPs displayed exceptional efficacy, achieving a remarkable 92% degradation of TC within a mere 40 minutes under visible light, surpassing the performance of all other tested photocatalysts. This superior performance can be attributed to Nd<sub>2</sub>O<sub>3</sub>'s efficient light absorption, effective charge separation, and high reactivity, facilitating the rapid degradation of antibiotics.

Mechanistically, photocatalysis involves the generation of electron-hole pairs upon light absorption, followed by reactive oxygen species (ROS) that degrade the antibiotic molecules. Substantially, the electron-hole pair generation and ROS formation optimal bandgap are suitable for efficient visible light absorption and catalyst performance, prompted by metal oxides.<sup>57</sup> The increasing charge separation efficiency and the

additional active sites by encapsulating carbon-based materials such as graphene oxide (GO) and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) enhance photocatalytic activity.<sup>58</sup>

Composite materials, including Ag/BiVO<sub>4</sub> and BiVO<sub>4</sub>/TiO<sub>2</sub>, exhibit synergistic effects, combining the properties of metal oxides with those of other materials to enhance light absorption, charge separation, and surface area, resulting in improved photocatalytic efficiencies.<sup>59</sup> The Nd<sub>2</sub>O<sub>3</sub> NPs remain important photocatalysts for breaking down many substances such as paracetamol, amoxicillin, ciprofloxacin, and TC. The study shows that Nd<sub>2</sub>O<sub>3</sub> NPs degrade TC more effectively under visible light than under UV exposure. This is especially important because visible light is more energy-efficient and environmentally friendly than UV light. The current study also describes the environmentally friendly manufacture of highly crystalline Nd<sub>2</sub>O<sub>3</sub> NPs using a plant extract and their superior photocatalytic activity for TC breakdown under visible light irradiation, achieving an efficiency of 92%.

## 5. Effect of Nd<sub>2</sub>O<sub>3</sub> NPs on bacterial cultures

The antibacterial efficacy of Nd2O3 NPs was analyzed using bacterial cultures i.e., S. aureus and E. coli Fig. 9(a and b). All the concentrations (25-100 µg mL<sup>-1</sup>) of Nd<sub>2</sub>O<sub>3</sub> NPs effectively inhibited the growth of both types of bacterial cells. However, increased growth inhibition was observed at 100 µg mL<sup>-1</sup>, and least bacterial growth inhibition was noticed at 25 μg mL<sup>-1</sup>. Therefore, this result, exhibited by increasing the Nd<sub>2</sub>O<sub>3</sub> NP concentration from 25 µg mL<sup>-1</sup> to 100 µg mL<sup>-1</sup>, affects the bacterial growth. The control antibiotic exhibits remarkable antibacterial activity against both bacterial cultures. Similarly, Nd<sub>2</sub>O<sub>3</sub> NPs prepared by the leaf extract of Andrographis paniculata exhibited excellent antibacterial activity against E. coli and S. aureus bacterial cultures. 55 Another report stated that Nd<sub>2</sub>O<sub>3</sub> NPs synthesized by calcination process also showed antibacterial potential of NPs against various bacterial cultures, including Micrococcus luteus, Staphylococcus aureus, Salmonella typhimurium, and Escherichia coli. 60 Possibly, the bacterial cell proliferation was controlled by oxonium ions discharged from the Nd<sub>2</sub>O<sub>3</sub> NPs.<sup>61</sup> Additionally, Nd<sub>2</sub>O<sub>3</sub> NPs of reactive oxygen species might be involved

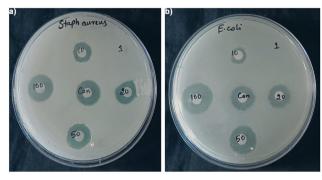


Fig. 9 Antibacterial activity of the Nd<sub>2</sub>O<sub>3</sub> nanoparticles against S. aureus

in oxidative stress in bacterial cells.<sup>62</sup> This results in malfunction of cellular biomolecules and finally leads to the ruin of cells.

#### 6. Conclusion

In summary, a novel supramolecular assembly of green-mediated Nd<sub>2</sub>O<sub>3</sub> NPs was assessed by their application in sustainability threats and biomedical applications. Further thermal treatment under a static air atmosphere changes the Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with the O atom. The oxygen defects give Nd<sub>2</sub>O<sub>3</sub> the highest stability, as confirmed by UV calculations. The resulting Nd2O3 photocatalyst demonstrates outstanding vis. light harvesting, charge carrier transition, and optical properties. In addition, it shows the highest electron density at the CB edge, which makes it a strong reduction photocatalyst. This result was further evidenced by more OH generation than in the control experiments. Furthermore, Nd<sub>2</sub>O<sub>3</sub> NPs exhibited excellent photocatalytic performance in the degradation of TC under visible light irradiation within 40 min. The Nd<sub>2</sub>O<sub>3</sub> NPs prepared by the C. urens plant extract showed their effective potency in the growth of bacterial cultures, E. coli and S. aureus. Therefore, Nd2O3 NPs emerge as promising candidates to meet the sustainable development goals.

The green-mediated synthesis of Nd<sub>2</sub>O<sub>3</sub> NPs showed encouraging photocatalytic and antibacterial efficacy; nevertheless, many hurdles arose during the investigation. A significant challenge was attaining uniformity in NP morphology and size distribution due to the diversity in the phytochemical makeup among different leaf batches. Seasonal and geographical differences in plant bioactive components affected the reducing and stabilizing efficacy of the extract, hence influencing NP homogeneity. Moreover, regulating the aggregation of NPs was a problem, particularly during the drying and calcination phases, which might influence surface area and the availability of active sites. A third limitation was the limited tunability of the bandgap; although a bandgap of 3.5 eV was attained, additional optimization is required for improved visible-light absorption. Furthermore, although there are potential antibacterial effects, the precise molecular processes by which ROS formed by Nd<sub>2</sub>O<sub>3</sub> disrupt bacterial cells remain inadequately elucidated and necessitate additional mechanistic investigations. Ultimately, enhancing the synthesis process for industrial applications is a difficult due to the necessity for meticulous regulation of green synthesis parameters and extract preparation conditions. Confronting these issues in forthcoming research will be essential for converting laboratory-scale discoveries into viable, scalable environmental and medicinal products.

#### Conflicts of interest

There are no conflicts to declare.

# Data availability

The data that support the plots in this paper and other findings of this study are available from the corresponding author upon

reasonable request. Financial support: Funded by Next Generation EU for PRIN 2022 PNRR: M4.C2.1.1 "Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN)" - Prot. P2022EWZFB -Unitised Regenerative Fuel Cell with Anion Exchange Membrane as Electrolyte (UNIRE), CUP B53D23025680001.

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