SYNTHESIS, CHARACTERIZATION, AND PHOTOCATALYTIC PROPERTIES OF LANTHANIDE-DOPED HEMATITE NANOPARTICLES

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ABSTRACT
This work aims to develop a highly efficient UV light-induced photocatalyst based on Sm-doped Hematite (α-Fe₂O₃) nanoparticles (NPs). Sm-doped α-Fe₂O₃ NPs were synthesized via a straightforward co-precipitation technique and subsequently analyzed for their morphological, structural, and functional attributes. Examination under scanning electron microscopy revealed the formation of NPs, often clustered in small aggregates. Transmission electron microscopy measurements indicated a NPs size range of approximately 18 nm. X-ray diffraction analysis confirmed octahedral-shaped with the crystalline nature and geometry of the synthesized NPs, with a determined crystallite size of 13 nm. The photocatalytic efficacy of the Sm-doped α-Fe₂O₃ catalysts was evaluated through their ability to degrade Rhodamine B (RhB) under solar light exposure. Remarkably, Sm-doped α-Fe₂O₃ exhibited outstanding degradation performance, achieving a 96.82% degradation of RhB within 120 minutes under specified conditions ((RhB) = 20 ppm; (catalyst) = 15-25-50 mg/L; pH = 7; T = 30 °C). The degradation process followed pseudo-first-order kinetics. This exemplary photocatalytic activity suggests that the synthesized NPs hold significant potential for the efficient removal of organic pollutants from industrial wastewater.

Keywords: Hematite nanoparticles; Lanthanide doped; Photocatalytic; X-ray diffraction, SEM,EDX,TEM

INTRODUCTION
The degradation of environmental components has recently emerged as a global crisis, demanding urgent action. Contaminated water presents a significant threat to ecosystem equilibrium, with its quality steadily declining due to the widespread use of chemicals by human activities [1]. Regrettably, despite advancements in science and technology, recent studies have revealed that 11% of the global population lacks access to clean drinking water. Industrial effluents often contain non-biodegradable organic pigments that can persist under adverse conditions [2]. These dyes are prone to various physicochemical and photochemical reactions, leading to the formation of numerous secondary compounds that can enter the food chain, causing severe illnesses in humans. Consequently, numerous strategies are under investigation in the quest for effective wastewater management solutions. Various commercially available equipment and techniques exist for removing organic dyes from wastewater [3]. Among these methods, modern photocatalysis stands out due to its distinctive mechanism of action and production of less harmful by-products. During the photocatalytic process, free radical species (such as OH and O₂⁻) are generated on the valence and conduction bands through energy utilization [4]. These unpaired electrons initiate redox reactions in the water, leading to the breakdown of organic dyes into harmless byproducts such as CO₂ and H₂O. Photocatalysts based on lanthanide metal oxides have been utilized for the past three decades. Studied by Fujishima and Honda in the 1990s as a photocatalyst for water purification, α-Fe₂O₃ has emerged as a promising visible-light-driven photocatalyst due to its affordability, abundance, non-toxicity, high stability, and favorable bandgap (Eg = 2.2 eV) [5]. However, its practical use is hindered by its limited total diffusion length (2-4 nm), short excitation lifetime, and restricted light penetration depth. Various strategies have been investigated to improve the suitability of hematite as a photocatalytic material, including nanostructure engineering to improve light absorption, diffusion length, and reaction sites, as well as combining it with other materials such as carbon, metals, and semiconductors to enhance carrier transport [6-7]. Among these approaches, intentional defect engineering has been shown to be a promising technique for improving performance.

Materials with unique physicochemical properties hold great potential for designing efficient photocatalysts. Among the various defects, oxygen vacancies in α-Fe₂O₃ NPs have been investigated extensively, with methods including heat treatment, plasma treatment, ball-milling, and aerosol-assisted chemical vapor deposition [8-11]. Importantly, the synthesis methods significantly influence the generation rate, distribution, role, and behavior of these vacancies. Co-precipitation synthesis stands out as one of the simplest and most cost-effective methods.
Understanding the generation mechanism and behavior of oxygen vacancies in this process is crucial for practical commercialization. In co-precipitation synthesis, FeOOH is initially formed, followed by the transformation to $\alpha$-Fe$_2$O$_3$. The incorporation of lanthanide metals such as La, Ce, Pr, Nd, Gd, Pm, Eu, etc., into $\alpha$-Fe$_2$O$_3$ NPs has been reported to enhance photocatalytic activity [12-15]. For instance, Sm-doped $\alpha$-Fe$_2$O$_3$ NPs synthesized via the co-precipitation method showed improved photocatalytic characteristics, attributed to its higher electron trapping capacity and enhanced oxidation-reduction of organic dyes. Substitution doping of Sm$^{3+}$ at the Fe$^{3+}$ sites in $\alpha$-Fe$_2$O$_3$ NPs has also been explored, leading to alterations in band gap and morphology, thereby improving photocatalytic activity.

In our study, we synthesized Sm-doped $\alpha$-Fe$_2$O$_3$ NPs through thermally induced polymorph transformation. Prior to this, NPs were synthesized using the co-precipitation method. The NPs underwent characterization to assess their structural, optical, and surface chemical properties. Subsequently, their photocatalytic efficiency was evaluated for the decolorization of toxic Rhodamine B (RhB) dye under UV-irradiation.

2. EXPERIMENTAL
2.1 Materials and Synthesis
The synthesis of $\alpha$-Fe$_2$O$_3$ NPs was conducted using the co-precipitation method. Solutions of Ferric chloride hexahydrate (FeCl$_3$•6H$_2$O, 99% purity, Sigma-Aldrich) and Samarium(III) chloride (SmCl$_3$•6H$_2$O, 99% purity, Sigma-Aldrich) precursors were prepared separately in water at room temperature, with a molar ratio of 1:2, respectively. These precursor solutions were then mixed under continuous magnetic stirring. After 1 hour of stirring, 1M solution of Polyvinylpyrrolidone (PVP) precipitating agent and NaOH was added dropwise while monitoring the pH of the solution. Stirring was halted when the solution reached a pH of approximately 11, and the mixture was allowed to settle undisturbed for 15 minutes. This process resulted in the formation of black precipitates, which were collected by filtration and washed thoroughly with distilled water and ethanol. The black precipitates were then dried in an oven at 80 °C for 12 hours to obtain $\alpha$-Fe$_2$O$_3$ NPs.

2.2 Characterization
The pure and Zr-doped $\alpha$-Fe$_2$O$_3$ NPs underwent characterization using various techniques. X-ray diffraction (XRD) analysis of the powder samples was performed using a Bruker X-ray diffractometer with Cu Ka ($\lambda=1.54$ Å) monochromatic wavelength. Vibrational spectroscopy was conducted using a Fourier-transform infrared (FTIR) instrument from Perkin Elmer. Powder samples were prepared into pallets with KBr, and spectra were recorded in the wavenumber range of 4000 to 400 cm$^{-1}$ in transmission mode. Surface morphology and particle size were examined using a field emission scanning electron microscope (FE-SEM), specifically the ZEISS Supra 55 VP model. Additionally, transmission electron microscopy (TEM) analysis was carried out using a JEOL 1010 instrument from Tokyo, Japan.

2.3 Measurement of Photocatalytic activity
A study employing photocatalysis was conducted in a custom-built reactor equipped with a magnetic stirrer and a UV lamp. The photocatalytic activities of synthesized Sm-doped $\alpha$-Fe$_2$O$_3$ NPs were investigated for the degradation of (RhB) dye solution under illumination from a 125 W (UV-C, 254 nm) Mercury lamp (Phillips). In the experimental setup, different concentrations (15-25-50 mg) of the photocatalyst were added to 100 ml of a 20 ppm dye solution. At regular intervals of 12 minutes, approximately 6 ml of the irradiated solutions were extracted, and the absorption spectra of the solutions were analyzed to monitor the photocatalytic activity.

3. RESULTS AND DISCUSSION
3.1. Structural analysis
X-ray powder diffraction was employed to examine the structure and phase stability of Sm-doped $\alpha$-Fe$_2$O$_3$ NPs. The powder samples revealed a crystalline structure, as depicted in Fig. 1. Based on the JCPDS Card No. 33-0664 [17], all observed peaks could be indexed in accordance with the predicted rhombohedral (hexagonal) structure of doped $\alpha$-Fe$_2$O$_3$ NPs (space group: R-3c) with specific lattice parameters. The diffracting peaks of all prepared samples were evident within the 2$\theta$ range, with corresponding miller indices such as (012), (220), (104), (113), (111), (024), (116), (018), (214), and (300) respectively. The uniform intensities observed across the peaks can be attributed to the consistent annealing temperature used during sample preparation, which directly influences the sample's crystallinity and charge mobility. No observable peak shifts were noted across the XRD patterns, consistent with previous findings [18]. This observation suggests that the dopants had no significant impact on the structure of the $\alpha$-Fe$_2$O$_3$ NPs.
The crystallite size (D) was determined using the Debye-Scherrer formula as shown in Equation 1.

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

The Debye-Scherrer formula utilizes a factor (K = 0.9), representing the Scherrer constant, alongside the wavelength (\(\lambda\)) of Cu K\(\alpha\), the Full Width at Half Maximum (FWHM) denoted by \(\beta\), and the diffracting angle (\(\theta\)).

The analysis of XRD data revealed an average crystallite size (D) of 13.44 nm, interplanar spacing (d) of 2.6223, lattice parameters (a=b) of 5.012, lattice parameter (c) of 13.71, volume (V) of 292.89, dislocation density (\(\delta\)) of 0.00630, strain (\(\varepsilon\)) of 0.00949, and crystallinity of 94.419%. This indicates that the size of Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs decreases due to an increase in nucleation center density in the doped samples. This finding aligns with previous research on Pt-Ru doped hematite NPs [19]. Studies conducted by further support this observation, suggesting that the decrease in crystallite sizes with an increase in dopant concentration results from enhanced nucleation of particles in the host sample [20].

**Fig. 1.** XRD pattern of hematite crystal lattices of Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs

### 3.2. Functional Group Analysis

FTIR analysis was conducted to determine the likely presence of reducing and stabilizing biomaterials in the fungal biomass extract. The resulting FTIR spectrum displayed several absorption bands that aligned with the functional groups of the Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs, as illustrated in Figure 2. Various absorption peaks were observed, including those centered at 3425, 2928, 2429, 1620, 1384, 1076, 461, and 594 cm\(^{-1}\), which were attributed to O–H stretching vibrations, C=O stretching vibrations, C–O stretching vibrations, and the bending vibration of C–OH. The peak at 2928 cm\(^{-1}\) indicated the C–H asymmetric and symmetric stretching vibrations of the methyl group [21]. Additionally, a peak at 1635 cm\(^{-1}\) could be attributed to the C=O stretching vibration band of polyphenol chemicals present in the PVP, which acted as a stabilizing and capping agent. Bands observed at 918-1110 and 1383 cm\(^{-1}\) were associated with the stretching vibration of C–O and polyphenol compounds, along with in-plane bending vibrations of OH in phenols. Furthermore, peaks at 459 and 582 cm\(^{-1}\) corresponded to Fe–O stretching vibrations. Peaks in the 500-1000 cm\(^{-1}\) wavelength range mainly originated from metal–oxygen group bonding [22], confirming the production of \(\alpha\)-Fe\(_2\)O\(_3\) NPs.

**Fig. 2.** FTIR spectrum of the developed synthesized Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs

### 3.3. Morphology Analysis

SEM and EDX analyses were conducted to assess the morphology and chemical composition of the Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs. In Figure 3a, fine grains with irregular shapes and some agglomeration were observed, indicating the presence of \(\alpha\)-Fe\(_2\)O\(_3\) NPs. Figure 3b displays the EDX spectrum of \(\alpha\)-Fe\(_2\)O\(_3\) NPs, detecting peaks corresponding to Fe and O elements, confirming the high purity of the synthesized NPs [23]. Furthermore, TEM investigation was employed to examine the morphology and size of the Sm-doped \(\alpha\)-Fe\(_2\)O\(_3\) NPs. TEM micrographs revealed octahedral-shaped particles evenly distributed without significant aggregation (Figure 4a). The Histogram image demonstrated well-dispersed particles, with an average diameter of approximately 18.32 nm, determined using ImageJ software (Figure 4b). These findings are consistent with previous studies. For instance, research by synthesize spherical \(\alpha\)-Fe\(_2\)O\(_3\) NPs with an average size of 70 nm [24]. Additionally, spherical \(\alpha\)-Fe\(_2\)O\(_3\) NPs ranging in size from 20 to 80 nm have been effectively manufactured using a similar approach [25].
3.4. Photocatalytic Activity Study
The photocatalytic activity of the α-Fe₂O₃ NPs for degrading methylene blue dye under sunlight irradiation was assessed. The degradation of RhB dye under UV-light irradiation was also observed. In the presence of the catalyst, the intensity of the peak at 550 nm decreased, and complete degradation was observed after 120 minutes. Figure 5 illustrates the photocatalytic activity. The photodegradation efficiency of the Sm-doped α-Fe₂O₃ NPs, as depicted in Figure 5a, indicates that 96% of the dye decomposed after 120 minutes of irradiation. Equation 2 was utilized to calculate the dye degradation percentage (%):

\[
\text{% degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

(2)

Co represents the initial absorption of the solution, while Ct represents the final absorption of the solution. The photodegradation reaction data can be described well by pseudo-first-order reaction kinetics, given by Equation 3, and Shown in Figure 5b.

\[
\ln \frac{C_0}{C} = kt
\]

(3)
The pseudo-first-order reaction rate constant (k) is determined by the concentrations (Co and C) at the beginning and at a specific time, respectively, with t representing the radiation exposure time. Table 1 outlines the calculated percentage degradation, rate constant, and regression coefficient for doped α-Fe₂O₃ NPs. Doped α-Fe₂O₃ NPs based nanoplatforms exhibit robust photocatalytic capabilities, along with non-toxicity, biocompatibility, and cost-effectiveness, suggesting their potential to replace traditional dye remediation techniques [26]. Nanoplatforms designed for wastewater treatment, emphasizing photocatalytic properties and environmentally friendly chemistry, are essential. Their exceptional chemical and thermal reliability, ability to absorb visible light, non-toxicity, abundance, and environmental friendliness render them valuable as photocatalysts for pollutant degradation [27].
Fig. 5. (a) Degradation percentage and (b) Photodegradation kinetics of synthesized doped α-Fe2O3 NPs for RhB dye

Table 1. % degradation, rate constant, and regression coefficient of synthesized Sm-doped α-Fe2O3 NPs for RhB dye

<table>
<thead>
<tr>
<th>Method of Synthesis</th>
<th>Concentrations (mg)</th>
<th>Degradation (%)</th>
<th>Rate constant (min⁻¹)</th>
<th>Regression coefficient (R²)</th>
</tr>
</thead>
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<td>15</td>
<td>90</td>
<td>0.0079</td>
<td>0.93043</td>
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<td></td>
<td>25</td>
<td>92</td>
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<td></td>
<td>50</td>
<td>96</td>
<td>0.0091</td>
<td>0.98523</td>
</tr>
</tbody>
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When electrons in Sm-doped α-Fe2O3 are excited to move from the valence band to the conduction band when UV light equal to or higher than its band gap energy is absorbed. In the conduction band, this action releases free electrons and leaves holes in the valence band. Water and oxygen molecules stick to the catalyst's surface, α-Fe2O3 NPs. The valence band's positive holes then start the oxidation of OH⁻ ions or water molecules at the catalyst surface, which produces strong oxidizing agents called •OH radicals [28]. Following their reaction with RhB dye, these hydroxyl radicals produce CO₂ and H₂O [29]. At the same time, molecular oxygen adsorbed onto the catalyst surface quickly absorbs the electrons that are already there where they undergo reduction to produce anions of superoxide radical (O₂⁻). The superoxide radical anion's oxidation potential enables it to react with the RhB dye, producing CO₂ and H₂O in the process [30]. Moreover, the findings from scavenging experiments highlight the crucial involvement of reactive oxygen species (ROS) in the photocatalytic breakdown of organic pollutants. This suggests that doping Sm not only enhances the inhibition of carrier charge recombination but also provides an additional active site response.

4. CONCLUSION

In this study, Sm-doped α-Fe2O3 NPs were effectively biosynthesized. Various analytical techniques including FTIR spectroscopy, XRD, SEM, and TEM were employed to characterize the synthesized Sm-doped α-Fe2O3 NPs. The doped α-Fe2O3 NPs exhibited spherical morphology for the α-Fe2O3 phases and rhombohedral crystal lattices, with crystallite sizes measured at 13.44 nm, confirming their existence and crystallinity via XRD analysis. FTIR spectra analysis identified the active molecules responsible for the inhibition and stabilization of the NPs, with characteristic peaks of the Fe-O bonding observed at 459 and 582 cm⁻¹. The energy dispersive X-ray spectroscopy (EDX) spectrum confirmed the presence of oxygen, samarium, and iron in the synthesized material. TEM imaging further confirmed the octahedral form of the Sm-doped α-Fe2O3 NPs, with a size range of 18.32 nm. These doped α-Fe2O3 NPs exhibit promising photocatalytic activity for degrading dyes in wastewater treatment, owing to their facile synthesis in large quantities using readily available iron precursors. Industries may benefit from large-scale production of NPs using green techniques for dye removal from various wastewaters. Moreover, the synthesized α-Fe2O3 NPs demonstrated high photocatalytic effectiveness, degrading 96.82% of Rhodamine B (RhB) dyes under 120 minutes of light exposure. These findings underscore the high potential of Sm-doped α-Fe2O3 NPs for dye degradation, suggesting their future application in mitigating hazardous dyes in contaminated water. Additionally, the production process of NPs is rapid, cost-effective, and environmentally benign.
ACKNOWLEDGMENTS
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CONFLICT OF INTEREST
The authors declare no competing financial interest.

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