

3D Cerium Doped In_2S_3 Immobilised Hydrogel for Efficient Photocatalytic Sulphamethoxazole Degradation And H_2O_2 Production-Mechanistic Insights and Applications

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3D Cerium Doped In₂S₃ Immobilised Hydrogel for Efficient Photocatalytic Sulphamethoxazole Degradation And H₂O₂ Production- Mechanistic Insights and Applications

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Abstract

With the increasing presence of pharmaceutical contaminants in aquatic ecosystems, there is need for the development of a sustainable method of wastewater treatment through photocatalytic oxidation. In this study, an effective cerium-doped indium sulfide (Ce-InS) hydrogel photocatalyst was developed that could concurrently degrade sulfamethoxazole (SMX) and produce photocatalytic hydrogen peroxide. For this purpose, Ce-doped In₂S₃ was loaded onto a hydrogel to enhance the performance of the material in terms of charge separation, light absorption and stability. Characterization studies on the physical, structural, morphological, and optical properties of the synthesized materials confirmed the successful synthesis of the Ce-InS hydrogel with a porous structure, uniform elemental composition, reduced electron-hole pair recombination and lowered optical band gap from 1.90 eV (powder form) to 1.44 eV (hydrogel). The photocatalytic degradation experiments showed good degradation efficiency with a value of about 91% achieved at the degradation of 10 ppm SMX under the visible-light condition. It is important to note that the degradation efficiency was enhanced from 73% to 91% by increasing the catalyst concentration (5-15 beads). At the same time, the increasing SMX concentration from 10 to 30 ppm resulted in the degradation efficiency decrease from 91% to 56%. The radical scavenging experiment confirmed that the hydroxyl radicals(•OH) were the main species responsible for the degradation process. Moreover, it was found that the Ce-InS hydrogel (90%) provided better results than the Ce-InS powder (77%) and pristine In₂S₃ (60%). In addition to achieving 91% SMX degradation, the Ce-InS hydrogel generated a maximum H₂O₂ concentration of **190 μM**, highlighting its dual-functionality as an efficient photocatalyst for simultaneous pollutant degradation and sustainable oxidant production under visible-light irradiation.

Keywords: Photocatalysis, Indium Sulphide, Hydrogel, Wastewater treatment, H₂O₂ Production

1. Introduction

Water pollution is one of the foremost environmental problems of the twenty-first century because of the fast pace of industrialization, urbanization, and population increase. There are large amounts of organic pollutants, drug residues, dyes, pesticides, and heavy metals being regularly released into water bodies, resulting in severe hazards to the environment and human beings [1,2]. There are drawbacks associated with conventional wastewater treatment techniques like adsorption, membrane separation, coagulation, and biodegradation processes that include partial purification of water, costliness, secondary pollution, and inefficiency against persistent organic compounds. Thus, the search for environmentally friendly and energy efficient technologies for purifying wastewater has become a critical research issue worldwide.

Various advanced oxidation processes have emerged over time, but semiconductor photocatalysis has gained much attention because of its potential in environmental purification and renewable energy conversion. The process makes use of sunlight to create electron-hole pairs in semiconductors, thereby creating reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\bullet\text{O}_2^-$) singlet oxygen ($^1\text{O}_2$) etc [3–5]. Such reactive species help in the degradation of various types of organic compounds to form simple compounds, such as carbon dioxide (CO_2) and water (H_2O). As compared to traditional methods, photocatalysis is advantageous in terms of mild conditions, lower energy requirements, no secondary pollution, and using abundant sources of solar energy.

One of the most valuable green oxidants is hydrogen peroxide (H_2O_2), and it has found diverse applications in environmental cleanup, chemical syntheses, pulp bleaching, textiles processing, sterilization of hospital equipment, and wastewater treatment. The demand for H_2O_2 will continue to grow due to its environmentally friendly decomposition into water and oxygen without any generation of toxic byproducts. Industrially, H_2O_2 is mainly prepared using the anthraquinone oxidation route that involves a significant amount of energy consumption, sophisticated equipment, toxic organic solvents, and centralized production units. In this regard, there has been extensive work towards the development of decentralized, sustainable, and solar-based production of H_2O_2 using photocatalysis through the selective water oxidation routes [6].

In terms of emerging water pollutants, pharmaceutical chemicals have been identified as one of the key pollutants of the environment due to the continuous release, persistence, and biological nature of the substances. Sulfamethoxazole (SMX), which belongs to the category of sulfonamide antibiotics and is being used extensively by people across the world, is often found in surface water, groundwater, and municipal wastewaters and even drinking water because of its extensive use and inefficiency of the conventional wastewater treatment plants to remove them from the waters[7]. Persistence of SMX in the aquatic ecosystem results in the spread of antibiotic-resistant bacteria and antibiotic resistance

genes, posing serious threat to both the environment and human health. Additionally, SMX is very stable chemically and biologically resistant and therefore difficult to degrade [8].

Photocatalytic processes rely heavily on the inherent characteristics of semiconducting photocatalysts such as light absorption capacity, charge carrier separation ability, band configuration, surface-active sites, and chemical stability. Several types of semiconducting materials such as TiO_2 , ZnO , BiVO_4 , Bi_2WO_6 , $\text{g-C}_3\text{N}_4$, CdS , and metal sulfides have been studied for the application of wastewater treatment and H_2O_2 production using photocatalysis[9–13] . Out of all of these semiconductors, indium sulfide (In_2S_3) has been identified as a potential photocatalyst. Indium sulfide is a visible-light-sensitive semiconductor that has an optimum band gap, chemical stability, non-toxicity, and favorable electronic configuration. However, due to fast recombination of photogenerated electron-hole pairs, surface-active sites, and poor charge carriers mobility, the performance of pristine In_2S_3 is greatly reduced[14].

Elemental doping has emerged as an efficient way of addressing these inherent drawbacks of semiconductor photocatalysts. The incorporation of proper dopant ions in the crystal lattice enables tailoring the electronic structure, controlling the band gap energy, creating defects, improving visible light absorption, facilitating charge separation, and increasing the surface catalytic properties. Rare earth metal ions have gained significant attention due to the unique electronic configurations and oxidation states, as well as the high density of defect chemistry. One such example is cerium (Ce) ion, which is capable of incorporating oxygen vacancy defects, trapping electrons, preventing charge recombination, and increasing the rate of charge transfer at interfaces due to the reversibility of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple and oxygen storage capacity [15].

In recent times, hydrogel assisted photocatalysis systems have been developed as a novel approach to improve the effectiveness and application prospects of photocatalytic processes. The hydrogels can be defined as 3D polymeric networks that show good absorbent properties, have plenty of functional groups, show high mechanical strength and have adjustable porosity. These polymers can be synthetic polymers such as acrylamide or biopolymers like carboxymethyl cellulose, chitosan, sodium alginate etc in which photocatalyst is immobilised to increase active sites, reusability and efficiency [16–19]. Due to these features, hydrogels allow for the homogeneous distribution of nanoparticles of the photocatalyst, inhibit their agglomeration, increase the adsorption of pollutants, accelerate mass transfer and offer additional reaction interfaces. In addition to these, hydrogel based photocatalysts demonstrate better recyclability, structural stability and ease of separation than typical powder photocatalysts and hence are highly promising for practical wastewater treatment applications.

In this current study, Ce-modified In_2S_3 -based photocatalyst is fabricated via a facile synthesis method for wastewater treatment and visible light-driven H_2O_2 production simultaneously. Introduction of Ce within the In_2S_3 structure would tune the electronic property, facilitate visible light harvesting, and improve the separation and transportation of photogenerated charge carriers, in addition to generating

numerous catalytically active sites. Besides, the use of hydrogel matrix would ensure uniform distribution of the catalyst, stability, as well as pollutant absorption, thus optimizing the photocatalytic activity of the catalyst. Sulfamethoxazole (SMX) has been chosen as a model organic pharmaceutical pollutant to determine the degradation efficiency of the newly developed photocatalyst. Photocatalytic H_2O_2 production ability, reaction pathway, generated reactive oxygen species (ROS), charge transfer dynamics, and stability of the novel catalyst have been thoroughly characterized. This study demonstrates an efficient method for designing rare earth metal-doped In_2S_3 -based hydrogel photocatalysts for wastewater purification and H_2O_2 production using sunlight simultaneously.

2. Materials and Methods

2.1. Materials and Reagents:

All the chemicals and reagents are mentioned in the supplementary file.

2.2. Preparation of Ce doped Indium sulphide:

54 mg of Cerious nitrate hexahydrate is taken and mixed with 10 ml ethanol in a beaker. It is then kept on the stirrer for 30 minutes with 30 ml of water added to the beaker. 2 gm of Indium sulphide is added to the beaker and transferred to the hydrothermal autoclave. The hydrothermal is then put inside the oven for around 24 hours. The sample is then allowed to settle down for around 10-15 minutes. The liquid above the sediments (powder) is taken out and the powder is put in a petri dish to heat for few more hours at 60-70 degree Celsius. The material is then scared out to obtain the final powdered product.

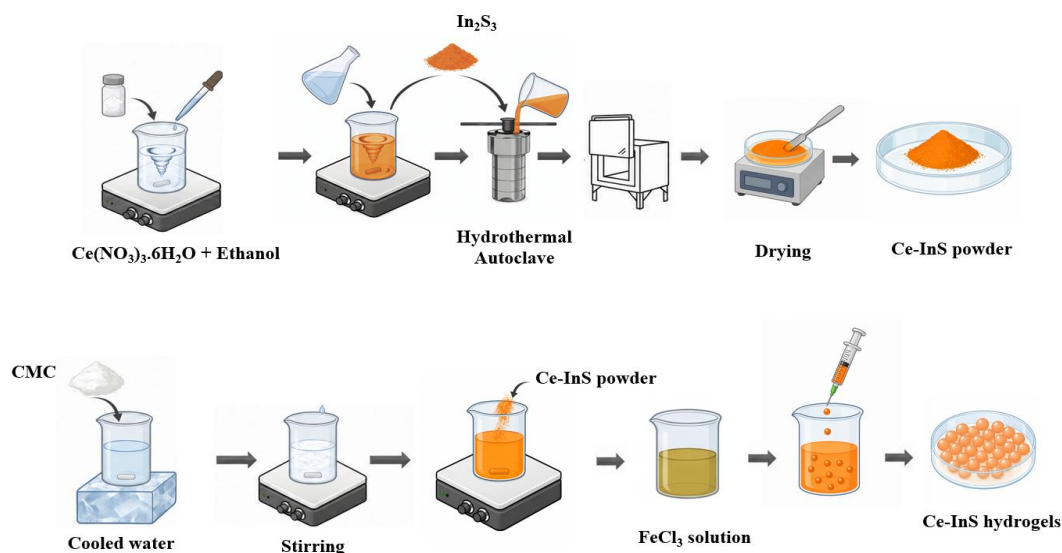


Fig 1: Preparation of Ce-InS Hydrogels

2.3. Preparation of Ce doped Indium sulphide hydrogels:

At first 60 ml of water is kept for cooling for 10-15 minutes and then 2.5 gm of CMC is added to the cooled water. The beaker is put into the stirrer for 15 minutes with 20 ml extra water to it. 1 gm of the

prepared material is taken into the beaker and mixed thoroughly. 0.2 M of FeCl_3 (3.22 gm) in 100 ml is taken in a beaker. After it has become a sticky form of mixture, then with the help of a syringe tiny spherical particles of the mixture are put into the FeCl_3 solution. The FeCl_3 solution with particles is put inside the fridge for 24 hours and the final hydrogels are then obtained.

3. Results and Discussion

Crystal structures of Ce-InS powders and Ce-InS hydrogels were analyzed using X-ray diffraction (XRD) and are shown in Fig. 2(a). It is clear that there are distinct diffraction peaks appearing at 2θ equal to about 27.5° , 33.3° , and 47.9° for Ce-InS powder indicating the high crystallinity of the material formed [20]. Well-defined and sharp diffraction peaks are indicative of the well-crystallized and well-organized structure of the Ce-doped In_2S_3 . However, XRD pattern of Ce-InS hydrogels shows a broad diffraction halo at low diffraction angle along with some weak peaks present at 31.9° and 45.7° . The broad peak can be seen in amorphous polymers while weak crystalline peaks confirm that crystalline Ce-InS particles are entrapped in the hydrogel matrix. Decrease in diffraction peak intensity after the formation of hydrogel is due to the fact that particles of photocatalyst are trapped in three-dimensional polymeric matrix, thus reducing the overall crystallinity without any change in the crystalline phase of Ce-InS[13].

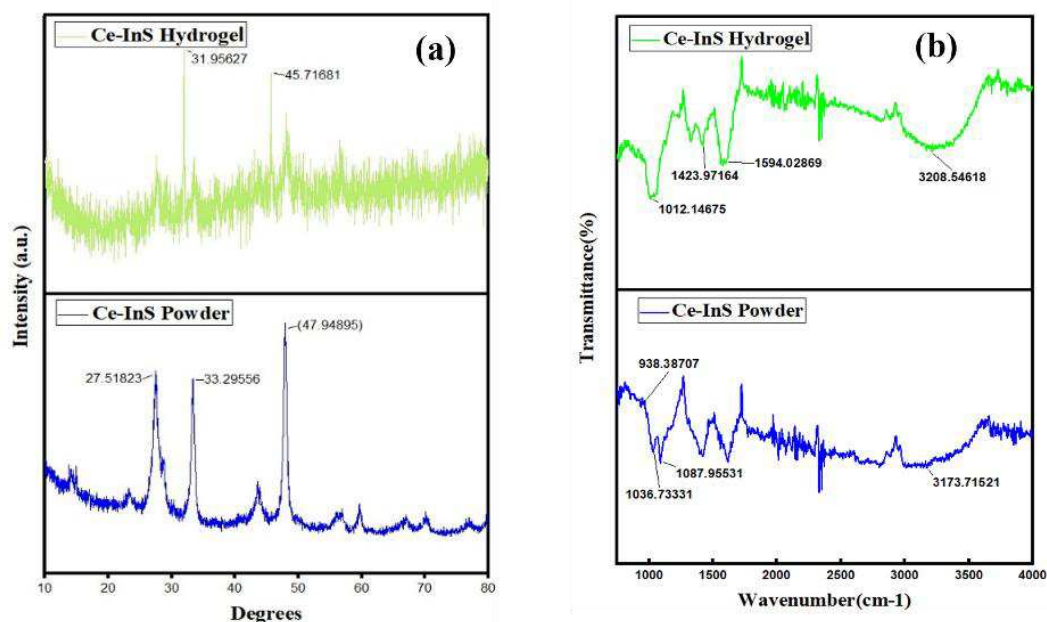


Fig 2: (a) XRD & (b) FTIR of Ce-InS and Ce-InS Hydrogel

Further information on the functional groups of the Ce-InS powder and Ce-InS hydrogel was provided by the Fourier transform infrared spectroscopy (FTIR) analysis, as presented in Fig. 2(b). It is observed that both samples contain a wide peak at the region of $3173\text{--}3208$ cm^{-1} which is related to the stretching

vibration of O-H and N-H functional groups [21]. Moreover, characteristic peaks appearing between 1012 and 1087 cm^{-1} can be associated with the C-O stretching vibrations and 938 cm^{-1} for Ce-In bond, and 1036 cm^{-1} for In-S bond which proves the existence of the sulfide skeleton. In contrast to the pristine Ce-InS powder, the Ce-InS hydrogel shows more intensive absorption peaks in the range of 1400-1600 cm^{-1} that could be attributed to C=O and C=C stretching vibrations of the polymeric hydrogel matrix[22]. It is worth noting that the characteristic peaks of inorganic Ce-InS skeleton do not change significantly when the hydrogel is formed, which suggests that the chemical structure of the photocatalyst remains practically the same upon encapsulation into the hydrogel network.

The morphology of the obtained Ce-InS powder and Ce-InS hydrogel were studied via FESEM, and the corresponding micrographs are illustrated in Fig. 3(a-f). Pristine Ce-InS powder is composed of dense clusters of microspheres that contain highly rough, wrinkled, and interconnected surfaces[23]. These microspheres are made up of many ultrathin nanosheets, which form a hierarchical structure with plenty of surface defects and active edges. This kind of morphology helps provide a higher specific surface area and more active sites, both of which are important for photocatalytic activity. No large regions of amorphous structure support the high crystallinity of the synthesized Ce-InS nanoparticles. Formation of Ce-InS hydrogel does not lead to any significant particle aggregation. Hydrogel matrix successfully holds the particles within its pores and maintains their hierarchical morphology. This interconnected porous network is believed to favor mass transport, pollutant absorption, and active site exposure [24].

Further information about the elemental composition and distribution of the Ce doped-InS hydrogel was provided by energy-dispersive X-ray analysis (EDX) presented in Fig. 3(g-m). From elemental mapping, it can be seen that the homogenous distribution of cerium (Ce), indium (In), and sulfur (S) was achieved for the hydrogel matrix, suggesting the successful doping of the In_2S_3 structure with cerium ions. There was also a small amount of oxygen found in the structure, which could have resulted either from the surface oxidation process or from physical adsorption during sample handling.

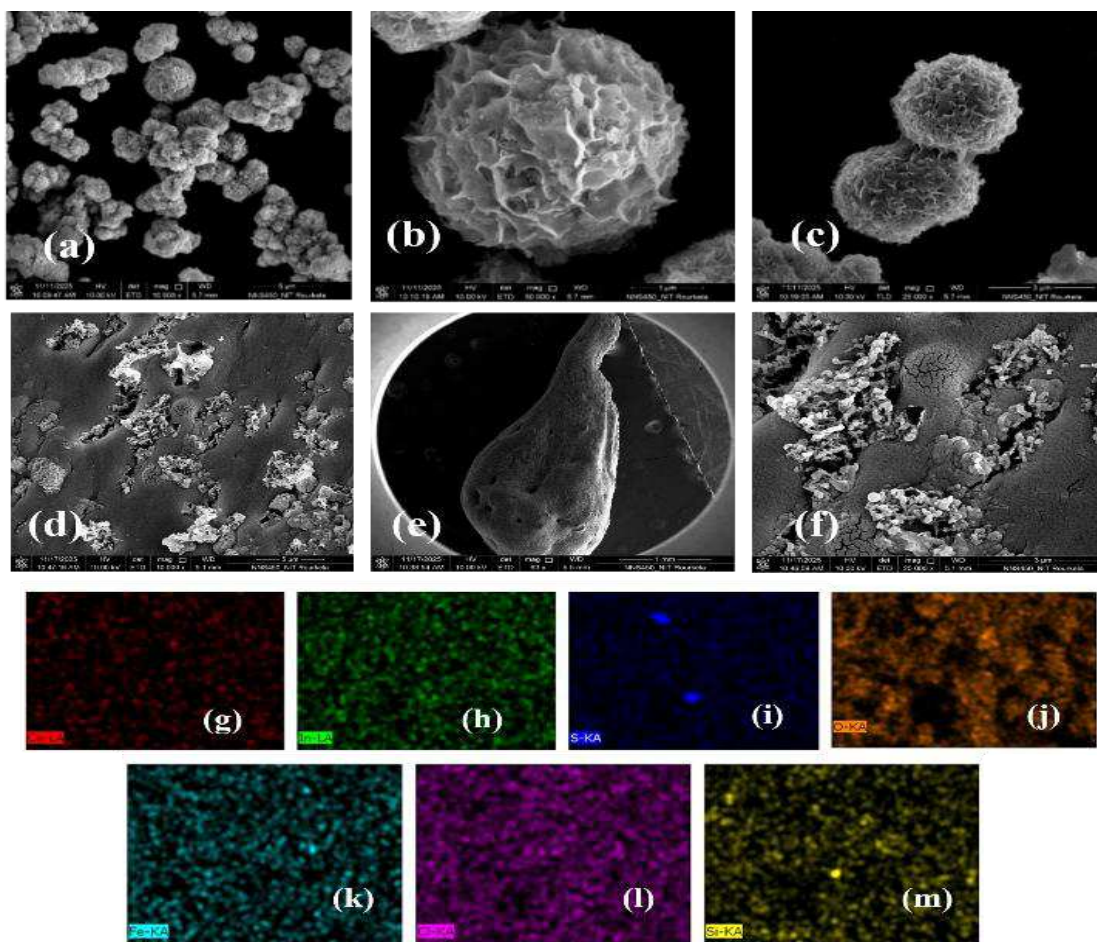


Fig. 3: (a-c) FESEM of Ce-InS (d-f) FESEM of Ce-InS hydrogel (g-m) EDX of Ce-InS hydrogels

The photoluminescence (PL) spectroscopic method was used to assess the charge carriers' separation and recombination processes in Ce-InS powder and Ce-InS hydrogel, as shown in Fig. 4(a). Pristine Ce-InS powder shows a broad PL peak around 440 nm, which usually originates from the radiative recombination of photogenerated charges within the defects or sulfur vacancies of the semiconductor crystal lattice structure [25]. High PL intensity implies effective charge carrier recombination, which may lower the efficiency of photocatalysis. In the case of the incorporation of Ce-InS into the hydrogel matrix, the PL intensity is greatly reduced, with the emission peak at 440 nm largely suppressed [7]. The maximum intensity drops from about 755 arbitrary units to 670 arbitrary units, implying a great decrease in the process of electron-hole recombination. Therefore, the hydrogel matrix facilitates charge separation by promoting the transport of electrons and hindering the pathway of radiative recombination. Thus, a large amount of photogenerated charge carriers can participate in photocatalytic

processes, which will improve both pollutant decomposition and photocatalytic H₂O₂ generation.

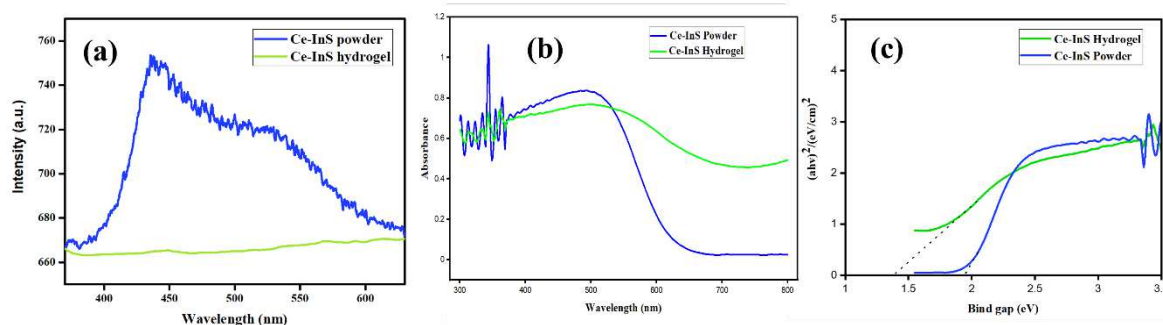


Fig 4: (a) PL Spectra & (b) DRS plot & (c) tauc plot of Ce-InS and Ce-InS Hydrogel.

Optical absorption behaviors of Ce-InS powder and Ce-InS hydrogel were studied by using UV-visible diffuse reflectance spectroscopy (DRS), and the obtained spectra are shown in Fig. 4(b). It is found that both materials absorb strongly in the visible region with a major absorption band at about 500 nm, illustrating excellent performance for the absorption of visible light [26]. The absorption edge of hydrogel broadens with respect to that of the pristine Ce-InS powder and shows an absorption tail at long wavelength region. Such redshifted absorption profile demonstrates improved light utilization, which might be due to enhanced light scattering and interaction effect between the catalyst and polymer.

Optical band gap was calculated using Tauc plots based on the Kubelka–Munk formula, as illustrated in Fig. 4(c). The optical band gap of the pure Ce-InS powder is 1.9 eV, while the band gap of the Ce-InS hydrogel is found to be 1.44 eV. This significant reduction of the band gap by about 0.46 eV reveals that the incorporation of Ce-InS in the hydrogel system reduces the band gap, allowing the photocatalyst to harvest photons with lower energy across a larger range in the visible spectrum. The reduction in the band gap promotes the easy excitation of electrons from the valence band to the conduction band by visible light irradiation, thus producing more photogenerated carriers.

4. Photocatalytic degradation of SMX

Performance of photocatalytic activity of synthesized Ce-InS hydrogel was assessed for the removal of SMX, which is considered as the pharmaceutical pollutant model. Before exposure to light, a first aliquot (about 4–5 mL) of SMX solution was withdrawn in order to obtain the initial concentration (C_0). Thereafter, the desired amount of Ce-InS hydrogel photocatalyst was added to the SMX solution and was vigorously agitated in darkness with an air pump for 30 minutes to reach adsorption–desorption equilibrium between the surface of the photocatalyst and the SMX molecule. After that time, a second aliquot was taken out from the solution for analysis. Other information is mentioned in supplementary file.

Afterwards, the photocatalytic reaction was set up by subjecting the reaction mixture to visible light using a 250 W photoreactor visible-light source, which was continuously aerated and stirred during the

entire reaction time to make sure there is complete dissolution of the catalyst and adequate dissolved oxygen. At the same time, the 100mg of PMS was introduced into the reaction system to promote the production of ROS. In the course of the photocatalytic reaction, about 4–5 mL of the reaction solution was collected at regular intervals of 10 min up to 60 minutes total reaction time. Afterwards, the collected reaction solutions were immediately separated from the catalyst to avoid further photocatalytic reaction. The remaining concentration of SMX in each collected reaction solution was analyzed using UV-Visible Spectrophotometry [7].

The photocatalytic degradation efficiency (%) was calculated using the following equation:

$$\text{Degradation Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the initial concentration of SMX after adsorption–desorption equilibrium and C_t is the concentration of SMX at irradiation time t .

4.1. Effect of catalyst concentration:

To elucidate the impact of catalyst dosage in the photocatalytic degradation of SMX, three catalyst dosages of 5, 10, and 15 Ce-InS hydrogel beads were tested under the initial SMX concentration of 10 ppm in visible-light illumination. The corresponding degradation efficiencies are shown in **Fig. 5(a)**. As shown, the degradation efficiency increased gradually with an increase in the catalyst dosage. About 73% of SMX was degraded using 5 beads, whereas the degradation efficiency reached 84% by doubling the catalyst dosage to 10 beads. By using 15 beads, the maximum degradation efficiency attained 91% after the reaction period. Such a high efficiency can be achieved due to the higher amount of active sites and better absorbance of visible light, resulting in the generation of higher amounts of ROS, such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and $\text{SO}_4^{\bullet-}$ radicals. Besides, a higher amount of catalyst surface leads to better adsorption of SMX molecules and thus accelerates the degradation process [27,28]. From these findings, it is clear that catalyst dosage is one of the key factors influencing the efficiency of photocatalysis, where 15 beads of hydrogel are optimal under the examined conditions.

4.2. Effect of SMX concentration:

The effect of initial pollutant concentration on photocatalytic degradation efficiency was tested by exposing 10 ppm, 20 ppm, and 30 ppm SMX solutions to a constant catalyst dosage of 10 Ce-InS hydrogel beads. The results of the study are presented in **Fig. 5(b)**. With the increase in the initial SMX concentration, the degradation efficiency drastically drops. Thus, with the initial SMX concentration of 10 ppm, the catalyst demonstrated about 91% degradation efficiency, while with the initial SMX concentration of 20 ppm and 30 ppm, its degradation efficiency dropped to 72% and 56%, respectively. The decrease in the catalyst degradation efficiency at higher SMX concentrations is due to the limited

number of active catalytic sites on the photocatalyst surface. With an increase in the pollutant concentration, more pollutant molecules are able to occupy active catalytic sites and saturate the catalyst surface. Higher pollutant concentrations also lead to lower light transmittance through the solution and consequently lower photon adsorption by the catalyst [29]. At higher pollutant concentrations, there are fewer active oxygen species generated than pollutant molecules, which leads to lower degradation kinetics [30,31].

4.3. Effect of time:

The 10 ppm SMX solution is subjected to 10 beads of photocatalyst for 3 hours with 7 ratios of final to initial concentration to study the impact of time (Fig.5c). The graph shows that the process of degradation of 10-ppm solution by 10 beads of photocatalyst is a time-dependent and non-linear process having a second order kinetics, which changes within 70 minutes of this process. One of the important aspects that need to be pointed out is the fact that nearly 80% of this degradation process takes place within 60 minutes. Also, there is a rapid increase in the reaction kinetics between 40 and 60 minutes, because there is a rapid decrease in relative concentration of reactants from 0.72 to 0.18, which indicates the most efficient catalysis in this period after the 40-minute induction period. As for the gradual decline in reaction kinetics within 70 minutes, it is possibly explained by the exhaustion of the target molecules during purification of the solution .

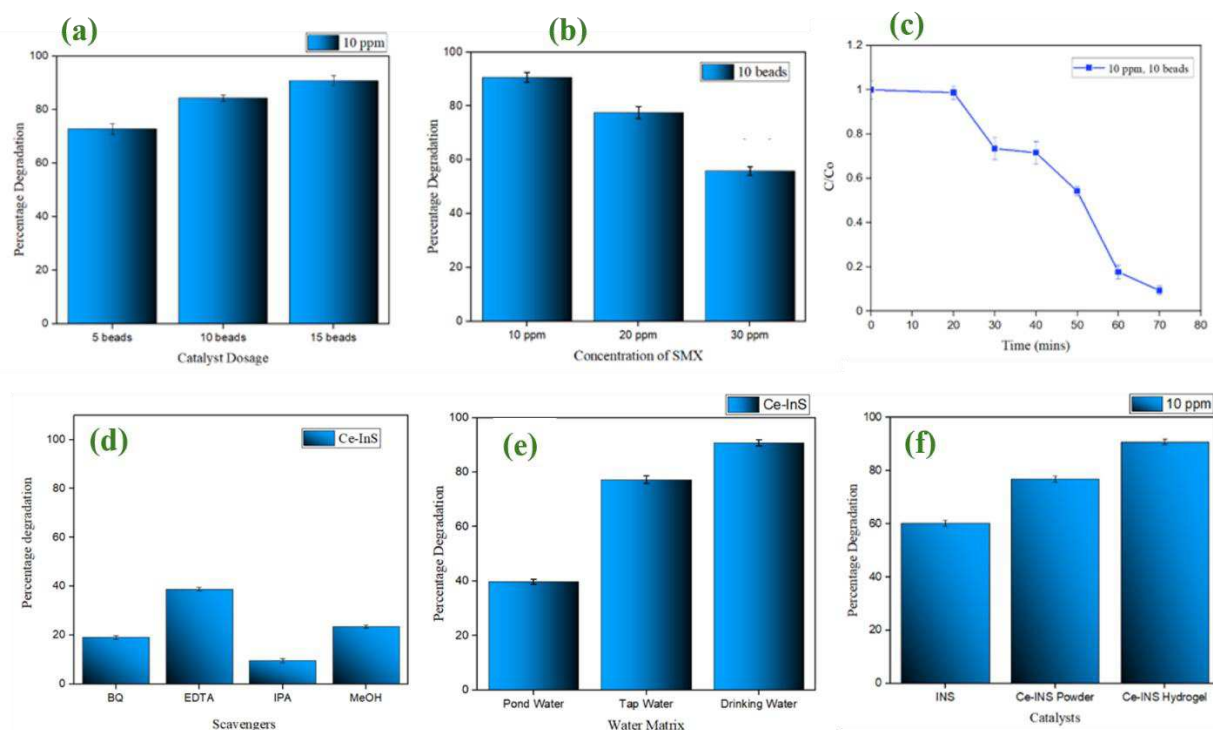


Fig 5: (a) Effect of catalyst dosage (b) Effect of Concentration (c) Effect of time, (d) Effect of scavengers (e) Effect of water matrix, (f) Effect of different type of catalyst

4.4. Effect of scavengers:

Scavenger tests were conducted using different radical scavengers such as isopropanol (IPA), methanol (MeOH), p-benzoquinone (BQ), and ethylenediaminetetraacetic acid (EDTA) for $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}/\bullet\text{OH}$, $\bullet\text{O}_2^-$, and h^+ , respectively, to explain the photocatalytic degradation reaction mechanism. The degradation efficiencies from this study are shown in **Fig. 5(d)**. The scavenging by IPA caused the greatest inhibition of photocatalytic activity by reducing the degradation efficiency to about 9.5%. The implication is that $\bullet\text{OH}$ radicals are the major reactive species responsible for the SMX degradation process [32,33]. On the other hand, the inclusion of BQ and MeOH reduced the photocatalytic activities of the system and caused a reduction of the degradation efficiencies to about 19% and 23%, respectively. It can be inferred that the contributions of $\bullet\text{O}_2^-$ radicals and $\text{SO}_4^{\bullet-}$ radicals are significant in the degradation process [34–36]. However, the addition of EDTA caused a comparatively lesser decrease in the degradation efficiency of about 38.5%. Therefore, it was found out that photogenerated holes are involved in the degradation process.

4.5. Effect of water matrix:

Further testing of the practicality of Ce-InS hydrogel photocatalyst was carried out using the photocatalytic degradation experiment of SMX in different water media: distilled water, tap water, and pond water with identical experimental parameters. The results of photocatalytic degradation efficiencies for each case are presented in **Fig. 5(e)**. It was found that the maximum degradation efficiency was achieved in distilled water and was about 91%, meaning low interference with the dissolved species. In case of using tap water as a solvent, the degradation efficiency dropped to approximately 77%. The main reason for such drop in efficiency was the presence of inorganic ions that could compete with the pollutants for reactive radicals or fill the active sites of the catalyst. Using pond water caused another drop in efficiency, when only about 40% of SMX was degraded. Such significant drop is explained by the presence of organic compounds, suspended particles, dissolved salts, and increased turbidity that may consume the active oxygen species, inhibit light penetration and occupy the active sites of the catalyst.

4.6. Comparative analysis between different type of catalysts:

As illustrated in **Fig. 5(f)**, the photocatalytic degradation efficiency of pristine In_2S_3 increased steadily from the pristine In_2S_3 , then to Ce-InS powder and lastly to Ce-InS hydrogel. The pristine In_2S_3 catalyst showed the lowest photocatalytic degradation efficiency of about 60%, meaning that it had low photocatalytic efficiency owing to fast recombination of the photo-generated electron-hole pairs, and also fewer numbers of active surface sites. After the incorporation of cerium, the degradation efficiency increased significantly to about 77% for the Ce-InS powder. This improved efficiency was achieved because of the presence of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox centers that enhance charge carriers separation and prevent recombination of electrons and holes and promote light absorption at visible region. Of all the

tested photocatalysts, the Ce-InS hydrogel has shown the highest photocatalytic activity and degraded almost 90% during the reaction time. This impressive improvement in the photocatalytic efficiency is due to the combined influence of the effect of cerium doping and hydrogel encapsulation. The porous nature of the hydrogel allows for higher accessible surface area and better adsorption of SMX molecules, mass transport, and dispersion of Ce-InS particles without their aggregation. Moreover, the hydrogel facilitates the efficient separation and migration of the photogenerated charges carriers and leads to generation of more reactive oxygen species in visible light conditions.

5. Photocatalytic Generation of H₂O₂:

The generation of H₂O₂ by means of photocatalysis over the Ce-InS hydrogel under visible light illumination was studied under conditions in the presence and absence of isopropanol (IPA) and is shown in **Fig. 6** below[37]. Significant increase in the generation of H₂O₂ was found in the presence of IPA **Fig. 6b**. In fact, the generation of H₂O₂ increased rapidly at the early stage of reaction to reach approximately 165 µM in the first 30 minutes. Following this, the rate of generation reduced gradually until a maximum concentration of around 190 µM was achieved, suggesting that the system has attained equilibrium between H₂O₂ generation and its degradation. The noticeable improvement in the yield of H₂O₂ due to the presence of IPA was because of its efficiency in scavenging holes (or •OH) and hence, reducing H₂O₂ decomposition.

On the other hand, the H₂O₂ production of the photocatalytic reaction system without IPA was much less than that of the previous reaction system for the whole reaction period (**Fig. 6a**). The H₂O₂ concentration remained comparatively low up to 70 minutes with gradual increase from 2.5 µM to 9 µM. After 70 minutes, there was a slight increase in the rate of H₂O₂ production leading to its maximum value of 22.5 µM at 80 minutes. The reason behind the much lesser production of H₂O₂ without IPA was the fast recombination of photogenerated charges and H₂O₂ degradation.

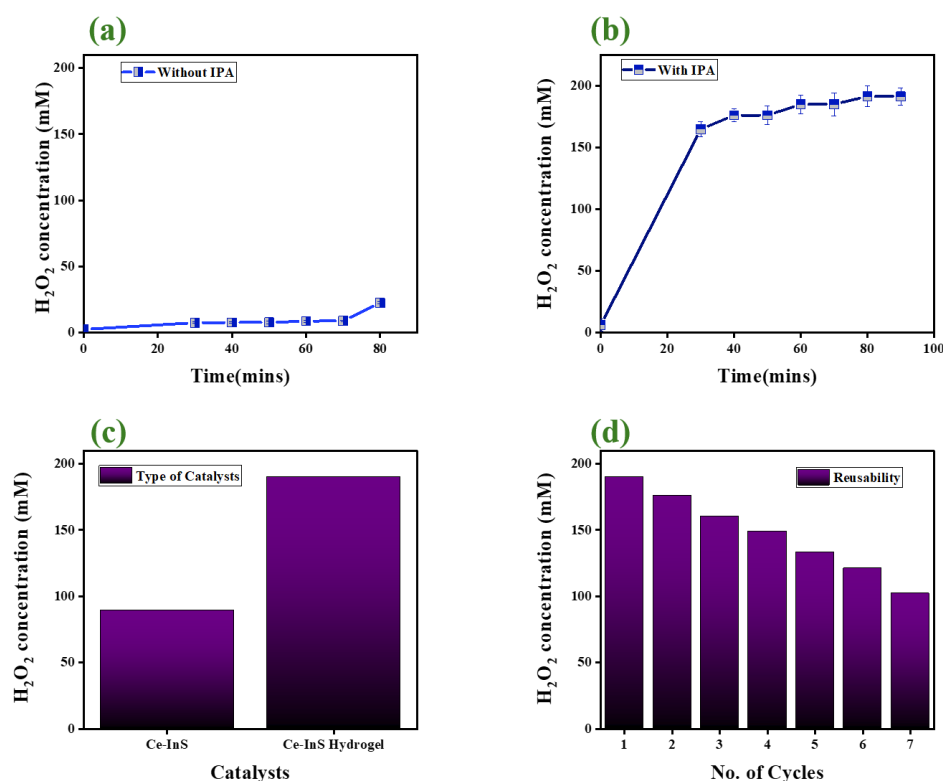


Fig 6. (a) with IPA (b) without IPA H₂O₂ production (c) H₂O₂ production by various catalysts, (d) Reusability of Ce-InS Hydrogel

Photocatalytic performances for H₂O₂ synthesis using the Ce-InS powder and Ce-InS hydrogel were compared, and the results are shown in **Fig. 6(c)**. It is apparent that the Ce-InS hydrogel performed much better in terms of H₂O₂ synthesis than the Ce-InS powder [38]. The Ce-InS powder produced around 90 μ M of H₂O₂, while the maximum H₂O₂ produced by the Ce-InS hydrogel reached about 190 μ M, showing more than double the efficiency of the former. Such enhancement in H₂O₂ synthesis can be mainly attributed to the synergistic effects between cerium dopants and the hydrogel structure. Three-dimensional porous hydrogel structure provides many active sites, ensures good diffusion and transportation of reactants, prevents aggregation of Ce-InS nanocrystals, and reduces the band gap and promotes separation of photogenerated electron-hole pairs. These effects contribute to the selective formation of H₂O₂ via two-electron oxygen reduction pathway[39,40].

To determine the stability and reusability of Ce-InS hydrogel photocatalyst, the study examined seven cycles of photocatalysis in terms of their H₂O₂ production, as shown in **Fig. 7(d)**. The photocatalyst proved to have good stability since there was significant photocatalytic activity during the several cycles, where H₂O₂ concentration slowly decreased from ~190 μ M for the first cycle to ~102 μ M for the seventh cycle. Even though there was some decrease in the rate of H₂O₂ production, the catalyst had more than 50% of its initial activity after seven consecutive cycles, which showed that the catalyst was structurally stable and had good stability. This was due to possible partial occupation of active sites, some loss of catalysts, and/or gradual surface deactivation during the repeated reactions of

photocatalysis. However, the hydrogel matrix successfully immobilized the Ce-InS nanoparticles, thereby preventing the leaching of the catalysts. It can be concluded that the Ce-InS hydrogel has high reusability and has great potential for real-world wastewater purification and sustainable H₂O₂ generation.

6. Degradation Mechanism of SMX

According to the results obtained from the active species trapping experiments and reaction pathway suggested (Fig. 7), the photodegradation of sulfamethoxazole (SMX) under visible light irradiation on the Ce-InS hydrogel catalyst occurs via synergic photocatalysis. When irradiated with visible light, electrons (e⁻) become excited from the valence band (VB) to the conduction band (CB) of the Ce-InS hydrogel, creating holes (h⁺) in the VB. Photogenerated electrons reduce oxygen to form superoxide radicals (•O₂⁻), whereas PMS works as a good electron scavenger that activates to form sulfate radicals (SO₄•⁻) [41]. In parallel, photogenerated holes oxidize Fe²⁺ to Fe³⁺ and lead to •OH formation due to the water oxidation [7,42]. Reactive oxygen species, mainly •OH along with SO₄•⁻ and •O₂⁻ radicals, work synergically for SMX degradation into low molecular weight compounds and their further complete mineralization to CO₂, H₂O and some other inert compounds [43–45].

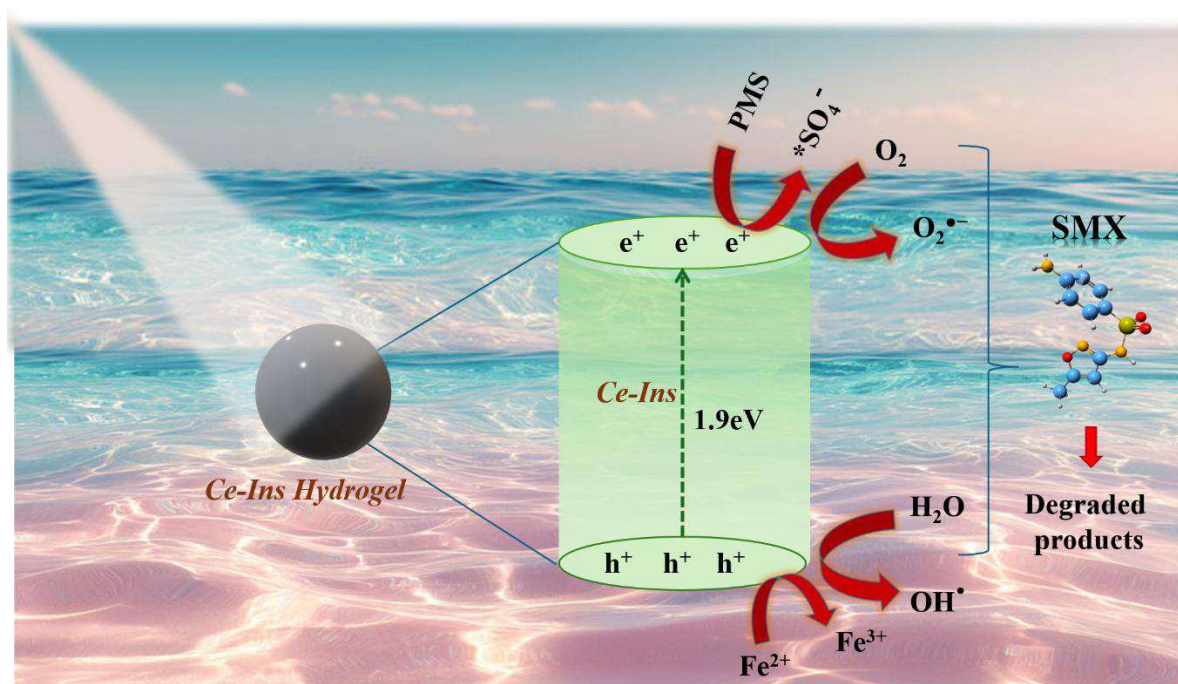
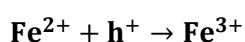
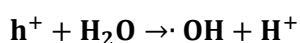
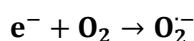
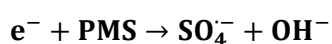


Fig 7. Band Level Diagram of Ce-InS Hydrogel





Conclusion

In this research work, a cerium-doped indium sulfide (Ce-InS) hydrogel photocatalyst was synthesized and used in the degradation of sulfamethoxazole (SMX) in addition to the generation of H_2O_2 under visible light irradiation. The characterizations carried out proved that the Ce-InS hydrogel photocatalyst was synthesized successfully. In the structure characterization studies, the preservation of the Ce-InS structure in the hydrogel material was confirmed. The results obtained from the morphological and optical characterization studies revealed that the Ce-InS hydrogel photocatalyst possessed a porous structure with an energy band gap of 1.44 eV compared to 1.90 eV for Ce-InS. The photocatalysis tests exhibited very good performances in terms of degradation activity toward 10 ppm SMX with a maximum degradation rate of approximately 91% under illumination with visible light. The degradation efficiency increased from 73% to 91% when the amount of catalyst was increased (from 5 to 15 beads). In turn, the increase of initial concentration of SMX from 10 to 30 ppm decreased the efficiency of degradation from 91% to 56% as a result of catalyst surface saturation. Up to 80% of the degradation process occurred during the first 60 minutes of illumination. In reactive species trapping tests, it has been found that hydroxyl radicals ($\cdot\text{OH}$) are the main active species, which leads to reduction of degradation efficiency down to 9.5% by IPA addition. Moreover, the catalyst possesses very good degradation efficiencies of 91%, 77%, and 40% in distilled water, tap water, and pond water, respectively. Comparison experiments have shown that the Ce-InS hydrogel (90%) exhibits better activities compared to Ce-InS powder (77%) and pristine In_2S_3 (60%). Overall, the developed Ce-InS hydrogel represents a promising, stable, and efficient visible-light-responsive photocatalyst for sustainable wastewater remediation and green H_2O_2 production.

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