Attuning doped ZnO-based composites for an effective light-driven mineralization of pharmaceuticals via PMS activation

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HIGHLIGHTS

• Composite photocatalysts merging Cu-, Ga- or In-doped ZnO with BaFe$_{12}$O$_{19}$ or Ni.
• All materials improved their activities in the presence of peroxymonosulfate.
• BaFe$_{12}$O$_{19}$-In1ZO induces over 97% mineralization of a multipollutant solution in 1 h.
• Composites display excellent reusability and stability over 10 cycles.
• Low substrate selectivity for the disposal of a broad array of pharmaceuticals.

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ABSTRACT

Water treatment technologies need to go beyond the current control of organic contaminants and ensure access to potable water. However, existing methods are still costly and often inadequate. In this context, novel catalysts that improve the mineralization degree of a wider range of pharmaceuticals through more benign and less consuming methodologies are highly sought after. ZnO, especially when doped, is a well-known semiconductor that also excels in the photocatalytic removal of persistent organic pollutants. In this study, we investigated the effect of doping ZnO nanoparticles with either copper, gallium or indium on the structure, morphology, photophysical properties and photocatalytic mineralization of pharmaceuticals. Their architecture was further improved through the fabrication of composites, pairing the best performing doped ZnO with either BaFe$_{12}$O$_{19}$ or nickel nanoparticles. Their suitability was tested on a complex 60-ppm multi-pollutant solution (tetracycline,

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levofoxacin and lansoprazole). The activation strategy combined photocatalysis with peroxymonosulfate (PMS) as an environmentally friendly source of highly oxidative sulfate radicals. The alliance of doped ZnO and BaFe$_2$O$_4$ was particularly successful, resulting in magnetic microcroquette-shaped composites with excellent inter-component synergy. In fact, indium outperformed the other proposed metal dopants, exceeding 97% mineralization after 1 h and achieving complete elimination after 3 h. All composites excelled in terms of reusability, with no catalytic loss after 10 consecutive cycles and minimal leakage of metal ions, highlighting their applicability in water remediation.

1. Introduction

Pharmaceutical products have become essential in many aspects of daily life. Their use extends not only to human consumption but also to the livestock industry. Antibiotics, analgesics, and anti-inflammatory drugs are among the most utilized families, with a global production of hundreds of tons per year (Grenni et al., 2018; Ortúzar et al., 2022; Samal et al., 2022). Unfortunately, their increasing presence in aqueous media as pollutants has become a significant environmental concern in recent decades. This is not only due to their potential toxicity but also to their unknown long-term impact on aquatic and terrestrial ecosystems (Cangola et al., 2024; Patel et al., 2019; Serra et al., 2021). The impact of global warming and the increase in world population exacerbate concerns about future drinking water supplies. Consequently, water remediation methods must address the current challenge of removing organic pollutants and ensuring access to safe drinking water. However, current methods are often expensive and can be overwhelmed by the persistence of many pharmaceuticals (Miklos et al., 2018; Motamedi et al., 2022; Pimentel et al., 2021). Furthermore, the vast and diverse range of molecular architectures they feature limits the design of a single, all-encompassing purification system. In this context, there is a high demand for novel strategies that enhance the mineralization of a wider range of pharmaceuticals using more sustainable and efficient methodologies. Photocatalytic water treatment represents a promising avenue of research due to its capacity to operate with low-cost, renewable, and clean energy sources (Gómez et al., 2022; Rashid et al., 2024; Serrà et al., 2021).

Titanium dioxide (TiO$_2$) is a popular choice for photocatalysts due to its stability, optical and electronic properties, low toxicity, and relatively low cost (Brillas and Garcia-Segura, 2023; Liu et al., 2021; Rashid et al., 2024). Zinc oxide (ZnO) is also a viable option with similar advantages, but it is more cost-effective and has better biocompatibility and environmental stability, making it an attractive substitute (Mirzaeifard et al., 2020; Samadi et al., 2016; Sharma et al., 2022). Various strategies can be employed to address the relatively high band gap of ZnO, which unfortunately limits its use to the ultraviolet region. One such strategy is to embed a doping element within the ZnO structure, which induces additional lattice defects and effectively narrows the band gap, resulting in red-shifted absorption towards the visible spectrum (Bembibre et al., 2022; Samadi et al., 2016; Yang et al., 2021). Additionally, these defects can act as electron traps, enhancing the lifetime of photo-induced electron/hole pairs by inhibiting the recombination process. An alternative approach is to integrate the photocatalyst into a bicomponent composite material. This heterojunction facilitates the splitting of electron/hole pairs between both materials, which generally results in improved activity compared to that of the individual components (Balakrishnan et al., 2023; Liu et al., 2024; Tayyab et al., 2022, 2024; Wang et al., 2023; Yang et al., 2021; Yue et al., 2024). In addition, the physical properties of the composite can be readily tailored by selecting an appropriate partner. Ferrites are optimal candidates due to their naturally low band gaps and capacity to impart magnetism to the resulting composite, facilitating catalyst recovery. They have been successfully employed in the removal of inorganic and organic pollutants, and microorganisms (Casbeer et al., 2012). To effectively separate holes and electrons, a p-n heterojunction can be formed, which is another option. ZnO, an n-type semiconductor, has been successfully paired with various p-type materials to achieve photocatalytic results (Chabri et al., 2016; Gnanasekaran et al., 2022; Saeed et al., 2023; Yu et al., 2021).

The aforementioned strategies were employed in the development of enhanced ZnO-based photocatalysts. Initially, the morphology, physical properties, and photocatalytic activity of ZnO nanoparticles were optimized by doping them with different elements, namely copper, gallium, or indium, in varying percentages. Secondly, the most effective architectures were integrated into composites with two commercially-available partners: BaFe$_2$O$_4$ nanoparticles, as an example of ferrite, or nickel nanoparticles for the formation of a NiO-ZnO p-n heterojunction. The photocatalytic process was assisted by advanced oxidation processes (AOPs), which activate highly reactive radicals in the media (Sabias et al., 2020). Peroxymonosulfate (PMS) was selected as the precursor of sulfate radicals due to its advantageous oxidative power (2.5–3.1 V vs. NHE) and relatively long half-life (30–40 μs), making it an eco-friendly option for light-mediated operations (Meng et al., 2023; Su et al., 2023). This study broadened its scope to include three examples of drugs with divergent functionalization on their molecular structures. Two representative antibiotics, tetracycline and levofloxacin, and the proton-pump inhibitor lansoprazole were selected. The resulting multipollutant solution was used as a model to evaluate the photocatalytic and PMS-activation efficiency of the pristine nanoparticles and the resulting composite materials. The findings presented have significant implications for the design and refinement of efficient and sustainable technologies for environmental remediation.

2. Experimental section

2.1. Synthesis and characterization of photocatalysts

2.1.1. Synthesis of pure, Cu-, Ga and In-doped ZnO nanoparticles

Pure ZnO, Cu-doped ZnO (CuZO), Ga-doped ZnO (GaZO) and In-doped ZnO (InZO) nanoparticles were synthesized via the sol–gel method. For each doped ZnO, three different [Doping metal]/[Zn] atomic ratios were considered, namely 0.01, 0.03 and 0.05. As a general method, the precursor Zn(CH$_3$COO)$_2$-2H$_2$O (16 g, 99%) was dissolved in methanol (112 mL) and the solution underwent magnetic stirring for 10 min at room temperature. Subsequently, precise quantities of either CuCl$_2$, Ga(NO$_3$)$_3$, xH$_2$O or InCl$_3$ were added to yield Cu-, Ga- or In-doped ZnO, respectively, which were calculated to obtain the abovementioned [Doping metal]/[Zn] atomic ratios of 0.01, 0.03 or 0.05, or no additive to furnish pure ZnO. After, the solution was magnetically stirred for another 15 min, transferred to an autoclave and subjected to drying under supercritical conditions using ethanol. The resulting nanopowders were then calcined in a muffle furnace at 400 °C for 2 h under aerated conditions. The synthesized samples were associated to unique codes based on the nominal dopant loading, e.g. Cu1ZO, Cu3ZO and Cu5ZO in the case of Cu-doped ZnO nanoparticles.

2.1.2. Synthesis of nanocomposites

The best-performing doped ZnO were combined with commercially available barium ferrite or nickel nanoparticles to synthesize composite materials through the solid-state reaction method. BaFe$_2$O$_4$ nanoparticles were acquired from Sigma-Aldrich (CAS: 12047-11-9) and Ni ones from Alfa Aesar (CAS: 7440-02-0). For the synthesis, 50 mg of

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doped ZnO and 50 mg of either BaFe$_2$O$_4$ or Ni nanoparticles were mixed in absolute ethanol (20 mL) and the resultant slurry was sonicated for 3 h. After, the samples were air-dried at 100 °C overnight, ground into a fine powder and subsequently calcined in a muffle furnace at 600 °C for 5 h under aerated conditions (heating and cooling rate of 2 °C min$^{-1}$).

2.1.3. Materials characterization

The characterization encompassed the materials' crystalline structure, morphology, chemical composition, and optical properties. The synthesized materials were characterized using a variety of techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) method, UV–Visible–NIR spectroscopy, and photoluminescence (PL). The X-ray diffraction analysis of the pure and X-doped ZnO nanopowders was conducted using a state-of-the-art instrument (XRD, D8 Advance, Bruker AXS, Germany) to unveil their crystalline structure. The morphology and phase constitution of the synthesized nanopowders were observed using field-emission scanning electron microscopy (FE-SEM, S4800II, Hitachi, Japan) equipped with EDX for enhanced elemental analysis, and transmission electron microscopy (TEM) carried out using a JEOL JEM 2010 type electron microscope with a LaB$_6$ electron gun, operating at 200 kV, equipped with a Gatan 794 Multi-Scan CCD camera. The specific surface area was determined by using the Brunauer–Emmett–Teller (BET) method from N$_2$ adsorption-desorption isotherms at 77 K using a Micrometrics Tristar-II. The light absorption properties were analyzed using a UV–Visible spectrophotometer (Shimadzu UV-3101PC) across a wavelength range of 200–1800 nm. PL spectra were obtained with a NanoLog Horiba modular spectrofluorometer, which used a Xenon lamp as an excitation light source with a wavelength of 325 nm. The emission was measured between 350 and 800 nm at room temperature.

2.2. Catalytic experiments

The mineralization assays were conducted using a multipollutant solution consisting of 20 ppm of tetracycline, 20 ppm of levofloxacin, and 20 ppm of lansoprazole in Milli-Q water. The pH was adjusted to 7. Independent experiments were performed to assess the intrinsic photocatalytic activity of each catalyst. Additionally, the impact of adding PMS was examined both in the absence and presence of illumination. A standard procedure was followed, in which 10 mg of catalyst was added to 10 mL of the multipollutant solution. The mixture was then stored in the dark for 30 min to establish adsorption-desorption equilibrium. Subsequently, the mixture was magnetically stirred at 600 rpm and irradiated with a 1.6 W white LED strip ($2.2 \times 10^{-3}$ W cm$^{-2}$) for 180 min for the photocatalytic analyses. In experiments involving PMS, 0.5 mL of a 16 mM PMS solution was added to the reactor just before starting. The PMS solution was prepared with Milli-Q water and adjusted to pH 7 before each experiment. At predefined time intervals ranging from 0 to 180 min, a 50 μL sample was extracted for mineralization analyses. Mineralization was characterized by measuring the loss of total organic carbon (TOC) content relative to the initial solution, using a Shimadzu TOC-VCSH instrument. The experiments were conducted in triplicate. The study investigated the potential recyclability of the nanocomposites under the aforementioned conditions, namely PMS-assisted and light irradiation, through 10 successive cycles. After each test, the catalyst was collected and reused with fresh solution. Additionally, a 50 μL aliquot of the sample was extracted at predefined intervals from 0 to 180 min for mineralization analyses. After recovering the catalyst from the decontaminated fractions through centrifugation, it was filtered using 0.22 μm syringe filters. It is worth noting that certain photocatalysts can be effortlessly retrieved through the application of a magnetic field. Nevertheless, the determinations were carried out following the same protocol. The filtered catalyst was then combined and adjusted to 100 mL to determine the amount of metallic ions released into the media. Metallic ion concentrations were determined utilizing inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300 PerkinElmer) for ppm scale and inductively coupled plasma-mass spectrometry (ICP-MS, NexIon, 2000 PerkinElmer) for ppb scale quantification. The impact of each metal ion on pharmaceutical mineralization was evaluated separately. The concentration of each metal in the respective tests was determined based on the ICP analyses. The concentration of Fe(III), Ni(II), and Cu(II) was 1 ppm, while the concentration of Zn(II) was 20 ppm. To prepare the metal ion solutions, chloride salts were used to create a [MX] = 100 ppm (MX = Fe(III), Ni(II), and Cu(II)) or 2000 ppm (MX = Zn(II)) solution. Next, 100 μL of one of these solutions was added to 10 mL of the model multipollutant solution for independent assays and submitted to irradiation in the presence of 0.75 mM of PMS.

3. Results and discussion

3.1. Synthesis and characterization of X-doped ZnO nanoparticles

The morphology of the synthesized ZnO and X-doped ZnO nanoparticles, annealed at 400 °C for 2 h, was examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1 shows the TEM images of pure ZnO and X-doped ZnO nanoparticles. All samples have a nanometric size of less than 100 nm. The pure and lightly doped samples (X1ZO and X3ZO) consist of spherical grains with a wide particle size distribution. TEM images indicate that the average nanoparticle size decreases slightly when adding dopant up to 3% and then increases for a higher dopant load.

The sample of pure ZnO displays hexagonal-shaped grains with regular facets. However, the doped samples show elongated particles with increasing dopant content and a loss of their regular facets. For instance, in the case of Ga-doped ZnO, lattice fringes were detected, with distances of 0.24 nm and 0.27 nm for the samples Ga1ZO and Ga3ZO, respectively. The interatomic distance of the crystal plane (101) of the hexagonal phase of ZnO (d = 0.25 nm) indicates the proximity of these values to the samples doped with Ga, confirming their crystallinity. The Ga5ZO sample exhibits larger and more elongated particles than the pure and low-doping samples, each surrounded by small grains. This behavior may be attributed to the differential growth of ZnO particles. It has been reported that exceeding a certain percentage of doping can cause lattice distortion due to the intercalation of Ga atoms in the crystal structure. This can lead to phase segregation and the presence of irregularly sized and shaped agglomerates. This behavior was observed in ZnO doped with In and Cu.

SEM analysis (Fig. S1) shows the presence of round agglomerates with dimensions ranging between 2 and 5 μm. The agglomerates exhibit spherical shapes and feature a rough, porous, fine-grained microstructure. The average grain size, also approached by means of SEM analysis, tends to lower values with the doping procedure. For instance, Cu doping induced a size reduction from 36 nm of pure ZnO to 28 nm of Cu3ZO. The histograms displaying the particle size distribution of pure and Cu-doped ZnO are represented in Fig. S2. To determine the elemental composition within the X-doped ZnO structure, energy-dispersive X-ray spectroscopy (EDS) measurements were performed on the XZO sample. The EDS analysis shows some similar presence of oxygen and zinc, with a relatively lower concentration of Ga, In, or Cu. This observation highlights the essential elements required for our structural composition, emphasizing the incorporation of dopant into the ZnO matrix. The effect of doping over the surface area of ZnO was also evaluated. Fig. S3 displays the Brunauer-Emmett-Teller (BET) adsorption-desorption isotherms of pure ZnO and In1ZO as an example of doped ZnO. Indeed, the incorporation of indium leads to a convenient fourfold increase in the surface area with respect to pure ZnO, escalating from 0.9 m$^2$ g$^{-1}$ to 10.1 m$^2$ g$^{-1}$ for pure ZnO and In1ZO, respectively.

XRD analysis was conducted to examine the details of our
synthesized materials. Fig. 2 displays the XRD patterns of pure and X-doped ZnO nanoparticles. The peaks were indexed to the wurtzite hexagonal-shaped ZnO with the space group $P\bar{6}3mc$, in accordance with the Joint Committee on Powder Diffraction Standards (JCPDS) card file 36–1451. The XRD patterns show nine diffraction peaks with different intensities, indicating the anisotropic growth of the samples. The peaks indexed in the X-ray diffraction pattern correspond to the reticular planes (100), (002), (101), (102), (110), (103), (200), (112), and (201) of wurtzite hexagonal ZnO (Benamara et al., 2023b). It is noteworthy that the same peaks were observed in both pure and X-doped ZnO samples, regardless of the dopant nature and concentration. This indicates that the crystal structures of all prepared ZnO nanoparticles maintain the wurtzite phase.

The analysis also included the variations in the average crystallite size and micro-strain. Cu-doped ZnO showed a decrease in the average crystallite size from 52 to 40 nm when the doping concentration increased from undoped to 5 at. % of copper (Table S1), as determined through the Williamson-Hall method. This decrease is consistent with the replacement of Zn$^{2+}$ ions, which have an ionic radius of 74 p.m., by slightly smaller Cu$^{2+}$ ions (73 p.m.) (Singhal et al., 2012). In Ga-doped ZnO, the weakly doped samples Ga1ZO and Ga3ZO experience a significant shrinkage due to the partial substitution of Zn$^{2+}$ by smaller Ga$^{3+}$ ions (ionic radius of 62 p.m.) (Table S2). On the other hand, the highly doped Ga5ZO shows narrower diffraction peaks compared to the other samples, indicating a larger estimated grain size of 141.1 nm. This increase can be attributed to a reduction in interplanar spaces caused by the different ionic charges (+2 for Zn and +3 for Ga). The incorporation of an additional positive charge necessitates the inclusion of more oxygen atoms in the mixed oxide network, which subsequently distorts it.

In the case of indium, the lattice parameters calculated from the (100) and (002) planes closely align with typical wurtzite ZnO values in the least doped sample, i.e. In1ZO. However, a higher percentage of dopant can slightly shift the diffraction peaks and even induce the appearance of additional signals. These signals belong to a secondary phase and were ascribed to the (222) and (440) planes of the cubic bixbyte crystal structure of In$_2$O$_3$ with the space group $Ia\overline{3}$ (JCPDS card file 06–0416) (Prasad et al., 2021). This suggests the formation of In$_2$O$_3$ rather than its proper incorporation as a dopant into the ZnO network. The crystallite size was estimated using the Scherrer equation by measuring the full width at half maximum (FWHM) of the diffraction peak. The average size decreased slightly from 65 nm (pure ZnO) to approximately 55 nm when In-doped (53, 56, and 54 nm for In1ZO, In3ZO, and In5ZO,
respectively). Note that the comparable ionic radii of In\(^{3+}\) and Zn\(^{2+}\) are similar to pure ZnO (Mourad et al., 2020). However, their different ionic charges result in a different crystal structure within the In-enriched domain.

Fig. 3 shows the optical properties of all samples, which were analyzed using UV-vis diffuse reflectance spectra (DRS) and photoluminescence spectra (PL). The band gap energy (E\(_g\)) of all nanoparticles was estimated using the Tauc model applied to the high absorption region of the UV-vis DRS absorption spectra. The annealing process at 400 °C for 2 h effectively decreased the band gap of pure ZnO from 3.37 (Lu et al., 2008) to 3.21 eV. The addition of dopants allowed for further fine-tuning to achieve slightly lower and more convenient values. This phenomenon is linked to the well-known Burstein-Moss band filling effect. Specifically, Cu\(_{3}\)ZO has the lowest E\(_g\) of all Cu-doped ZnO materials, with a value of 3.17 eV (Fig. 3a).

Additional (Cu) doping activates an absorption band starting at 385 nm, indicating an improvement in light exploitation efficiency due to enhanced absorption capacity. The absorption band for Cu\(_{3}\)ZO is at its maximum and is hypsochromically shifted as the Cu concentration increases from 1 to 5 at.%.

A similar trend is observed for Gallium (Fig. 3c), but the absorption band derived from its doping originates within the near-infrared region (ca. 1200 nm) in the case of Ga\(_{1}\)ZO. Similarly, increasing the doping rate causes a blue shift in this band, optimizing the absorption rate within the visible range for Ga\(_{3}\)ZO and facilitating the transport of charge carriers between the valence and conduction bands. In the case of indium, the increase in absorption covers a range from blue to infrared and is related to the increase in doping percentage (see Fig. 3e). Additionally, the band gap energy was reduced, which is related to the creation of a donor level from the In\(^{3+}\) ions below the conduction band, inducing a curvature at the band’s edge (Mourad et al., 2019).

The PL spectra were captured at room temperature for pure and X-doped ZnO samples. The ultraviolet emission of pure ZnO is prominently situated at 390 nm and corresponds to the near band edge (NBE) peak, whereas the band within the visible light range (approximately 560 nm) stems from inter-band defects. In the case of Cu-doped ZnO (Fig. 3b), the blue-green emission increases while the orange-red one decreases with an increasing dopant percentage. This indicates that the inclusion of Cu in the ZnO structure promotes the presence of zinc/oxygen vacancies and interstitial zinc while reducing the amount of oxygen interstitials (Benamara et al., 2023a; Reddy Boppidi et al., 2020; Yang et al., 2012). In addition, the valency of copper (Cu) in the ZnO structure can be fine-tuned to achieve slightly lower and more convenient values. This assumption is based on the respective radii of Cu\(^{+2}\) (0.096 nm), Cu\(^{3+}\) (0.072 nm), and Zn\(^{2+}\) (0.074 nm) ions. Consequently, the primary impurities in Cu-doped ZnO may include Cu\(^{+2}\), Cu\(^{3+}\) substitutes, and Cu\(^{+2}\) interstitials. The presence of both Cu\(^{+2}\) and Cu\(^{3+}\) substitutes, along with Ga\(^{3+}\) interstitials, leads to a reduction in the concentration of zinc vacancies (V\(_{Zn}\)) and an increase in the concentration of interstitial zinc (Z\(_i\)). This shift is responsible for the disappearance of violet emission and the emergence of blue emissions (Yang et al., 2012). Ga-doping leads to an increase in the emission peak at 390 nm, followed by a reduction in the green-yellow area. This could be attributed to the insertion of Ga atoms on Zn vacancies, which increases the rate of donor-related defects of ZnO (Fig. 3d). The UV emission peak is significantly enhanced in Ga\(_{3}\)ZO, which also has the largest average grain size. These two characteristics are closely related because a larger crystallite size reduces the concentration of non-radiative defects, thereby maximizing the PL intensity in the UV region. In-doped samples exhibit strong defect peaks at approximately 440 nm, which effectively mask the intrinsic peak (Fig. 3f). This observation suggests that the substitution of Zn\(^{2+}\) by trivalent In\(^{3+}\) induces zinc vacancies to preserve charge neutrality (Pati et al., 2015). The bands within the orange-red region, related to the presence of oxygen interstitials, could also respond to that substitution. The interplay of defects sheds light on the photoluminescent behavior induced by indium doping in ZnO. It is worth mentioning that the NBE peaks of the doped samples exhibit a bathochromic shift with respect to that of pure ZnO. It is related to the introduction of deep level inter-bands within the material, which leads to a decrease of the band gap energy and permits an enhanced light absorption. Additionally, the band peaking at 560 nm undergoes a significant blue shift, which is particularly pronounced for Cu and In doping. This could be attributed to structural modifications in the ZnO lattice induced by the dopants, which further modulates its electronic and optical properties (Khashan and Mahdi, 2017; Licurgo et al., 2020; Madhavanunni Rekha et al., 2023).

3.2. Catalytic performance of pure and X-doped ZnO, BaFe\(_{12}\)O\(_{19}\) and Ni nanoparticles

Catalytic tests were conducted on pure ZnO, X-doped ZnO, commercially available BaFe\(_{12}\)O\(_{19}\), and Ni nanoparticles using a multi-pollutant solution containing 20 ppm of tetracycline, 20 ppm of levofloxacin, and 20 ppm of lansoprazole at a pH of 7. First, the model solution was irradiated without a catalyst. The results showed that it is almost impervious to light exposure, with only 1% mineralization after 3 h. The impact of the annealing process on the synthesis of pure ZnO (400 °C for 2 h) was also evaluated in terms of photocatalytic performance (see Fig. 4a). This step leads to a reduction in E\(_g\) and improved crystallinity, resulting in higher mineralization. The mineralization increased from 9% to 18% after 3 h. The optimum doping concentration for each dopant was determined through an initial survey under light irradiation. Fig. 4a–c shows the mineralization evolution induced by...
each catalyst (pure and X-doped ZnO) under photocatalytic conditions over a period of 3 h.

It has been observed that the presence of a doping metal is critical in improving the catalytic activity of pure ZnO. In1ZO, which is the best performing X-doped ZnO, shows an almost 4-fold increase in mineralization up to 67% after 3 h. However, when the indium concentration was further increased from the optimum 1%, mineralization gradually decreased to 59% and 50% for In3ZO and In5ZO, respectively. According to the XRD analysis, the underperformance may be due to the formation of localized In$_2$O$_3$ instead of homogeneous doping with an indium overloading. On the other hand, in the cases of Cu and Ga, a dopant concentration of 1% falls short, with Cu3ZO (57%) and Ga5ZO (50%) being the most favorable, respectively. It is worth noting that Cu doping is the most sensitive to the dopant percentage and follows a comparative trend in the photodegradation of other pollutants (Mittal et al., 2014). As reported, a 3% doping optimally prevents the recombination of electron–hole pairs resulting in higher production of active OH$^\bullet$ radicals, whereas a higher dopant percentage evolves into a cyclic process that avoids their formation (Sclafani et al., 1993). Therefore, Cu3ZO, Ga5ZO, and In1ZO were chosen as representatives for subsequent tests and composite synthesis.

Fig. 4d–f presents the catalytic performance of pure ZnO, Cu3ZO, Ga5ZO, In1ZO, BaFe$_{12}$O$_{19}$, and Ni nanoparticles under irradiation, incorporating 0.75 mM of PMS in darkness, and incorporating 0.75 mM of PMS under irradiation. The effect of PMS was evaluated by treating the solution without catalyst, resulting in mineralization values of only 4% and 7% after 3 h in darkness and under light irradiation, respectively. This confirms the necessity of a catalyst for the process.

In the absence of PMS, the photocatalytic activities of BaFe$_{12}$O$_{19}$ and Ni nanoparticles were lower compared to those of X-doped ZnO. BaFe$_{12}$O$_{19}$ achieved 45% mineralization after 3 h, a value slightly lower than Ga5ZO, whereas Ni nanoparticles stagnated at 27%. The oxidation processes unlocked via PMS triggering, even in darkness, were more effective than an isolated photocatalytic treatment. All nanoparticles increased their mineralization rates when comparing the two conditions, with values above 70% after 3 h, except for pure ZnO which had a rate of 48%. X-doped ZnO nanoparticles showed similar results to photocatalysis, with mineralization rates ranging from 70% (Ga5ZO) to 80% (In1ZO). BaFe$_{12}$O$_{19}$ (75%) and Ni (77%) showed even greater improvement, with the latter exhibiting a ca. 3-fold increase. During the light-driven activation of PMS, BaFe$_{12}$O$_{19}$ and Ni catalysts demonstrated superior performance compared to all X-doped ZnO catalysts, achieving mineralization values exceeding 50% after 20 min and over 90% after 3 h. These results suggest that BaFe$_{12}$O$_{19}$ and Ni are highly dependent on PMS for effective water remediation. Alternatively, PMS enhances the activity of X-doped ZnO to a lesser degree due to its intrinsic
semiconductor behavior that already promotes the formation of oxidizing radicals under photocatalytic conditions. Therefore, these results suggest the integration of X-doped ZnO nanoparticles with either BaFe$_{12}$O$_{19}$ or Ni to create composite catalysts.

3.3. Synthesis and characterization of composites

Composite materials were formed via the solid-state reaction method by combining the best-performing Cu$_3$ZO, Ga$_5$ZO, and In$_1$ZO compounds with either BaFe$_{12}$O$_{19}$ or Ni nanoparticles in a 1:1 (wt/wt) ratio. This article discusses the characterization of all six composites. The analysis of the nanoparticles included an examination of their morphology and architecture before and after the calcination process used in the synthesis of the composites. To facilitate comparison, the nanoparticles were analyzed both as received and after being calcined at 600 °C for 5 h. The nanoparticles of BaFe$_{12}$O$_{19}$ were found to be spherical and hexagonally distorted with diameters ranging from 40 to 110 nm when analyzed as received (Fig. S5a). In contrast, the Ni nanoparticles had a spherical shape with a broader particle size distribution ranging from 30 to 420 nm (Fig. S5b). The non-calcined nanoparticles exhibited magnetic properties in both cases, allowing for easy collection using an external magnetic field. After the calcination step, BaFe$_{12}$O$_{19}$ retained its magnetic characteristics during the formation process, but the architecture and morphology were significantly affected. Fig. S6a shows that the BaFe$_{12}$O$_{19}$ nanoparticles underwent a transition from the nanoscale to sintered aggregates with sizes ranging from 3 to 22 μm during the heating process. In contrast, the sintering of Ni nanoparticles (Fig. S6b) was less significant, and only a few aggregates exceeded 1 μm. However, the magnetic properties were not preserved, likely due to overoxidation to NiO.

Fig. 5 compiles the FE-SEM micrographs and EDS mapping of all BaFe$_{12}$O$_{19}$ and Ni-based composite materials. Remarkably, X-doped ZnO nanoparticles did not sinter into aggregates when merged together, unlike BaFe$_{12}$O$_{19}$. This resulted in the formation of magnetic microcrquette-shaped composites, where the core was predominantly constructed from sintered BaFe$_{12}$O$_{19}$ nanoparticles and the outer coating comprised a densely-packed layer of X-doped ZnO nanoparticles (Fig. 5a–c). The simultaneous composition of BaFe$_{12}$O$_{19}$ and ZnO was observed for all three types of X-doped ZnO nanoparticles. This behavior was confirmed by the elemental maps. The micrometric aggregates formed by Ni and X-doped ZnO particles presented by their Ni counterparts ranged between 0.2 and 5 μm, with the elemental maps demonstrating again the composition and integration of both materials (Fig. 5d–f). It is also important to note that some ZnO particles underwent sintering in combination with Ni. It should be noted that in this process, the Ni particles were also oxidized to form a p-n heterojunction.
which resulted in a significant loss of their initial magnetism.

The impact of the synthetic process over the surface area of the materials was also evaluated by means of the BET method. Specifically, the values of both pristine nanoparticles were compared with those of their respective composites BaFe$_{12}$O$_{19}$–In1ZO and Ni–In1ZO as representatives (Fig. S7). Pristine BaFe$_{12}$O$_{19}$ nanoparticles outclass their Ni counterparts with BET surface areas of 22.6 and 4.7 m$^2$ g$^{-1}$, which could contribute to the better catalytic performance detected for the formers. Regarding the composites, both combinations hold on with slightly lower values of 14.3 (BaFe$_{12}$O$_{19}$–In1ZO) and 4.2 m$^2$ g$^{-1}$ (Ni–In1ZO), even considering the sintering process observed via SEM. Therefore, the architecture of the former composite endows with a superior surface area to that of the In1ZO nanoparticles (10.1 m$^2$ g$^{-1}$).

In summary, for ferrites, microcroquettes with a core of barium ferrite and an outer layer of X-doped ZnO nanoparticles were observed (no sintering of this material was observed). In contrast, for nickel, the formation of agglomerates composed of particles of both materials was observed - it is important to note that both nickel and ZnO particles were larger than those observed before the composite formation process. The XRD spectra of the BaFe$_{12}$O$_{19}$–XZO and Ni–XZO composites show almost all the characteristic peaks of BaFe$_{12}$O$_{19}$ and ZnO nanoparticles or Ni and ZnO nanoparticles. In no case was an additional peak obtained after the formation of the composites.

### 3.4. Catalytic performance of composites

The catalytic efficiency of all composite materials was evaluated on the model, multipollutant solution (tetracycline, levofloxacin, lansoprazole, 20 ppm each) under irradiation, incorporating 0.75 mM PMS in the dark, and incorporating 0.75 mM PMS under irradiation. Fig. 6 shows the evolution of mineralization over a period of 3 h.

As a general assessment, the photocatalytic response of the composites is unaffected with respect to that of the doped ZnO precursors, probably due to the underperformance of the pristine BaFe$_{12}$O$_{19}$ and Ni nanoparticles under the same conditions. However, in the presence of PMS, the composites clearly advanced their isolated precursors, whether in the dark or under irradiation, progressing at a faster rate and achieving superior mineralization. Indium reaffirms itself as the best doping option for ZnO also when incorporated in a composite, surpassing copper and gallium in all conditions. In fact, Ni–In1ZO and
BaFe$_{12}$O$_{19}$–In$_{1}$ZO stand out for promoting an almost quantitative mineralization (i.e., >99.5%) after 3 h under photocatalytic PMS-assisted conditions. Even though the former progressed faster at an early stage (i.e., 0–40 min), BaFe$_{12}$O$_{19}$–In$_{1}$ZO surpassed it thereafter, climbing to 97% after 60 min and peaking at 99.8% after 150 min. This supports a remarkable synergy between the two components. Table S3

Fig. 6. Mineralization of the multipollutant solution achieved with the BaFe$_{12}$O$_{19}$-based (a, b and c) and Ni-based (d, e and f) composites in different conditions: (a and d) under irradiation, (b and e) with PMS in the dark and (c and f) with PMS under irradiation. The mineralization achieved without catalyst (blank experiments) are also indicated in each case. The experiments were performed in triplicate with an error below 1.6%. Experimental conditions: [pollutants] = 20 ppm each (tetracycline, levofloxacin and lansoprazole), [PMS] = 0.75 mM, catalyst dosage = 1 mg mL$^{-1}$.

Fig. 7. Reusability and stability tests performed through 10 cycles under irradiation and the presence of PMS: (a) Mineralization rates induced by the best-performing BaFe$_{12}$O$_{19}$–In$_{1}$ZO composite after 60 and 180 min on each cycle (experiments performed in triplicate, with an error below 1.5%); (b) Concentration of Fe, Ni, In, Cu (ppb scale, left, error: 1 ppb) and Zn (ppm scale, right, error: 0.5 ppm) leaked through the whole process by each catalyst, determined via ICP-MS. Experimental conditions: [pollutants] = 20 ppm each (tetracycline, levofloxacin and lansoprazole), [PMS] = 0.75 mM, catalyst dosage = 1 mg mL$^{-1}$.
compiles state-of-the-art reports on the PMS-assisted disposal of tetracycline for comparison. Regarding the composites incorporating Cu and Ga, the most preferred partner was Ni, which increased the mineralization to 98.6 and 96.7%, respectively. On the other hand, the incorporation of Cu3ZO and Ga3ZO into BaFe$_{12}$O$_{19}$ could not improve the already notable performance of the precursor BaFe$_{12}$O$_{19}$ nanoparticles. Considering that the calcination process used to prepare the composites strongly modified the morphology of the initial nanoparticles, the mineralization induced by the calcined BaFe$_{12}$O$_{19}$ and Ni was analogously analyzed. However, this step had a very limited effect on the catalytic activity of the compounds, especially in the case of BaFe$_{12}$O$_{19}$ (Fig. S8).

Reusability, a key point in the evaluation of a potential catalyst, was also investigated. Fig. 7 shows the mineralization obtained with BaFe$_{12}$O$_{19}$-In1ZO as catalyst over 10 consecutive cycles after 60 and 180 min. It should be noted that the loss of catalytic activity is negligible in both cases. This is also true for the other In and Cu based composites, indicating excellent reusability regardless of the composition. The reusability tests of Ni-In1ZO, BaFe$_{12}$O$_{19}$-Cu3ZO and Ni-Cu3ZO are shown in Fig. S9. The amount of metal ions leaked during the reusability tests (i.e., 10 cycles) was checked by ICP-OES (Zn, on the ppm scale) and ICP-MS (Fe, Ni, Cu and In, on the ppb scale). Fig. 7b summarizes the concentration of the analyzed metal ions released by all four composites. The release of Zn, which is the only element present in all four composites, is the most significant and shows small differences with respect to the composition of the catalysts, ranging from 19 to 28 ppm. On the other hand, the release of the other metals is quite conditioned by the composition, especially by the doping metal. As observed, the choice of In tends to mitigate the release of either Fe or Ni with respect to Cu. Comparing Ni-In1ZO and Ni-Cu3ZO, 360 ppb of Ni were detected for the former and 606 for the latter. The difference is even more abysmal when combined with BaFe$_{12}$O$_{19}$, reducing the amount of leached Fe from 812 (BaFe$_{12}$O$_{19}$-Cu3ZO) to 77 (BaFe$_{12}$O$_{19}$-In1ZO) ppb. BaFe$_{12}$O$_{19}$-In1ZO also outperforms in the retention of the dopant metal, with a release of only 5 ppb of In. The fact that the magnetic character is retained on the BaFe$_{12}$O$_{19}$-based composites, further aiding the recovery and reusability process, further highlights the advantages of the BaFe$_{12}$O$_{19}$-In1ZO architecture.

Considering that metal ions may also be involved in the activation of PMS, additional mineralization tests were performed to evaluate the effect of leached metals. Therefore, comparative concentrations of the detected cations (1 ppm for Fe(III), Ni(II) and Cu(II); 20 ppm for Zn(II); In(III) was not considered due to its extremely low concentration) were independently added as their chloride salts to the model multipollutant solution. Each solution was exposed to analogous conditions, i.e. irradiation in the presence of PMS (0.75 mM) without any catalyst. The solution was exposed to analogous conditions, i.e. irradiation in the presence of PMS (0.75 mM) without any catalyst. The highest mineralization rate after 3 h corresponded to Fe(III) (11%), followed by Cu(II) and Ni(II) (9%), and finally Zn(II) (7%), which was the element present in higher concentration. Considering that under the same conditions, without any additive or catalyst, the solution already undergoes a mineralization of 7%, it can be concluded that the presence of dissolved metal ions hardly interferes or supports the process.

4. Conclusions

Recent research has underscored the imminent water crisis in arid regions, primarily stemming from the contamination of water sources by emerging and persistent organic pollutants. This urgency necessitates the development of effective and inexpensive water treatment methods. In this context, a series of ZnO nanoparticles doped with varying percentages of copper, gallium or indium have been successfully synthesized using the sol-gel method. The doping process has proven instrumental in altering the morphology, crystallinity, and optical properties of pure ZnO, thereby enhancing its intrinsic photocatalytic activity. Notably, both the nature and the percentage of the dopants play pivotal roles in the concurrent mineralization of model pharmaceuticals, namely tetracycline, levofloxacin and lansoprazole. Particularly, a 1% indium doping significantly enhances ZnO’s catalytic performance across all test conditions, implying a fourfold increase compared to the undoped counterpart. Moreover, the remediation process was effectively supported by PMS activation, which was able to improve the mineralization rates of all photocatalysts. The combination of the most promising compositions (i.e., Cu5%, Ga5%, and In1%) with either BaFe$_{12}$O$_{19}$ or Ni nanoparticles provided heterojunctions with excellent synergy, which greatly supported their separate activities. Furthermore, BaFe$_{12}$O$_{19}$ provides microcrocquette-shaped composites that retain their magnetism, which greatly facilitates the separation and reusability of the catalyst. In fact, BaFe$_{12}$O$_{19}$-In1ZO emerges as the most optimal composite composition, exceeding a 97% mineralization after 1 h and achieving a complete disposal after 3 h. Cu- and Ga-doped ZnO, slightly outperform when fused as a NiO/ZnO p-n heterojunction. The different chemical nature of the selected pharmaceuticals suggest that the proposed materials exhibit low substrate selectivity, thereby enabling the effective removal of a wide range of pollutants. Collectively, all composites exhibited excellent reusability with no catalytic loss and negligible leakage of metal ions after 10 consecutive cycles, further supporting their capability in water remediation. In summary, the strategic combination of BaFe$_{12}$O$_{19}$ and doped ZnO within the realm of PMS activation research presents a robust approach to enhancing photocatalytic degradation efficiency, facilitating catalyst recovery and reuse, and addressing a broad spectrum of pollutants. This approach addresses key challenges in water remediation technology, especially critical in regions facing acute water contamination issues.

CRediT authorship contribution statement

Roger Bujaldón: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Majdi Benamara: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Ramzi Dahhri: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Elvira Gómez: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Albert Serró: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

Authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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