



Tinidazole degradation assisted by solar radiation and iron-doped silica xerogels

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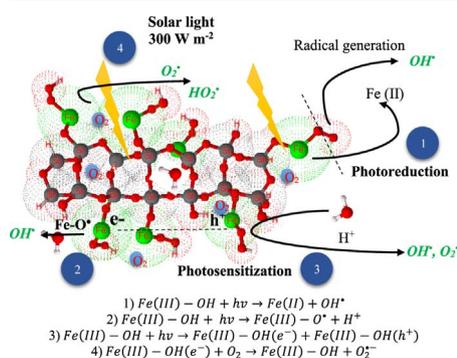
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HIGHLIGHTS

- TNZ photodegradation process is increased to 98% by adding iron-doped silica xerogel.
- Xerogel textural properties are modified by the doped Fe(III).
- XGS-Fe(III) band gap demonstrated that these materials behave as semiconductor materials.
- The XGS-Fe(III) activity is related to the radical formation HO[•] mainly.
- An action mechanism for XGS-Fe(III) photoactivity has been proposed involving photo redox reaction and photosensitization.

GRAPHICAL ABSTRACT



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ABSTRACT

The main objective of this study was to assess the photoactive properties of iron-doped silica xerogels under solar radiation. For this purpose, silica xerogels (XGS) were doped with different doses of Fe(III) by the sol-gel method. Tinidazole (TNZ) was considered as model compound for the degradation study. XGS samples were texturally and chemically characterized by N₂ (77 K), standard test sieves, XRD, FTIR, SEM, HRTEM, PL, XPS, and DRS. The results showed that in aqueous solution of 0.4 M Fe(III), XGS was doped with 3.64% iron and contained 33.01% silicon and 63.36% oxygen (XGS-Fe(III)-0.4 M). The addition of Fe(III) modified the textural properties of the xerogels. Thus, XGS-Fe(III)-0.4 M had a smaller specific area (587 m² g⁻¹) than non-doped XGS-BCO (645.92 m² g⁻¹), with a decrease in pore volume and average pore diameter of 50% and 63.6%, respectively. The band-gap energy (E_g) value was reduced from 3.55 eV (XGS-BCO) to 2.32 eV (XGS-Fe(III)-0.4 M) due to the inclusion of iron zoned in the form of iron oxy-hydroxide. Therefore, this is a photoactive material under solar radiation, with an E_g value < 4 eV. The percentage TNZ degradation was 41% for XGS-BCO and 68% for XGS-Fe(III)-0.4 M after 1 h of treatment. Previous irradiation of XGS-Fe(III)-0.4 M increased the percentage TNZ degradation to 98%. The radicals generated in the process were quantified. The degradation rate was increased at higher XGS-Fe(III) doses and neutral pH. The low-molecular-weight degradation byproducts obtained are not

Abbreviations: PPCPs, pharmaceuticals and personal care products; TNZ, tinidazole; AOPs, advance oxidation processes; XGS, silica xerogels; TEOS, tetraethyl orthosilicate; IPrOH, isopropanol; TNM, tetranitromethane; DMSO, dimethyl sulfoxide; XGS-BCO, non-doped xerogel; XGS-Fe(III), Fe(III) doped xerogels; HPLC, high-performance liquid chromatography; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy; DRS, diffuse reflectance spectroscopy; FTIR, Fourier transform infrared spectroscopy; XRD, X-ray diffraction; HRTEM, high-resolution transmission electron microscopy; PL, photoluminescence; DNPH, 2,4-dinitrophenylhydrazine; HCHO-DNPH, hydrazine; E_g, band-gap energy

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toxic for HEK-293 cells. Fe(III)-doped xerogels are a good alternative option for drug removal from polluted waters.

1. Introduction

Antibiotics are an example of pharmaceuticals and personal care products (PPCPs), which have been detected in wastewater treatment plants (WWTPs) and freshwater worldwide [1,2]. The main sources of antibiotic pollution are the pharmaceutical and agricultural industries, hospitals, and healthcare centers. Antibiotics play a major role in environmental pollution, even at low concentrations [3,4]. There is a lack of regulation and standards for PPCPs, which can be persistent and bioaccumulable, with a wide range of potential effects that include acute and chronic human harm and ecotoxicological damage [5–7]. PPCPs include nitroimidazoles, such as tinidazole (TNZ) [8], which are active pharmaceuticals against human and animal infections caused by anaerobic and protozoan bacteria, including vaginosis bacteria [8,9]. Their addition to feed for fish and poultry has led to their presence in fish farm waters and the meat industry [10,11], while concentrations between 0.1 and 90.2 $\mu\text{g L}^{-1}$ have been detected in hospital effluents [12,13]. Approximately 20–25% of the ingested dose of TNZ is excreted in urine, with around 12% being excreted in feces and the remainder eliminated as different metabolites [14]. Nitroimidazoles found in industrial and municipal wastewater treatment plants cannot be effectively remediated by conventional treatment technologies [15–18] due to their low biodegradability, high water solubility, and complex molecular structure. Therefore, novel approaches are required for their removal.

Advanced oxidation processes (AOPs) are more powerful techniques that aim at the complete decomposition of organic contaminants in aqueous systems into carbon dioxide and water or their transformation into less harmful compounds through high concentrations of oxidant radicals (OH^\cdot , $\text{SO}_4^{\cdot-}$, $\text{O}_2^{\cdot-}$, HO_2^\cdot) [19–24]. There has been very limited research on the degradation of TNZ by these processes, and its complete mineralization has not been achieved. Several studies have reported percentage TNZ removal of < 75% by ultrasound irradiation and H_2O_2 [25], ozone and activated carbon [26], gamma radiation [27], and solar radiation [28,29].

Photocatalytic processes are an important group of AOPs, in which luminous radiation promotes electronic activation of the semiconductor material acting as catalyst. After irradiation at a certain wavelength (always in the visible or UV region), the photocatalyst generates electron/hole pairs responsible for the formation of radical species (mainly OH^\cdot) that participate in pollutant degradation. These radicals derive from reduction or oxidation reactions produced by electron or positive holes, respectively [30–32]. TiO_2 is one of the most widely used catalyst

materials, applied alone or in combination with other materials (dopants and/or supports), because it absorbs 4% of solar radiation and has a low band-gap energy at approximately 3.0 eV [33]. The efficacy of other semiconductors, such as iron compounds, has also been explored, with some promising results [34,35]. Iron is one of the elements used in AOPs to degrade organic compounds, mainly as natural or synthesized mineral phase or as chemical reagent in Fenton or Fenton-like processes [36,37]. Other authors have also reported on the efficacy of using Fe(III) species doped on TiO_2 surface [38–41].

The application of Fe(III) on photocatalysts has proven to be an efficient method to achieve a high photocatalytic performance. Because of the relatively low redox potentials of $\text{Fe}^{3+/2+}$ compared with the conduction band position of photocatalysts, photogenerated electrons from photocatalysts can be readily scavenged by Fe(III) ions, inducing the efficient separation of electron-hole pairs and thereby favoring photocatalytic reactions [42,43].

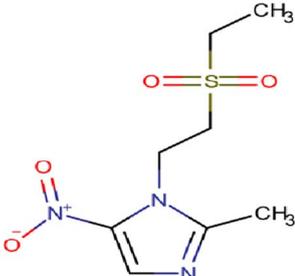
There have been few studies on TNZ removal by photocatalytic methods. Umar et al. [44] used $\text{TiO}_2/\text{sunlight}$ and Zhao et al. [45] fabricated a photocatalyst ($\text{g-C}_3\text{N}_4/\text{BiNbO}_4$), which both exhibited significantly enhanced photocatalytic activity in TNZ degradation under visible light irradiation.

The synthesis and modification of silica xerogels (XGS) has opened up a new line of research on catalysts [46,47] due to their physicochemical properties, which include: highly homogeneous molecular arrangements, extensive specific areas, good mechanical resistance, and the possibility of functionalization by forming a monolayer of nanometric-size materials [48].

The sol-gel process is a simple two-stage method involving the hydrolysis and condensation of a precursor in solution. After condensation, the XGS is formed by drying under atmospheric conditions at < 100 °C [49,50].

With this background, the main aim of this study was to identify the causes of the photocatalytic behavior of Fe(III)-doped XGS in the presence of solar radiation. For this purpose, we synthesized silica xerogels doped with Fe(III). The specific objectives were to study: (i) the textural properties of Fe(III)-doped XGS by XPS, XRD, FTIR, SEM, HRTEM, PL and DRS; (ii) the degradation kinetics of TNZ on Fe(III)-doped XGS under solar radiation in different experimental conditions (Fe(III) concentration doped in XGS silica, XGS-Fe(III) particle size, TNZ concentration, XGS-Fe(III) concentration, medium pH and XGS-Fe(III) previously exposed to solar radiation); (iii) quantification of OH^\cdot and $\text{O}_2^{\cdot-}$ radicals and determination of degradation byproducts; (iv) the mechanism underlying TNZ degradation; (v) byproduct cytotoxicity in

Table 1
Molecular structure and properties of TNZ.

Nitroimidazole	Molecular structure	Molecular weight (g mol^{-1})	Volume (Å^3)	Solubility ^a (mol L^{-1})	pK_{ow} ^b	pK_a
Tinidazole (TNZ) $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4\text{S}$		247.27	258	0.008	0.35	2.58

^a Water solubility, 298 K.

^b Octanol-water partition coefficients.

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