Facile synthesis of ZnO nanoparticles and its photocatalytic activity in the degradation of 2-phenylbenzimidazole-5-sulfonic acid

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Abstract

Sphere-shaped zinc oxide nanoparticles were synthesized following an eco-friendly synthesis method, at mild temperature, using zinc acetate dihydrate as precursor. A comparative characterization was performed with and without a post-calcined step at 300 °C during 15 minutes. The synthesized zinc oxide nanoparticles were characterized by FE-SEM, EDS, XRD, BET and UV-Vis spectroscopy. After the calcined step, wurtzite was the only crystalline structure present in the sample. The photocatalytic activity of the calcined zinc oxide nanoparticles proved to be high since more than 90% of degradation of 2-phenylbenzimidazole-5-sulfonic acid was reached after 180 min of reaction time. The effects of different factors (i.e. radiation source, oxygen source, and catalyst) on the catalytic reaction were evaluated and, as expected, it was found that all these factors are required, and act synergistically in the photodegradation process.

Keywords: ZnO, 2-phenylbenzimidazole-5-sulfonic acid, photodegradation, nanoparticles, catalysis.

1.0 Introduction

Water scarce has become one of the most widely investigated issues related to environmental problems. In recent years, the use of sunscreens has experienced remarkable growth due to the constant awareness of the skin damage caused mainly by ultraviolet (UV) radiation [1]. This overconsumption has caused the direct and indirect enter of these compounds in water sources. Direct input may include the washing off effect after human recreational activities in beaches, rivers, and lakes, while indirect pathways are more frequently related to domestic wastewater effluents and water treatment plants [1-3]. UV-filters are commonly used not only as components of sunscreen products, but also in cosmetics and plastics to avoid any damage from the sun radiation [4]. The UV-filters are organic contaminants very resilient to biodegradation since several studies have demonstrated the presence of at least one UV-filter in sediments and sludge, and groundwater sources [1, 5]. Moreover, recent studies suggest that these compounds have the capability to penetrate and to bioaccumulate in organisms after being detected in liver tissues, breast milk, human blood and urine [6, 7]. Blüthgen et al [4] demonstrated that low concentrations of a UV-filter can lead to the alteration of genes and hormonal pathways in zebrafish. Some of the UV-filters most frequently found in water samples are benzophenone-3, octyl dimethyl-p-aminobenzoate, and 2-phenylbenzimidazole-5-sulfonic acid (PBSA) [3]. PBSA is an FDA approved water soluble UV-filter with a strong absorption in the UV-B spectral region (290 – 320 nm) [8]. One of the most serious concerns about this compound is the ability to photogenerate reactive oxygen species such as $^1\text{O}_2$ and O_2^- , and therefore cause DNA damage. In fact, the generation of these oxygen radicals was proposed by Zhang et al [9], using a

theoretical approach based on the density-functional theory. Also, Bastien et al [10] concluded that PBSA offers a good photoprotection, but it is also capable of generating photosensitization, causing oxidation of guanine bases by UV-A and UV-B radiation.

The UV-filters, as well as other pharmaceutical and personal care products, can not be degraded by traditional techniques that only transfer the pollutant from one medium to another, without destroying or transforming the parent compound [11-13]. However, photocatalysis as one of the advanced oxidation processes (AOP's), has the capability to degrade recalcitrant organic compounds in relatively short periods of time, at lower cost. In addition, efficiency of the degradation process can be improved under different oxidizing agents, and by improving the experimental reaction parameters [8]. The photocatalysis has been extensively studied and its efficiency proved by degrading organic solvents, antibiotics, and polycyclic aromatic compounds [14-16].

In the last decade, several semiconductors have been proposed and synthesized as suitable photocatalysts to perform these processes. One of these catalysts is ZnO, which possesses high theoretical band gap energy of 3.3 eV [17]. ZnO can be synthesized by several routes, including sonochemical, precipitation, microwave-assisted combustion, and hydrothermal methods [18-21]. The final product obtained can be modified when the precursor, temperature or type of reaction is modified (see table 1 at Supplementary Information). ZnO has been employed as a photocatalyst for the degradation of dyes and phenolic compounds [21, 22]. Furthermore, it has also been investigated for other several applications including its potential use in the development of gas sensors and for manufacturing dye-sensitized solar cells [23, 24].

In this research ZnO nanoparticles (ZnONPs) have been synthesized via precipitation process, using zinc acetate dihydrate as the precursor. This catalyst has been characterized by

FE-SEM, EDS, BET, UV spectroscopy, and XRD, and tested in the photocatalytic degradation of PBSA.

2.0 Methods and Materials

2.1 Reagents

All reagents were used as received without further purification or treatment. NaOH 98.9%, Zinc acetate dihydrate 99.9%, ethanol 95%, and hydrogen peroxide 50% wt, were provided by Fisher Scientific®. Hydrochloric acid 1.0 M standard solution was provided by Sigma-Aldrich, and 2-phenylbenzimidazole-5-sulfonic acid 98%, was acquired from ACROS Organics (Morris Plains, NJ). All the experimental solutions were prepared using ultra pure water (Milli-Q water, 18.2 MΩcm⁻¹ at 25 °C).

2.2 Synthesis of ZnONPs

ZnONPs were synthesized via precipitation, using an eco-friendly method, without applying high temperatures or high pressure systems. A precursor solution of the zinc salt was prepared by diluting 4 g of Zn(OAc)₂•2H₂O in 150 mL of water. Separately, 1.17 g of NaOH were diluted in an aqueous solution of 12.5% ethanol (v/v). Both solutions were maintained under constant stirring for 30 minutes. After that, the NaOH alcohol solution was slowly transferred to the precursor solution, and kept under continuous stirring at room temperature for 2 hours. The reaction was as follows:

As a result of the reaction, a white precipitate was obtained. This precipitate was separated by centrifugation at 7,000 rpm for 10 minutes. After sevenfold repetition of the

centrifugation–resuspension cycle, the purified precipitate was dried at 60 °C overnight. Finally, the ZnONPs were calcined at 300 °C for 15 min, and stored in sealed tubes until use.

2.3 ZnONPs Characterization

ZnONPs were characterized by field emission scanning electron microscopy (FE-SEM) using a Philips FEG XL-30S operating at 10 kV. The elemental composition was determined using an EDAX Genesis 2000 EDS at 20 kV. X-ray diffraction (XRD) patterns were obtained in Theta/2Theta configuration, in the range of 20–80 °, at 2 °min⁻¹, using a Bruker D8-Advance X-ray diffractometer at 40 kV and 40 mA. *Brunauer–Emmett–Teller* (BET) specific area was measured using a Micromeritics ASAP 2020. The experimental band gap energy was estimated according to the absorption spectrum threshold, using a Shimadzu UV-2401PC spectrophotometer.

2.4 Photocatalytic activity of ZnONPs

To test the photocatalytic activity of the ZnONPs, a homemade photoreactor was built as described in our previous research [25]. In general, the photoreactor is composed of seven white light bulbs and three mirrors surrounding the system where the reaction takes place. A catalyst loading of 1.2 gL⁻¹ was used as the standard amount, according to previous experiments. The initial pH was adjusted from 3 to 11 with 0.5 M NaOH or HCl, and the system was kept in dark for 30 min in order to reach the adsorption-desorption equilibrium [26]. Then, the oxygen sources which consist of a 0.05% solution of H₂O₂, and air bubbling were added, and the radiation source was switched on. The photoreactor was covered with a black blanket in order to avoid any other incident radiation and light leakage. The photocatalytic system was maintained

under constant stirring and irradiation, and the reaction was monitored for 180 min, by taking aliquots every 30 min. These aliquots were previously filtered with 0.45 μm membrane filters, and analyzed with a Shimadzu UV-2401PC spectrophotometer [25]. The photocatalytic degradation of PBSA was also confirmed by fluorescence spectroscopy, using a Varian Cary Eclipse spectrophotometer. All the experiments were performed in triplicate. The results shown in this work represent the average, and the standard deviation is also shown with the aid of error bars.

3.0 Results and Discussion

3.1 ZnONPs characterization

The ZnONPs were synthesized, and sphere-like particles of homogenous shapes were obtained, showing diameters of less than 100 nm (see Figures 1a and 1b). This result is similar to those obtained by Banerjee et al [18], when a sonochemical approach was employed, using zinc acetate and ethanol as precursor materials. The small size of the nanoparticles can explain the high surface area of $413\text{ m}^2\text{g}^{-1}$ for the calcined ZnONPs according to N_2 adsorption isotherms at 77 K.

Figure 1: FE-SEM images obtained for calcined ZnONPs: a) aggregates of particles are shown at 75,000X; b) at higher magnification (200,000X) is observed that aggregates are composed of sphere-like particles of less than 100 nm.

The elemental analysis of the synthesized ZnONPs showed the presence of zinc and oxygen, characteristics of ZnO (see Figure 2a and 2b) [27]. The additional presence of carbon is attributed to both remaining carbon as byproduct of the reaction, and carbon contamination present on the sample surface. Moreover, the inset of figure 2b shows a decrease of the carbon contribution after calcination of the sample, confirming the removal of the zinc salt. The presence of sodium, from NaOH, or other elements, was not detected, confirming that precursors were removed after calcination of ZnONPs.

Figure 2. Elemental analysis (EDS) of the ZnONPs after drying overnight at 60 °C (a); and after calcination in air at 300 °C (b). The inset of figure 2b shows the carbon signal before and after calcination.

Figure 3 shows the XRD patterns of the ZnONPS after drying at 60 °C, and calcination at 300 °C, respectively. Before calcination, the ZnONPS shows additional diffraction signals, star-labeled, attributed to the zinc precursor or contamination in the surface [28]. However, these diffraction signals are no longer detectable after the sample was calcined. The diffraction pattern of the calcined ZnONPs showed typical signals at 31.8 °, 34.4 °, 36.2 °, 47.5 °, 56.6 °, 62.9 °, 66.4 °, 67.9 °, 69.1 °, 72.6 ° and 77.0 °, that were assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) reflections, respectively (see Figure 3). According to literature and to the JCPDS no. 36–1451, all these diffraction signals have been indexed to wurtzite crystal structure [19, 21, 27, 29].

Figure 3. XRD of ZnONPs after drying overnight at 60 °C (a); and after calcination at 300 °C for 15 minutes (b).

Additionally, the wavelength at the onset of reflection was taken (see Figure 4), and the band-gap energy was calculated using the equation $E_{bg}=1240/\lambda$ [28], showing a high band-gap

energy of 3.36 eV. As is shown in Figure 4, a maximum absorption was observed at ca. 369 nm. The results obtained are similar for those previously reported for ZnO [20, 28].

Figure 4. UV-Vis absorption spectrum measured for calcined ZnONPs.

The calcined ZnONPs showed small particle size of less than 100 nm with a high band gap energy and crystallinity, and no presence of detectable impurities from the Zn precursor, and therefore are appropriate to be used in the photocatalytic experiments.

3.2 ZnONPS photocatalytic activity

3.2.1 Effect of the initial pH

The pH effect was studied by varying the initial pH from 3 to 11, using a 50 μM PBSA solution. As shown in Figure 5a, the photocatalytic activity increases simultaneously with the pH, showing a maximum at pH 9. Sobana et al [30] reported a similar photocatalytic performance using ZnO for the photocatalytic degradation of azo dyes. In this research they found that the photocatalytic degradation of azo dyes, in presence of ZnO, increased as the pH

increased reaching a threshold as shown in figure 5a. Furthermore, a similar photocatalytic investigation of PBSA using TiO_2 demonstrated comparable results since the optimum pH conditions were found at pH 8.9 [31]. The photocatalytic activity decreases in acid media, due possibly to ZnO corrosion under these conditions [22]. The literature suggests that at pH higher than 4.0 the deprotonation of the OH group occurs. Generally, surface water sources show pHs ranging from 6.5 to 8.5. Under these environmentally relevant conditions the sulfonate monoanion (PBSA-H) should be the dominant species with the imidazole group as a strong chromophore, and could be responsible for the photochemistry of this compound. A second deprotonation occurs at very basic conditions (pH>11). Under basic conditions (pH 9) the ZnONPs showed the higher photocatalytic performance, degrading more than 50% of the initial PBSA content.

Figure 5. Effect of initial pH: Photodegradation percent obtained from pH 3 to pH 11, and dominant species (a); and, kinetic reaction rate at pH 9 (b).

As shown in Figure 5b, a characteristic pseudo-first order reaction rate was obtained, showing a constant rate of $4.4 \times 10^{-3} \text{ min}^{-1}$, which is similar to related investigations [31].

3.2.2 Influence of PBSA initial concentration

The photocatalytic performance of the ZnONPs was tested at pH 9, varying the initial PBSA concentration from 10 to 50 μM . As shown in Figure 6a, the photocatalytic performance

decreases simultaneously with the decreasing of the initial PBSA concentration. This degradation pattern is similar to other experiments previously described in the literature since in both cases the degradation through the time diminished as the initial concentration increases [32, 33]. Optimum PBSA initial concentration was found ranging from 10 to 20 μM , showing photodegradation percentages above 90%. When the concentration is higher than 20 μM , the interaction between PBSA molecules increases, diminishing the photodegradation. Also, at higher concentrations, the excess of the PBSA molecules saturates the ZnONPs surface and thereby a decrease in the photodegradation rate is observed.

Figure 6. Photocatalytic performance of ZnONPs at different initial PBSA concentrations. Photodegradation results after 180 min, under constant irradiation, with a catalyst loading of 1.2 gL^{-1} at pH 9 (a); and photocatalytic study of the degradation of PBSA under different initial concentrations (b). The standard deviations for the measurements shown in figure B are less than 0.1.

Figure 6b shows the reaction progress over time. When the initial concentration is 10 μM , 93% photodegradation was obtained, while with an initial PBSA concentration of 20 μM a slight decrease was observed, obtaining ca. 90% of photodegradation after 180 min. However, using one-way ANOVA was determined that this difference was not statistically significant ($p \text{ value} > 0.05$). Furthermore, it is observed that during the first 90 min of reaction the photocatalytic performance is similar with initial PBSA concentrations of 10, 20 and 30 μM .

However, after 120 min of irradiation, and an initial PBSA concentration of 30 μM , the catalytic performance of the ZnONPs decreases. These results may be associated to a competition effect for the catalytic active sites between PBSA molecules and the photoproducts formed.

The studies regarding photodegradation of sunscreen active ingredients are scarce. However, few authors have reported that progressive attacks of PBSA by hydroxyl radicals can result in cleavage or ring opening by-products. The AOPs often yield numerous degradation intermediates and photoproducts due to the non-selective reaction of the radicals with the organic pollutant. In the case of PBSA it can be mineralized into water and CO_2 . Moreover, the sulfonic group can be released as SO_4^{2-} , and the nitrogen atoms of the imidazole structure into NH_4^+ , and NO_3^- ; however, this may occur at a much lower rate than the degradation of the parent compound [31]. According to a recent study, the formation of NH_4^+ , and NO_3^- species depends on the pollutant chemical structure and the presence of catalysts, since typically the nitrogen atoms are converted into inorganic N, in the form of NH_4^+ , and due to a consecutive photo-oxidation, the NO_3^- is generated [34]. Recently, it has been reported that only 17% of the total organic carbon (TOC) was removed, even when most of the parent compound was degraded [31]. Furthermore, it has been reported that only ~30% of the total sulfate was mineralized when ~90% of PBSA was degraded [34]. These results suggest that the photoproducts obtained can be even more photoresistant, and probably require longer treatments, promoting the successive attacks that lead the PBSA degradation, including the hydroxylation, sulfonate elimination and ring opening mechanism steps [34].

3.2.3 Control experiments

The influence of the ZnONPs, oxygen sources, and the presence of the irradiation was studied using an initial PBSA concentration of 10 μM at pH 9, and 1.2 gL^{-1} of the catalyst. The fluorescence intensity was measured using an excitation wavelength of 302 nm (Figure 7).

Figure 7. PBSA degradation results showed as fluorescence intensities for photocatalysis, photolysis, catalysis (in absence of irradiation source), and under anoxic conditions (a); and fluorescence emission spectra obtained after different reaction times, using optimal catalytic conditions for the photodegradation of PBSA (b). The standard deviations for the measurements shown in figure A are less than 0.07.

For anoxic conditions, a constant N_2 purge was employed to remove the oxygen content in solution. Under these experimental conditions, PBSA remains almost constant since the photodegradation does not occur. This is due to the fact that under anoxic conditions the generation of oxygen-based radicals is avoided, and therefore the degradation does not occur. Moreover, during the preliminary stage of this research we obtained less than 30% of degradation with H_2O_2 or air bubbling solely. However, when both oxygen sources are combined, the degradation increased substantially (data not shown). Additionally, it was observed that the solely employment of the ZnONPs on the PBSA degradation is negligible in absence of the irradiation source. This occurs mainly because under dark conditions the catalyst is not activated, and no generation of electron-hole pairs is observed [28]. Under photolysis conditions, less than 20% of degradation occurred, suggesting that both, photolysis or catalytic pathways are not the main degradation routes for PBSA.

4.0 Conclusion

Sphere-like ZnONPs, with particle size of ca. 100 nm, were easily and eco-friendly synthesized, using a zinc salt as the precursor. The presence of a pure wurtzite crystal structure was confirmed after calcination at 300 °C for 15 min. ZnONPs were characterized by having a very high surface area of 413 m²g⁻¹, which could explain the high photocatalytic activity, since more than 90% photodegradation of PBSA was recorded after 180 min. The results obtained have demonstrated that PBSA experiences degradation mainly by a photocatalytic process. To the best of our knowledge, this investigation represents the first photocatalytic study of the degradation of PBSA employing synthesized ZnONPs, and opens a promising direction for future researches.

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