A comparative study of the performance of zinc oxide and iron oxide doped-zinc oxide photocatalysts toward the oxidization of phenol under UV-radiation and sunlight

M V Karavasilis¹, ², M A Theodoropoulou¹, ³ and C D Tsakiroglou¹, ⁴

¹ Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences, Stadiou str, Platani, 26504 Patras, Greece
² University of Patras, Department of Chemistry, 26504 Patras, Greece
³ Hellenic Open University, 26335 Patras, Greece
⁴ Corresponding author e-mail: etsakir@iceht.forth.gr

Abstract. In the present work, a comparative analysis of the photocatalytic degradation of phenol, was done for two different types of immobilized photocatalytic nanoparticles immobilized on 5mm sodalime beads by a facile and cost-effective method: (1) Zinc oxide (ZnO) and (2) Iron doped Zinc Oxide (Fe-ZnO). Tests of phenol degradation by using the immobilized catalyst were conducted in batch photoreactors under UVA light of 22W and summertime sunlight. These tests allowed us to evaluate the phenol degradation rate and photocatalyst durability under controlled conditions.

1. Introduction
The rapid growth of urban areas and industry during recent decades has contributed to the extensive pollution of water resources. Among the physicochemical methods commonly used for the degradation of recalcitrant organic pollutants from wastewaters, heterogeneous photocatalysis is an emerging and well-promising advanced oxidation process. In general, photocatalysis consists of three steps: (i) the generation of electrons (e⁻) in the conduction band (CB) and holes (h⁺) in the valance band (VB) upon irradiating the catalyst surface with radiation of intensity greater than or equal to that of the band gap of the catalyst; (ii) the separation of photogenerated electron–hole pairs from each other and their vigorous movement to catalytically active sites at semiconductor surface; (iii) the surface redox reactions, where the holes of the valence band act as strong oxidizing agents and the electrons of the conduction band act as strong reducing agents [1]. Under the presence of organic molecules/ions and water, the generated holes have a high oxidation potential and produce hydroxyl radicals, while the electrons reduce the oxygen adsorbed on the catalyst [2] [3].

There are two main ways through which photocatalysis can be applied. (1) The micro- or nano-particles of catalyst are suspended in the aqueous solution of pollutants. The main advantage of such a configuration is the high pollutant degradation rate thanks to the high specific surface area of micro- / nano-particles, but when upscaling the process at continuous flow conditions, the main disadvantage is that the photocatalytic particles have to be separated from the effluent and recycled to the bulk phase. (2) The catalytic particles may be immobilized on various substrates (e.g. activated carbon, alumina, glass, etc.) overcoming the separation process and facilitating the method application to large flow-
through systems. However, the main disadvantage of photocatalyst immobilization is the significant decrease of the specific surface area which is almost proportional to the rate of surface reactions. This disadvantage could be overcome with the proper design of the reactor, the adjustment of controllable parameters to values that favour the degradation of pollutants, and the selection of the appropriate substrate so as to maximize the photocatalytic activity[4].

Numerous photocatalysts have been studied during the last decades, but those based on ZnO have been identified as candidates able to degrade efficiently organic pollutants, due to their high photosensitivity, stability, and energy band gap (3.37 eV). In particular, transition metals such as silver, platinum, iron might improve the charge transfer by trapping the photochemical load carriers and enhancing the performance of the photochemical degradation process, caused by the recombination of electrons with holes prior to the peroxide activation process.[5] Moreover, it was also showed that iron doping could improve the chemical stability of ZnO nanoparticles in aqueous media [6]. Also a bandgap shift to lower energy region was observed, which enhances the transfer of electrons from the valence band to the conduction band, and in turn, increases the photocatalytic efficiency [7].

2. Materials
Chemicals of analytical grade and tri-distilled water were used for the preparation of photocatalysts and solutions: Phenol C_{6}H_{6}O, Iron(III) nitrate nonahydrate Fe(NO_{3})_{3}•9H_{2}O, potassium hexacyanoferrate (III) K_{3}[Fe(CN)]_{6} and sodalime spheres of diameter 5 mm were purchased from Merck, Zinc acetate dihydrate Zn[CH_{3}COO]_{2}•2H_{2}O (ZAC), hydrofluoric acid HF, Sulphuric acid H_{2}SO_{4}, ethanol 95% purity, acetone, hydrochloric acid HCl, were purchased from Honeywell, and 4-Aminoantipyrine was purchased from Glentham Life Sciences.

3. Synthesis of ZnO and Fe-ZnO photocatalysts immobilized on sodalime

3.1. ZnO immobilization
The deposition of nanoparticles on the surface of sodalime beads is done by the following steps: (a) the beads are submersed into dense hydrofluoric acid for 10 min to roughen their surface and then are washed with tri-distilled water; (b) the beads are immersed in the sodium hydroxide solution for 30 min at 80°C; (c) the beads are separated from the solution and placed in boat-shaped refractory boxes; (d) the boxes are filled with a 0.5M zinc acetate precursor solution until covering the beadpack; (e) the boxes are placed inside programmable ovens and kept for specific time intervals at gradually increasing temperatures 80°C, 110°C, 140° and 430°C; (f) the solid material is removed from the boxes and is rinsed with deionized water to remove residual nanoparticles and isolate the ZnO-coated beads [8].

3.2. Fe-ZnO immobilization
An analogous procedure was followed for the immobilization of Fe-ZnO nanoparticles on sodalime beads. The same steps were followed by changing only the precursor solution and mixing 0.2M of Zinc Acetate with 0.05M of Iron Nitrate.
3.3. Photocatalytic activity
The photocatalytic activity of immobilized catalysts was examined with respect to their capacity to degrade phenol dissolved in aqueous phase, either under UVA light by using a 22W UV-oven emitting at 370 nm, or under the summertime sunlight. All tests were performed in transparent 50mL beakers. The initial concentration of phenol was 10 ppm and the liquid volume was adjusted to 40mL. Atmospheric air was injected in the solution through an air pump at a flow rate of 0.3 L/min. The UV-oven was placed inside a thermostatted chamber at 25°C and the pH was recorded as a function of time by a sensor connected with a data logger (Vernier LabQuest stream). For each catalyst, eight cycles of experiments were completed to evaluate any differences in photocatalytic reaction efficiency and potential aging effects. During each test, aqueous samples were collected from the solution from time to time to measure the phenol concentration with a UV-Vis spectrophotometer (UV-1900 Shimadzu) at wavelength 505.5 nm by using the 4-AAP method [9]. Moreover, with the same types of photocatalysts, experiments were conducted outdoors under sunlight and the observed reaction kinetics was compared to the corresponding one measured under UVA light.

4. Results and discussion

4.1. Photocatalyst characterization

4.1.1. X-ray diffraction (XRD). The XRD diffraction patterns for ZnO and Fe-ZnO are shown in Figure 2. Peaks of both samples coincide each other. It confirms the crystalline nature and hexagonal phase (wurtzite structure) of ZnO with lattice constants a=3.249Å and c=5.206Å. The reflections observed at 31.7°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, 67.9°, 69.1°, 72.5°, 76.9° can be indexed to [100], [002], [101], [010], [110], [004], [202] planes of ZnO.
Figure 2. XRD patterns of ZnO and Fe-ZnO.

4.1.2. SEM images. The morphology of synthesized materials was examined with scanning electron microscopy (SEM), employing a Zeiss SUPRA 35VP instrument. The surface of the sodalime bead is covered almost fully by a uniform and dense layer of ZnO (Figure 3a), with the sizes of nanoparticles ranging from 45–220 nm (Figure 3b). Regarding the Iron doped structures, a dense layer of self-organized nanotubes is created with a cross section area 30-70nm², which are covered with nanoparticles of mean size 7nm (Figure 3c, d).

4.1.3. Photoluminescence. To assess the photocatalytic efficiency versus the recombination rate of photo-induced electron–hole pairs, the photoluminescence (PL) spectrum of ZnO and Fe-doped ZnO immobilized on sodalime beads surface was measured with a spectrophotometer (Cary Eclipse Fluorescence Agilent) over the wavelength range 350–650 nm. The spectra of both materials exhibit a wide peak at 395nm but it’s worth mentioning that the intensity of PL decreases by one order of magnitude when the ZnO is doped with iron (Figure 4a). This may be due to the fact that, the lower the excitonic PL intensity, the stronger the capacity of the dopants to capture photo-induced electrons and the higher the separation rate of photoinduced electrons-holes. Doping may offer competitive pathways for recombination resulting in quenching of the emission [10]. According to Cheng et.al [11] as the iron concentration increases, the crystal lattice exhibits fewer interstitial oxygen vacancies compared to pure ZnO. Habba et.al [12] found that the electrons are also trapped by the defects in the ZnO-Fe structure, thus leading to a lower electron–hole pair recombination rate, thus increasing the photocatalytic activity, and enhancing the reaction rates.
Figure 3. SEM images of (a,b) immobilized ZnO and (c,d) immobilized iron doped ZnO.

4.1.4. UV-Vis analysis. The two materials present similar shape of UV-Vis spectrum with 4nm difference in maximum peak (Figure 4b). By Tauc plot [13] method, a shift in energy band gap was observed with values 3.2eV and 3.11eV for undoped ZnO and iron doped ZnO, respectively (Figure 4b).

Figure 4. (a) PL spectrum and (b) UV-Vis spectrum with the apply of Tauc plot method.

4.1.5. XPS analysis. Surface analysis measurements were performed in a UHV chamber (P~5×10^{-10} mbar) equipped with a SPECS Phoibos 100-1D-DLD hemispherical electron analyzer and a unmonochromatized dual-anode Mg/Al x-ray source for XPS. The XP Spectra were recorded with AlKa at 1486.6 eV photon energy and an analyzer pass energy of 15 eV giving a Full Width at Half Maximum (FWHM) of 0.87 eV for Ag3d5/2 line. The analyzed area was a rectangle 15x7mm². The atomic ratios were calculated from the intensity (peak area) of the XPS peaks weighted with the corresponding relative sensitivity factors (RSF) derived from the Scofield cross-section taking into account the electron transport properties of the matrix and the energy analyser transmission function. For spectra collection and treatment, including fitting, the commercial software SpecsLab Prodigy (by Specs GmbH, Berlin) was used. The sample was in powder form and pressed on a foil.

Figure 5a shows the survey scan of Fe/ZnO sample where C, O, Na and Zn peaks are present. Figure 5b shows the detailed Fe2p core level spectrum. The Fe2p_{3/2} is at 711.1eV and the satellite at ~720eV are characteristic for Fe_{2}O_{3} chemical state. From the peak areas of Fe2p and Zn2p_{3/2} and the % atomic concentration derived are, 13.5% for Fe and 86.5% for Zn.
5. Photocatalytic activity

Eight comparative cycles of photocatalysis were performed for both materials and the results were used to estimate the kinetic rate constants. Regarding the tests conducted at 25°C in thermostatted chamber, it’s worth mentioning that UVA- leds emitting at 370 nm are attached throughout the internal surface of oven, within which the beaker with aqueous solution has been placed (Figure 6a). During each test, the pH was recorded and a typical transient behaviour during one cycle of photocatalysis is shown in Figure 6b. Assuming pseudo-first order kinetics, the kinetic constant of phenol photocatalytic degradation was estimated for undoped ZnO and iron-doped ZnO. Apart from the first cycle, in next cycles of catalyst reuse, the kinetic constant for Fe-doped ZnO was two (2) and three (3) times higher than that for undoped ZnO (Figure 7a). Regarding the tests conducted under sunlight, the temperature varied between 36°C-48°C and the kinetic constant was almost identical for undoped and doped catalysts (Figure 7b) and of the same order of magnitude with those resulting from tests under UVA light (Fig.7a, b).

Figure 8 shows the losses of catalyst mass during the successive photocatalysis cycles. It is evident that much less mass of particles is detached from the substrate for Fe-doped ZnO catalyst, which means that the presence of iron strengthens the stability of photocatalyst in aqueous media.

![Figure 5. (a) XPS Survey scan of Fe/ZnO sample (b) Detailed Fe2p XPS peak of Fe/ZnO sample.](image)

![Figure 6. The process of experiments, (b) a typical pH diagram during the whole experiment.](image)
Figure 7. Comparison of the pseudo-first order, $k_1$, reaction rate constants of undoped and doped ZnO catalysts during batch experiments under (a) UVA light, and (b) sunlight.

Figure 8. (a) Catalyst mass during all cycles of photocatalysis tests, and (b) percentage of mass loss.

6. Conclusions
In this study undoped and Fe-doped ZnO nanoparticles were synthesized and immobilized on the surface of sodalime beads, and tested with regard to the phenol photocatalytic degradation capacity in aqueous media. Very different structures of nanoparticle organization on substrate surface were confirmed from SEM images. Testing the two types of immobilized photocatalysts in multiple cycles, faster kinetics of phenol degradation at advanced iterative cycles of the process, and stronger attachment of nanoparticles on the substrate surface were confirmed for Fe-doped ZnO. The improved photocatalytic efficiency of Fe-doped ZnO catalysts is attributed to the faster electron-hole pair recombination which is reflected in PL and UV-Vis spectra. Preliminary studies show that both catalysts have comparable photodegradation capacity under sunlight.

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