

# Characterization and Photocatalytic Performance of Newly Synthesized ZnO Nanoparticles for Environmental Organic Pollutants Removal from Water System

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## 2. Materials and Methods

### 2.1. Synthesis of ZnO nanoparticles (ZnO-NPs)

According to the applied procedure, 100 ml of 0.5 M solution of the appropriate precursor was mixed with 100 ml of 0.5 M solution of sodium hydroxide (reagent grade,  $\geq 98\%$ , pellets (anhydrous), Sigma Aldrich) at room temperature. The solution was kept under continuous stirring for 2 h. The resulting white precipitate was collected by filtration, rinsed with deionized water, dried at 80 °C for 24 h and calcined at four different temperatures – 300 °C, 400 °C, 500 °C, and 700 °C for 5 h under static air conditions.

### 2.2. Materials characterization

The structure and morphology of ZnO-NPs were characterized by scanning electron microscope (SEM JEOL JSM-6460LV). The texture of the samples was investigated by means of specific surface area determined by fitting the BET isotherm equation, mean pore diameter and pore volume were determined from the desorption part of the N<sub>2</sub> isotherm by the Barrett-Joyner-Halenda (BJH) method. Pores were classified according to Brunauer-Deming-Teller method based on hysteresis loops of adsorption-desorption isotherms. Corresponding data for textural characterization were obtained by dynamic low temperature N<sub>2</sub> adsorption/desorption (LTNA) method, with He as a carrier gas, using a Micromeritics ASAP 2010 instrument. X-ray diffraction (XRD) measurements were performed on a Rigaku Miniflex 600 unit (Cu K $\alpha$  radiation,  $\lambda = 0.15406$  nm) using a counting step of 0.3 ° and a counting time per step of 3 s. The average diameters of crystallites were derived using the Scherrer equation.

### 2.3. Measurements of photocatalytic activity

The aqueous solutions were prepared using ultrapure water. All stock solutions were protected from light and stored at room temperature. Experiments were carried out using 20 mL of emerging pollutant solution, with an initial concentration of 0.03 mM (mass concentration of CLO = 7.191 mg/L, mass concentration of AMI = 8.322 mg/L and mass concentration of SUL = 9.864 mg/L) for all experiments, while catalyst loading was 1.0 mg/mL for all nanoparticle types. When the pH value was examined, dilute aqueous solutions of NaOH (ZorkaPharm, Šabac, Serbia) and HClO<sub>4</sub> (60%, Merck, Darmstadt, Germany) were used. The aqueous suspension of the catalyst was sonicated (50 Hz) in the dark for 30 min before irradiation, in order to uniformly disperse the particles of photocatalyst and to obtain adsorption equilibrium. The simulated sunlight energy flux was measured using a Delta Ohm HD 2102.2 radiometer (Padua, Italy) using an LP 471 UVA sensor with a spectral range of 315–400 nm, while in the case of visible radiation energy measurement, the radiometer was connected to an LP 471 RAD sensor (spectral range 400–1050 nm). Irradiation under SS was carried out using a 50 W halogen lamp (Philips) with the intensity of 0.1 W/cm<sup>2</sup> in the visible region and  $2.2 \times 10^{-4}$  W/cm<sup>2</sup> in the UV region. The suspension was thermostatted at 25.0 °C in the

stream of O<sub>2</sub> (3.0 mL/min), and then irradiated. During irradiation, the suspension was stirred at a constant rate under the continuous O<sub>2</sub>-flow. The obtained suspensions were filtered through Millipore (Millex-GV, 0.22 µm) PVDF membrane filters. The preliminary check confirmed the absence of pollutants adsorption on the filters.

#### 2.4. Analytical Methods

Kinetic studies of all investigated pollutants were monitored by ultrafast liquid chromatography with diode array detector (LC-DAD) using Shimadzu UFLC Nexera, equipped with an Eclipse XDB-C18 column (150 mm × 4.6 mm i.d., particle size 5 µm). All chromatograms were recorded in the wavelength range from 190–300 nm. Mixtures of acetonitrile (ACN, 99.9%, Sigma-Aldrich) and water were used as mobile phase for analysis of all studied pollutants, which was acidified with mass fraction of 0.1% H<sub>3</sub>PO<sub>4</sub> (85%, Sigma-Aldrich). In the case of CLO the UV/vis DAD detector was set to 210 nm (wavelength of maximum absorption of CLO) and the ACN : water ratio was 60 : 40 (v/v), following isocratic regime with flow rate of 1.0 mL/min. Conditions for SUL analysis using UFLC-DAD had UV/vis DAD detector at 232 nm (wavelength of SUL maximum absorption). The mixture of mobile phase, ACN and water, was 40 : 60 (v/v), following isocratic regime (flow rate was 1.0 mL/min). Also, samples of AMI were analyzed with an Inertsil ODS-4 column (2.1 mm × 50 mm *i.d.*, particle size 2 µm, 35 °C). The UV/Vis DAD detector was set at 206 nm (wavelength of AMI maximum absorption). The ratio of mobile phase for ACN and water, was 30 : 70 (v/v), following isocratic regime (flow rate was 0.4 mL/min).

Delta Ohm HD 2102.2 (Padova, Italy) was used for the UV energy fluxes measurements. The radiometer was fitted with the LP 471 UVA sensor (spectral range 315–400 nm), and in the case of visible energy radiometer was fitted with the LP 471 RAD (spectral range 400–1050 nm).

All experiments were performed at natural pH ~7, except in the case of examining the effect of the initial pH value of the suspension. The change in pH value during the degradation was monitored using a combined glass electrode (pH-Electrode SenTix 20, WTW) connected to the pH-meter (pH/Cond 340i, WTW).