



Green synthesis of fluorapatite from waste animal bones and the photo-catalytic degradation activity of a new ZnO/green biocatalyst nano-composite for removal of chlorophenols



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ABSTRACT

Wastewater from petroleum refineries contains toxic, carcinogenic and recalcitrant chlorophenols. This comes with the mandatory environmental aspect of the recycling of the organic wastes. This work aimed to prepare; fluorapatite (FAP) by a simple calcination process of waste animal bones (ABs), ZnO nanoparticles by a wet chemical method and ZnO/FAP binary oxide nano-bio-composite by a simple mechano-mixing technique and study their photo-catalytic degradation properties on chlorophenols. The obtained catalysts were characterized by high-resolution X-ray diffractometer, Fourier transform infrared spectroscopy, scanning electron microscope, transmission electron microscope, Brunauer Emmett-Teller and Barret-Joyner-Halenda methods and N₂ adsorption-desorption isotherms. The three prepared catalysts showed excellent photo-catalytic degradation activity under UV-irradiation towards 3-chlorophenol and 2,3-dichlorophenol. The photo-degradation followed the Langmuir-Hinshelwood L-H kinetic model with R² ≥ 0.962; however, the rate constant was strongly affected by the type of the catalyst and chlorophenols. New proposed mathematical correlations were elucidated to assess the relationship between the cumulative removal of the studied chlorophenols and the production of their photocatalytic oxidation intermediates. In the view of the ubiquity, environmental compatibility, and cost-effectiveness; the prepared green FAP from ABs as a readily available, sustainable and cheap waste byproduct of food industry proved to be a favorable photo-catalyst for remediating petroleum refineries wastewater. In an attempt to enhance the photo-catalytic degradation activities of ZnO towards the chlorophenols, the mechano-mixing process suggested a new approach to produce commercial amounts of nano-bio-composites of ZnO/FAP nanostructures with high quality and suitable structural and morphological features that would revolutionize the field of biomaterials.

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1. Introduction

Wastewater from petroleum refineries contains chlorophenols, which represents a serious ecological problem because of their high toxicity, carcinogenicity and resistance to biodegradation [1,2]. The European Union (EU) categorized 132 dangerous substances (based on their toxicity, stability, and bioaccumulation) that should be monitored in waters. Amongst these substances are organochlorinated compounds (or chlorophenols) and substances that can be converted to organochlorinated compounds [3]. The reported levels of chlorophenols (CPs) in contaminated environments, range from 150 µg/L to 100–200 mg/L [4]. However, small amounts of these compounds (at ppb to ppm) can be tested in water [5].

There are some literature data concerning photo-catalytic degradation of mono- and di- chlorophenols CP; 2-CP, 3-CP, 4-CP, 2,3-DCP and 2,4-DCP by TiO₂ nanoparticles NPs [6–8], ZnO NPs [9,10] and the enhancement of their photo-catalytic degradation by the bi-functional ZnO-TiO₂ catalysts [11].

Egypt suffers from huge amounts of rubbish, that can reach to approximately 70 million tonnes/year, and animal bones (ABs) are estimated to contribute to approximately 1% of it. The ABs are sold per ton between 39.44 \$ and 50.71 \$. ABs can be used in modern industries to produce conches or buttons, while fats and greases extracted from ABs can be used to produce soap, detergents or glue and gelatinous materials and then the remaining can be taken, grinded and re-used in the production of animal fodders or in the purification and leaching of raw sugar.

In order to find a kind of material with enhanced adsorption and photo-catalytic performance, this work aimed to prepare a new green nano-biocatalyst from the readily available, sustainable

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and cheap resource; ABs and study its photo-catalytic degradation properties on CPs. This study aimed also to synthesize ZnO NPs and investigate the possibility of the application of the simple mechano-mixing technique for the preparation of nano-bio-composite of ZnO/green biocatalyst, in an attempt to enhance the photo-catalytic degradation activities of ZnO towards the CPs.

2. Materials and methods

2.1. Chemicals

3-chlorophenol (3-CP) and 2,3-dichlorophenol (2,3-DCP) with purity of 98% (Sigma-Aldrich) were used in this study as model organic compounds for mono- and di- CPs, respectively. Acetonitrile and water (HPLC grade) were obtained from POCH. All other chemicals were purchased from Merck and used without further purification.

2.2. Catalyst preparation

2.2.1. Preparation of fluorapatite

The waste buffalo animal bones ABs were collected from local butcheries, and then they were washed with tap water, dried at 105 °C for 2 h in an oven and then grinded using a grinding mill (pulverisette6, FRITSCH, Germany) with rotational speed of 400 rpm and time 10 min. Then, they were sieved to constant sizes (<0.07 mm). Calcination was performed in a muffle furnace at 700 °C for 2 h [12]. The calcined catalyst was then stored in dark screw-capped vessels to avoid reaction with humidity and CO₂ in air before usage.

2.2.2. Preparation of zinc oxide nanoparticles

The ZnO NPs were synthesized by wet chemical method using zinc nitrate and sodium hydroxide precursors. 0.5 M aqueous ethanol solution of zinc nitrate tetra hydrate (Zn(NO₃)₂·4H₂O) was kept under constant stirring for 1 h using magnetic stirrer set at 200 rpm to assure the complete dissolution. 0.9 M aqueous ethanol solution of sodium hydroxide (NaOH) was also prepared in the same way. After the complete dissolution of the zinc nitrate, the 0.9 M NaOH aqueous solution was added under high speed constant stirring (500 rpm), drop by drop (for 45 min) touching the walls of the vessel. Then, the vessel was sealed and the reaction was allowed to proceed for 2 h. After the completion of the reaction, the solution was allowed to settle overnight and then, the supernatant solution was separated by decantation. The remaining solution after decantation, was centrifuged for 10 min, and then the ZnO NPs were separated from the rest of Zn(OH)₂ solution, washed three times with deionized water and ethanol to remove the byproducts which would be bounded with the NPs. Then, dried in air atmosphere at 60 °C for 12 h to assure the complete conversion of Zn(OH)₂ to ZnO.

2.2.3. Preparation of ZnO/Fluorapatite nano-bio-composite catalyst

The photo-catalytic nano-bio-composite catalyst, namely, ZnO·Ca₅(PO₄)₃F, was prepared by mechano-mixing technique [13]. A requisite amount of ZnO NPs was mixed with Ca₅(PO₄)₃F NPs in a ratio maintained at 50%, then the obtained mixture was milled thoroughly in planetary ball mill for 5 h to obtain a fine powder then the mixture was dried at 110 °C for 2 h.

2.3. Catalyst characterization

To determine the crystalline phases of the prepared catalysts, X-ray diffraction patterns were determined on a high-resolution X-ray diffractometer (XRD; PANalytical XPERT PRO MPD, the Netherlands) coupled with Cu k α radiation source ($\lambda = 1.5418 \text{ \AA}$)

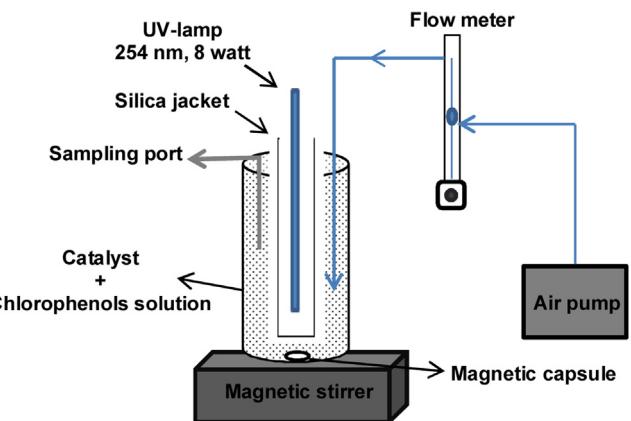


Fig. 1. Schematic diagram of the experimental set-up of the UV photo-reactor.

operated at 40 kV and 40 mA. The diffraction patterns were recorded at room temperature in the angular range of 4–70° (2θ) with a step size of 0.02° (2θ) and a scan step time of 0.5 (sec). The crystalline phases were identified using the ICDD-PDF database. The crystalline size of the catalyst was calculated from the XRD data using Scherrer's formula, as reported by Qin et al. [14]:

$$D \approx \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystal size of the NPs, θ (radian) is the diffraction angle, λ is the X-ray wavelength (1.5418 Å), and β is the width of the XRD peak at half height.

Analytical Fourier transform infrared (FTIR, Perkin Elmer Spectrum One, USA) instrument was used to investigate the chemical composition of the prepared catalysts. The samples were measured as KBr discs by mixing the sample with KBr (spectroscopic grade) where the solid samples were transferred into the cell after melting using an infrared lamp. The spectra of all the studied samples were measured in the range of 400–4000 cm⁻¹ with a suitable scan resolution of 4 cm⁻¹ and a scan rate of 16 cm/min.

The surface morphology of the prepared catalysts was studied using the scanning electron microscope (SEM; JEOL-model JSM-5300, Japan) and the particles size of the prepared catalysts was investigated by the transmission electron microscope (TEM; Jeol Jem 2100F, 80–200 kV, Japan).

The specific surface areas of the prepared catalysts were measured by Brunauer Emmett-Teller(BET) method using low temperature N₂ adsorption-desorption (NONA3200e, Quantachrome, USA). The samples were tested for pore volume and pore size distribution using the Barret-Joyner-Halenda (BJH) method.

All characterizations were done in replicates to assure reproducibility.

2.4. Photo-catalytic activity

A batch type cylindrical photochemical quartz reactor (Fig. 1), with continuous stirring of 250 rpm and aeration using air bubble distributor (1 dm³/min), was used at room temperature 25 ± 1 °C. A 300 cm³ of distilled water with an initial pH of 6 that contained 100 mg/L 3-CP or 2,3-DCP and 1 g/L catalyst, was initially kept in the darkness for 30 min for adsorption-desorption equilibrium. Afterward, the prepared mixture was exposed to UV irradiation using 254 nm (8 W) VILBER-LOURMATT-8C lamp. Samples of 5 cm³ were collected at prescribed time intervals, centrifuged for 3 min at 3000 rpm. Then the supernatant was separated to determine the photo-degradation rate of the chlorophenols CPs by high performance liquid chromatography HPLC.

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