Synthesis and evaluation of Fe_3O_4@HDL@Ag/Ag_3PO_4 composites for photocatalytic degradation of acetaminophen

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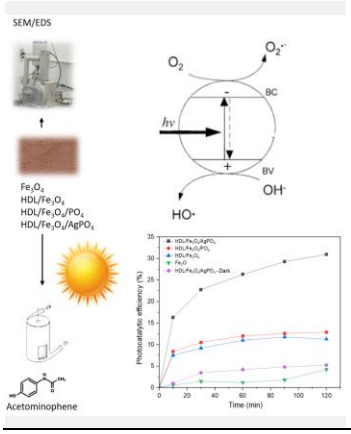

Acetaminophen is considered an emerging contaminant and is not removed by conventional water treatment processes due to its high solubility in water. Heterogeneous photocatalysis, a process capable of generating oxidizing species capable of destroying contaminant molecules, can be favorable for the removal of this drug. In this initial investigation, silver phosphate was studied as a photocatalyst due to its high activity in the visible region and the plasmonic effect, but its recovery from the liquid phase is challenging. As an alternative, materials with magnetic properties were synthesized, such as composites formed by magnetite immobilized in layered double hydroxides. Therefore, this study investigated the synthesis of Fe_3O_4@HDL@Ag/Ag_3PO_4 materials, which were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), and evaluated for their photocatalytic performance for acetaminophen degradation under visible light, showing potential for environmental applications.

Introduction

Emerging pollutants present in water and industrial effluents, such as acetaminophen, pose significant risks due to their toxicity, making it necessary to purify contaminated water. Conventional processes such as adsorption and ozonation have the drawback of low treatment yields, mainly due to the characteristics of pharmaceutical pollutants. An advanced technological alternative with "green" oxidation properties is heterogeneous photocatalysis, which is attracting increasing attention [1].

Heterogeneous photocatalysis is an advanced oxidative process (AOP) in which absorbed photons stimulate electrons of a semiconductor, raising them from the valence band to the conduction band, generating electron-lacuna pairs and participating in redox reactions [1].

Silver phosphate is highly efficient at decomposing pollutants in the visible region due to the plasmonic effect, but has the limitation of being difficult to separate from the liquid medium. As an alternative, materials with magnetic properties are synthesized, such as composites formed by magnetite (Fe_3O_4) immobilized in layered double hydroxides (HDLs) to control the distribution and size of the particles. In this context, the aim of this study is to obtain Fe_3O_4@HDL@Ag/Ag_3PO_4 heterostructures with a high level of structural organization, which are characterized and evaluated for the degradation of acetaminophen [1].

Material and Methods

The materials used in the synthesis were: iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, ≥ 99%, Sigma-Aldrich), iron (III) chloride hexahydrate ($FeCl_2{\cdot}6H_2O$, ≥ 98%, Sigma-Aldrich), ammonium hydroxide (NH_4OH), sodium hydroxide, (NaOH ≥ 97%, Química Moderna), zinc nitrate hexahydrate (≥ 98%, Sigma-Aldrich), chromium nitrate nonahydrate (≥ 99%, Sigma-Aldrich), sodium hydrogen phosphate (Na_2HPO_4, ≥ 98%, Química Moderna) and silver nitrate ($AgNO_3$, ≥ 99.8%, Vetec).

To synthesize magnetite, 50 mL of a solution containing 1.228 g of $FeCl_2{\cdot}4H_2O$ and 2.640 g of $FeCl_3{\cdot}6H_2O$ were initially prepared. Fe_3O_4 was precipitated by adding 5 mL of NH_4OH under stirring at a constant temperature of 60 °C for 30 minutes. The particles were washed and then dried at 80 °C for 18 h [2]. To synthesize the Fe_3O_4@HDL heterostructure, 0.1 g of Fe_3O_4 was dispersed in 60 mL of NaOH solution (7 g L^{-1}). After ultrasonication for 20 min, 40 mL of the solution containing Zn and Cr (molar ratio 2:1) was added to the alkaline solution under vigorous stirring. The resulting mixture was autoclaved at 100 °C for 12 h. The products were separated by centrifugation, washed with ethanol and deionized water. To intercalate the phosphate ions, 1.2 g of Fe_3O_4@LDH were dispersed in 200 mL of aqueous Na_2HPO_4 solution (0.25 mol L^{-1}) with continuous mechanical stirring at room temperature for 6 h. The products were collected by centrifugation. Finally, to synthesize the Fe_3O_4@HDL@Ag/Ag_3PO_4 heterostructure, 0.8 g of Fe_3O_4@HDL-PO_4^{3-} were dispersed in 100 mL of deionized water and then 15 mL of $AgNO_3$ solution (0.1 mol L^{-1}) was added to the solution with continuous stirring for 0.5 h. The products were separated by centrifugation, washed three times with pure water and then dried at 60 °C for 12 h [1].

Regarding the characterization of the photocatalysts, SEM (Vega 3 LMU Tescan equipment) at 20 kV was

used to analyze the morphology and size of the particles; the chemical elements present in the photocatalysts were analyzed using the EDS technique (Oxford equipment) coupled to the SEM. Photocatalytic tests were carried out in batch for 30 min in the dark to ensure adsorption equilibrium and for 120 min under simulated solar irradiation from a mercury iodide vapor lamp at a distance of 16 cm from the liquid surface, at constant temperature and agitation. For the experiments, the 100-mL reactor was filled with 50 mL of an aqueous acetaminophen solution with a concentration of 5 mg L^{-1} and a catalyst content of 50 mg L^{-1} (concentrations were based on tests previously carried out by the research group). Aliquots of 1 mL were collected at pre-determined time periods, filtered through a PVDF filter (13 mm, 0.45 µm) and analyzed by high-performance liquid chromatography (HPLC - Shimadzu - model LC20), equipped with a C18 column (Phenomenex, 250 mm × 4.6 mm) and a UV-Vis detector (SPD20A). The mobile phase consisted of methanol:water (25:75) at a flow rate of 1.0 mL min^{-1}; the injection volume and temperature were 50 µL and 35 °C, respectively.

Results and Discussion

Figure 1 shows the SEM micrographies for Fe_3O_4 and the synthesized heteroestructures.

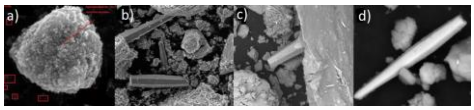

Figure 1: SEM micrographs: a) Fe_3O_4; b) Fe_3O_4@HDL; c) Fe_3O_4/PO_4^{3-}@HDL; d) Fe_3O_4@HDL@Ag/Ag_3PO_4.

According to Figure 1, the obtained Fe_3O_4 nanoparticles are roughly spherical and the HDL-based heterostructures are crystalline, agglomerated, disordered and overlapping. It was observed that, in addition to the HDL blocks, the synthesis procedure led to the formation of ZnO rods [3].

Figure 2 shows that, in addition to the presence of Fe, chemical elements from the metallic precursors used to obtain HDL, such as Zn and Cr, were also confirmed. PO_4^{3-} was intercalated into HDL by ion exchange with HPO_4^{2-} anions and $AgNO_3$ was used to intercalate Ag into the structure.

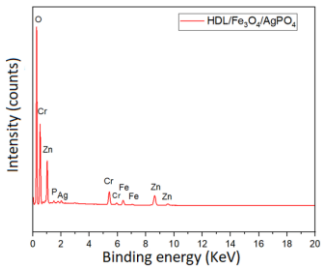

Figure 2: EDS Analysis for the Fe3O4@HDL@Ag/Ag3PO4 heteroesctruture.

Regarding the photocatalytic tests (Figure 3), it can be seen that there was an increase in efficiency for Fe_3O_4@HDL and Fe_3O_4@HDL@PO_4 and, as can be seen in the SEM micrographs, ZnO rods were formed; this efficiency may therefore have been influenced by the presence of ZnO, which the literature already mentions as having excellent photocatalytic properties [3]. However, it can be observed that the presence of silver phosphate (Ag_3PO_4) significantly increased the photocatalytic activity of Fe_3O_4@HDL@Ag/Ag_3PO_4. Figure 3 also shows that a reaction was carried out in the presence of Fe_3O_4@HDL@Ag/Ag_3PO_4 and in the absence of light; a much lower result can be observed when compared to the same material evaluated in the presence of light. This investigation shows that the photocatalytic contribution is significant, as desired [1].

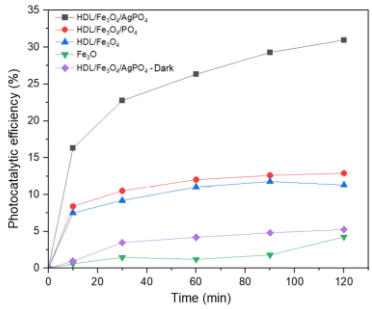

Figure 3: Photocatalytic efficiency of synthesized materials.

Conclusions

Using the proposed synthesis methods, it was possible to obtain different photocatalysts and to characterize these materials. The photocatalytic properties and performance of each of the materials discussed in relation to the degradation of the model contaminant acetaminophen showed interesting results for the treatment of aqueous solutions containing the drug.

Acknowledgments

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