Valorization of a waste iron material as a catalyst for amoxicillin degradation by Fenton and Photo-Fenton reactions

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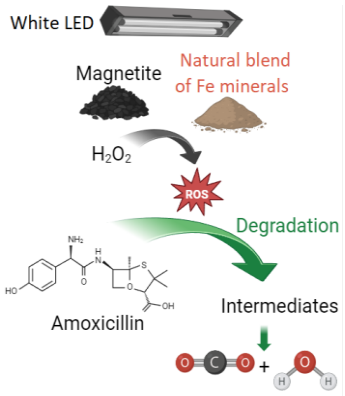

Magnetite and an iron residue from the mining industry were evaluated as catalysts in the degradation of amoxicillin, a widely used antibiotic. Parameters such as the concentration of H_2O_2, catalyst concentration, and exposure to light were analyzed. With the synthesized magnetite, 67.1% removal was achieved, while with the iron residue, a removal of 69.4% was obtained. This result is promising, indicating that the industry residue material has a higher catalytic activity than the synthesized solid. Additionally, it was observed that the photo-Fenton process was more effective than the Fenton process, probably due to the increased formation of radicals through light irradiation. These results suggest that the catalysts are promising for removing persistent organic pollutants in wastewater.

Introduction

Amoxicillin is a *β*-lactam antibiotic widely used to treat bacterial infections. Approximately 78% of amoxicillin is excreted unchanged through the urine [1]. Its wide use has made amoxicillin one of the most commonly detected antibiotics in wastewater [2]. Because amoxicillin can be toxic to some organisms, and microorganisms can develop resistance to this antibiotic, it is essential to use an effective treatment for its degradation.

Advanced oxidation processes (AOPs) are alternatives for removing persistent organic pollutants (POPs) from wastewater [3]. AOPs are based on the generation of a powerful oxidizing species *in situ*. Among the AOPs is the Fenton reaction, which uses Fe^{2+} or Fe (II) on a catalyst and H_2O_2 to generate hydroxyl radicals [3]. The Fenton reaction can be homogeneous or heterogeneous. The main disadvantage of homogeneous Fenton-type reactions is the working pH range (2-4), since in this range, the Fenton reaction can be propagated by the redox behavior of the Fe^{3+}/Fe^{2+} pair [3]. At a higher pH, it leads to the precipitation of iron sludge in the form of iron hydroxides [4]. Therefore, it is necessary to use significant amounts of acid to acidify the medium and then neutralize the treated solutions. To overcome this drawback, heterogeneous Fenton-type reactions have been evaluated, which allow the use of a near-neutral pH, these reactions have shown favorable results in neutral and even alkaline media [5]. Also, heterogeneous catalysts are widely studied due to the possibility of recovery and reuse.

To valorize a residue of the mining industry, a natural material composed of several iron minerals was evaluated as a catalyst for the degradation of amoxicillin through a Fenton and photo-Fenton heterogeneous processes at a natural pH. For comparison, synthetic magnetite was also evaluated as a catalyst for such a reaction.

Materials and Methods

The iron natural material was dried at 110°C. For the synthesis of magnetite, 13 mmol of $FeSO_4 \cdot 7H_2O$ and 35 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 15 mL of 0.5 M H_2SO_4. Then, the two solutions were mixed and diluted to 50 mL with 0.5 M H_2SO_4. The mixture was heated to 70 °C, and then 43% KOH solution was added at a flow rate of 500 µL/min for 30 min, followed by a change to 100 µL/min for 30 min to obtain a final pH of 9.15. Subsequently, the magnetite crystals were aged at 70 °C for 24 hours washed with deionized water to a pH of 7.0 and dried at 60°C for 24 h.

The crystalline phases of the catalysts were determined by X-ray powder diffraction (XRD) using an XRD 7000 MAXima instrument (Shimadzu Scientific Instruments) from 5° to 70° with a scanning step of 0.02° and a Cu anode (Kα 1.5406 Å).

The catalytic activity was analyzed through the Fenton and photo-Fenton reaction for the degradation of amoxicillin. For this, 8 mL of a 20 mg/L solution of amoxicillin was mixed with 4 mg of the catalyst for 24 hours in the dark to analyze the adsorption processes. Subsequently, for Fenton experiments, 10 µL of 30% H_2O_2 was added to the mixture (11 mM H_2O_2). For photo-Fenton reactions, a white LED light (24 W) was turned on and H_2O_2 was added as described before. This process was carried out in 8 different glass reactors to avoid catalyst loss. The samples were withdrawn at different reaction times (0, 15, 30, 60, 120, 240, and 360 min). The catalyst was separated by centrifugation or in the case of magnetite with a

magnet, and the samples were filtered and analyzed by HPLC on a Thermo UltiMate 3000 instrument with a Kynetex C18 column. (2.6 µm, 100 × 4.6 mm) and an UltiMateTM 3000 Multiple Wavelength Detector at 230 nm.

Results and Discussion

The diffraction pattern of natural iron material (Figure 1) shows peaks associated with goethite (α-FeOOH), hematite (α-Fe_2O_3), and siderite ($FeCO_3$). The diffraction pattern of synthesized magnetite (Figure 2) only shows peaks characteristic of this phase.

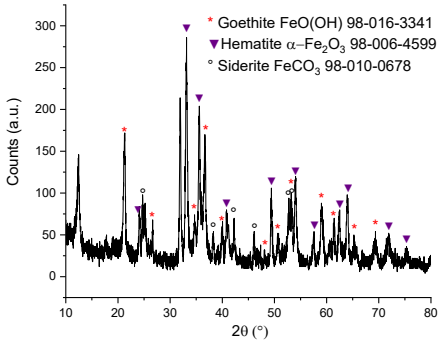

Figure 1. XRD pattern of iron residue.

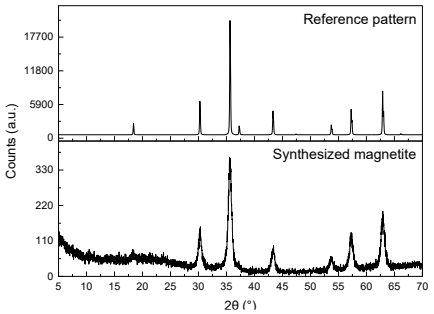

Figure 2. XRD pattern of the synthesized magnetite and reference pattern (ICSD: 96-900-2320).

The catalytic evaluation of iron material and magnetite in the degradation of amoxicillin suggests that amoxicillin has a stronger interaction with magnetite, as after 24 hours in darkness, it has a higher removal percentage (data not shown), which may be related to the reaction pH (≈6.50) magnetite has a more positively charged surface than the iron residue, making the interaction stronger with the carboxylate group the amoxicillin. However, the degradation process is greater with iron residue material. In both cases, greater removal of amoxicillin is achieved with visible light than in darkness (see Figure 3), obtaining more oxidized species in the presence of visible light, due to the increased formation of reactive oxygen species under irradiation.

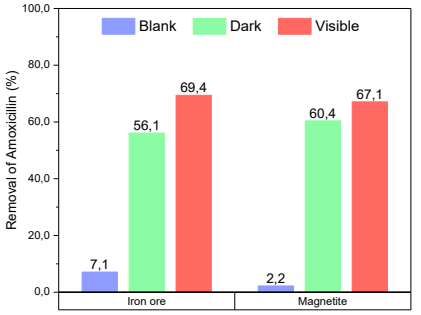

Figure 3. Removal of amoxicillin with iron residue and magnetite at 6 hours in darkness (dark), visible light (visible), and the blank.

With the iron material, more oxidized products were obtained than with magnetite. This was analyzed based on the retention time of the peaks in HPLC, as a shorter retention time indicates a lower interaction with the stationary phase, which is nonpolar. Therefore, products with shorter retention times would be more polar (more oxidized) (data not shown). This agrees with what is observed in Figure 3, where a greater removal of amoxicillin is achieved with the iron material.

Conclusions

The catalytic evaluation suggested that the adsorption process of amoxicillin on magnetite is greater than in the iron residue. Nevertheless, a greater degradation is observed using the iron residue material, which is important and promising to valorize an industrial waste. In addition, greater degradation of amoxicillin is observed by the photo-Fenton than for the Fenton process using both catalysts, which suggests that degradation with visible light is more efficient due to the generation of more reactive oxygen species.

Acknowledgments

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