Degradation of amoxicillin through the Fenton and photo-Fenton processes using Fe-PCH obtained from a raw clay

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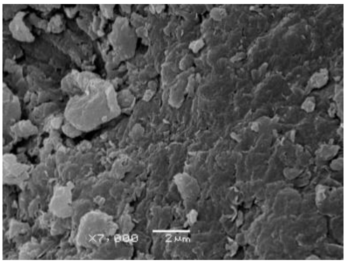

A raw Uruguayan clay was modified to obtain an iron-modified porous clay heterostructure (Fe-PCH). The clay and the Fe-PCH were characterized by TGA, XRD, XRF, nitrogen adsorption-desorption isotherms and SEM. The prepared material has a high specific surface area (386 m^2 g^{-1}) and a high volume of micropores and mesopores, 0.176 and 0.118 cm^3 g^{-1}, respectively. Fe-PCH was evaluated as catalyst in the Fenton and photo-Fenton process applied to the degradation of amoxicillin. The micropollutant was completely degraded by the photo-Fenton process with visible LEDs, while the Fenton process, under the conditions studied, allowed the degradation of 91% of the amoxicillin present. Thus Fe-PCH constituting a very promising material for water remediation.

Introduction

Micropollutants, found in water at low concentrations, are considered harmful to human health and the environment. This includes amoxicillin, a broad-spectrum semisynthetic antibiotic widely used in both human and veterinary medicine. It is often excreted from the body without being completely metabolized. Due to its widespread use, amoxicillin and its degradation products can be found in waterbodies. This can lead to imbalances in the aquatic ecosystem and contribute to the development of bacterial resistance [1].

Wastewater treatment plants are not capable of removing micropollutants such as amoxicillin. Therefore, these are present in surface and underground waters, and even in drinking water. However, heterogeneous Fenton and photo-Fenton processes, which requires a suitable catalyst, constitute a promising alternative for the degradation of amoxicillin.

Porous clay heterostructures (PCHs) are solids with high specific surface area and combined microporous and mesoporous structure. These materials are obtained by the modification of a cationic layered silicate with a surfactant and a silica precursor, followed by heat treatment to remove the surfactant. They are of great interest due to their potential application as adsorbents, catalyst supports and porous matrices for the encapsulation and controlled release of drugs [2,3]. The aim of this work was to prepare iron-modified PCH (Fe-PCH) from a raw Uruguayan clay and evaluate its catalytic activity in the degradation of amoxicillin by the Fenton and photo-Fenton processes.

Material and Methods

The catalyst was prepared from a Uruguayan raw clay, a calcium montmorillonite with few impurities. The clay was suspended in 0.2 mol L^{-1} of cetyltrimethylammonium chloride (CTAC) aqueous solution with magnetic stirring for 20 h at room temperature. It was then recovered, washed and suspended in a solution of 22 g L^{-1} of hexadecylamine (HDA) in ethanol for 1 h at 30 °C. Then, 3 mL of tetraethoxysilane (TEOS) was added to the suspension and stirring was continued for 20 h. The resulting solid was washed and suspended in 1 mol L^{-1} $Fe(NO_3)_3$ with magnetic stirring for 3 h at room temperature for iron incorporation by template-ion exchanged (TIE) method [4]. Next, it was recovered, washed, air dried and calcined at 650 °C for 6 h to obtain the Fe-PCH.

The solids were characterized by thermogravimetric analysis (TGA), nitrogen adsorption-desorption isotherms, X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF) and scanning electron microscope (SEM).

Catalytic tests were carried out to degrade amoxicillin (AMX) using Fe-PCH as catalyst and Fenton and photo-Fenton conditions. A batch cylindrical photo-reactor made of borosilicate glass and surrounded by visible LEDs (6500 K, 72 W) was used. The experimental conditions were $[AMX]_o$ =50 mg L^{-1}, $[H_2O_2]_o$ = 10 mmol L^{-1}, 1 g L^{-1} of catalyst and pH_o =3. During the tests the AMX concentration, TOC and iron in solution were determined.

Results and Discussion

X X-ray diffraction results (Figure 1) show that the basal spacing of the clay (d_{001}) increases in the Fe-PCH precursor. This indicates that CTAC and TEOS have been introduced into the interlaminar space of the clay.

The Fe content of the clay and the Fe-PCH determined by XRF (Table 1) confirmed the effective incorporation of iron in the catalyst.

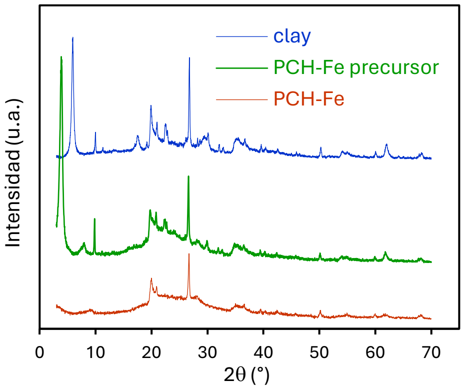

Figure 1. X-ray difractograms.

The textural properties of the solids (Table 1) were determined from the nitrogen adsorption-desorption isotherms. Fe-PCH has higher values of specific surface area and pore volume than the clay. This confirms the generation of a nanoporous structure in Fe-PCH, with the presence of micropores and mesopores. These properties suggest that Fe-PCHs has adequate properties for catalytic processes that involve iron as active species.

Figure 2 shows the results of the catalytic and adsorption tests performed. Fe-PCH catalyst shows catalytic activity in AMX degradation under Fenton conditions, achieving a removal of 91% at the end of the test. Besides, in the photo-Fenton test the degradation rate of AMX is higher, achieving its total removal in 180 min. Although AMX is degraded in these tests, the removal of TOC from the reaction medium is lower, reaching 33% for the photo-Fenton test. On the other hand, the stability of the catalyst could be verified, since at the end of the Fenton and photo-Fenton tests the concentration of iron in solution was less than 1 mg L^{-1}.

Since Fe-PCH is a material with high specific surface area and pore volume, a test was carried out to evaluate its ability to remove AMX by adsorption. The results (Adsorption test in Figure 2) show that this mechanism is not significant.

Furthermore, since the raw clay has a certain iron content, its catalytic activity was also evaluated. Figure 2 shows that although the raw clay shows some catalytic activity (removal of 28% of AMX at the end of the test under Fenton conditions), the iron incorporated in Fe-PCH turns out to have higher catalytic activity than the present originally in the clay structure.

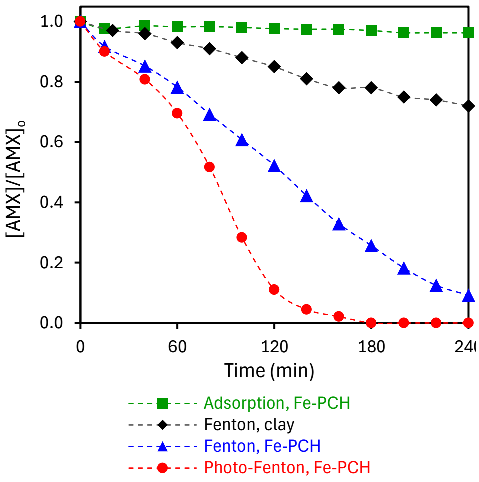

Figure 2. Result of catalytic test of amoxicillin degradation

Table 1. Textural properties and chemical composition for the clay and the PCH-Fe

Sample	S_{BET} ($m^{2\cdot}$ g^{-1})	V_p (cm^3 g^{-1})	$V_{\mu p}$(cm^3 g^{-1})	V_{mp}(cm^3 g^{-1})	Si (%)	Al (%)	Fe (%)
Clay	28	0.043	0.012	0.031	28.5	8.34	1.06
Fe-PCH	386	0.294	0.176	0.118	36.2	5.19	1.55

Conclusions

The modification of the raw clay allowed to obtain a nanoporous material (Fe-PCH) with a high specific surface area and pores volume, in whose structure it was possible to incorporate iron. Fe-PCH probe to be active as catalyst in the degradation of amoxicillin using the Fenton and photo-Fenton process, thus constituting a very promising material.

Acknowledgments

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