Removal of paracetamol, dexamethasone, and metformin by photo-Fenton.

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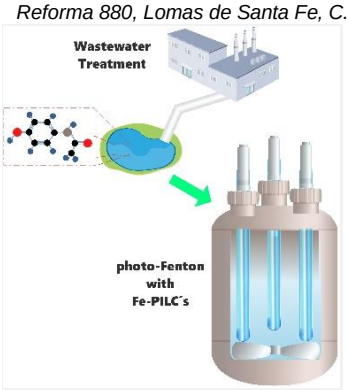

Photo-Fenton process catalyzed with iron pillared clays (Fe-PILC's) is an attractive alternative for the removal of paracetamol, metformin, and dexamethasone without the necessity of acidic conditions. Fe-PILC's were synthesized, characterized and its photocatalytic activity was tested is the degradation and mineralization of each parent compound as well as in a mixture of them.100% removal of each of drug was achieved and metformin is the molecule that required less time to be completely degraded, followed by paracetamol and finally dexamethasone. In addition, 73.5% of mineralization was achieved when a mixture of the three pharmaceuticals was treated.

Introduction

Inadequate wastewater treatment has led to an increasing number of pollutants in water bodies. This is especially dangerous when these are source of drinking water for some communities. Such is the case of the Madín Dam, which is responsible for supplying drinking water to Naucalpan and Atizapán, both places located in central Mexico [1].

In this context, it is essential to develop complementary technologies for conventional wastewater treatment able to effectively remove pollutants including, for example, dyes, pesticides and pharmaceuticals [2].

Paracetamol (PCM), metformin (MET) and dexamethasone (DEX) are among the common products re in domestic effluents due to its wide worldwide consume [1]. In addition, the prescription of this kind of drugs was considerably increased since the COVID-19 pandemic [3].

Advanced oxidation processes (AOPs) are technologies that are prominent for their great capacity to oxidize organic compounds and have positioned themselves as a promising strategy for water purification [4]. The heterogeneous photo-Fenton process is an AOP that combines UV radiation, hydrogen peroxide and an iron catalyst. This combination allows to increase the rate of generation of hydroxyl radicals for the removal of organic pollutants [5]. In addition, clays as a support for iron species allows to conduct the photo-Fenton process without necessity of maintaining acidic conditions unlike the classic homogeneous phase Fenton processes. This work aimed to remove paracetamol, dexamethasone, and metformin in aqueous samples by photo-Fenton reaction using iron pillared clays as catalyst.

Materials and methods

2.1 *Reagents*

Pillared clays were prepared from Bentonite (pure grade) supplied by Fisher Scientific. Sodium hydroxide (NaOH, 98%), Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.7%) and hydrochloric acid (HCl, 37.2%) were employed in the synthesis of pillared clays and supplied by Fermont. Hydrogen peroxide (H_2O_2, 30%) was supplied by Fermont. Acetaminophen ($C_8H_9NO_2$, 99%, MW:151.16, mp:168-172°C) and 11-dimethylbiguanide hydrochloride ($C_4H_{11}N_5 \cdot$ HCl, 97%, MW:165.62, mp:223-226°C) were purchased from Sigma Aldrich.

2.2 *Catalyst synthesis and characterization*

Iron pillared clays (Fe-PILC's) were synthesized by and ion exchange procedure [6], and them were characterized by X-ray diffraction (XRD) and atomic absorption (AAS).

2.3 *Degradation of paracetamol, metformin, and dexamethasone*

Degradation and mineralization of PCM, MET, DEX and its mixture (MIX) was performed by a photo-Fenton process using Fe PILC's as iron source. For this purpose, an intermittent reactor containing 1 L of the parent compound was employed. Different initial concentrations of the molecules to be degraded were tested: PCM (0.25 and 0.5 µg/L), MET (20 and 40 µg/L) and DEX (30 and 60 ng/L). The tested mixture (MIX) was prepared from 0.5 µg/L, 20 µg/L and 60 ng/L PCM, MET and DEX solutions, respectively. All the experiments were conducted at room temperature and the light source consisted in three 5.5-Watt UV mercury lamps (λ= 254 nm). The reaction products were monitored with high-performance liquid chromatography (UHPLC) while the MIX mineralization degree was followed by total

organic carbon (TOC) analysis.

Results and discussion

3.1 *Catalyst characterization*.

The incorporation of iron within the clay layers was verified by XRD analysis given by an increase in the basal space, from 9.6 Å (natural clay) to 21.43 Å. On the other hand, by AAS it was found that the iron content was 10.5% per gram of Fe-PILC.

3.2 Degradation of paracetamol, metformin, dexamethasone, and their mixture.

In Table 1 are summarized the results about the reaction rate achieved and the final pH of the sample through different photo Fenton experimental conditions. In addition, Figure 1 shows the degradation profile for PCM, MET and DEX.

A 99.67 and 88.27 % PCM removal was attained in 60 min when the initial concentration of the pollutant was 0.5 and 0.25 µg/L, respectively. After PCM samples treatment, pH turned to acidic conditions and this is related to the presence of the main derivatives of PCM, like carboxylic acids. On the other hand, metformin was positioned as the molecule with the higher degradation rate, reaching 100% in only 10 min regardless its initial concentration. The corresponding reaction rates were 68 x 10^{-11} and 101 x 10^{-11} mol s^{-1} L^{-1} for 20 and 40 µg L^{-1}, respectively. For the case of DEX experiments, during the first 5 min it was removed 65% and 88% of the original compound when the initial concentrations were 0.03 µg L^{-1} and 0.06 µg L^{-1}, respectively. It was found that the DEX removal occurred at a slower rate in comparison to PCM and DEX and it was required up to 400 min to achieve a 100% removal. In consequence, reaction rates of DEX removal are the smallest of this study as is presented in Table 1. Lastly, in the case of the mixture of the three pollutants (MIX) it was reached a 73.46% mineralization in 420 min corresponding to a reaction rate of 996 x 10^{-11} mol s^{-1} L^{-1}.

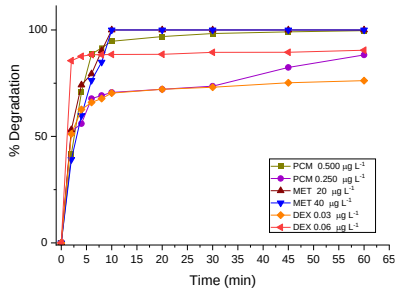

Figura 1. Degradation profile of PCM, DEX, and MET at different initial concentrations.

Table 1. Removal of paracetamol, metformin, and dexamethasone by photo-Fenton catalyzed by Fe-PILC's. [a]

Drug	Initial Concentration (µg L^{-1})	[H_2O_2 x 10^{-3}] (µL L^{-1})	Catalyst loading (mg L^{-1})	$pH_{initial}$	pH_{final}	$-r_{a0}$ x 10^{-11} (mol s^{-1} L^{-1})
PCM	0.250	2.7	0.5	6.34	5.5	1.17
	0.500	5.4		5.42	4.6	1.38
MET	20	73		6.21	4.5	101.05
	40	140		5.51	4.3	68.622
DEX	0.03	0.32		7	6.5	0.0519
	0.06	0.63		6.53	4	0.2324
MIX	0.500, 20 y 0.06	115000		6.75	4.25	996

[a] All experiments were performed at 278 K.

Conclusions

Iron pillared clays (Fe-PILC's) were synthesized by ion exchange with an iron content of 10.5% for the degradation of several pharmaceutical products by means of a photo-Fenton process. It was assessed different initial concentrations of paracetamol, metformin and dexamethasone. In all the cases, a 100% removal of each molecule was achieved although at a different reaction rate. Metformin was eliminated at higher rates in comparison to paracetamol and dexamethasone. In addition, a 73.5% mineralization of a mixture consisting of paracetamol, metformin and dexamethasone was achieved in 420 min. Fe-PILC's are a convenient iron source for Fenton processes and it can be extended to the removal of another organic compounds looking for viable technologies for water treatment.

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