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Enhanced degradation of metronidazole by sunlight via photo-Fenton process under gradual addition of hydrogen peroxide

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ABSTRACT

The present paper has investigated the application of solar energy as renewable, abundant, free and clean energy driven advanced oxidation process (photo-Fenton), for the mineralization of metronidazole (MTZ) as the most important drug of the group of 5-nitroimidazole. The hydrogen peroxide (H_2O_2) was added slowly and gradually over time in order to limit side reactions. The kinetics of organic matter decay was monitored by the chemical oxygen demand (COD) and the absorbance measurements. The experimental results showed that the solar photo-Fenton system leads successfully to 96% of COD removal for 960 mg L^{-1} COD_0 under optimal experimental conditions (1 mmol L^{-1} $Fe(II)_0$, H_2O_2 dosing rate of 2 mmol min^{-1}, pH 3 and at 60 °C) after 12 min. The MTZ concentration decay and the COD removal obeyed a pseudo-first-order kinetics. Compared with Fenton process, the exposition of the reactor to sunlight enhanced the mineralization process by 16%.

1. Introduction

The widespread use of antibiotics in human and veterinary medicine is the cause of their introduction into the aquatic environment. Several negative effects can be induced after their bioaccumulation [1,2]. Among these effects, the risk assessment should cover their toxic or allergenic effects when they are in the state of traces in complex mixtures of pollutants in sewage and surface waters [3]. Moreover, another problem is related to the antibiotic-resistant bacteria, causing the loss of therapeutic properties of these drugs [4,5].

The use of appropriate methods for the treatment of water containing antibiotics is necessary. Recently, the advanced oxidation processes (AOPs) have proven to be highly effective in the removal of the majority of the contaminants from wastewaters [6–9]. Among all AOPs, the Fenton and photo-Fenton processes have been frequently used techniques.

Oxidation of organic pollutants by Fenton process is based on hydroxyl radicals (HO•) produced from hydrogen peroxide molecules in the presence of ferrous ions (catalyst) as shown in Eq. (1).

$$H_2O_2 + Fe(II) \rightarrow HO^{\bullet} + OH^{-} + Fe(III) \quad (1)$$

Ferrous ions are slowly regenerated as shown in Eq. (2) [10].

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HOO^{\bullet} + H^{+} \quad (2)$$

When the Fenton reaction is conducted by solar irradiation (photo-Fenton), additional reactions occur in the presence of light that produce hydroxyl radicals from hydrogen peroxide photolysis, or increase the production rate of hydroxyl radicals [11], thus increasing the efficiency of the oxidation process Eq. (3).

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \quad (3)$$

Moreover, the reduction of ferric to ferrous ions is promoted with the generation of additional •OH radicals, as shown in Eq. (4) [12].

$$Fe(III) + H_2O \xrightarrow{h\nu} HO^{\bullet} + Fe(II) + H^{+} \quad (4)$$

Due to the toxicity, potential mutagenicity and carcinogenicity of MTZ, wastewaters contain MTZ pose a major risk to the environment and human health [13,14]. Therefore, the removal of the MTZ from wastewater is necessary. Many studies were focused on the treatment of MTZ wastewater by AOPs [15–20]. In this context, the specific objective of this study was to establish the characteristics of solar photo-Fenton oxidation process for the effective removal of MTZ from synthetic wastewater. A series of experiments was conducted to determine the most important process variables of the solar photo-Fenton reagent such as H_2O_2 dosing rate and Fe^{2+}

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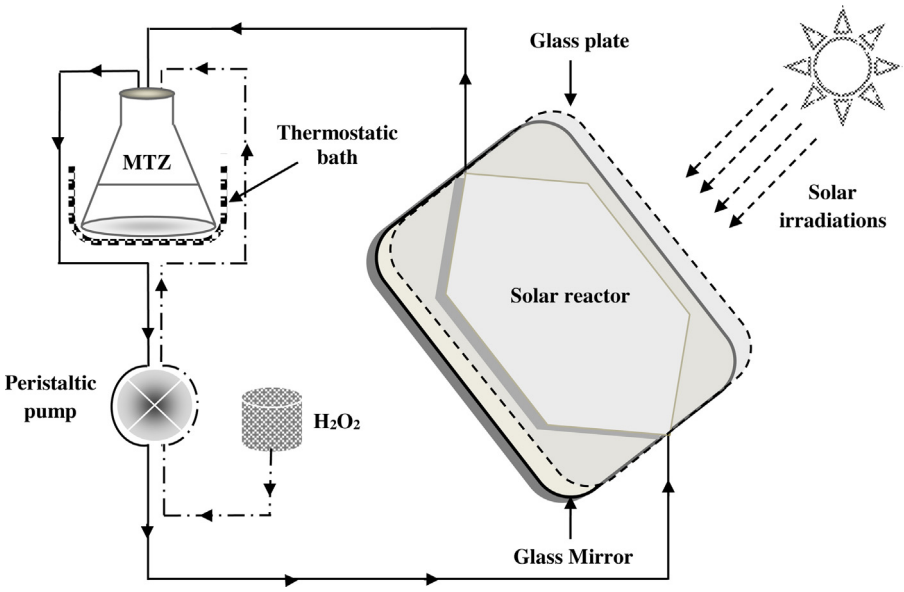

Fig. 1. Scheme of solar photo-Fenton reactor.

concentration, and experimental parameters such as pH, treatment time, temperature and the effect of solar irradiation.

2. Experimental

2.1. Chemicals

MTZ was taken from Winthrop Pharma Tunisia. All solutions were freshly prepared with double-distilled water. The sulfuric acid of analytical grade was employed for pH adjustment. Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was obtained from Riedel-de Haën (Seelze-Hannover, Germany) and used as catalyst. Hydrogen peroxide (110% v/v), H_2SO_4, Na_2SO_4 and NaOH were provided by Merck (Darmstadt, Germany).

2.2. Solar reactor design

The schematic illustration of the experimental device used in this work is shown in Fig. 1. The solar reactor is consisted of a rectangular mirror glass (50 × 80 cm) on which is placed in parallel at 5 mm a glass plate of the same size. The exposed volume of 460 mL has an hexagonal shape. The reactor is fixed at a platform of aluminum placed 34° to the horizontal. The mirror is used to reflect solar irradiations in order to give more energy to the exposed MTZ solution. This later is circulated from the bottom to the top to fill the entire volume of the reactor.

The experiments were carried out at the National Engineering School of Sfax, Tunisia (approximately 3 m amsl, latitude: 34° 44′ N, longitude: 10° 45′ E) between June and August 2015. The solar irradiation intensity was about 850 W m^{-2}. The temperature was controlled using a thermostat (Julabo Labortechnik GMBH, Sellback, Germany). A peristaltic pump (Cole-Parmer Instrument, Chicago, Illinois 60648 USA) was used to circulate the treated volume (1 L) through the reactor with a flow rate of 82 mL min^{-1}. This pump was simultaneously used to generate the flow of the hydrogen peroxide with a constant rate of 1 mL min^{-1}.

2.3. Analysis

The COD measurement during the processing permitted the evaluation of the kinetics of organic matter decay. Its values were determined by the dichromate method [21] using a spectrophotometer (Shimadzu UV-Mini 1240 UV–vis Spectrophotometer).

For the absorbance measurements, samples taken during the treatment were analyzed by a spectrophotometer (Shimadzu 1650 PC).

The MTZ concentration was determined by Square Wave Voltammetry (SWV) method under optimal experimental conditions as described in our previous work [22]. Samples of 2 mL were withdrawn from the reactor at selected intervals for MTZ analysis. These samples were diluted 10-fold with double-distilled water and the pH was adjusted to 11. SWV analyses were carried out by a potentiostat-galvanostat (VoltaLab PST050), using a conventional three-electrode cell. The cathode was a boron-doped diamond (7×10^{-2} cm^2) electrode and the anode was a Pt electrode (1 cm^2). The reference electrode was a saturated calomel electrode (SCE).

3. Results and discussion

3.1. Effect of the dosing rate of H_2O_2 on the mineralization of MTZ

In solar photo-Fenton process, hydrogen peroxide and ferrous ion are two major chemicals, determining the operating efficiency as well as cost. Theoretically, in absence of UV radiations, the total mineralization of 1 mol of MTZ needs 42 mol of HO• according to the Eq. (5).

$$C_6H_9N_3N_3O_3 + 42\,HO^{\bullet} \rightarrow 6\,CO_2 + 24\,H_2O + 3\,NO_3^- + 3\,H^+ \quad (5)$$

From Eq. (1), one mole of H_2O_2 produces one mole of HO•. So, one mole of MTZ needs 42 mol of H_2O_2. For initial MTZ concentration of 500 mg L^{-1} (2.92 mmol L^{-1}), 122 mmol of H_2O_2 are required. Since H_2O_2 was introduced gradually into the reactor for 30 min, its dosing rate was estimated to be about 4 mmol min^{-1}.

Moreover, high quantities of ferrous ions might produce a great amount of Fe(III) sludge. The treatment of the sludge requires a large amount of chemical and manpower [23,24]. For this reason, a few amount of Fe(II) (1 mmol L^{-1}) was added to the solution.

To determine the optimal dosing rate of H_2O_2, experiments were performed for H_2O_2 dosing rate in the range of 0.5–4 mmol min^{-1} at pH 3. The initial MTZ concentration was 500 mg L^{-1} corresponding to an initial COD of 960 mg L^{-1}.