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Degradation of four pharmaceuticals by solar photo-Fenton process: Kinetics and costs estimation

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ABSTRACT

Solar photo-Fenton process for degradation of four types of pharmaceuticals namely amoxicillin, ampicillin, diclofenac, and paracetamol was studied. Experiments were carried out by solar compound parabolic collectors (CPCs) reactor with borosilicate tubes and capacity of 4.0 L. Oxidation of each pharmaceutical was investigated individually using 100 mg/L synthetic solution. The influence of irradiation time, initial pH value, and dosage of Fenton reagent were investigated. Paracetamol, and amoxicillin were completely removed after 60 and 90 min of irradiation respectively. Complete degradation of ampicillin and diclofenac was occurred after 120 min. The removal of pharmaceuticals was significantly affected by changing pH values from 3 to 10. Complete removal of all pharmaceuticals was achieved under acidic conditions (pH 3). The optimum H_2O_2 and $FeSO_4.7H_2O$ dosage were 1.5 and 0.5 g/L, respectively. The results of photo-Fenton experiments fitted the pseudo-first order kinetic equation with high correlation. Costs estimation of 30 m^3/d full scale solar photo-oxidation plant was assessed.

Introduction

Recently, the pharmaceutical industry became widespread because of the growing needs of its different products which are used for human and animal medications [1]. The wastewater of the pharmaceutical companies contains several bio-recalcitrant organics which are difficult to be removed by conventional wastewater treatment processes [2,3]. Pharmaceuticals rich wastewater are not only generated from industry but also low concentrations of several types of pharmaceuticals were reported to be exist in municipal wastewater, surface and ground water [1,4]. Among all the pharmaceutical compounds, antibiotics and drugs are considered the most significant because of its high usage and consumption in both veterinary and human medicine [5,6]. Moreover, the presence of low concentration of antibiotics in the wastewater leads to improvement of bacteria resistance against the existing antibiotics [7]. Accordingly, wastewater containing pharmaceuticals compounds should be treated prior discharging into the sewer networks and/or surface water.

Usually, the attention received by conventional biological treatment far exceeds that of other treatment methods, in part due to its low cost, high stability, and easy operating. However, the presence of toxic and bio-recalcitrant organics detracts the viability of biological treatment process [8]. Advanced oxidation processes (AOPs) have been reported as particularly efficient technologies for removal of bio-resistant organics like pesticides, pharmaceuticals, and phenolic compounds [9]. In AOPs powerful reactive hydroxyl radicals ($HO^{\bullet}$) are produced by specific chemical reactions in aqueous solutions [10]. ($HO^{\bullet}$) is able to destroy even the most resistant organic molecules and convert them into less persistent compounds and benign end products such as CO_2, H_2O and inorganic ions [11,12]. Fenton reaction is an advanced oxidation process that generate a highly reactive ($HO^{\bullet}$) by the combination of Fe^{2+} and H_2O_2[13]. The photo-Fenton process is a typically enhanced Fenton reaction with higher rate and faster mineralization of recalcitrant organics than the dark reaction process and can take the advantage of utilizing UV irradiation from the solar light [14,15]. In the reaction of the photo-Fenton process Fe^{2+} ions are oxidized by H_2O_2 to Fe^{3+} and one equivalent ($HO^{\bullet}$) is generated [5,16]. In aqueous solutions the resulted Fe^{3+} act as the

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light absorbing species that produce another radical while the initial Fe^{2+} is reproduced as illustrated in Eqs. (1) and (2) [17]:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {}^{\bullet}OH + OH^{-} \quad (1)$$

$$Fe^{+3} + H_2O + h\upsilon \rightarrow Fe^{+2} + {}^{\bullet}OH + H^{+} \quad (2)$$

According to the light sensitivity of the photo-Fenton reaction with respect to the sunlight spectrum, the utilization of a solar light is reported to be very economic and simple alternative when compared to UV lamps specially for treatment of wastewater at a full scale [18,19]. Several researchers reported that compound parabolic collectors (CPC) technology is suitable for application of solar photo-Fenton process [20–22] because UV light is reflected and intensified towards the solution moving in the reactor tubes [15,22].

The aim of the present study is to evaluate photo-Fenton reaction for treatment of pharmaceutical wastewater. For this purpose, high concentration solutions of common antibiotics namely amoxicillin and ampicillin and two drugs namely diclofenac and paracetamol were tested. Compound parabolic collectors (CPCs) reactor depending on the solar light was used. The effects of several parameters such as irradiation time, initial pH, and Fenton reagent dosage on the degradation of pharmaceuticals were investigated. Pseudo-first order kinetic model was tested. In addition, Costs of full scale reactor were estimated.

Materials and methods

Chemicals

Amoxicillin was purchased from GlaxoSmithKline. Ampicillin, paracetamol, and diclofenac were obtained from Eipico and used as received without further purification. Ferrous sulfate hydrate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (H_2O_2), sulfuric acid, and methanol was purchased from Sigma–Aldrich company.

Experimental procedures

Solar photo-Fenton experiments were carried out using compound parabolic collectors (CPCs) reactor placed in Borg, Alarab City, Egypt (Latitude 30°52′, Longitude 29°35′) on the roof of environmental engineering department. The photo-reactor module is ($0.36\,m^2$) and consists of six borosilicate tubes with diameter 25.4 mm and length 750 mm mounted on a curved polished aluminum reflector sheet with radius of curvature 92 mm. The illuminated volume of CPCs is 2.3 L. The reactor is connected from inlet and outlet with a tank containing the pharmaceutical solution and provided with stirrer to keep the homogeneity of feedstock. The solution was continuously circulated in closed cycle with flow rate of 2 L/min. A schematic diagram of the experimental set-up is shown in Fig. 1.

The reactor was fed with 4 L of the pharmaceutical solution. Pharmaceuticals were treated individually in separate solutions. Initial concentration was 100 mg/L of one pharmaceutical for all experiments. First, pH was adjusted by H_2SO_4, or NaOH. Then H_2O_2 (0.5–2.0 g/L) and $FeSO_4 \cdot 7H_2O$ (0.1–0.75 g/L) were added. The solar irradiation was measured by Met one Portable Weather Station (Model 466A) installed in the same location. The normalized illumination time (t_{30w}) was used to compare between photo-catalytic experiments instead of exposition time (t). The normalized illumination time was calculated by the Eqs. (3) and (4) [16,23].

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \left(\frac{UV}{30}\right)\left(\frac{V_i}{V_t}\right) \quad (3)$$

$$\Delta t_n = t_n - t_{n-1} \quad (4)$$

where t_n: the observed experimental time for each sample, UV: the average solar ultraviolet radiation (W/m^2) measured during Δt_n, $t_{30\,W}$: the normalized illumination time, which refers to a constant solar UV power of $30\,W/m^2$ (typical solar UV power on a perfectly sunny day around noon), V_t: the total reactor volume and V_i: the total irradiated volume.

Analytical methods

The concentrations of pharmaceuticals were quantified by Shimadzu HPLC using C-18 phenomenex reverse phase column, degasser (20A5), pump (LC-20AT), and prominences Diode Array Detector (SPD-M20A). The samples were filtered by microsyringe filters (0.2 μm). The mobile phase was (60:40) 0.025 moles KH_2PO_4 buffer solution in ultra pure water and acetonitrile at a flow rate of 0.50 mL/min. and temperature of 60 °C. H_2O_2 concentration was quantified by $KMnO_4$ titration method described by (Savarino and Thiemens) [24].

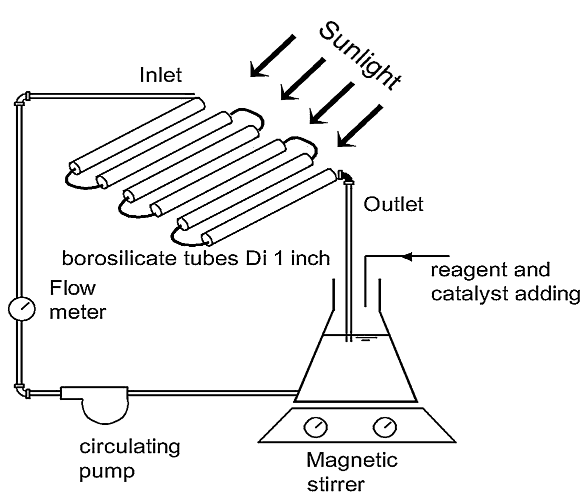

Fig. 1. Schematic diagram of the solar reactor.

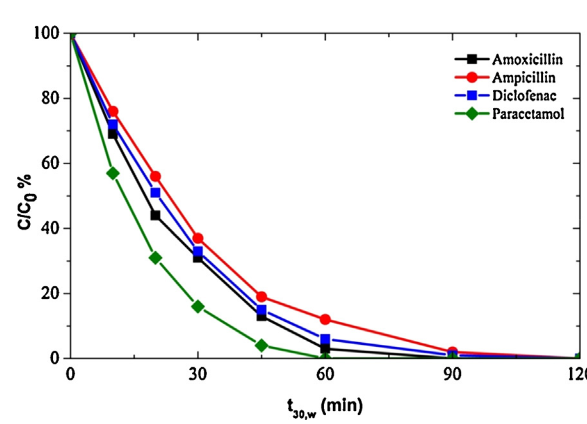

Fig. 2. Effect of irradiation time on degradation of pharmaceuticals, initial concentration of all pharmaceuticals = 100 mg/L, initial pH 3.0, H_2O_2 dose = 1500 mg/L, $FeSO_4 \cdot 7H_2O$ dose = 500 mg/L.