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Sonophotolytic degradation of synthetic pharmaceutical wastewater: Statistical experimental design and modeling

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ABSTRACT

The merits of the sonophotolysis as a combination of sonolysis (US) and photolysis (UV/H_2O_2) are investigated in a pilot-scale external loop airlift sonophotoreactor for the treatment of a synthetic pharmaceutical wastewater (SPWW). In the first part of this study, the multivariate experimental design is carried out using Box–Behnken design (BBD). The effluent is characterized by the total organic carbon (TOC) percent removal as a surrogate parameter. The results indicate that the response of the TOC percent removal is significantly affected by the synergistic effects of the linear term of H_2O_2 dosage and ultrasound power with the antagonistic effect of quadratic term of H_2O_2 dosage. The statistical analysis of the results indicates a satisfactory prediction of the system behavior by the developed model. In the second part of this study, a novel rigorous mathematical model for the sonophotolytic process is developed to predict the TOC percent removal as a function of time. The mathematical model is based on extensively accepted sonophotochemical reactions and the rate constants in advanced oxidation processes. A good agreement between the model predictions and experimental data indicates that the proposed model could successfully describe the sonophotolysis of the pharmaceutical wastewater.

1. Introduction

During the last few decades, the production and consumption of pharmaceutical compounds have been increased significantly. Nowadays, huge volumes of pharmaceutical compounds are used for the prevention and the treatment of diseases in both human and animals. Consequently, an enormous amount of wastewater is generated in pharmaceutical industries (Laera et al., 2011; Mohapatra et al., 2014). The presence of high concentrations of biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solid (TSS), and the low biodegradability make industrial pharmaceutical wastewater as one of the most toxic industrial wastes. Since the wastewater contains various quantities of organic and inorganic solvents, catalysts, raw materials, and reaction intermediates, finding efficient treatment procedure is intricate (Gupta and Hung, 2004; Sreekanth et al., 2009). The widespread occurrence of pharmaceuticals and personal care products (PPCPs) in an aquatic environment is an important problem with unknown consequences. During the last decade, the number of studies focusing on the prevalence of PPCPs in water environments has increased drastically (Fent et al., 2006; Guerra et al., 2014; Miège et al., 2009; Yan et al., 2014). Also, numerous treatment technologies could be found in the open literature which concerns the removal of these contaminants from aquatic environment. Coagulation–flocculation, adsorption through activated carbon, aerobic activated sludge process, and membrane bioreactors are frequent examples of such technologies (Chang et al., 2008; Ghafoori et al., 2014c; Mowla et al., 2014; Mutamim et al., 2012; Oz et al., 2004; Snyder et al., 2007; Suarez et al., 2009).

Conventional biological methods are considered as the most economical choice of treatment for pharmaceutical wastewater, however, it has been reported in several research studies that certain types of the PPCPs are nonbiodegradable and persistent to the biological systems. Therefore, these refractory substances would discharge into the surface and ground water resources where their presence in drinking water potentially produce harmful effects on both humans and ecosystems (Battimelli et al., 2010; Brausch and Rand, 2011; Mannucci et al., 2010; Strenn et al., 2004). Therefore, in order to prevent such potential detrimental effects, the application of advanced and more powerful treatment systems seems to be indispensable. Advanced oxidation processes (AOPs) are one of the most effective treatment

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technologies which have been intensively employed as a tool to decompose the bioresistant organic contaminants (Tabrizi and Mehrvar, 2004; Bustillo-Lecompte et al., 2014; Cao and Mehrvar, 2011; Ghafoori et al., 2012, 2014a, 2014b; Hamad et al., 2014; Johnson and Mehrvar, 2008; Martins and Quinta-Ferreira, 2011; Mohajerani et al., 2010a,b; Sanches et al., 2010; Trovó et al., 2011; Yu et al., 2013). AOPs such as UV/H_2O_2, Fenton, etc. could be described as an oxidation method based on the generation of sufficient reactive species such as hydroxyl radicals (•OH) in a procedure leading to the degradation of target contaminants (Beltran et al., 1993; Contreras et al., 2003; Ghafoori et al., 2013; Tabrizi and Mehrvar, 2004). A new and developing method among AOPs involves the application of ultrasound irradiation (US) or sonolytic process. Several advantages of sonolytic process such as avoiding consumption of chemical oxidants or catalysts, safety, and lower demand for the clarification of aqueous solution, make their application simple and desirable (Song et al., 2005; Xu et al., 2013). Sonochemical reactions are principally due to a phenomenon named acoustic cavitation. The phenomenon is the process of formation, expansion, and sudden implosion of gas micro-bubbles. The phenomenon leads to the generation of high local pressure (as high as 1000 atm) and high temperature (as high as 5000 K). The hemolytic cleavage of water molecules under such extreme conditions results in the generation of hydroxyl radicals as follows (Equation (1)) (Torres et al., 2008; Na et al., 2012):

$$H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H \quad (1)$$

Generally, the passage of the US waves at frequencies in the range of 20–1000 kHz through liquid water can produce cavitation in aqueous solutions (Durán et al., 2013). Ultrasound can be used alone or in combination with other AOPs (UV alone, UV/H_2O_2, etc.) for the generation of hydroxyl radicals. During this combination, the synergic effect between the US waves and the UV irradiation has resulted in improved degradation efficiencies (Bahena et al., 2008; Mohajerani et al., 2010b, 2012a; Monteagudo et al., 2014).

AOPs are considered as multifactor systems. Various parameters such as the concentration of organic substances, light source intensity, oxidant dosage, reaction time, pH, US frequency and output power, and other operating conditions impress the system performance (Coenen et al., 2013; Ghafoori et al., 2013). Therefore, the correct characterization of such systems requires considering cross-factor and single-factor effects. Using experimental design, the identification of factors influencing the multivariable system is conceivable. The experimental design has been applied successfully to identify the most influential factors in multivariable systems. Also, the response surface methodology (RSM) is able to optimize the operating conditions in multifactor systems by considering the interactions among variables (Ghafoori et al., 2012). Furthermore, the RSM has been shown to be a reliable statistical tool in studying chemical treatment processes to achieve an optimal response with a minimum number of experiments.

Also, in the open literature, the number of studies regarding the reaction mechanism and kinetics of the sonochemical processes are scarce (Okitsu et al., 2005; Xu et al., 2013). In addition, there is a requirement for more detailed information with respect to the role of organic compounds and H_2O_2 in reactions and mechanistic model to describe the detail reactions involved in the sonochemical process in wastewater treatment.

Therefore, in the first part of this study, an experimental design was used to investigate the sonophotolytic degradation of a synthetic pharmaceutical wastewater by the US/UV/H_2O_2 process. Also, the effects of the initial TOC concentrations of the wastewater, the initial H_2O_2 concentration, and the ultrasonic power on the sonophotodegradation of the synthetic pharmaceutical wastewater by the US/UV/H_2O_2 process were investigated. The optimal values of parameters were determined by means of three-factor three-level Box–Behnken Design (BBD), combined with response surface methodology (RSM) and quadratic programming. In the second part of this study, a novel rigorous mathematical kinetic model including all the detailed reactions of sonophotolytic process in an aqueous solution was developed to predict the TOC percent removal as the output variable with time in the US/UV/H_2O_2 process. The model predictions were compared to the experimental data where the kinetic rate constants were also estimated.

2. Materials and methods

2.1. Materials

The synthetic pharmaceutical wastewater (SPWW) used in this study was prepared based on a list of component reported in the study of Badawy et al. (2009). They detected these components in a wastewater generated by a pharmaceutical company in Cairo, Egypt. The wastewater contains chloramphenicol, diclofenac, salicylic acid, and paracetamol which are the main products of the company. Also, some by-products such as nitrobenzene, benzoic acid, and phenol were detected in the raw wastewater. Table 1 indicates the composition of each component present in the wastewater. It should be noted that in the study by Badawy et al. (2009), samples were taken six times during a year. In the present study, three sets of concentrations were chosen for conducting the experiments. The characteristics of these three sets of experiments including TOC are indicated in Table 1. The initial pH of the SPWW was 3.9 ± 0.1. Distilled water was used to prepare the synthetic wastewaters. H_2O_2 (30% wt) was purchased from Sigma Aldrich and was used as received.

2.2. Experimental setup and procedure

Fig. 1 shows the schematic diagram of the experimental setup. The sonophotoreactor is an airlift external loop reactor. The riser is 9.72 cm in diameter and 110 cm in height. For the downcomer, height and diameter are 90 and 3.25, respectively. Also, the total volume of the reactor is 7 L. As shown in Fig. 1, the setup is equipped with a single ended UV lamp (Ushio America Inc.) and a commercial ultrasonic processor (Branson, S-250D sonifier). The UV lamp was inserted at the center of the riser with 84.6 cm in height and 1.55 cm in diameter. It operates at 253.7 nm wavelength with 13 W output power. The sonifier has a 13 mm diameter tip which is capable of working in continuous and pulse mode. It has a constant frequency of 20 kHz and a variable output power up to 200 W. In this study, all experiments were performed with sonifier at continuous mode. To inject air into the riser, there is a perforated circular tube air sparger 5 cm above the reactor bottom. The sparged air enhances mixing in the reactor. In all experimental runs, the air flow rate was set to 2 L min^{-1}. It was proven that this was the optimum value for the air flow rate in the previous study (Mohajerani et al., 2012b).

Photolytic, sonolytic, and sonophotolytic processes were used to treat the SPWW in batch mode. Three pharmaceutical wastewater samples with initial TOC concentrations of 10, 20 and 30 mg L^{-1} were directed to the sonophotoreactor under various operating conditions.

The SPWW was thoroughly mixed by a magnetic stirrer in the feed tank. Desired amount of H_2O_2 was added at the beginning of the experiment to the feed tank. The sonophotoreactor was filled from the feed tank using a peristaltic pump. In each run, 40 mL samples were taken from the reactor every 30 min to analyze the TOC concentration. All experiments were repeated in triplicates