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Potential use of solar photocatalytic oxidation in removing emerging pharmaceuticals from wastewater: A pilot plant study

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ABSTRACT

A pilot plant was used to evaluate the potential of solar photocatalytic processes in the treatment of wastewater containing emerging contaminates. Four groups of commonly used pharmaceuticals (antibiotics, estrogens, acidic, and neutral) were selected as model compounds and were treated with different combinations of solar advanced oxidation processes including solar-photolysis, homogenous solar oxidation with ferric ions, heterogeneous solar oxidation with titanium dioxide, and solar ozonation. Oxidation experiments were performed in Doha, Qatar (25.2854°N, 51.5310°E) under natural sunlight and at ambient temperature, in a semi-batch photoreactor. Treatment performance was evaluated based on the efficiency of the processes in removing the target compounds and in mineralizing the organic content of the aqueous solution. The improvement in biodegradability and the reduction in the toxicity of the aqueous solution before and after the treatment were also evaluated. The results show that solar photolysis and solar oxidation with ferric ions are not effective in removing or mineralizing aqueous solutions containing the selected contaminates, while solar-driven oxidation processes with ferric ions, titanium dioxide, and ozone rapidly removed these pharmaceuticals from the wastewater and to some extent decreased the organic carbon content of the solutions. The removal efficiencies with solar photolysis and solar oxidation with ferric ions did not exceed 12.7% and 28.3%, respectively. Adding H_2O_2 to solar oxidation with ferric ions or utilizing TiO_2 increased the percentage removal to the range 80–96%. Ozonation and solar ozonation processes removed 90–100% of the *pharms* in very short time. Performance indictor analysis showed that combining solar photocatalytic oxidation process with ozonation significantly improved the removal performance, increased the degree of mineralization, reduced the chemical requirements, and reduced the demand for ozone and energy. The kinetic profile of the combined processes is higher than that of the single oxidation process; thus, the combined oxidation processes is recommended for efficient treatment. The oxidation processes with their effective degradation capacity improved wastewater biodegradability and reduced its acute toxicity.

1. Introduction

The presence of emerging contaminates (ECs), such as pharmaceuticals and pesticides, in the effluents of conventional wastewater treatment plants, and the detection of these ECs in surface-water systems, such as rivers, lakes, streams, and aquifers have attracted much attention over the last five years (Ternes, 2001, Kolpin et al., 2002, Huber et al., 2004). These potentially hazardous materials pose risks to the ecosystem and to public health and, in most cases, are responsible for the development of microbiological resistance. Most of these ECs have high acute toxicity and low or zero biodegradability. They are thus expected to remain in the environment for a long time, unless eliminated by an effective treatment process. The concentrations of these contaminates detected in the effluents of conventional wastewater treatment plants (WWTPs) are significant (Kolpin et al., 2002; Al Momani et al., 2004; Almomani et al., 2016b; Kanakaraju et al., 2018). Contamination of groundwater by ECs has been reported from a variety of sources (Ternes et al., 2002; Stuart et al., 2012;). Worries about the continuous increase in the concentrations of these ECS in different parts of the environment must be highlighted, and the search for more thorough wastewater treatment technologies is a necessary task (Lapworth et al., 2012).

In most developing countries with limited water resources, the reuse of waster is a common practice. For safe reuse, water should be free of toxic or disease-causing compounds, as well as of non-biodegradable substances (Radjenovia et al., 2007). Effective advanced treatment

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processes to completely remove these substances are therefore urgently required.

Advanced oxidation processes (AOPs) are considered to be promising candidate for eliminating these pollutants from aqueous solutions (Gogate and Pandit, 2004; Saritha et al., 2007; Dwivedi et al., 2016; Kanakaraju et al., 2018). AOPs can be employed as an effective and promising technology for the removal of any traces of ECs from water and wastewater (Al Momani and Jarrah, 2010; Almomani and Baranova, 2013). AOPs are based on the production of highly oxidative radicals to degrade or mineralize a range of organic contaminates from wastewater in a very short time. Hydroxyl radicals can be produced in different ways in AOPs, thus allowing better compliance with different treatment requirements (Liu et al., 2014, Tijani et al., 2014). With such technologies, problematic compounds can be partially or totally oxidized into smaller by-products that can easily be removed through conventional biological processes. Applying this strategy would potentially reduce the size of both oxidation and biological reactors, and may thus reduce both capital and operating costs. This synergy has the potential to open up a new niche in the water treatment field for treating contaminants that conventionally reserved for other treatment technologies (e.g., activated carbon).

In advanced oxidation processes, hydroxyl radicals can be generated using ozone, heterogeneous photocatalytic processes, or homogeneous photocatalytic processes. Ozone, which has an oxidation potential of ~2.07 V at low pH, has been widely used in water treatment, as it can react directly or indirectly with many organic compounds, leading to significant oxidation (El-Din et al., 2006; Zhang et al., 2006). In heterogeneous photocatalytic processes, the energy of a photon absorbed at the surface of the photo-catalyst excites an electron from the valence band to the conduction band, generating a positive hole in the valence band and triggering a process that leads to the generation of hydroxyl radicals that can be used in the degradation of pollutants. Titanium dioxide is widely used as photo-catalyst as a result of its high chemical stability, nontoxicity, low cost, highly oxidizing power, and its ability to absorb solar radiation (Malato et al., 2002; Malato et al., 2009). Homogeneous AOPs use in most cases iron salts (Fe(III)) as a photo-catalyst. The oxidation of Fe(III) in the photo-catalytic process leads to the generation of iron(III)–aqua complexes, primarily $Fe(OH)^{2+}$, which undergo photolysis to generate hydroxyl radicals. Hydrogen peroxide can be added to promote the formation of more radicals in what is known as the photo-Fenton process. As a photo-catalyst, iron is non-toxic, readily available, and can be efficiently used under acidic conditions (Vedrenne et al., 2012). Different combinations of various AOPs can be used to enhance the production of hydroxyl radicals and to more rapidly degrade of pollutants. A number of previous studies have shown the synergistic effects of combination processes on treatment performance (Abderrazik et al., 2002; von Gunten, 2003, Rodríguez et al., 2013).

The concept of solar AOPs has recently evolved in treating wastewater containing organic matter (Rodríguez et al., 2005, Al Momani, 2007a, Al Momani et al., 2007b, Polo-Lopez et al., 2014; Almomani et al., 2016a; Almomani et al., 2016b). The objective of using solar oxidation is to utilize abundant solar energy to treat wastewater containing bio-recalcitrant compounds. Works addressing the use of solar-driven photocatalytic processes to treat ECs in water are limited (Klamerth et al., 2009, Bernabeu et al., 2011, Miranda-Garcia et al., 2011). In addition, according to our literature review, only four works have investigated solar-driven ozonation at a pilot scale (Oyama et al., 2011, Shin et al., 2013, Marquez et al., 2014, Polo-Lopez et al., 2014). Thus, the present work aims to complete the gap in this research topic and to study the treatment of emerging contaminates in wastewater with solar energy. The study also aims to evaluate and compare the treatment efficiency when solar irradiation is used in different AOPs.

Table 1
Name, Chemical formula and the initial concentration of pharmaceuticals used in solar oxidation experiments.

Name (chemical formula)	Use	Used Concentration (mg/L)
Antibiotics		
Azithromycin ($C_{38}H_{72}N_2O_{12}$)	Macrolide antibiotic	1.1
Roxithromycin ($C_{41}H_{76}N_2O_{15}$)	Macrolide antibiotic	1.1
Estrogens		
17α-ethinylestradiol (EED) ($C_{20}H_{24}O_{2)}$	Synthetic steroid hormone	1.1
Estrone ($C_{18}H_{22}O_2$)	Natural steroid hormone	1.0
Acidic pharmaceuticals		
Diclofenac ($C_{14}H_{11}Cl_2NO_2$)	Antiphlogistic	0.9
Fenoprofen ($C_{15}H_{14}O_3$)	Antiphlogistic	0.7
Neutral pharmaceuticals		
Caffeine ($C_8H_{10}N_4O_2$)	Psychostimulant	0.6
Ifosfamide ($C_7H_{15}Cl_2N_2O_2P$)	Antineoplastic	0.8

2. Materials and methods

2.1. Studied pharmaceuticals

The pharmaceuticals used in this study belong to four groups of commonly used medications (antibiotics, estrogens, acidic pharmaceuticals, and neutral pharmaceuticals). The name, chemical formula, and initial concentration of each pharmaceutical used in this study are presented in Table 1. The concentrations of these pharmaceuticals in different water and wastewater samples have been presented in our previous work (Almomani et al., 2016b). All of the pharmaceuticals were obtained from Sigma-Aldrich with a purity of > 98%. The concentrations used—although higher than the actual values found in raw wastewater (often as high as 10^2 μg/L–10^{-1} mg/L) allowed accurate and fast quantitative chemical analysis with the equipment available to us.

2.2. Chemicals

Iron (III) perchlorate hydrate purchased from Sigma–Aldrich was used as the source of Fe(III) catalyst in homogeneous solar oxidation experiments. Titanium dioxide heterogeneous photocatalysis was prepared from tetrabutylorthotitanate ($Ti(OC_4H_9)_4$), acetyl acetone (C_5H_8O), n-propanol(C_3H_8O) and deionized water according to the procedure explained in our previous work (Almomani et al., 2016b). Other chemicals; sodium chloride (> 99%), sodium sulfate (> 99%), sodium carbonate (> 99%), sodium nitrate (> 99%) and sodium phosphate 12-hydrated (> 99%) were all purchased from Panreac and used as received in some experiments.

Laboratory reagents used in analysis were sodium thiosulfate pentahydrate (Merck), potassium indigo-trisulfonate (Sigma–Aldrich), acetonitrile (Fisher Scientific), phosphoric acid (85%, Fisher Scientific) hydrochloric acid (37%, Sigma–Aldrich),and sodium hydroxide (Panreac).

2.3. Wastewater samples

The solar photo-oxidation experiments were carried out on wastewater samples collected from the effluent of a secondary treatment train from the north treatment plant in Doha, Qatar. Water samples were filtered through a 0.45 μm Millipore filter and stored at 4 °C prior to use. Table 2 shows the characteristics of the wastewater used in the experiment.