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The design of a sunlight-focusing and solar tracking system: A potential application for the degradation of pharmaceuticals in water

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HIGHLIGHTS

- A sunlight focusing, solar tracking and continuous reaction system was constructed.
- The SFST system significantly improved the photodegradation of pharmaceuticals.
- UV-enhanced coated SFST with the addition of persulfate has development potential.

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ABSTRACT

Photolysis is considered one of the most important mechanisms for the degradation of pharmaceuticals. Photodecomposition processes to remove pharmaceuticals in water treatment presently use artificial UV light incorporated in advanced oxidation processes. However, UV lighting devices consume a substantial amount of energy and have high operational costs. To develop low energy treatment systems and make good use of abundant sunlight, a natural energy resource as a green technology is needed. As such, a system that combines sunlight focusing, solar tracking and continuous reaction was designed and constructed in the present study, and its application potential as a pharmaceutical water treatment option was tested. Two representative photolabile pharmaceuticals, ciprofloxacin and sulfamethoxazole, were chosen as the target pollutants. The results indicate that the sunlight-focusing system consisting of a UV-enhancing-coated parabolic receiver can concentrate solar energy effectively and hence result in a more than 40% improvement in the direct photolysis efficiency of easily photoconvertible ciprofloxacin. The sunlight-focusing coupled with a solar tracker (SFST) system can improve the sunlight-focusing efficiency by more than 2-fold, thus leading to the maximization of the efficient use of solar energy. Sulfamethoxazole, which is difficult to photoconvert, was successfully degraded by more than 60% compared to direct photolysis through the designed SFST system in the presence of persulfate. The treatment system exhibited good and consistent performance during clear and cloudy days of summer. It is proven that the UV-enhanced coated SFST system with the addition of persulfate indeed has development potential for application in the degradation of pharmaceuticals in water.

1. Introduction

Several pharmaceuticals possess activity when they are present as parent compounds in the environment and exhibit toxicity or an inhibitory effect, or both, on microorganisms (Carvalho and Santos, 2016; Fu et al., 2017; Välitalo et al., 2017). Due to their chemical or physical characteristics, pharmaceuticals such as antibiotics, anti-cancer drugs and analgesics cannot be completely removed by the treatment processes used in common wastewater treatment plants, and therefore, they are found in the effluent of wastewater treatment plants (Eggen and Vogelsang, 2015; Hamza et al., 2016; Jiang et al., 2014; Pal et al., 2010; Santos et al., 2009; Yamamoto et al., 2009). In particular, the trace pharmaceuticals and antibiotics present in the environment have been found to increase the drug resistance of bacteria (Klavarioti et al., 2009; Kolpin et al., 2002; Lin et al., 2008). Pharmaceuticals and antibiotics can be removed from the environment through natural degradation mechanisms including hydrolysis, adsorption, biological degradation and photolysis. However, because some pharmaceuticals and antibiotics possess biological toxicity or an inhibitory effect, they cannot

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be easily removed through biological adsorption, metabolism or conversion in natural water bodies, and thus, photolysis is considered an important natural attenuation and removal mechanism in the literature (Lin et al., 2008; Lin and Reinhard, 2005; Tixier et al., 2002).

Ciprofloxacin and sulfamethoxazole are two of the common antibiotics frequently detected in environmental water bodies (Ashbolt et al., 2013; Kümmerer, 2009; Wilkinson et al., 2017). They are shown to naturally photodegrade, with half-lives ranging from a few minutes to a few hours (Chen et al., 2011; Guo et al., 2013; Ryan et al., 2011; Wang and Lin, 2014). The photolysis of ciprofloxacin is primarily through direct photolysis, and the degradation rate is very fast. Wang and Lin showed that in deionized (DI) water (pH = 5.5) under an initial concentration of 10 μM and a light intensity of 765 W/m^2, the photolysis half-life of ciprofloxacin is approximately 13 ± 3 min (Wang and Lin, 2014). However, the direct photolysis rate can be influenced by environmental media and exhibits pH dependency; its acid dissociation constants (pK_a) are 6.1 and 8.7. Therefore, it has high photochemical reactivity under neutral to basic environments (Guo et al., 2013; Torniainen et al., 1996; Wammer et al., 2013). Babić et al. showed that the photolytic degradation mechanisms of ciprofloxacin vary with the experimental conditions; under acidic conditions, the degradation reactions involve the cleavage of the quinolone ring, whereas under basic conditions (pH = 8), side-chain reactions occur (Babić et al., 2013; Zhang et al., 2013).

The photodegradation rate of sulfamethoxazole is less than that of ciprofloxacin. Wang and Lin showed that in DI water (pH = 7) under an initial concentration of 10 μM and a light intensity of 765 W/m^2, the photolysis half-life of sulfamethoxazole can reach 1.5 ± 0.1 h (Wang and Lin, 2014). In natural bodies of water, in addition to the direct photolysis, the presence of photolabile matter in water can promote indirect photolysis, thus increasing the degradation rate. The natural photodegradation mechanism of sulfamethoxazole in DI water primarily involves breaking of the sulfonamide bond and rearrangement of isoxazole (Ryan et al., 2011; Trovó et al., 2009). Because the natural photodegradation of sulfamethoxazole is also significantly influenced by the reaction medium and pH, its photodegradation rate under different pH values (pH = 3 and pH = 10) has shown 10-fold variation (Hamza et al., 2016).

In current water treatment processes, photolysis is often applied to advanced oxidation processes (AOPs). For example, UV light combined with O_3 and the chlorine oxidation process have a significant effect on removing some pharmaceuticals and organic pollutants (Chan et al., 2012; Klavarioti et al., 2009; Wols and Hofman-Caris, 2012), which UV and visible light can photolyze (Chan et al., 2012; Criquet and Leitner, 2009). For UV light or UV light combined with chemical oxidation (UV/O_3, UV/H_2O_2 and $UV/S_2O_8^{2-}$), the advantageous fact is that most pharmaceuticals can absorb UV light and their structures are directly damaged. Alternatively, the UV energy can excite oxidants in bodies of water to form radicals, e.g., HO• and $SO_4{\bullet}^-$, which can further degrade pharmaceuticals in water. Among these, persulfate ($S_2O_8^{2-}$, PS) can be excited by light with a wavelength of 248–351 nm to produce $SO_4{\bullet}^-$, which can degrade organic pollutants in water (Lin et al., 2011). Ahmed and Chiron showed that by using simulated solar irradiation as a light source, PS as an oxidant at a concentration 40-fold that of the pollutants, and ferrous iron (Fe(II)) as a catalyst at a concentration half that of the oxidant, carbamazepine in wastewater can be fully degraded in 30 min (Ahmed and Chiron, 2014). In addition to excitation by light, PS can also be excited by thermal or chemical energy (Liang et al., 2004; Yang et al., 2010). Research has also shown that a low pH favors the generation of more $SO_4{\bullet}^-$, whereas a high pH creating a basic environment promotes the conversion of $SO_4{\bullet}^-$ to HO• (Criquet and Leitner, 2009; Guan et al., 2011; Liang and Su, 2009; Lin, 2001). In the temperature range of 20–70 °C, the higher the temperature is, the more $SO_4{\bullet}^-$ is generated (Huang et al., 2002; Lin, 2001; Yang et al., 2010). Yang et al. showed that compared to H_2O_2 and HSO_5^- (peroxymonosulfate, PMS), PS is more easily excited by heat activation to produce radicals. As a result, PS oxidation activated by heat (>50 °C) is an effective degradation technology (Yang et al., 2010). Furthermore, the $SO_4{\bullet}^-$generated from the excitation of PS by UV/254 nm has a higher selectivity towards the degradation of carboxylic acid-type organic pollutants than that of HO• generated by H_2O_2 (Criquet and Leitner, 2009; Liang and Su, 2009).

Most research relies on simulated sunlight for photolysis, thereby lacking information about the application of photolysis by sunlight irradiation in real environments. However, the UV-based treatment processes must use electricity to drive the UV light source, thus requiring a high energy consumption and operational cost. Recently, more research has focused on replacing the energy-demanding UV lamps with simulated sunlight for natural photolysis; it has also been shown that natural light has a significant effect on degrading some pollutants (Batchu et al., 2014; Chan et al., 2012; Jiang et al., 2014; Klavarioti et al., 2009; Koumaki et al., 2015; Lin and Reinhard, 2005; Weidauer et al., 2016; Wols and Hofman-Caris, 2012; Yong et al., 2015). Therefore, there remains much room for developing the application of solar energy.

Presently, sunlight-focusing equipment is primarily used to supply light, heat, and electricity for photovoltaic cell development. Commercial products primarily include solar kettles, solar water heaters, concentrating solar power cells, and photovoltaic cells. The advantage of the application of solar energy lies in the absorption efficiency of the wavelengths of sunlight and its energy conversion efficiency (Elshik et al., 2017; Lee et al., 2016; O'neill, 2017). The current solar light degradation system has only been designed for photocatalytic treatment processes based on a fixed-bed reactor (Bandala et al., 2004; Malato et al., 2002; Nair et al., 2016; Tanveer and Tezcanli Guyer, 2013). Bandala et al. studied four solar photoreactors—parabolic trough concentrator, tubular collector (TC), compound parabolic collector (CPC), and V-trough collector—and concluded that the total amount of energy collected by the photoreactors is similar and that CPC has the best overall performance in terms of accumulated energy. The shape, reflective surface and acceptance angle of the concentrator were found to affect solar ray concentration (Bandala et al., 2004; Malato et al., 2002; Nair et al., 2016; Spasiano et al., 2015). The addition of oxidants such as hydrogen peroxide and sodium persulfate were found to improve the efficiency of the photocatalytic treatment process (Malato et al., 2002). Without the need for a photocatalyst, this study, which is the first of its kind, aims to establish a system that couples sunlight-focusing with solar tracking for the treatment of pharmaceutical pollutants in synthetic pharmaceutical water. In addition, the effect of added PS on the degradation efficiency of pharmaceuticals is studied to explore the development potential of applying this sunlight-focusing system to the treatment of water containing pharmaceutical pollutants. In this study, two photolabile pharmaceuticals were chosen: ciprofloxacin, which can be rapidly and directly photolyzed ($t_{1/2}$<1 h), and sulfamethoxazole, which represents a compound that cannot be easily photolyzed, having a longer half-life ($t_{1/2}$>1 h). The investigation of the degradation of these two pharmaceuticals was used to evaluate the feasibility and potentiality of the developed system.

2. Experimental materials and methods

2.1. Chemicals

The acetonitrile (HPLC grade, 99.9%), methanol (HPLC grade, 99.9% purity) and phosphoric acid (ACS grade, 85% purity) mobile