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Enhancement of UV-assisted TiO_2 degradation of ibuprofen using Fenton hybrid process at circumneutral pH

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ABSTRACT

A synergistic UV/TiO_2/Fenton (PCF) process is investigated for the degradation of ibuprofen (IBP) at circumneutral pH. The IBP decay in the PCF process is much faster than that with the conventional UV, UV/H_2O_2, Fenton, photo-Fenton, and photocatalysis processes. The kinetics analysis showed that the IBP decay follows a two-stage pseudo-first order profile, that is, a fast IBP decay (k_1) followed by a slow decay (k_2). The effects of various parameters, including initial pH level, dosage of Fenton's reagent and TiO_2, wavelength of UV irradiation, and initial IBP concentration, are evaluated. The optimum pH level, $[Fe^{2+}]_0$, $[Fe^{2+}]_0/[H_2O_2]_0$ molar ratio, and $[TiO_2]_0$ are determined to be approximately 4.22, 0.20 mmol/L, 1/40, and 1.0 g/L, respectively. The IBP decay at circumneutral pH (i.e., 6.0–8.0 for wastewater) shows the same IBP decay efficiency as that at the optimum pH of 4.22 after 30 min, which suggests that the PCF process is applicable for the treatment of wastewater in the circumneutral pH range. The $\ln k_1$ and $\ln k_2$ are observed to be linearly correlated to $1/pH_0$, $[IBP]_0$, $[H_2O_2]_0$, $[H_2O_2]_0/[Fe^{2+}]_0$ and $\ln[TiO_2]_0$. Mathematical models are therefore derived to predict the IBP decay.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are composed of a diverse group of medicines, which include prescription and over-the-counter therapeutic drugs, veterinary drugs, fragrances, cosmetics, sunscreen products, diagnostic agents, and nutraceuticals. A growing number of environmental concerns are raised owing to their biological activity, increase in usage and persistence in the environment [1]. The existence of PPCPs in aquatic organisms possibly affects human health and interferes with the balance of the ecosystem through a continuous and multigenerational exposure to the polluted water [2].

Ibuprofen (IBP), 2-(4-isobutylphenyl) propionic acid, is widely used as a nonsteroidal anti-inflammatory drug especially prescribed for the treatment of pain, fever and rheumatic

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disorders [3]. As a result of its widespread applications, the global production of IBP has exceeded 15000 t/year [4]. IBP occupied the 17th place on the list of the most prescribed drugs in the United States [5] in 2005. In Spain, IBP was the third best-selling pharmaceutical in 2011. After application of the therapeutic dose, 15% IBP is excreted from the body in the unaltered form and is subsequently able to enter into municipal wastewater [6]. Additionally, a major contributor to the aqueous environmental concentration of the non-metabolized and metabolized forms of ibuprofen is medical waste that has not been properly managed. Many studies have shown that the removal of IBP is not appropriate through the conventional treatments employed by wastewater treatment plants because the technologies used are not sufficiently effective [7]. Previous studies have reported that in China, IBP has been detected in a reservoir at a concentration greater than 1 μg/L [8], while in the drinking water, concentrations of up to 23.3 ng/L have been reported [9]. The toxicological effect of ibuprofen metabolites originating from human and microbial activity in the aquatic environment have been reported to influence cyclooxygenase reactions, and, therefore, affect the reproduction of aquatic animals and the photosynthesis of aquatic plants [10,11]. Therefore, a number of studies on eliminating IBP from an aquatic environment have recently been carried out [12–14].

Coagulation and flocculation are poor for the elimination of IBP owing to the chemical nature and low concentration of IBP in an aqueous environment [15]. Efficient IBP removal has been achieved by adsorption and membrane treatment, but the high operational cost limits its application [16], Moreover, the adsorption and membrane treatment is simply a physical separation process, where the IBP moves from the aqueous phase to another phase as the unchanged species rather than being mineralized. Sunlight degradation, with the advantages of low cost and destruction of the chemical structure, has been estimated by A. Pal and co-workers [17]. Their results showed that sunlight degradation cannot be adopted for IBP removal in real-life application because the reaction is slow with a half-life of 9900 h. The advanced oxidation processes (AOPs) have been used for IBP degradation through the supply of active radicals (i.e., $^{\bullet}OH$, $O_2^{\bullet-}$) in the literature such as Fenton, photo-Fenton oxidation, and TiO_2 photocatalysis [6,18]. Photocatalysis is an effective process that shows good performance at neutral pH, which falls in the working pH of wastewater treatment plants and biodegradation process [7,19]. Therefore, there is no need to adjust the pH by using extra acid or alkali before and after treatment. However, the TiO_2 heterogeneous photocatalysis follows moderate first-order kinetics, for example, 60% IBP (0.24 mmol/L) degradation in 60 min [10], because the heterogeneous oxidation only occurs on the TiO_2 surface [20,21]. For comparison, the homogeneous Fenton reaction is much faster owing to the oxidation proceeds in the whole solution [22,23]. The Fenton reaction encompasses the reaction of hydrogen peroxide (H_2O_2) with Fe^{2+} under acidic conditions to form reactive oxygen species (ROS, usually $^{\bullet}OH$) that can degrade organic compounds [24]. The complex reaction mechanism of the Fenton reaction can be summarized as follows [25]:

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

However, the Fenton reaction is only competitive under acidic conditions and a pH adjustment before and after the treatment is required [14]. Considering that the water treatment at neutral pH is less harmful to the environment, it would be more appealing to develop a fast process that proceeds at the circumneutral pH level.

In this study, with the aim of integrating the advantages of both the heterogeneous photocatalysis and homogeneous photo-Fenton reactions, a combined process, namely photo/TiO_2/Fenton (PCF), was designed. The objective is to explore the IBP decay using the PCF process at circumneutral pH level. The effect of various parameters, including initial solution pH levels, dosage of Fenton's reagents and TiO_2, wavelength of UV irradiation, and initial IBP concentrations, were examined. Moreover, mathematical models were derived for the prediction of IBP degradation in the PCF process in terms of the dosage of TiO_2 and Fenton's reagents, initial IBP concentration, and initial pH levels.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytic reagent grade, and all solvents were of HPLC grade and used as received without further purification. IBP ($C_{13}H_{18}O_2$, α-methyl-4-(isobutyl)phenylacetic acid) was purchased from Wako Pure Chemical Industries. Fenton's regents, that is, ferrous sulfate and hydrogen peroxide, were obtained from Aldrich and Riedel-de Haën, respectively. Titanium dioxide (TiO_2, Degussa P25, 80% anatase and 20% rutile) was used as the catalyst with a BET surface area of 50 m^2/g and a density of 3.85 g/cm^3. TiO_2 has an average aggregate size of 200 nm and is made up of 30 nm primary particles. The mobile phase solvent for HPLC analysis (i.e., acetonitrile) was obtained from Tedia. A resistivity of 18.2 MΩ for the distilled-deionized water was used to prepare the mobile phase and stock solution, which was obtained from a Bamstead NANOpure water treatment system (Thermo Fisher Scientific Inc., USA).

2.2. Experimental procedures

The degradation of IBP was conducted in a Rayonet RPR-200 photochemical reactor manufactured by the Southern New England Ultraviolet Co. Two phosphor-coated low-pressure mercury lamps were installed in the photoreactor. All the experiments were conducted through the following steps. First, 100 mL IBP was added into a quartz beaker (56 mm ID × 125 mm H) followed by the addition of TiO_2 with stirring for 30 min in the dark to achieve the adsorption equilibrium. The reaction was initiated by the addition of an appropriate amount of ferrous salt and hydrogen peroxide into the reactor with the simultaneous switching on of the UV lamps. The pH values were adjusted by 0.10 mol/L nitric acid and/or 0.10 mol/L sodium hydroxide whenever required. To ensure a thorough mixing, mechanical stirring was provided continuously before and during the reaction. An exact aliquot (0.5 mL) was withdrawn