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Comparative study of sulfamethazine degradation in visible light induced photo-Fenton and photo-Fenton-like systems

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ABSTRACT

A comparative study between the visible light induced photo-Fenton system (light/Fe^{2+}/H_2O_2, P-F) and photo-Fenton like system (light/Fe^{2+}/$S_2O_8^{2-}$, P-FL) was carried out for the degradation of antibiotic sulfamethazine (SMZ). It was found that white-LED light could enhance the SMZ degradation in both photochemical systems. The optimum dosage ratio of [Fe^{2+}]:[Oxidant] was determined as 1:10 in the two systems. However, compared to the P-F system, the P-FL system would consume five times of catalyst/oxidant (i.e. 1 mM [Fe^{2+}]/10 mM [persulfate]) amount to achieve approximately complete decomposition of SMZ within 30 min. The P-FL system could also effectively degrade SMZ at a broad pH range of 2–5 (the P-F system was 3–4). Furthermore, the present of common inorganic ions exhibited different effects on the SMZ degradation as for the two systems. Although good mineralization and detoxicity of the synthetic wastewater were observed in the two systems, identifications of the released sulfate and intermediates/product suggested different SMZ degradation pathways. Cleavage of the S—N bond under hydroxyl radical ($^{\bullet}OH$) attacking was dominant in the P-F system, while sulfate radical ($SO_4^{\bullet-}$) attacking of the amine group in the benzene ring followed by cleavage of C—N bonds in the heterocyclic ring was the main SMZ degradation pathway in the P-FL system.

Introduction

Nowadays, the environmental concern of pharmaceuticals and personal care products (PPCPs) has been becoming more intensive. Sulfonamides, a typical class of PPCPs, are widely used in human and veterinary medicine as antibacterial drugs and growth promoters [1]. In the aquatic environment, appearances of sulfonamides and their metabolites could easily be found [1,2]. It would lead to potential adverse effects on human health and the aquatic ecosystem [1].

Advanced oxidation processes (AOPs) are commonly accepted as potential techniques to decompose recalcitrant organic pollutants in water or wastewater treatments. The most common AOPs include H_2O_2/UV, O_3/UV, photocatalysis and Fenton process [3–6]. Among them, Fenton process is relatively economic and simple. Based on generation of activated, relatively non-selective radical (such as hydroxyl radical, $^{\bullet}OH$), Fenton is effective to destroy refractory organics at near diffusion-controlled rates. It can enhance the biodegradability of wastewater in favor for subsequent biological treatment. Persulfate (PS) could be another potential alternative oxidant for AOPs even for extensive use [7], due to its characteristics of high solubility and stability at the ambient temperature. The persulfate anion ($S_2O_8^{2-}$) is a strong oxidant ($E^\circ = 2.01$ V) that can be activated by heat, UV or Fe^{2+} to produce a stronger sulfate radical ($SO_4^{\bullet-}$, $E^\circ = 2.60$ V) [8,9].

One of the most disadvantages of Fenton methodology is slow regeneration of Fe^{2+} ions in the homogenous process [10]. Plus photochemical-enhanced methods (UV or visible light) could be good options to improve the efficiencies of heterogeneous/homogeneous Fenton systems in the degradation of target pollutants. The advantages are generally ascribed to the photo-regeneration of Fe^{2+} and photochemical decomposition of the pristine oxidants (such as H_2O_2 and persulfate) [11,12].

There are numerous studies concerning H_2O_2-based or persulfate-based photochemical Fenton or Fenton like systems. In these studies, many kinds of recalcitrant organic pollutants, e.g. azo dyes, pesticides and pharmaceuticals, have been successfully decomposed and mineralized [11–14]. The performances of a H_2O_2-based Fenton system and a PS-based Fenton like system would be expected to be distinguished. Nevertheless, until now there is still few researches in clarifying the differences between the photochemical Fenton and Fenton-like systems.

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To give a better understanding in the different performances achieved in H_2O_2-based Fenton systems and PS-based Fenton-like systems, two visible white-LED illuminated photochemical systems, i.e. Fe^{2+}/H_2O_2 (P-F system) and Fenton system Fe^{2+}/persulfate (P-FL system) were established for the degradation of an antibiotic sulfamethazine (SMZ). Our targets were to (a) examine the enhanced degradation of SMZ achieved in either P-F system or P-FL system, (b) optimize several important experimental parameters (initial catalyst/oxidant dosage and pH) affecting the SMZ degradation in above both systems, (c) investigate the role of two present common anions (Cl^- and HCO_3^-) affecting the SMZ degradation in the two systems, and (d) explore possible pathways during the SMZ degradation.

Materials and methods

Chemicals

Sulfamethazine (>99%) was obtained from Sigma–Aldrich company, without any purification. The chemicals ferrous sulfate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (H_2O_2, 30% v/v), and potassium persulfate ($K_2S_2O_8$) were supplied by Merck company. Other chemicals, such as HCl (37% w/w), NaOH, NaCl, Na_2CO_3, H_2SO_4, 1,10-phenanthroline ($C_{12}H_8N_2$), $Na_2S_2O_3$, KI, and soluble starch were all from Sigma–Aldrich company. Deionized water with resistivity of 18.2 MΩ cm (Millipore Co.) was used for all solutions preparation.

Experimental procedures

Experiments of the SMZ photochemical oxidation were carried out in a series of parallel Vis-LED photoreactors. Each comprised a 500 mL borosilicate glass reactor wrapped by a 2-m flexible white LED strip (SMD 5050, 30 pcs/m, 7.5 W m^{-1}). The spectrum of the white LED clearly showed blue light emitted at about 450 nm and more broadband Stokes-shift light emitted at roughly 500–600 nm. In a typical run, an aqueous mixture of 400 mL was prepared with predetermined SMZ concentration (50 mg L^{-1}). 0.1 M $HClO_4$ or NaOH was used to adjust the solution pH. In the experimental cases of anion effects, either NaCl or $NaHCO_3$ was added into the solution to prepare a background of concentrated chloride (Cl^-) or bicarbonate ion (HCO_3^-). The photochemical reaction was initialized by the addition of a certain amount of Fenton/Fenton-like reagent (addition of $FeSO_4$ solution into the SMZ solution with predetermined amount of H_2O_2). During the reaction, the mixture was magnetically stirred (600 rpm) at ambient temperatures. At predetermined intervals, water samples were withdrawn and the reaction was stopped by adding a dorp of *tert*-butyl alcohol (for SMZ analysis) or NaOH (for TOC measurement). Afterwards, the samples were immediately filtered by 0.45 μm membrane and sent for analysis. All experiments in this study were conducted in duplicate. The average values of data were adopted due to all standard errors were within 5%.

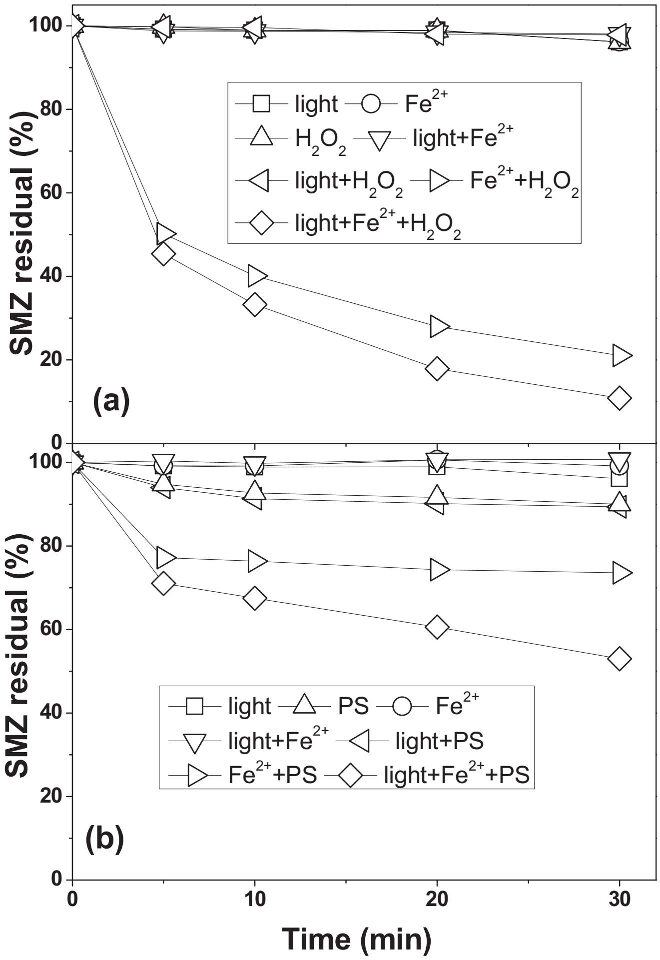

Fig. 1. Degradation of SMZ in comparative systems versus the reaction time in the case of (a) the P-F system, and (b) the P-FL system (initial parameters: 50 mg L^{-1} SMZ, 0.2 mM Fe^{2+}, 1 mM H_2O_2 or $K_2S_2O_8$, 15 W white-LED light and initial pH 3).

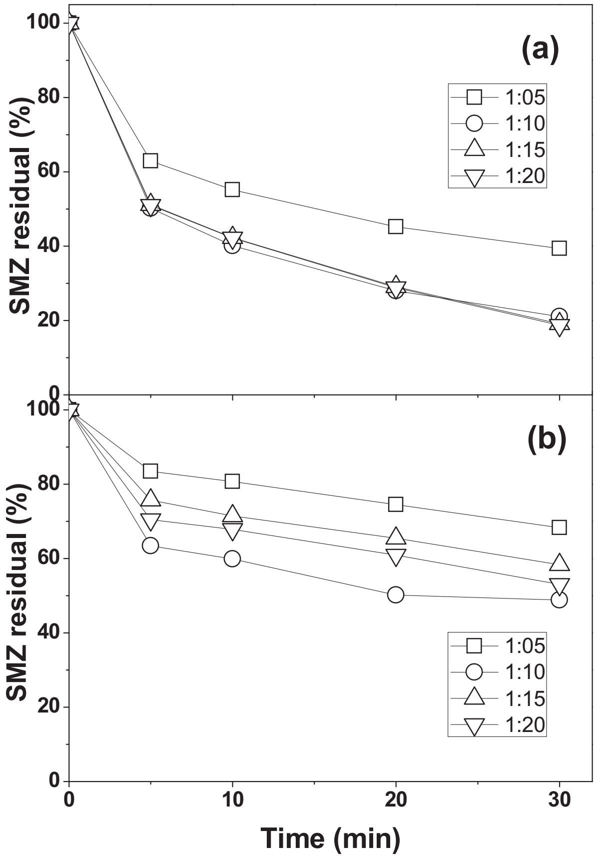

Fig. 2. Effect of initial dosage ratio of $[Fe^{2+}]$:[Oxidant] on the SMZ degradation with a fixed $[Fe^{2+}]_0$ of 0.2 mM (a) the P-F system (b) the P-FL system (other initial parameters: 50 mg L^{-1} SMZ, 1.0-4.0 mM H_2O_2 or $K_2S_2O_8$, 15 W white-LED light and initial pH 3).