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Efficient sonoelectrochemical decomposition of sulfamethoxazole adopting common Pt/graphite electrodes: The mechanism and favorable pathways

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ABSTRACT

In this study, efficient degradation of sulfamethoxazole (SMX) with a high synergy factor of 14.7 was demonstrated in a sonoelectrochemical (US-EC) system adopting common Pt and graphite electrodes. It was found that the US-EC system could work effectively at broad pH range of 3–9, but would achieve good performances with appropriate electrochemical conditions at 20 mA/cm^2 and 0.1 M Na_2SO_4. Both ·OH attacking and the anode oxidation would be responsible for the SMX degradation in the US-EC system, while the multiple promotional roles of US would be played homogenously and heterogeneously. US could not only effectively accelerate the decomposition of cathode-generated H_2O_2 into ·OH, but also lead to the enhancement in the heterogeneous reactions on the two electrodes, i.e. the cathode generation of H_2O_2 as well as the anode oxidation of SMX and H_2O/OH^-. Besides, the US-EC system would decompose SMX molecule via similar and simple pathways, by using either Na_2SO_4 or NaCl electrolytes. It was interesting to note that the US-EC system could successfully avoid the formation of complex chlorinated byproducts that detected in the referring EC system with NaCl. This finding would make the sonoelectrochemical processes favorable in treating practical wastewaters by alleviating the environmental impact of disinfection byproducts.

1. Introduction

As new generation hot emerging contaminants, pharmaceutical and personal care products (PPCPs) have received increasing concerns worldwide in the past two decades, due to their potential adverse impacts in humans and in ecosystems even at trace level occurrences [1]. Sulfamethoxazole (SMX) is one of the most widely used sulfa antibiotics. It has been detected at different concentration levels (ng L^{-1} to μg L^{-1}) in various municipal sewage treatment plants, surface water, hospital effluents and drinking water, posing a potential environmental risk due to its extensive usage and resistance to natural biodegradation [2].

Like many other PPCPs, SMX is recalcitrant to the conventional biological water and wastewater treatment processes [3]. Advanced oxidation processes (AOPs) have been therefore applied as alternative methods for the treatment of aqueous PPCPs. It has been reported that many AOPs, such as O_3/UV, UV/H_2O_2, Fenton/Fenton-like oxidation, γ-radiolysis, sonolysis, and electrochemical oxidation could be capable of effective degrading numerous toxic and/or recalcitrant organic pollutants [1].

Among these above AOPs, electrochemical advanced oxidation processes (EAOPs) are attractive due to their environmental compatibility, amenability of automation, high energy efficiency, versatility and safe operation under mild conditions [4]. In a typical EAOP, hydrogen peroxide is electrochemically supplied by the two-electron reduction of O_2, preferentially at a carbonaceous cathode, while the simultaneous action of the anode gives rise to the well-known and popular anodic oxidation (AO) [5]. Basing on the in-situ generation of strong oxidizing agent hydroxyl radicals (·OH), EAOPs can efficiently mineralize a large number of aromatic and aliphatic organic compounds [6].

The electrochemical oxidation efficiency are generally limited in the EAOPs adopting common electrodes [7,8]. Developing advanced electrodes, e.g. boron-doped diamond anodes (BDD) [9–11], dimensionally stable anodes (DSA) (e.g., Ti/IrO_2, Ti/SnO_2, and Ti/PbO_2) [2], and carbon nanotubes anodes/cathodes with high surface area [12,13] have received great interesting. These novel

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anodes/cathodes pose more positive oxygen evolution potentials and/or higher reactive sites, favoring the electrochemical oxidation for pollutant decontaminations. However, high cost and complicated synthesis procedures as well as the unconfirmed long-term electrode life will be great challenges for their industrial applications [6,14].

Combing EAOPs with ultrasound, i.e. energy-based sonoelectrochemical AOPs (US-EC), is one of the most novel AOPs and has received intensive interesting due to its favorable features such as mild operational condition, efficient functioning at room temperature and no additional requirement of chemicals [15,16]. US irradiation can improve the efficacy of electrochemical (EC) processes manifolds and thus lead to more efficient destruction of refractory organic pollutants [16–18]. Nevertheless, these studies mainly used novel and expensive electrodes such as BDD, DSA [19,20]. The work efficiency and synergistic effect of US-EC systems adopting common and simple electrodes still remains uncertain. The positive decomposition pathways of emerging organic pollutants in the combining systems also need to be clarified.

Therefore, a US-EC process adopting common Pt anode and graphite cathode was established in this study for the efficient degradation of SMX. The objectives were to: (a) demonstrate the synergistic effect of the US-EC system on the SMX degradation, (b) investigate the effects of important parameters on the SMX degradation, (c) propose the reaction mechanism in the system and the promotional role of US, and (d) examine the intermediates and reveal a simpler and favorable SMX degradation pathway by using either Na_2SO_4 or NaCl electrolyte.

2. Experimental

2.1. Chemicals

Purified sulfamethoxazole ($C_{10}H_{11}N_3O_3S$, >98%) was obtained from Sigma-Aldrich Co. Analytic grade Methanol and tert-butyl alcohol (TBA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Catalase (CAT, 2000–5000 U/mg protein) was got from Biosharp company. Acetonitrile, acetic acid and all other common chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further perification. All solutions in this study were prepared by deionized water.

2.2. Experiment procedures

All sonoelectrochemical and related electrochemical experiments were carried out in a jacketed cylindrical glass reactor equipped with an electrochemical workstation (Wuhan CorrTest Instruments Co.). A square platinum flag (2×2 cm^2) and a columnar graphite electrode (d = 6 mm) which supplied by Gaossunion Company (China) were adopted as anode and cathode, respectively. Pt was chosen as the working electrode in this study because of its relatively high overpotential and convenient to gain. The distance between the electrodes was set as 1.5 cm. Ultrasound was introduced into the reactor upon a plate generator with the frequency of 40 kHz and the power of 100 W (KQ2200, Kunshan Shumei Co.). In each experimental run, 100 mL predetermined solution was added into the reactor and the reaction started as the work station and sonicator simultaneously switched on. During the reaction, the solution was mechanical mixed and the temperature was kept at 30 ± 1 °C by circulating cooling water. At set intervals, samples were taken out and immediately sent for analysis.

2.3. Analysis

The concentrations of SMX were quantified by a high performance liquid chromatography (HPLC, LC-15C, Shimadzu), equipped with a C18 column and a UV detector. The mobile phase was a mixture of 1% acetic acid (50%) and acetonitrile (50%), with a flow rate of 0.8 mL min^{-1}. The detector temperature was set at 35 °C and the wavelength was set at 275 nm. The degradation intermediates were identified by HPLC-ESI-MS (1100 LC, Agilent, USA). The mobile phase was a mixture of 1% acetic acid solution (50%) and acetonitrile (50%), with a flow rate of 0.6 mL min^{-1}. A coupled electrospray ionization (ESI) source was operating in both positive and negative ion mode under the following conditions: spray potential was 3.5 kV, desolvation temperature was 300 ^{0}C.

3. Results and discussion

3.1. Comparative degradation of SMX in different systems

A series of comparative experiments were carried out using 0.1 M Na_2SO_4 electrolyte. As shown in Fig. 1a, the US alone system could only lead to very marginal degradation of SMX after 60 min

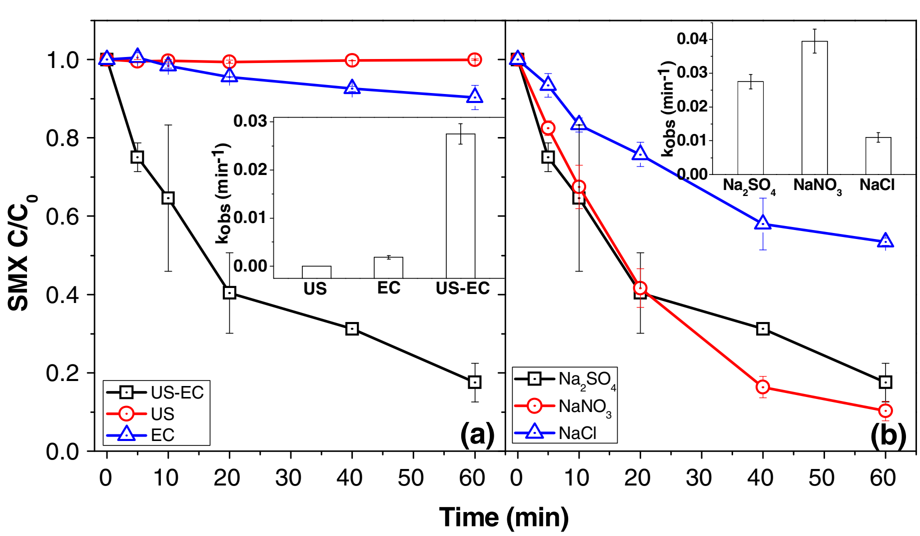

Fig. 1. Degradation of SMX in (a) the three comparative systems with 0.1 M Na_2SO_4 electrolyte, (b) the US-EC system with three different electrolytes (0.1 M). Insets present the corresponding k_{obs}(SMX) values. Initial conditions were: 20 mg L^{-1} SMX, 20 mA cm^{-2} current density, initial pH 6, temperature 30 ± 1 °C.

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