



Degradation of tetracycline hydrochloride by electro-activated persulfate oxidation



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ABSTRACT

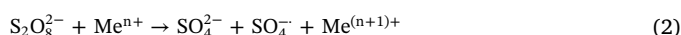
Removal of tetracycline hydrochloride (TCH) in aqueous solution was conducted by coupling electrolysis with persulfate oxidation, wherein a synergistic effect occurred. Batch tests were performed to investigate the influence of various operation parameters, including current density, persulfate concentration and initial pH. It is remarkable that TCH pollutants could be removed effectively by means of electro-activated persulfate oxidation, in which both hydroxyl and sulfate radicals offer the predominant oxidizing species. The removal efficiency of total organic carbon (TOC) reached 31.3% within 4 h, while up to 43.0% with further prolongation of reaction time to 12 h. In this study, electro-activated persulfate oxidation is verified to be an effective manner for TCH degradation in wastewater.

1. Introduction

Tetracycline (TTC) is typically one of tetracycline antibiotics, which are widely used in clinical treatment and livestock industry, thus resulting in their occurrence in the environment via various routines including medical wastewater discharge, agricultural runoff and so on [1,2]. As reported, tetracycline antibiotics are frequently detected in sediments, surface waters and ground waters [3–5]. These residues in the environment have raised great concerns due to high drug-resistance and eco-toxicity, probably posing a serious threat to ecology and human health. Fig. S1 in the Supporting information shows the chemical structure of TTC with multiple ionizable functional groups associated with three macroscopic acid dissociation constants (pK_a) [2,6].

Advanced oxidation processes (AOPs) depend on the use of highly reactive oxidizing radicals, are becoming increasingly popular as a tool of the degradation of organic compounds (e.g. TTC) [2,7]. Most of the presently used AOPs are based on the hydroxyl radical ($HO\cdot$) which can destroy a wide range of organic compounds quickly and non-selectively, however the instability of $HO\cdot$ limits its application [8]. Recently, another type of AOPs has drawn attention, which is based on sulfate radical ($SO_4\cdot^-$) with a longer half-life than $HO\cdot$ [7,9,10]. As reported, $SO_4\cdot^-$ prefers electron transfer reaction while $HO\cdot$ participates in a diversity of reaction with equal preference [11–13]. As opposed to $HO\cdot$, $SO_4\cdot^-$ exhibits high reactivity towards certain (e.g. carboxylic, anilinic, and phenolic) functional groups of target pollutants (e.g. for tetracycline antibiotics) [8].

A strong oxidizing agent of sodium persulfate ($Na_2S_2O_8$) is typically used in the sulfate radicals-based AOPs, due to its high stability at room temperature, relatively low cost and benign end products [14]. When sodium persulfate dissociates in water, it forms the persulfate anion ($S_2O_8^{2-}$) with a standard redox potential (E^0) of 2.01 V [7]. $S_2O_8^{2-}$ could be activated to generate $SO_4\cdot^-$ with a higher standard redox potential ($E^0 = 2.5\text{--}3.1$ V, depending on the pH [2]), by means of heat energy, UV radiation, microwave radiation or electron transfer of transition metal ions (Eqs. (1) and (2)).



Activated persulfate oxidation via above activation methods has been broadly used for destroying contaminants in wastewater [7,9,15,16]. Recently, electro-activated persulfate (Eq. (3)) for organic compounds degradation is described in different studies [12,17–19].



At the industrial scale, persulfate is commonly produced electrochemically via electrolysis of sulfate containing solutions using platinum electrodes [20]. Moreover, it is suggested that persulfate could be regenerated at the anode (Eq. (4)) in system of an activated persulfate degradation reaction [20–22].



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In conjunction with cathodic activation (Eq. (3)), this would perpetuate a source of sulfate radicals. Therefore, combining electrochemistry and activated persulfate can lead to continuous generation of strong oxidants of $S_2O_8^{2-}$ and $SO_4^{\cdot-}$, thus degrading contaminants quickly and effectively.

In this study, tetracycline hydrochloride (TCH) is degraded in the electrochemical (EC) process combined with persulfate (PS) addition (e.g. EC/PS process). To our knowledge, this is the first report about the degradation of TCH in the EC/PS process. The effect of various operating parameters such as current density, persulfate concentration and initial pH is investigated to assess the feasibility of TCH removal by electro-activated persulfate oxidation in the EC/PS process. The mineralization of TCH in terms of TOC removal is also investigated.

2. Materials and methods

2.1. Materials

TCH ($C_{22}H_{24}N_2O_8 \cdot HCl$, 98%) was purchased from Beijing Bailingwei Technology Co., Ltd. (China). Sodium peroxydisulfate ($Na_2S_2O_8$, 98.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anhydrous sodium sulfate (Na_2SO_4 , 99.0%) was obtained from Beijing chemical works (Beijing, China). Ethanol (CH_3CH_2OH , 99.7%) and *tert*-butanol ($C_4H_{10}O$, 98.0%) employed as radicals scavengers, were purchased from Beijing chemical works (Beijing, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) respectively. Sulfuric acid (H_2SO_4 , 95–98%) and sodium hydroxide (NaOH, 96.0%) used for pH adjustment, were purchased from Beijing chemical works (Beijing, China). Sodium hydrogen carbonate ($NaHCO_3$, 99.5%) and potassium iodide (KI, 99.0%) used for PS analysis, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with Milli-Q water ($> 18 m\Omega cm$) purified with a deionizing system.

2.2. Experimental

Fig. 1 presents the scheme of the experimental equipment. Batch experiments were performed in an electrolytic reactor (300 mL glass cylinder) containing 250 mL electrolyte solution. Both cathode and anode plates were made of platinum (99.95 wt%) with dimensions of 10 mm × 70 mm × 0.1 mm, which 45 mm length of each was immersed in the electrolyte solution. The electrodes were arranged parallel to each other at a distance of 4.0 cm. A Model HB17601SL3A direct current (DC) power supply from Zhejiang Wenzhou Hongbao electric group Co., Ltd. (China) was employed to provide the constant current. A Model 76-Sa temperature control device from Shanghai specimen model factory (China) was used to keep the temperature constant.

Before each run, a fresh stock solution of TCH was prepared in deionized water and the initial concentration (C_0) was kept at 50 mg/L. 50 mM of sodium sulfate was added as a supporting electrolyte to

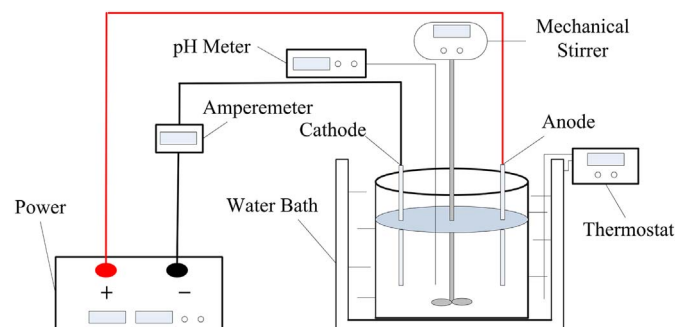


Fig. 1. A scheme of the experimental apparatus.

ensure adequate conductivity of mixed solution (11.55 mS/cm). The initial pH (pH_0) of TCH solutions was natural pH 4.42 measured with an OHAUS STARTER 3100 pH-meter. The solution pH was adjusted to desired value by sulfuric acid (H_2SO_4 , 0.01 M) or sodium hydroxide (NaOH, 0.1 M). The reaction solution was kept in an ice-water bath to avoid any reaction occurring during preparation and pH adjustment. Before the beginning of electrolysis, a certain amount of PS was added into electrolyte solution with constant stirring ($30 r min^{-1}$) by using a JB90-SH mechanical stirrer from Shanghai specimen model factory (China). At predetermined time intervals, samples were collected and immediately analyzed for TCH and PS concentration. In another set of tests, a series of reactors were conducted. One of these reactors was periodically withdrawn from electrolysis, instantly placed in an ice-water bath ($0^\circ C$) to quench the oxidation reaction. The samples obtained were used for total organic carbon (TOC) analyses. Control experiments in process of PS or electrolysis alone were carried out concurrently. In this study, all the experimental tests were undertaken in duplicate to ensure reproducibility.

2.3. Analysis

The absorbance of TCH was measured at $\lambda_{max} = 358 nm$ using a Model 752 UV-visible spectrophotometer from Shanghai Sunny Hengping Scientific Instrument Co., Ltd. (China). The calibration curve using TCH solutions ranging from 1 to 50 mg/L showed a high linear correlation coefficient (i.e., $R^2 = 0.999$). Removal efficiency (RE) of TCH was calculated according to Eq. (5).

$$RE = \frac{A_0 - A}{A_0} \times 100\% \quad (5)$$

where the A_0 and A were the absorbance of the sample at time 0 and t , respectively. The concentration of residual PS was measured via UV spectrophotometric method with potassium iodide [23]. The TOC of the samples were determined by a Model TOC-L CPH analyzer (Shimadzu, Japan).

3. Results and discussion

3.1. Comparison of electrolysis, persulfate and electro-activated persulfate oxidation

Fig. 2 shows the TCH removal efficiency by means of electrolysis,

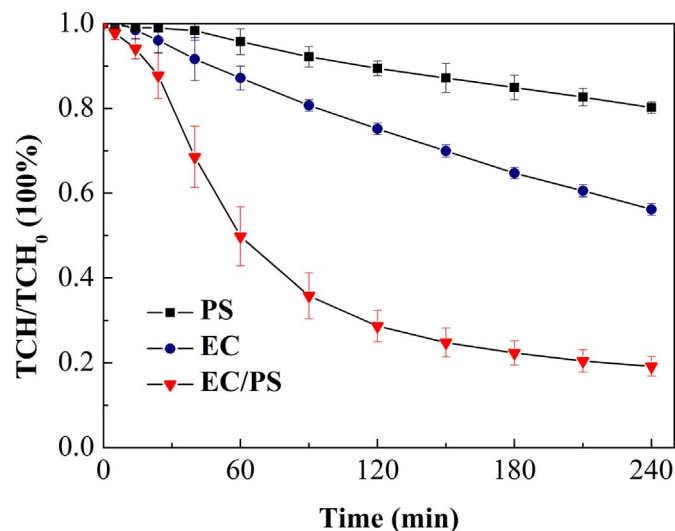


Fig. 2. Removal of TCH by means of electrolysis (EC), persulfate (PS) alone and electro-activated persulfate (EC/PS) oxidation respectively ($TCH_0 = 50 mg/L$, $PS_0 = 12.6 mM$, $j = 13.33 mA/cm^2$, $Na_2SO_4 = 50 mM$, $pH_0 = 4.42$, Temperature $25^\circ C$).

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