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Mineralization of aniline in aqueous solution by electro-activated persulfate oxidation enhanced with ultrasound

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HIGHLIGHTS

- Sulfate radicals are mainly responsible for elimination of aniline.
- Sulfate radicals are formed via cathodic reduction of persulfate anions.
- The yield of sulfate radicals is significantly enhanced with assistance of ultrasonic irradiation.
- Degradation intermediates are identified as azobenzene, nitrobenzene, hydroquinone, *p*-benzoquinone and so on.

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ABSTRACT

Mineralization of aniline in wastewater was performed using electro-activated persulfate oxidation assisted with ultrasonic irradiation. Experiments were carried out under batch-wise mode to investigate the influence of various operation variables on the sonoelectrolytic behavior, such as ultrasonic power intensity, electrode potential employed, sonoelectrolytic temperature, persulfate anion concentration, acidity of wastewater and nitrogen gas dosage. It is notable that the aniline contaminants could be almost entirely eliminated by means of sonoelectro-activated persulfate oxidation, in which sulfate radicals served as principal oxidizing agents, of which amounts were significantly elevated with assistance of acoustic streams. Ethanol and tert-butyl alcohol were used as scavengers to clarify the reactive radicals. Based on the results given by gas chromatograph–mass spectrometer (GC–MS), it was postulated that aniline preliminarily underwent oxidation to form iminobenzene radicals, followed to convert into azobenzene, nitrobenzene and nitrosobenzene respectively. Hydroquinone and *p*-benzoquinone were also detected as reaction intermediates. Generally, the sonoelectro-activated persulfate process is a potential method for treatment of aniline in wastewater.

1. Introduction

Aniline is an important petrochemical compound used primarily for the synthesis of isocyanate, an intermediate for the manufacture of polyurethane. Aniline derivatives are also key precursors for the production of accelerators and antioxidants in the rubber industry. The other principal applications include the manufacture of dyes, herbicides and pharmaceuticals [1]. Due to highly toxic and severe damage to the liver of animals, the wastewater effluent containing aniline should be cautiously treated before released into the environment [2].

Several technologies have been developed to dispose aniline in wastewater owing to its recalcitrance for biodegradation. Based on the results shown [3–6], TiO_2 photocatalysis in the presence of carbonate ions would be effective for the abatement of aniline in wastewater. The main degradation intermediates were identified to be azobenzene and benzoquinone. Besides, some researchers investigated the removal of aniline by means of ozonation [7,8], O_3/UV [9] or O_3/US manner [10], wherein ozone would be substantially decomposed to hydroxyl radicals via cavitation phenomenon. In some publications, aniline was treated using electrochemical oxidation [11,12]. Additionally, many studies have been issued on the mineralization of aniline through Fenton's reagent [13], electro-Fenton method [14–17] or fluidized-bed Fenton process [18,19].

In last decade, persulfate anions (E^0 = 2.01 V) have received much attention for treatment of hazardous compounds due to its stability in aqueous solution [20]. The stronger oxidant, sulfate radicals (E^0 = 2.6 V), could be generated from persulfate anions activated with heat energy, UV radiation, or electron transfer of

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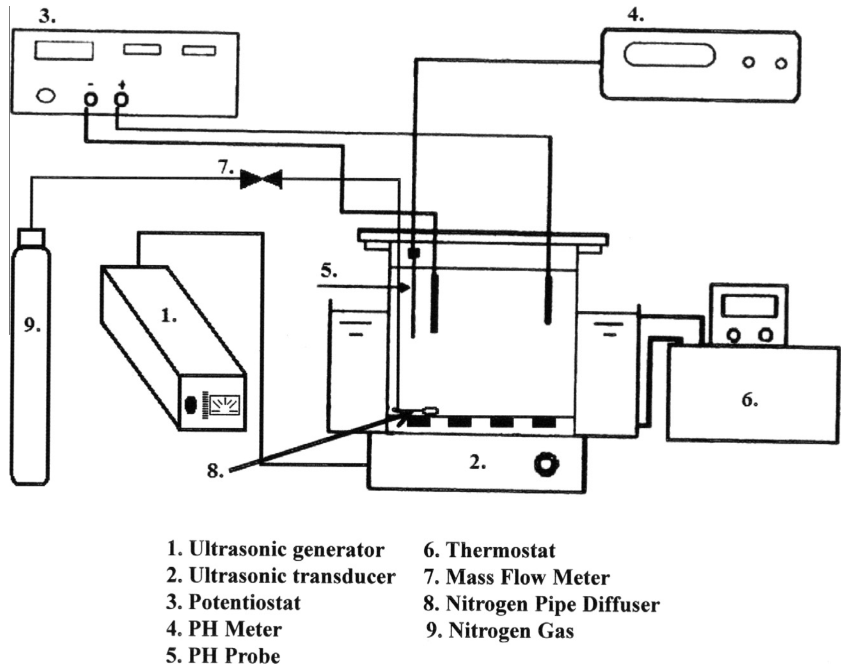

Fig. 1. A scheme of the experimental equipment employed in sonoelectro-activated persulfate oxidation.

transition metal ions. Sequentially, sulfate radicals may be partially converted into hydroxyl radicals and hydrogen peroxide [21–23]

$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{-\cdot} \quad (1)$$

$$S_2O_8^{2-} + Me^{n+} + \rightarrow SO_4^{-\cdot} + SO_4^{2-} + Me^{(n+1)+} \quad (2)$$

$$SO_4^{-\cdot} + H_2O \rightarrow H^+ + SO_4^{2-} + HO^{\cdot} \quad (3)$$

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \quad (4)$$

Recently, the thermally activated persulfate anions have been used to dispose aniline in wastewater, wherein the main oxidizing agent is supposed to be sulfate radicals [24]. In addition, it has been verified that persulfate anions activated with homogeneous ferrous ions were effective for elimination of aniline [25,26]. Above all, it has been proved that sulfate radicals could be produced via electrolytic activation of persulfate anions [27,28], shown as follows

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{-\cdot} + SO_4^{2-} \quad (5)$$

Nevertheless, the yield of sulfate radicals is constrained by the mass transfer rate of persulfate anions toward the cathode [29]. In our previous study, it was found that ultrasonic irradiation could accelerate the mass transfer rate of solute in solution by acoustic streams [30]. Accordingly, this research aims to assess the feasibility of mineralization of aniline in wastewater by sonoelectro-activated persulfate oxidation under various operating parameters, such as ultrasonic power intensity, electrode potential applied, sonoelectrolytic temperature, persulfate anion concentration, acidity of wastewater and nitrogen gas dosage.

2. Material and methods

2.1. Sonoelectro-activated persulfate oxidation testing

Fig. 1 depicts the scheme of the experimental apparatus. Ultrasonic irradiation was provided by an ultrasonic generator (320 W output, variable power control) at a frequency of 160 kHz, controlled by a MOSFET IC circuit and located at the bottom of the reactor. The reactor was a double jacket cylinder (PIIN JIA Technol. JC-A16 Model). As far as the electrode materials were concerned in the laboratory, both cathode and anode plates were conventionally made of platinum (99.9 wt%, 20 mm × 20 mm × 1 mm, PIIN JIA Technology Co.) [31]. Experiments were carried out batch-wisely under atmospheric pressure at the temperature range of 303–318 K. Prior to the testing, proportionate amounts (450 mL) of wastewater with aniline concentration of 75 mg L^{-1}, manufactured using deionized water and aniline (⩾99.5%, Fluka), and sodium persulfate (⩾99.5%, Fluka) were blended well in the reactor, wherein the temperature of wastewater was maintained at the set point by means of a circulating water bath (VWR Scientific Co. 1167 Model). In this study, the sonoelectrolytic testing was performed under constant electrode potential through a dc power supply (INS Power). Within the course of tests, periodic samples were withdrawn from the reactor, instantly placed in an ice bath (277 K) to terminate the oxidation reaction. Sequentially, the samples obtained were undertaken total organic compounds (TOC) analyses. In another set of experiments, the quantitative nitrogen gas controlled by the mass flow meter (BROOKS 5850E Model) was introduced into the wastewater simultaneously through a porous pipe-diffuser located under the cathode, wherein the operation conditions were identical to those as mentioned. Besides, ethanol (⩾99.5%, Fluka, 1 M) and tert-butyl alcohol (⩾99.5%, Fluka, 1 M) were also added into the wastewater respectively.

To evaluate the influence of ultrasonic power intensity on the elimination of aniline, three tests with a variety of power intensity (160–320 W) were conducted. The sonoelectro-activated persulfate oxidation tests were carried out as well under the electrode potentials of 3 V up to 6 V. To gain an insight on the anodic oxidation process, wherein the anode was Pt sheet and the cathode was stainless steel (AISI 304) sheet [32], electrolyses were also conducted under the electrode potentials of 3 V up to 6 V. For the purpose of exploring the effect of acidity of wastewater on the degradation of aniline, a series of tests at the pH values of 3.0 up to 7.0 were performed. Moreover, four tests with various persulfate