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Decomposition of nitrotoluenes in wastewater by sonoelectrochemical and sonoelectro-Fenton oxidation

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ABSTRACT

Oxidative degradation of dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) in wastewater was conducted using electrochemical and electro-Fenton processes respectively, combined with ultrasonic irradiation, wherein a synergistic effect is observed. Experiments were carried out to elucidate the influence of various operating variables on the sonoelectrolytic behavior, such as electrode potential, sonoelectrolytic temperature, acidity of wastewater, oxygen dosage, and dosage of ferrous ions. It deserves to note that the nitrotoluene contaminants could be completely decomposed by sonoelectro-Fenton method, wherein hydrogen peroxide was in situ generated from cathodic reduction of oxygen, supplied partially by anodic oxidation of water. During the sonoelectrolytic process, in spite of existence of degassing phenomenon, the high yield of hydrogen peroxide was produced due to the significantly enhanced mass transfer rate of oxygen toward the cathode, caused by ultrasonic irradiation. Because higher removal efficiency of DNTs and TNT obtained at ambient conditions, it is believed that the sonoelectrolytic method is potentially applied to dispose wastewater from toluene nitration processes.

1. Introduction

Toluene nitration processes have attracted considerable interest of researchers on account of broadly industrial applications of dinitrotoluene (DNT) and trinitrotoluene (TNT), such as precursors of dyes, polyurethane and explosives, respectively [1]. Traditionally, the nitration process is mainly performed with vigorous agitation of toluene and nitrating acid, consisting of a mixture of nitric acid and concentrated sulfuric acid. In the course of separating section, the nitrotoluene product decanted from the settler would be preliminarily mixed with alkaline aqueous solution to neutralize entrained sulfuric acid and nitric acid. Subsequently, the residual contaminants in nitrotoluene were eliminated by virtue of process water washing. The above aqueous streams constitute the great bulk of wastewater. Due to the toxicity and plausible carcinogenicity caused by DNT isomers and TNT derivatives, the effluent wastewater from toluene nitration processes should be properly disposed [2].

To date, many studies have focused on oxidative degradation of nitrotoluene in wastewater by means of advanced oxidation processes. Based on the reports in the literature [3–5], photocatalysis using TiO_2 has been proved to be effective for the destruction of 2,4,6-TNT contained in wastewater. The possible degradation pathways of nitrotoluene on the surface of TiO_2 have been also elucidated. Besides, Li et al. [6,7] explored the remediation of soil utilizing Fenton's reagent, wherein the removal efficiency of 2,4,6-TNT was significantly enhanced with increasing the reaction temperature. Several researchers investigated oxidative degradation of nitroaromatic compounds through UV/Fenton's reagent [8,9] or UV/H_2O_2 manner [10,11]. In another respect, some publications have been issued on the decomposition of 2,6-DNT utilizing O_3, H_2O_2/O_3 or UV/O_3 methods [12,13].

Recently, ultrasound has been applied for treatment of nitrotoluene in wastewater [14–17]. It has been shown that during sonication tests the pyrolytic reaction is mainly responsible for the destruction of nitrotoluene in wastewater, wherein the influence of reaction temperature on the sonolytic behavior is the most important. The removal efficiency of nitrotoluene under sonolysis could be enhanced significantly on the addition of TiO_2 due to the supply of adsorbent and/or excess nuclei, leading to generation of more cavitation bubbles. Additionally, the destruction efficiency of nitrotoluene using UV/TiO_2 could be obviously increased by virtue of ultrasound, wherein TiO_2 serves as both photocatalyst and nuclei, resulting in enhancement of cavitation bubble numbers. Alternatively, persulfate anion combined with ultrasound has been used to dispose dinitrotoluene in wastewater. It has been found that sulfate radicals serve as principal oxidants, derived from activation of persulfate anion with ultrasound.

It has been well recognized that hydrogen peroxide can be electrolytically generated by means of reduction of oxygen dissolved at the cathode made of graphite [18,19], carbon-polytetrefluorethyl-

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ene [20,21] or platinum [22,23]. Upon addition of ferrous salts, the Electro-Fenton's reagent is produced, which gives rise to formation of hydroxyl radicals as follows [24–26]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

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

In addition, ferrous ions may be recovered from reduction of ferric ions at the cathode. The water molecule could be oxidized into oxygen at the anode shown as follows:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

Due to continuously generation of hydrogen peroxide and ferrous ions, nitrotoluene in wastewater would be effectively destructed by hydroxyl radicals derived from Electro-Fenton's reagents.

In our previous studies [22,23,27], it has been proved that nitrotoluene in spent acid or in wastewater would be successfully eliminated using electrochemical and electro-Fenton oxidation respectively, wherein hydrogen peroxide is main oxidant, being in situ generated from cathodic reduction of oxygen, supplied partially by anodic oxidation of water. Nevertheless, the yield of hydrogen peroxide is constrained by the mass transfer rate of oxygen toward the cathode. Consequently, this research investigates the feasibility of removal of nitrotoluene in wastewater by electrochemical and electro-Fenton processes enhanced with ultrasound independently. The influences of electrode potential, sonoelectrolytic temperature, acidity of wastewater, oxygen dosage and dosage of ferrous ions on the removal efficiency of nitrotoluene were also explored.

2. Experimental methods

2.1. Sonoelectrolytic testing

Fig. 1 presents the scheme of the sonoelectrolytic system. Ultrasonic irradiation was supplied by an ultrasonic generator at a frequency of 120 kHz, which was connected to an ultrasonic transducer (φ 80 × 30 mm, 80 W) controlled by a mosfetic circuit and located at the bottom of the reactor. The reactor was made of stainless steel 304 with inner dimensions of φ 80 × 145 mm and outer dimensions of φ 100 × 145 mm (PIIN JIA Technology Co., JC-A16 Model). Experiments were performed in a batch-wise mode under atmospheric pressure at 30, 40, 50 and 60 °C, respectively. As far as the electrode materials were traditionally used [28], both cathode and anode plates were made of platinum (99.9 wt.%) with dimensions of 20 × 20 × 1 mm (PIIN JIA Technology Co.). At the beginning of tests, proportionate amounts (450 mL) of wastewater (rendered by military ammunition plant), accompanied with or without iron (II) sulfate heptahydrate (⩾99.5%, Fluka), were situated in the reactor. In the course of sonoelectrolysis, oxygen gas controlled by the mass flow meter (BROOKS 5850E Model) was introduced into the wastewater through a porous pipe-diffuser located under the cathode. The sonoelectrolytic temperature was adjusted using a circulating water bath (VWR Scientific Co., 1167 Model). In this study, the constant electrode potential mode was adopted by virtue of dc power supply (INS Power) throughout the testing, during which the wastewater was periodically sampled from the reactor and undergone TOC analyses to evaluate the residual organic compounds content.

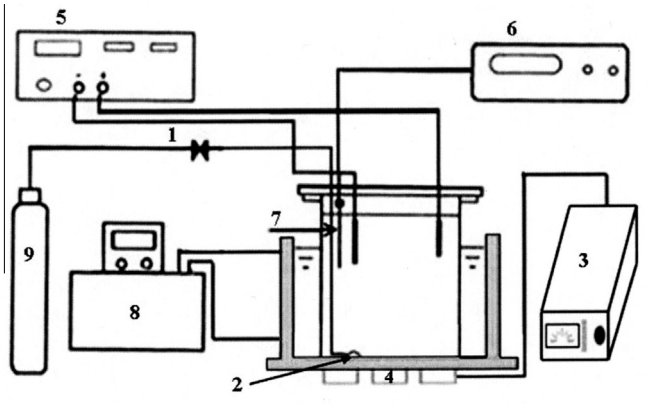

Fig. 1. A scheme of the experimental apparatus employed in sonoelectrolytic tests.

In order to investigate the influence of electrode potential on the destruction of nitrotoluene, four tests with various electrode potentials (3–6 V) were carried out. Besides, for the purpose of exploring the effect of oxygen dosages on the degradation of nitrotoluene, a series of tests with oxygen flow rates of 50–150 mL min^{-1} were performed. The sonoelectrolytic tests were also conducted at the pH values of 0.1–3.0 to elucidate the influence of acidity of wastewater on the decomposition of organic compounds. Moreover, a variety of tests with Fe (II) concentrations of 50–200 mg L^{-1} were undertaken to evaluate the optimal conditions for decomposition of nitrotoluene. In this study, all the experimental tests were undertaken in duplicate to verify the assurance of data.

2.2. Total organic compounds (TOC) analysis

For the duration of sonoelectrolytic tests, the wastewater was periodically sampled and directly analyzed utilizing a Tekmar Dohrmann Phoenix 8000 instrument equipped with an ultra-violet (UV) reactor and a nondispersive infrared (NDIR) detector. The organic compounds in samples were completely transformed into carbon dioxide by sodium persulfate with assistance of UV irradiation, which was subsequently quantified by the NDIR detector. In another respect, the inorganic compounds were acidified by phosphoric acid and removed via carbonic acid. To meet the requirement of concentrations of TOC in samples, the calibration curve is established among the range (0–500 mg L^{-1}) by the potassium hydrogen phthalate standard solutions.

2.3. Hydrogen peroxide concentration analysis

To verify hydrogen peroxide being derived from oxygen reduction, the concentrations of electrogenerated hydrogen peroxide by sonoelectrolysis and electrolysis individually in the deionized water (pH 0.1) instead of wastewater under identical operating conditions with previous sonoelectrolytic tests were determined by a titanic sulfate method [29]. The light absorbance of titanic-hydrogen peroxide was measured using an UV–vis spectrophotometer (LAMBDA 850 Model, Perkin Elmer) at a wavelength of 410 nm. The sample (ca. 4 mL) was directly situated in a quartz holder and analyzed among the range of 0–500 mg L^{-1}, corrected by the standard solutions of hydrogen peroxide.