A dual-cathode electro-Fenton oxidation coupled with anodic oxidation system used for 4-nitrophenol degradation

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ABSTRACT

The degradation of 4-nitrophenol was investigated using a novel electrochemical oxidation system, in which the anodic oxidation at $Ti/SnO_2–Sb_2O_5–IrO_2$ electrode and the electro-Fenton oxidation with two cathodes were involved. In this system, gas diffusion electrode (GDE) was used to generate H_2O_2 by O_2 reduction and graphite electrode was employed for the reduction of Fe^{3+} regenerating Fe^{2+}. When the potential values of GDE and graphite cathode were controlled at -0.80 and -0.10 V/SCE respectively, the optimum Fe^{2+} concentration for 4-nitrophenol degradation was about 0.10 mM, much lower than the concentration of 0.25 mM obtained in the single-cathode system. Due to the combination of electro-Fenton oxidation and anodic oxidation, an effective degradation and a high mineralization current efficiency (MCE) were achieved. After 600 min treatment, 74.5% of the original TOC was removed by the dual-cathode oxidation system. Moreover, it was confirmed that 57.0% of the original nitrogen could be removed in gaseous form from the simulated wastewater. These results indicate that this electrochemical oxidation process might provide an alternative for the degradation of organic pollutants.

1. Introduction

Over the past two decades, the application of advanced oxidation processes (AOPs) characterized by the in situ generation of hydroxyl radical ($\cdot$OH) in the degradation of organic contaminants has become the focus of increasing research [1,2]. Among the various AOPs, electrochemical oxidation processes, mainly include electro-Fenton oxidation and anodic oxidation have attracted much attention in recent years, benefiting from their ability to destroy bio-refractory organic compounds and environmental compatibility [3–5].

In an electro-Fenton oxidation process, H_2O_2 is continually generated in acidic solutions by the reduction of O_2 at the cathodes such as graphite [6], carbon-felt [7] and carbon-polytetrafluoroethylene [8]. When Fe^{2+} is presented as the catalyst, Fenton reaction will take place in the contaminated solution, generating $\cdot$OH to destruct the various organics. This process has been applied to treat many industrial wastewaters containing organic compounds including phenol [7], aniline [9], herbicides [10], dyes [11], and so on. As a crucial factor in electro-Fenton process, the influence of Fe^{2+} on the degradation of organic pollutants has been carefully investigated. The

optimum Fe^{2+} dosage is associated with the various experimental conditions. However, more attention should be paid to the generation of Fe(III) complexes which causes the decrease in the efficiency of electro-Fenton process [12,13]. Based on many studies, some organic acids (carboxylic acids) are always formed during organics degradation by Fenton or electro-Fenton process, and these carboxylic acids can react with Fe(III) generating complexes. Since it is very difficult to destroy these Fe(III) complexes by $\cdot$OH generated in electro-Fenton process [14,15], some efforts to reduce the generation of Fe(III) complexes may be conducted by reducing the initial Fe^{2+} concentration or by other methods to obtain a complete organics degradation. Additionally, as we all know, iron ions may be removed from wastewaters after the treatment of electro-Fenton oxidation by adding alkaline chemicals, resulting in the generation of chemical sludge. The burden resulted from the sludge treatment is an important disadvantage of electro-Fenton process. It is evident that the decrease in Fe^{2+} dosage will reduce the amount of chemical sludge and save chemicals.

Furthermore, for the purpose of extensive industrial application in the treatment of organic wastewaters, further enhancing the current efficiency of electrochemical oxidation process is necessary. In many studies, its average value is not beyond 50% [3]. As a result of low current efficiency, high energy consumption is required for the effective pollutants removal, which is the main disadvantage of this process. In most studies of electro-Fenton processes focus has been put on the functions of cathodes, usually omitting

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functions of anodes. Few studies were conducted on the destruction of organic pollutants wherein equal attention has been put on both anodic and cathodic actions. In fact, if H_2O_2 is electro-generated on the cathode surface under optimum conditions, simultaneously, the anodic oxidation of organic contaminants is also used by the greatest extent, the goals of enhancing current efficiency and reducing energy consumption will be attained. Recently, the possibility of destroying organics by the electro-Fenton oxidation using a gas diffusion electrode in parallel with the anodic oxidation of boron-doped diamond or Pt has been demonstrated and is attracting more and more attention [16,17].

Nitrophenols are toxic organic compounds widely used in the manufacture of pesticides, dyes and other chemicals, which are commonly present in many industrial wastewaters [18]. These compounds resist biodegradation and have potential toxicity toward humans and animals. Because conventional biological methods are found to be ineffective for the degradation of nitrophenols due to their toxicity, there is an increasing interest in the development of environmentally clean technologies to destroy such compounds in aqueous medium.

It is the object of this paper to report the degradation of 4-nitrophenol in aqueous electrolyte by a dual-cathode oxidation system (DOS). In this process, electro-Fenton oxidation and anodic oxidation were united in one electrochemical reactor using $Ti/SnO_2–Sb_2O_5–IrO_2$ as anode, gas diffusion electrode as the first cathode for H_2O_2 generation, and graphite electrode as the second cathode for Fe^{2+} regeneration. Besides enhancing the current efficiency of electrochemical oxidation process, the main aims of this work were to minimize the initial concentration of Fe^{2+} required for the effective electro-Fenton oxidation and investigate the nitrogen conversion during 4-nitrophenol degradation by DOS.

2. Experimental

2.1. Chemicals and electrodes

All chemicals were analytical grade reagents and used as received. All solutions were prepared with ultra pure deionized water (conductivity < 0.8 μS cm^{-1}). The supporting electrolyte consisted of a 0.10 mol L^{-1} Na_2SO_4 solution and 4-nitrophenol was added to this solution as the simulated pollutant for the degradation experiments. The original concentration of 4-nitrophenol was 200 mg L^{-1} and the pH of all electrolytes was adjusted to 3.0 using H_2SO_4 solution.

$Ti/SnO_2–Sb_2O_5–IrO_2$ anode was prepared by thermal decomposition of appropriate mixtures of precursor salts dissolved in isopropanol [19]. The graphite electrode with a carbon content of 99.5% was used as the second cathode. The preparation of gas diffusion electrode (GDE) is described as follows.

Graphite powder (99.9% purity) and polytetrafluoroethylene (PTFE) emulsion were mixed according to a mass ratio of 2:1 ($W_{carbon}:W_{PTFE}$), followed by the addition of a small amount of ethanol and NH_4HCO_3. After the mixture was well mixed by ultrasonic stirring, it was shaped into the cylinder with a diameter of 24 mm using an extruder, and then was dried at 330 °C for 60 min in a muffle furnace. After that, the prepared material was dipped into acetone for 24 h. Finally, it was dried at 100 °C for 45 min.

2.2. Electrolytic systems

The main electrolytic experiments were performed in an open and undivided tank reactor containing 200 mL of solution stirred with a magnetic bar at 500 rpm. The potential of work electrodes was controlled by a CHI760D Electrochemical Workstation (Shanghai Chenhua instrument Co. Ltd., China). The solution temperature was regulated at 25 ± 1 °C by circulating external thermostated water through a double-jacket. The GDE was fed with an air flow rate of 25 mL s^{-1} to continuously generate H_2O_2 from O_2 reduction. The graphite cathode was used for the reduction of Fe^{3+}. But this cathode was not used in single-cathode oxidation system (SOS). The geometric area in contact with the solution was 38 cm^2 for the anode and the graphite, while this area was 30 cm^2 for GDE. The distance between anode and cathode was 15 mm. In all electrolytic experiments, a saturated calomel electrode (SCE) was used as a reference electrode.

2.3. Electro-generation of H_2O_2 at GDE

The experiments were performed under potentiostatic condition using 200 mL of 0.10 mol L^{-1} Na_2SO_4 solution at pH 3.0 in the electrolytic system described in Section 2.2. In these experiments, the graphite electrode was not used in order to investigate the generation of H_2O_2 at GDE. During the course of electrolysis, samples were drawn at desired time intervals to determine the concentration of H_2O_2.

2.4. Bulk electrolysis for 4-nitrophenol degradation

The degradation of 4-nitrophenol was carried out in the electrolytic system described in Section 2.2. For each run, 200 mL of the solution containing 200 mg L^{-1} 4-nitrophenol and 0.10 mol L^{-1} Na_2SO_4 (pH 3.0) was poured into the reactor. $FeSO_4 \cdot 7H_2O$ of various amounts was added into the solution. The potential values of GDE and graphite electrode were controlled at −0.80 and −0.10 V/SCE respectively in DOS by the bi-potentiostat. At appropriate time intervals, samples were taken for chemical analysis. Prior to each experiment, GDE was subjected to a hot treatment at 330 °C for 60 min, and then washed by deionized water to obtain a stable H_2O_2 production. All experiments were performed at least twice, and data shown were from one representative experiment.

2.5. Analytical methods

H_2O_2 concentration was determined by light absorption of the titanium-hydrogen peroxide colored complex at λ = 410 nm with a detection limit of 1.2 mg L^{-1}. Fe^{2+} was determined by 1,10-phenanthroline spectrophotometric method (China national standard: HJ/T345-2007). Quantification of 4-nitrophenol was achieved by light adsorption at 401 nm in alkaline medium. Total organic carbon (TOC) was measured using TOC-VCPH Analyzer (Japan). Ammonia nitrogen was measured by Nessler's reagent colorimetric method (China national standard: HJ/535-2009). NO_2^- and NO_3^- concentration were determined by a Dionex ICS-3000 ion chromatograph system with a IonPac AS 9 column. Before the measurement, samples were diluted with deionized water and subjected to the pretreatment of eliminating SO_4^{2-} by the addition of CaO. The detection was conducted using a mobile phase of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at a flow rate of 2.0 mL min^{-1}. Total nitrogen (TN) was measured by alkaline potassium persulfate digestion-UV spectrophotometric method (China national standard: GB11894-89). pH value was monitored with a pHS-25C acidity meter. Additionally, the UV–vis adsorption spectra of the samples were recorded in the wavelength range from 200 to 600 nm using a TU-1901 spectrophotometer (Beijing Puxi Instrument Co. Ltd., China).
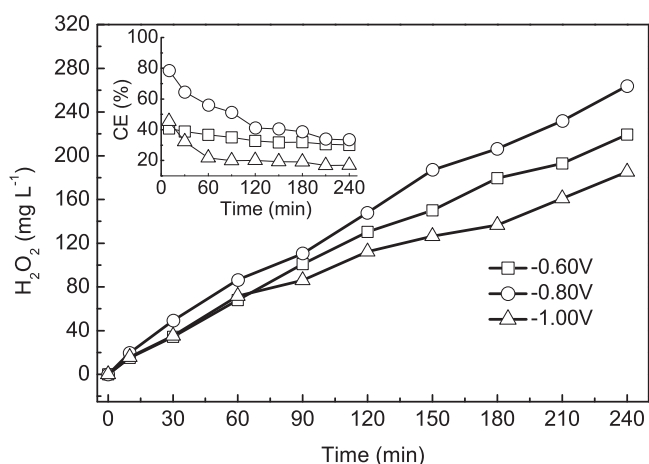
Fig. 1. Measured H_2O_2 production and current efficiency (CE) at various cathodic potential.

3. Results and discussion

3.1. Electro-generation of H_2O_2 by GDE

The ability of GDE for H_2O_2 generation by O_2 reduction (Eq. (1)) was checked under the condition of various cathodic potentials at pH 3.0. An apparent increase in H_2O_2 production and a decrease in current efficiency (CE) for H_2O_2 accumulation with reaction time are shown in Fig. 1. CE values were calculated from Eq. (2).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$CE(\%) = \frac{nFcV}{1000MQ} \times 100 \tag{2}$$

where $n = 2$ represents the stoichiometric number of electrons transferred in reaction (1), F is the Faraday constant (96,486 C mol^{-1}), c is the concentration of accumulated H_2O_2 (mg L^{-1}), V is the solution volume (L), 1000 is a conversion factor, M is the molecular weight of H_2O_2 (34 g mol^{-1}), and Q is the charge consumed during the electrolysis.

As clearly seen, the GDE at the potential of −0.80 V exhibits a higher catalytic activity toward O_2 reduction generating H_2O_2 than at −0.60 and −1.00 V. In this case, a H_2O_2 accumulation of 263 mg L^{-1} along with an average CE of 46.8% was achieved by the electrolysis of 240 min. Additionally, it should be pointed out that the real H_2O_2 production was more than the measured production because of the H_2O_2 decomposition caused by several processes [20,21]. When the cathodic potential is at −1.00 V, the current increases obviously because of H_2 evolution by H^+ reduction (Eq. (3)), leading to the decrease in H_2O_2 accumulation and current efficiency. Therefore, in the following experiments, the potential of GDE was constantly controlled at −0.80 V to obtain a stable H_2O_2 production.

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

3.2. Comparative degradation by SOS and DOS with various Fe^{2+} concentrations

A comparative study on the degradation of 4-nitrophenol solution was conducted by a conventional single-cathode oxidation system (SOS) and a novel dual-cathode oxidation system. For the purpose of comparison, the potential of GDE was controlled at −0.80 V with an average current of 40 mA in the two processes to obtain an approximate H_2O_2 production. The potential of graphite cathode in DOS was controlled at −0.10 V (average current of 6.5 mA) because an effective reduction of Fe^{3+} generating Fe^{2+}

could be achieved in this condition [22]. The percent removal of 4-nitrophenol by SOS (Fig. 2a) and DOS (Fig. 2b) with various Fe^{2+} concentrations is shown in Fig. 2. It is apparent that Fe^{2+} plays a key role in the degradation of 4-nitrophenol by the two processes. Since the single oxidation of H_2O_2 is unable to destroy 4-nitrophenol, the degradation is ascribed to the combined actions of electro-Fenton oxidation and anodic oxidation in the presence of Fe^{2+}. A significant removal was also attained in the absence of Fe^{2+} (0 mM) owing to the anodic oxidation of Ti/SnO$_2$–Sb$_2$O$_5$–IrO$_2$. The mechanism of organics degradation by this kind of anode has been proposed by several researchers [23,24]. It can be observed that the increase of initial Fe^{2+} concentration from 0 to 0.10 mM greatly enhances 4-nitrophenol removal by DOS. Considering the removal rates and the minimization of Fe^{2+} dosage, the optimum concentration for an effective degradation was 0.10 mM (Fig. 2b), whereas it was 0.25 mM for SOS (Fig. 2a), much higher than 0.10 mM for DOS. This difference was confirmed by TOC removal (Fig. 2c). It is observed that the best Fe^{2+} concentrations are 0.10 and 0.25 mM for TOC removal by DOS and SOS respectively. Generally, as a result of the presence of graphite cathode, the degradation of 4-nitrophenol by DOS was faster than by SOS at the same initial Fe^{2+} concentration except at 0.25 mM, especially when the concentration was lower than 0.15 mM. The relatively poor degradation obtained by 0.50 mM exhibits an excess addition of Fe^{2+}, and the quenching effect of •OH caused by Fe^{2+} from reaction (4) can explain this result [25]:

$$^\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{4}$$

It is well known that the mixture of Fe^{2+} and H_2O_2 in acid solution can generate •OH to destroy organic pollutants accompanying the generation of Fe^{3+} (Eq. (5)). The instantaneous concentration of •OH is proportional to the H_2O_2 and Fe^{2+} concentration [26].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow \ ^\bullet OH + H_2O + Fe^{3+} \tag{5}$$
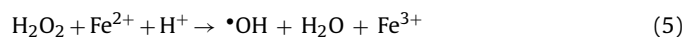
$$[^\bullet OH] = \lambda k [Fe^{2+}][H_2O_2] \tag{6}$$

where k is the second-order rate constant ((μmol L^{-1})$^{-1}$ min^{-1}); λ is the average life of •OH (min); [Fe^{2+}] and [H_2O_2] are the concentration of ferrous ion (μmol L^{-1}) and H_2O_2 (μmol L^{-1}), respectively. Since Fe^{2+} is consumed more rapidly than it is regenerated [27,28], the regeneration of Fe^{2+} becomes an important factor for the lasting of Fenton reaction [27,29]. To accelerate the reduction of Fe^{3+} can provide sufficient Fe^{2+} ions generating more •OH for organics degradation (Eq. (6)). Because the main function of GDE is the electro-generation of H_2O_2, the regeneration of Fe^{2+} by the cathodic reduction in SOS is very weak [30], whereas the regeneration of Fe^{2+} can be enhanced by the reduction at the graphite cathode in DOS (Eq. (7)). The rapid change between the Fe(III)/Fe(II) couple in DOS lead to the effective degradation of 4-nitrophenol with a lower initial Fe^{2+} concentration.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} (\text{at graphite cathode}) \tag{7}$$
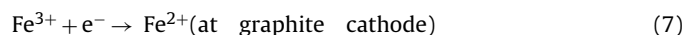
The typical evolutions of Fe^{2+} concentration during the course of 4-nitrophenol degradation by DOS and SOS were shown in Fig. 2d. Note that a similar trend was found operating with the initial Fe^{2+} concentration of 0.10 or 0.50 mM. A rapid concentration decrease in 30 min was caused by Fenton reaction (Eq. (5)), followed by a concentration increase from 30 to 60 min indicating the presence of Fe^{3+} reduction both in the two processes, and after 60 min the concentrations only varied slightly. From Fig. 2d, it is clear that the concentrations obtained from DOS are always greater than those from SOS, which also applies to the evolution of Fe^{2+} at other initial concentrations and further evidences the function of Fe^{3+} reduction at the graphite cathode. In fact, there are several species such as H_2O_2, HO$_2$•, O$_2$•$^-$, and organic radical
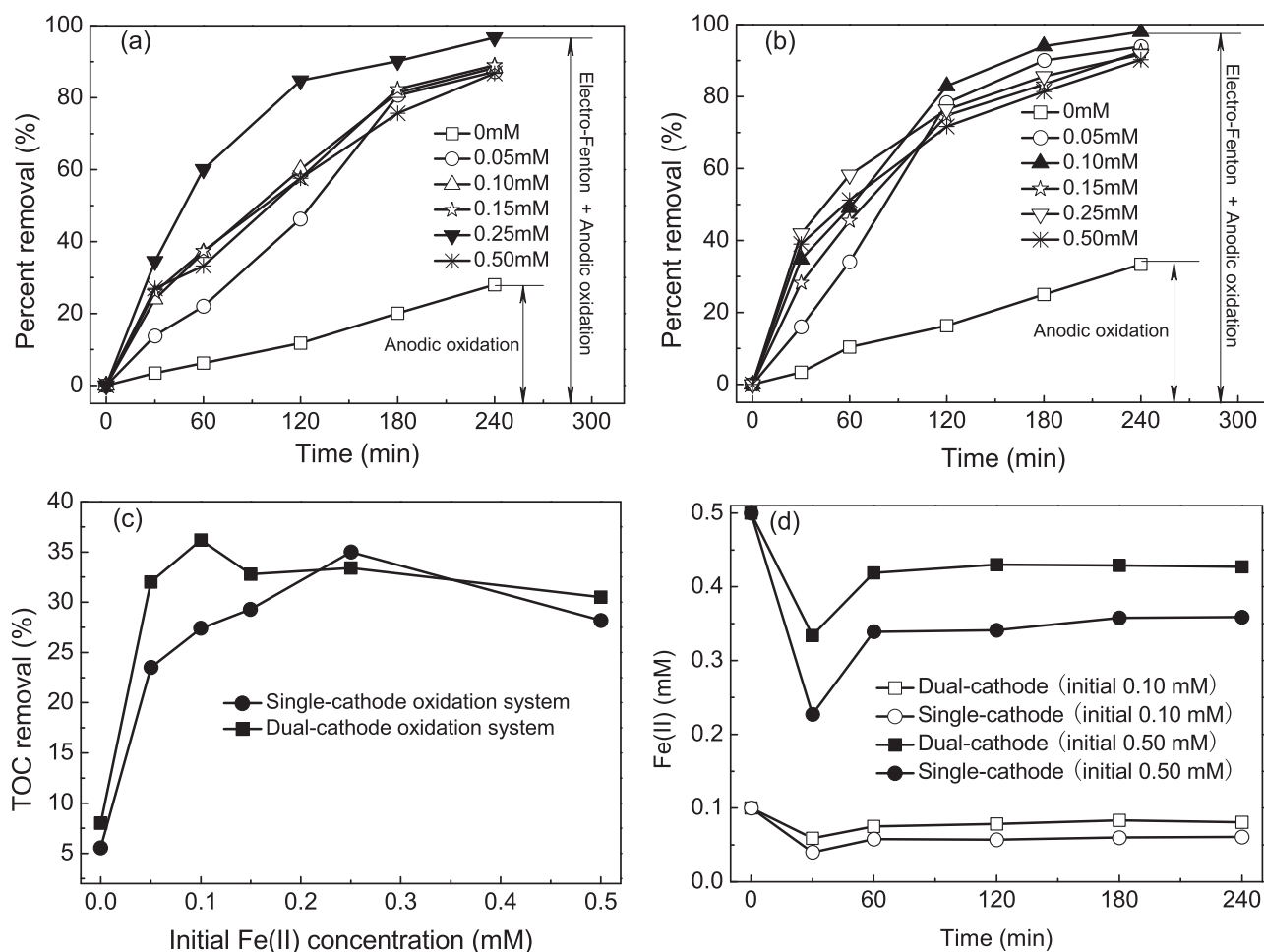
Fig. 2. The percent removal of 4-nitrophenol with various initial concentration of Fe^{2+} in single-cathode (a) and dual-cathode (b) oxidation systems. TOC removal obtained by the electrochemical treatment of 240 min at various initial concentrations of Fe^{2+} (c). Evolution of Fe^{2+} concentration during the degradation of 4-nitrophenol solutions with the initial Fe^{2+} concentrations of 0.10 and 0.50 mM (d).

($R^\bullet$), which can lead to a slow reduction of Fe^{3+} in SOS [3]. Nevertheless, apart from the reduction caused by the above species, the presence of graphite cathode further accelerates the reduction of Fe^{3+} in DOS. Recently, Isarain-Chávez et al. reported the mineralization of drug β-blocker atenolol by an electro-Fenton process with a four-electrode oxidation system emphasizing the effectiveness of Fe^{3+} reduction at carbon-felt cathode for organics degradation [17]. Their experiments were conducted under constant current condition by two power supply systems, while only one bi-potentiostat was employed in our work to control the constant potential for GDE and graphite cathode simultaneously, which is more advantageous to restrain side reactions enhancing the current efficiency.

Fig. 3 summarizes the generation of $^\bullet OH$ and the role of the graphite cathode to better understand the organics degradation mechanism in DOS. There are two ways for the generation of $^\bullet OH$ in this process: one is the oxidation of H_2O at the anode surface, the other is Fenton reaction in solution. Therefore, both anodic oxidation and electro-Fenton oxidation were accounted for the degradation of 4-nitrophenol by DOS with an enhanced reduction of Fe^{3+}. According to the removal of 4-nitrophenol and TOC (Fig. 2c), electro-Fenton oxidation was the predominant mechanism for 4-nitrophenol degradation, whereas anodic oxidation was the secondary mechanism under the ideal Fe^{2+} concentration.
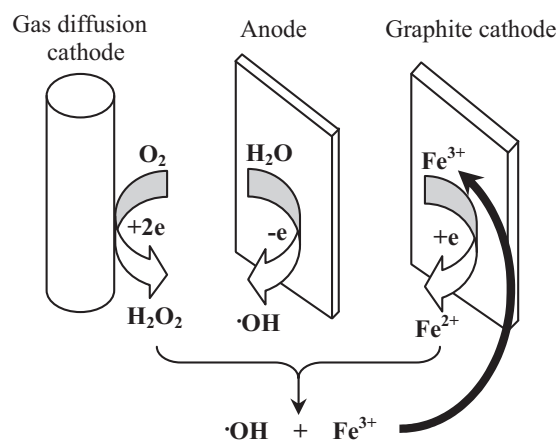

Fig. 3. Illustration of the mechanism for $^\bullet OH$ generation and Fe^{3+} reduction in dual-cathode oxidation system.

3.3. Degradation of 4-nitrophenol by DOS

To learn more about the degradation of 4-nitrophenol by DOS, the degradation experiments were carried out at −0.80 V for GDE and −0.10 V for graphite cathode using 0.10 mM Fe^{2+} with a longer
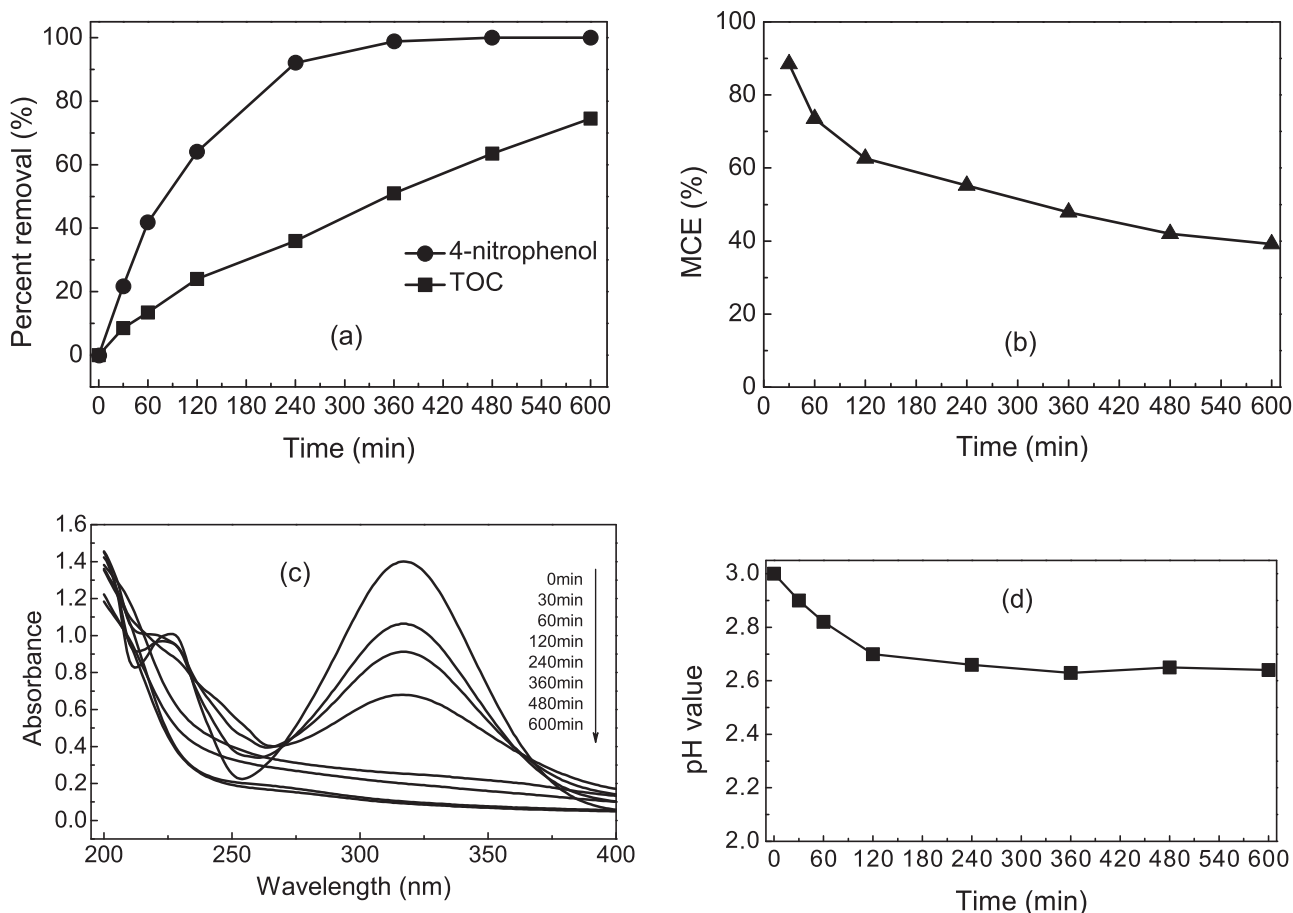
Fig. 4. TOC, 4-nitrophenol removal (a) and MCE (b) as a function of reaction time. UV–vis absorption spectra of the 4-nitrophenol solution (c) and pH variation (d) during the electrochemical treatment. The potential of GDE and graphite cathode was controlled at −0.80 and −0.10 V respectively. The initial concentration of Fe^{2+} was 0.10 mM.

electrolysis time. Percent removal versus electrolysis time profiles for 4-nitrophenol and TOC was shown in Fig. 4a. 4-Nitrophenol removal noticeably increased as electrolysis time was increased from 0 to 240 min showing a rapid degradation. A 4-nitrophenol removal of 98.8% was achieved by the electrolysis of 360 min, much greater than TOC removal (51.0%), indicating that part of 4-nitrophenol was degraded to soluble intermediates rather than completely oxidized to CO_2 and H_2O. TOC removal increased from 51.0% to 74.5% as electrolysis time was increased from 360 to 600 min indicating the further degradation of organic intermediates. Moreover, as the treatment proceeded, the solution changed from colorless to red-brown and then gradually disappeared with prolonged reaction time, which also suggested that some intermediates were formed during the degradation.

Mineralization current efficiency (MCE) is a key parameter to evaluate the effectiveness of electrochemical processes. In this work, on the basis of the measured TOC, the MCE at a given time t (h) was calculated using Eq. (8) [31]. Where F is the Faraday constant (96,487 C mol^{-1}), V is the solution volume (L), $\Delta(TOC)_t$ is the TOC decay (mg L^{-1}), 4.32×10^7 is the conversion factor for units homogenization (3600 s h^{-1} × 12,000 mg mol^{-1}), m is the number of carbon atoms of 4-nitrophenol (6C atoms) and I is the applied total current (A). The number n of electrons consumed per 4-nitrophenol molecule during mineralization was taken as 28 considering that it is converted into CO_2 and NO_3^- ions according to the following reaction (Eq. (9)). The further discussion was presented in the next subsection.

$$MCE\ (\%) = \frac{nFV\Delta(TOC)_t}{4.32 \times 10^7 mIt} \times 100 \qquad (8)$$

$$C_6H_4OHNO_2 + 12H_2O \rightarrow 6CO_2 + NO_3^- + 29H^+ + 28e^- \qquad (9)$$
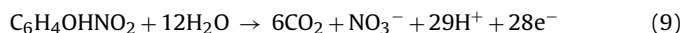
The efficiencies determined for the experiments of Fig. 4a were presented in Fig. 4b. A MCE value of 88.5% was obtained at 30 min, which decreased to 39.2% at the end of the electrolysis. The higher MCE values were observed at the early stage of the electrolysis indicating a fast conversion of organics into CO_2, followed by a deceleration at long electrolysis times as a consequence of the loss of organic matter and the formation of more difficultly oxidizable organic intermediates. Generally, the MCE of the present work was greater than that reported in literature [32,33], indicating a more complete use of energy in the electrochemical degradation of organics. The high MCE achieved in this work mainly was due to the realization of using anodic oxidation and electro-Fenton oxidation for organics degradation in one electrolysis system. The constant cathodic potential of −0.80 V favored the generation of H_2O_2 and effectively restrained the side reaction of producing H_2. Finally, although a high MCE can be obtained, a longer electrolysis time is still required for the complete degradation of organics.

The UV–vis absorption spectra of 4-nitrophenol solution before and after the degradation by DOS were shown in Fig. 4c (all samples were diluted ten times by deionized water). A main absorption band for 4-nitrophenol was at 317 nm and the absorption intensity reflected its concentration in solution. The peak intensity decreased by about 95% within 240 min confirming the rapid degradation of 4-nitrophenol in this system. The absorption peak disappeared after 360 min indicating a complete destruction of the molecular structure of 4-nitrophenol, which could be evidenced by the removal of 4-nitrophenol shown in Fig. 4a. In addition, nitrate ions (NO_3^-) were generated in the course of 4-nitrophenol degradation
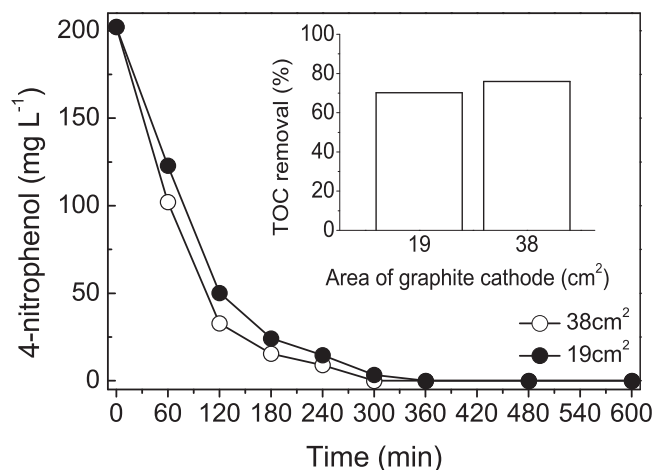
Fig. 5. Decay of 4-nitrophenol concentration with reaction time at different effective areas of graphite and percent TOC removal by the treatment of 600 min. The experiments were conducted under the same conditions as Fig. 4 except the effective area of graphite.

Fig. 6. Evolution of NH_4^+, NO_2^-, NO_3^- and TN during the degradation of 4-nitrophenol under the same conditions as Fig. 4.

Fig. 7. Illustration of the mechanism for nitrogen conversion in the course of 4-nitrophenol degradation by DOS.

discussed in the later section, which has an intense absorption at about 210 nm. As a result, the absorption of nitrate ions along with the organics caused the absorbance value only decreased slightly, even increased at 200–210 nm.

Fig. 4d shows the evolution of solution pH during the treatment. It can be observed that pH value decreases to 2.65 from the initial value of 3.00 in 240 min and changes slightly in the subsequent reaction time. Since the optimum pH for Fenton reaction is about 2.8 [3], this oxidation system is able to remain the reasonable pH for organics degradation.

The decay of 4-nitrophenol concentration and the TOC removal at 600 min obtained with different effective area of graphite cathode are shown in Fig. 5. The decay rate of 4-nitrophenol and TOC removal at 38 cm^2 are higher than those at 19 cm^2 exhibiting a relatively faster degradation under the former condition. When the effective area changed from 38 to 19 cm^2, the average current passed through graphite cathode reduced from 7 to 4 mA weakening the reduction of Fe^{3+} generating Fe^{2+}. As a result, the degradation rate became slower when the effective area of graphite cathode decreased with an initial Fe^{2+} concentration of 0.10 mM. It should be pointed out that the anodic oxidation power was not the main reason for the different degradation rate as proved by the little difference in anodic current. The above results indirectly demonstrate again that the graphite cathode can affect organics degradation by enhancing Fe^{3+} reduction in DOS.

3.4. Nitrogen conversion during the course of 4-nitrophenol degradation by DOS

While the degradation of 4-nitrophenol resulted in a decrease in organic carbon content, the new pollution factor of inorganic nitrogen might be generated simultaneously for the presence of $-NO_2$ group. Although some work on the degradation of 4-nitrophenol by advanced oxidation processes has been conducted, nitrogen conversion and removal was not attracted much attention [34,35]. In the present work, the concentrations of NH_4^+, NO_2^-, NO_3^- and total nitrogen (TN) were determined to understand the mechanism of nitrogen conversion and the nitrogen removal during 4-nitrophenol degradation by DOS. As can be seen from Fig. 6, the concentration of NO_2^- increases in the time range of 0–120 min followed by gradual concentration decay, whereas the concentration of NO_3^- increases continuously in 480 min. The concentration evolutions of NO_2^- and NO_3^- demonstrate that the destruction of 4-nitrophenol is accompanied by the elimination of $-NO_2$ group
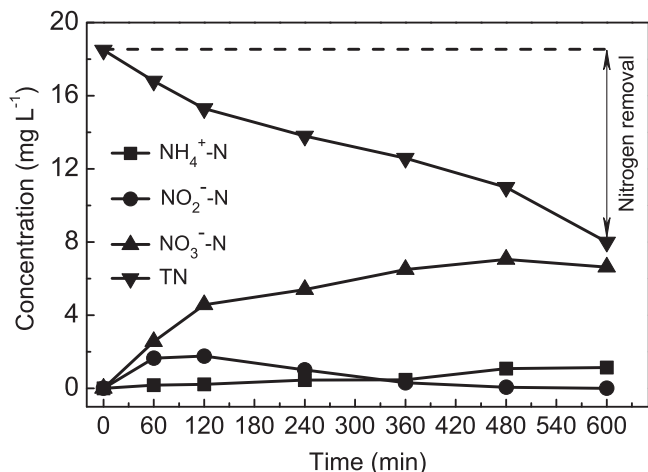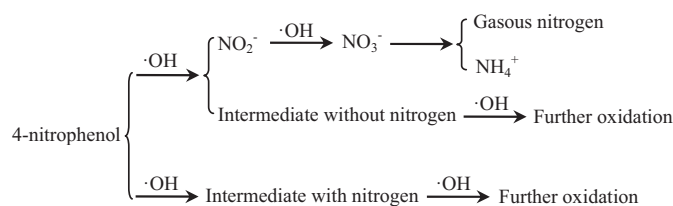
generating NO_2^-. Because NO_2^- ions are unstable, they will be easily oxidized to NO_3^- ions by •OH. Although several researchers have reported the accumulation of NO_3^- ions during the degradation of 4-nitrophenol by AOPs, little was known about TN removal and the variation of NH_4^+ concentration [34,36]. However, in this work, it was interesting that the significant decrease in TN concentration and the continuous increase in NH_4^+ concentration were obtained by DOS. About 57.0% of the original nitrogen was removed from the solution by the electrolysis of 600 min. Since organic nitrogen and inorganic nitrogen have been included in TN, the significant decrease in TN concentration indicated that a major nitrogen removal by gaseous nitrogen (N_2 or NO_x) was achieved along with the mineralization of organic carbon. Both the decrease of TN concentration and the continuous increase of NH_4^+ concentration showed the presence of the reduction of NO_3^-. The reduction function of graphite cathode as well as GDE might be used to explain the well nitrogen removal.

In addition, 1.15 mg L^{-1} for NH_4^+, 0.00 mg L^{-1} for NO_2^-, 6.63 mg L^{-1} for NO_3^- and 8.00 mg L^{-1} for TN were determined at the end of electrochemical treatment (600 min). The total inorganic nitrogen in the solution was about 7.78 mg L^{-1}, lower than the TN concentration (8.00 mg L^{-1}), which indicated the presence of organic nitrogenous compounds.

Based on the above discussion, the mechanism of nitrogen conversion during the course of 4-nitrophenol degradation by DOS was proposed (Fig. 7). Yuan et al. reported a different path for the initial degradation of 4-nitrophenol, in which the reduction of 4-nitrophenol generating 4-aminophenol was proposed because no significant amounts of NO_3^- and NO_2^- ions were detected after 13% mineralization of 3.6 mM 4-nitrophenol [37]. However, the mechanism of the initial degradation of 4-nitrophenol was denitrated by the oxidation of •OH in DOS confirmed by the accumulation of NO_3^- and NO_2^- ions. We believe that the difference in electrode materials and experiment conditions can explain the above different

results. Finally, to completely understand the nitrogen conversion in the process, further efforts on the determination of the species of gaseous nitrogen and the identification of by-products will be necessary.

4. Conclusions

A dual-cathode oxidation system was proposed for the degradation of 4-nitrophenol in order to reduce the amount of Fe^{2+} used in electro-Fenton oxidation and enhance the effectiveness of electrochemical advanced oxidation process. Major conclusions are as follows:

(1) Compared with the conventional single-cathode oxidation system, the amount of Fe^{2+} optimized for the effective degradation of 4-nitrophenol in the dual-cathode oxidation system could be reduced significantly due to the reduction of Fe^{3+} at the graphite cathode. Besides saving chemicals, this characteristic would lessen the generation of Fe(III) complexes during organics degradation enhancing the performance.

(2) Both electro-Fenton oxidation and anodic oxidation are accounted for 4-nitrophenol degradation in DOS, and the former is the main mechanism under the optimum Fe^{2+} concentration condition. When the degradation of 4-nitrophenol $(200\,mg\,L^{-1})$ was carried out at $-0.80\,V$ for GDE and $-0.10\,V$ for graphite cathode with $0.10\,mM\,Fe^{2+}$, 74.5% TOC removal with 39.2% MCE was achieved by the electrolysis of 600 min.

(3) The nitrogen conversion in the degradation of 4-nitrophenol by DOS mainly involves the denitration generating NO_2^-, the oxidation of NO_2^- generating NO_3^- and the reduction of NO_3^- generating gaseous nitrogen as well as NH_4^+, which leads to a significant nitrogen removal of 57.0%.

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