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Treatment of nitrophenols by cathode reduction and electro-Fenton methods

Songhu Yuan [1], Meng Tian, Yanping Cui, Li Lin, Xiaohua Lu[*]

Environmental Science Research Institute, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China

Abstract

This study deals with the degradation of various nitrophenols by cathode reduction and electro-Fenton methods. Phenols (Poh), 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), and 2,4-dinitrophenol (2,4-DNP) are treated and different degradation sequences are obtained. The relationship between the structure and activities of nitrophenols is discussed. Using 4-NP as a model nitrophenol, the electrochemical behaviors on graphite cathode and Pt anode are analyzed by cyclic voltammetry. The contribution of different reactions to the degradation of 4-NP is investigated in divided cells. The degradation of 4-NP is much faster in the cathode cell than in the anodic cell. In the cathode cell, the degradation of 4-NP is significantly enhanced by the introduction of aeration and Fe^{2+}. Ultraviolet–visible (UV–vis) spectra reveal different reaction pathways for the degradation in the anodic cell and cathode cell. Treatment of high concentration of 4-NP in the undivided cell shows that more than 98% removal of 4-NP and about 13% removal of total organic carbon (TOC) are obtained for both processes, while the subsequent biodegradability test shows that electro-Fenton can eliminate the toxicity and improve the biodegradability of 4-NP. Negligible quantity of nitrate and nitrite ions detected in both processes indicates that there is no direct release of $-NO_2$ and $-NO$ groups from 4-NP and its degradation intermediates. Intermediates such as hydroquinone and bezoquinone are detected by gas chromatography/mass spectrum (GC/MS). The degradation pathway of 4-NP in electro-Fenton process is proposed as the cathode reduction followed by hydroxyl oxidation.
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1. Introduction

Nitrophenols are among the most common organic pollutants in industrial and agricultural wastewaters. These compounds are involved in the synthesis of many chemicals, particularly in the field of pesticides. Some of their derivatives are used as insecticides, herbicides and dyes. They are present in the industrial effluents of chemical plants that manufacture explosives, dyestuffs and products for leather treatment, as well as in agricultural irrigation effluents. Nitrophenols are considered as hazardous wastes and priority toxic pollutants by the U.S. Environmental Protection Agency [1]. It is therefore important to assess the fate of these compounds in the environment and develop effective methods to remove them from water.

Recently, a new advanced oxidation process induced by electrochemistry, electro-Fenton has attracted much interest [2–8]. This process consists of either adding Fe^{2+} or reducing Fe^{3+} electrochemically with the simultaneous production of H_2O_2 upon the reduction of O_2 on the electrodes such as graphite [2], mercury pool [3], carbon fiber [4,5] or carbon-polytetrafluoroethylene O_2-fed cathodes [6–8]. Compared with traditional Fenton's reagent oxidation, electro-Fenton can avoid the high cost of H_2O_2 [8], maintain an almost constant concentration of H_2O_2 [6–8] and regenerate Fe^{2+} more effectively [10]. Electro-Fenton can oxidize organic compounds quickly and economically. Many persistent pollutants have successfully been degraded by this method [2–8]. Oturan et al. [4] investigated the degradation of 4-nitrophenol (4-NP) by electro-Fenton using carbon fiber as cathode in undivided cells. Intermediates of hydroquinone, benzoquinone and 4-nitrocatechoel were identified and quantified. Around 85–90% of nitrogen initially contained in 4-NP was recovered as nitrate ion at the end of process. A dominant hydroxyl oxidation pathway was proposed for

* Corresponding author. Tel.: +86 27 87792159; fax: +86 27 87792159.
E-mail addresses: yuansonghu622@hotmail.com (S. Yuan),
lxh@hust-esri.com (X. Lu).
[1] Tel.: +86 27 62798401.

the degradation and cathode reduction process was not involved in the literature. Brillas et al. [6–9] investigated the mineralization of aniline by electro-Fenton using an O_2-diffusion PTFE cathode. The authors studied the peroxi-coagulation process and photoelectro-Fenton method [7–9], and extended the bench scale to a pilot flow reactor [9]. The degradation of the target substance was reported as hydroxyl oxidation as well [7–9].

In the electro-Fenton system, when O_2 is reduced to H_2O_2 on cathode, some reducible substances will be reduced in the mean time. This direct cathode reduction may represent one possible pathway for the degradation of the substances, particularly when reducible compounds such as nitrophenols are present. However, there are few literatures about the contribution of cathode reduction to the degradation of pollutants in the electro-Fenton process. Canizares et al. [11,12] carried out anodic oxidation of 4-NP and 2,4-dinitrophenol (2,4-DNP) using boron doped diamond anode in an undivided cell. The dominant degradation pathway was proposed as the direct release of $-NO_2$ group from the aromatic ring on anode. A partial decomposition of nitrophenol by reduction on cathode was also assumed.

Additionally, the number and the position of $-NO_2$ group affect the activities of nitrophenols. Although nitrophenols have been studied widely by electrochemical methods [4,11–16], there is no literature that discusses the relationship between the structure and activities of nitrophenols in electrochemical processes. The objectives of this study are: (1) to explore the relationship between the structure and activities of nitrophenols by cathode reduction and electro-Fenton methods; (2) to investigate the contributions of cathode reduction and hydroxyl oxidation to the degradation of 4-NP in cathode reduction and electro-Fenton processes.

2. Materials and methods

2.1. Chemicals and materials

Chemicals were obtained from Sigma (2-nitrophenol (2-NP), 4-NP), Shanghai Reagent Factory One, China (3-nitrophenol (3-NP), indicator reagent), Chemical Plant of East Normal University, Shanghai, China (2,4-DNP, indicator reagent) and Shanghai Chemical Reagent Co. Ltd. (phenol (Poh), analytical grade). $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (analytical grade) was used as the sources of Fe^{2+}. Dichloromethane (analytical grade) was used in the liquid–liquid extraction procedures. Deionized water (8.2 mΩ cm) obtained from a Millipore Milli-Q system was used for the preparation of synthetic wastewater and the other solutions. All the other reagents used were above analytical grade. A graphite stick (Ø25 mm × 90 mm) and a platinum black (type 260, Shanghai Luosu Scientific Co. Ltd., China) were used as cathode and anode, respectively.

2.2. Procedures and equipment

2.2.1. Undivided cell

Cathode reduction was carried out in an undivided glass cell of 250 mL capacity containing the above-stated graphite cath-

ode and platinum black anode. The cell was filled with 200 mL of nitrophenol aqueous solution (0.20 mmol/L for all phenols). H_2SO_4 (1.0 mol/L) was added to bring the pH to 3.0 and Na_2SO_4 (25 g/L) was used to enhance the conductivity. The pH was kept constant by the continuous addition of H_2SO_4 (or NaOH) to the cell. The electro-Fenton process was performed using a 0.5 mmol/L $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution. The cell voltage was provided with a laboratory dc power supply (GPC-3060D). A constant current of 50 mA was maintained in both cathode reduction and electro-Fenton experiments. Stirring was applied to the solution using a magnetic stirrer (GPS-77-03). All experiments were carried out at room temperature. For the degradation of high concentration of 4-NP, 3.6 mmol/L was chosen as initial concentration.

2.2.2. Divided cells

In the divided cells, both anodic cell and cathode cell were filled with 200 mL of 4-NP aqueous solution (0.2 mmol/L). A salt bridge which consisted of 2% agar solution saturated with KCl was used to connect the anodic cell and cathode cell. All the other conditions were the same as those in the undivided cell. Aeration of air was introduced through a micropore aeration head with an air compressor.

2.2.3. Cyclic voltammetry

Electrochemical measurements were performed using a conventional three electrode cell in conjunction with a computer controlled multichannel potentiostats (VMP2/Z, Princeton applied research). For the study of cathode behavior of 4-NP, graphite piece (0.5 cm^2) was used as the working electrode, and Pt black as the counter electrode. For the study of anodic behavior of 4-NP, Pt black was used as the working electrode and graphite (Ø25 mm × 90 mm) as the counter electrode. $Hg/Hg_2Cl_2 \cdot KCl$ (saturated) was used as the reference electrode in both processes. Voltammetry experiments were carried out in the unstirred buffer solution (100 mL). Acetic acid (25 mmol/L) and sodium acetic (25 mmol/L) were used as buffer solution (pH 4.7). The deaerated solution was acquired by purging the solution with pure nitrogen (99.99%) for 30 min to remove oxygen prior to the experimental runs and the solution was protected under nitrogen atmosphere during the experiments.

2.3. Analysis of the samples

2.3.1. 4-NP

The samples (5 mL) were taken out at regular time intervals and neutralized to pH 8 immediately to impede further reaction. The samples containing Fe^{2+} were centrifuged for 3 min at 3000 rpm. All the samples were stored at 4 °C until analysis within 4 h. All nitrophenols were analyzed by high performance liquid chromatography (HPLC) system (Hitachi pumps L-7100 and Hitachi Dynamic mixer) equipped with a Ultraviolet–visible (UV–vis) detector L-7420 and a reverse-phase Hypersil C-18 column (250 mm × 4.6 mm i.d., 5 μm). The mobile phase was a mixture of methanol and 1% acetic acid aqueous solution with ratios of 80:20 (v/v) for all the nitrophe-

nols. The wavelength of 280 nm was set for Poh, and 320 nm for 2-NP, 3-NP, 4-NP and 2,4-DNP. The flow rate of the mobile phase was 0.8 mL/min. The volume of injection was 20 μL. Calibration curves were drawn for the quantitative analysis of the nitrophenols.

2.3.2. UV and TOC

UV spectra were scanned on a Cary 50 UV–vis spectrophotometer (Varian, USA). The total organic carbon (TOC) contents of electrolyzed solution were determined on an Apollo 9000 TOC analyzer (Dohrmann, USA). In TOC analysis the samples were ignited at 700 °C on platinum-based catalyst, and the carbon dioxide formed was swept by pure oxygen as the carrier gas through a nondispersive infrared (NDIR) detector.

2.3.3. Nitrate and nitrite

The concentration of nitrate and nitrite ions produced during electrolysis was measured by ionic chromatography (IC, Dionex 120 equipped with a conductivity detector), on a 4-mm anionic exchange column (IonPack AS4A-SC-Dionex). The volume of injection was 25 μL and the mobile phase was a mixture of 0.94 mmol/L sodium carbonate and 0.83 mmol/L sodium bicarbonate solution with a flow rate of 0.73 mL/min.

2.3.4. Biodegradability

Biodegradability test was performed with a BODTrak[TM] analyzer (Hach Company, USA) using the standard reagent package provided by Hach Company. A given volume of municipal sewage was used as seed water to provide microorganism and used as reference meanwhile. The oxygen consumption curve was recorded automatically.

2.3.5. Intermediates

Typically a 10 mL sample (8 h electrolysis, 3.6 mmol/L 4-NP) containing 4-NP and intermediates was acidified to pH < 2 with H_2SO_4 (1.0 mol/L). Then it was extracted twice with 30 mL of dichloromethane each time. The combined extract was dehydrated with anhydrous sodium sulfate and concentrated to about 2 mL by rotating evaporator (Shanghai Medicine Instrument Company, China). The extract was stored at 4 °C until analysis within 8 h.

Identification of intermediates was performed using a gas chromatography (GC, Varian 3900) equipped with a capillary column (FactorFour[TM]: VF-5 ms, 30 m × 0.25 mm, 0.25 μm) and coupled to a mass spectrometer (MS, Saturn 2100T), which is equipped with electron ionization (EI) source and programmed with the Saturn Chemstation software (Saturn WS). A split ratio of 15:1, solvent delay of 3 min, and scan range from *m/z* 50 to 500 at 3 scan/s were used. The oven temperature was programmed from 50 °C (1 min) to 300 °C (1 min) at a ramp rate of 8 °C/min. The injection volume of extract was 1 μL. The Nist library was used for tentative species identification as a supplement to mass spectral and retention time characteristics. All library matched species exhibit the degree of match better than 60%.

3. Results and discussion

3.1. Degradation of various nitrophenols

In this study, we compared the degradation of nitrophenols including 2-NP, 3-NP, 4-NP, and 2,4-DNP, achieved by cathode reduction and electro-Fenton methods in an undivided cell. The resulting degradation kinetics is plotted in Fig. 1.

In order to achieve a better understanding of the degradation efficiency obtained by the different tested methods, pseudo first-order rate constants were calculated and Table 1 displays the values.

As expected, the degradation of nitrophenols is relatively faster in the electro-Fenton process than in the cathode reduction process. In cathode reduction, the sequence of the degradation is obtained as 2,4-DNP > 2-NP > 4-NP > 3-NP ≫ Poh. In the cathode reduction process, anodic oxidation can lead to the generation of O_2, which can be reduced to H_2O_2 on the cathode subsequently. Therefore, nitrophenols might be decomposed by cathode reduction, anodic oxidation, H_2O_2 oxidation and polymerization on Pt anode [18]. Since phenol is more oxidable and hence less reductive than nitrophenols, the pseudo first-order rate constant is only 0.0036 min^{-1}, which is much smaller than those of nitrophenols. Because –NO$_2$ is a strong electron withdrawing group, the reducibility of aromatic ring will be enhanced by the addition of –NO$_2$ to benzene ring. Therefore, it can be suggested that cathode reduction of nitrophenols predominates
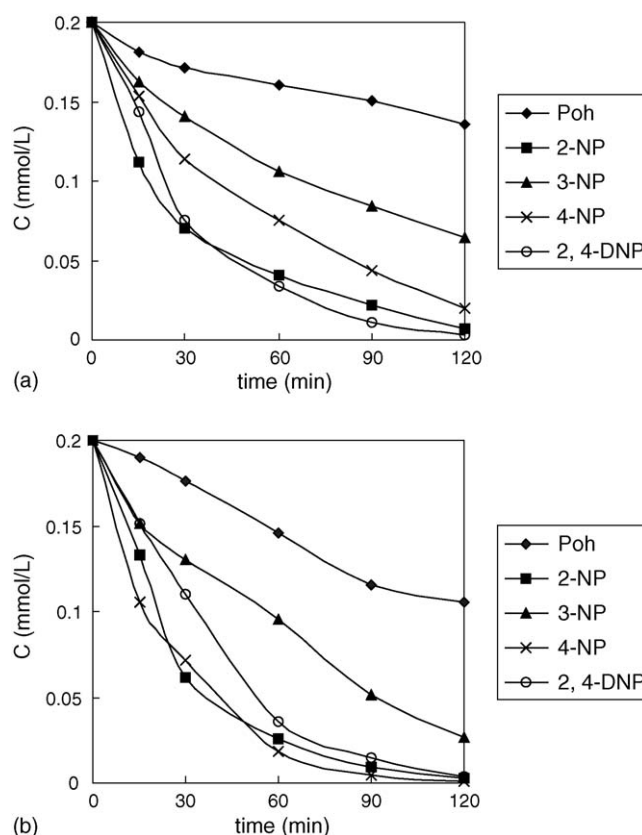

Fig. 1. Degradation kinetics of various nitrophenols: (a) cathode reduction; (b) electro-Fenton.

Table 1
Pseudo first-order rate constants of the degradation of nitrophenols by cathode reduction and electro-Fenton methods

Nitrophenols	Cathode reduction		Electro-Fenton	
	Rate constant (min^{-1})	Correlation coefficient	Rate constant (min^{-1})	Correlation coefficient
Poh	0.0036	0.984	0.0084	0.993
2-NP	0.0276	0.994	0.0363	0.998
3-NP	0.0091	0.997	0.0161	0.989
4-NP	0.0186	0.994	0.0428	0.998
2,4-DNP	0.0341	0.998	0.0351	0.994

in the cathode reduction process. The position effect indicates that 3-NP is the most oxidable nitrophenol among the three mono-nitrophenols. For multi-substituted nitrophenols, the electron effect contributed by –OH is shared by each –NO$_2$ group, leading to a higher nucleophilic character. This is the reason why multi-substituted nitrophenols have larger rate constants than mono-nitrophenols. So conclusions can be drawn that the degradation rates of nitrophenols by cathode reduction increases with the increase of the number of –NO$_2$ group, and that 2- and 4-nitrophenol can be reduced more easily than 3-nitrophenol.

On the other hand, the degradation sequence of 4-NP > 2-NP > 2,4-DNP > 3-NP $\gg$ Poh is found in the electro-Fenton process. Hydroxyl radicals, produced by the combination of H$_2$O$_2$ and Fe^{2+}, have a strong ability to attack the positions in aromatic ring with high electron density. Besides the reactions in the cathode reduction process, hydroxyl oxidation of nitrophenols is another competitive degradation pathway in the electro-Fenton process [17]. By comparing the rate constants obtained by the cathode reduction and electro-Fenton methods, the larger rate constants in the electro-Fenton process indicate the possible contribution of hydroxyl oxidation. Moreover, 4-NP and 2-NP can be oxidized by hydroxyl radicals more easily than 3-NP. It can be seen from Table 1 that the rate constants of the degradation of nitrophenols ($\geq$0.0161) are much larger than that of phenol (0.0084). So it is proposed that cathode reduction contributes to the degradation of nitrophenols more significantly than the other degradation pathways. In this system, the degradation sequence is interpreted as the comprehensive effect of cathode reduction and the other oxidation processes, including hydroxyl and anodic oxidation. The detailed contribution will be discussed in the following section using 4-NP as a model nitrophenol.

3.2. Electrochemical behavior of 4-NP

As suggested above, 4-NP might be decomposed by cathode reduction and anodic oxidation in both processes. The electrochemical behaviors of 4-NP on graphite cathode and Pt anode were investigated by cyclic voltammetry as shown in Fig. 2.

Fig. 2(a) shows the continuous cyclic voltamograms of 3.2 mmol/L 4-NP on graphite electrode in the acetic buffer (pH 4.7) with different scan rate. During the cycle of 50 mV/s (Fig. 2(a, 2)), two peaks appear at about 0.18 and −1.00 V in the cathode sweep, and another peak appears at about 0.30 V in the anodic sweep. The difference of the peaks of 0.30 and 0.18 is 0.12 ($\approx$2 × 0.059), so a two-electron reversible oxidation/reduction reaction can be suggested for the two peaks. The

same reversible peaks were also found by Hu et al. [19], where the peaks appeared at 0.25 V with a glass carbon electrode. The peaks were assumed by the author to be the two-electron oxidation/reduction of 4-nitrosophenol to 4-hydroylaminophenol, where 4-nitrosophenol was formed by the four-electron reduction of 4-nitrophenol. So the redox couple in this study can be also supposed to be the transformation of 4-nitrosophenol to 4-hydroylaminophenol [19]. A significant irreversible peak at −1.00 V indicates that graphite cathode is able to catalyze the reduction of 4-nitrophenol [19–22]. A linear regression of peak current density versus square root of the potentials scan rate results in a straight line ($R^2 = 0.978$), suggesting a diffusion control process in the studied range. The same result
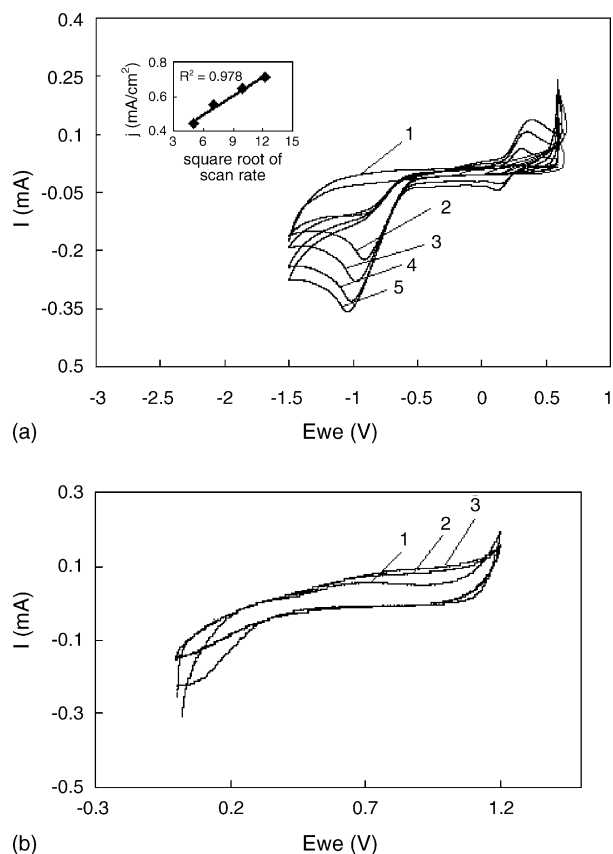

(a)

(b)

Fig. 2. Cyclic voltammetry of 4-NP, 3.2 mmol/L 4-NP, 25 mmol/L acetic buffer (pH 4.7). (a) Graphite electrode, scan range from 0.6 to −1.5 V: (1) acetic buffer, 50 mV/s; (2) 4-NP, 25 mV/s; (3) 4-NP, 50 mV/s; (4) 4-NP, 100 mV/s; (5) 4-NP, 150 mV/s. (b) Pt electrode, scan range from 0.0 to 1.2 V, 100 mV/s: (1) acetic buffer; (2) 4-NP, first cycle for the scan; (3) 4-NP, second cycle for the scan.

has been reported by Luz et al. [20], where the number of electrons involved in the reduction of 4-nitrophenol was calculated as 3.93. Therefore, the reduction of 4-nitrisophenol to 4-hydroxylaminophenol is proposed in this paper.

The anodic behavior of 4-NP is shown in Fig. 2(b). A week anodic peak at 0.8 is observed. However, there is no significant difference between the two cycles determined, suggesting no polymerized film generated on Pt anode. This behavior is different from the literature [18], where a polymerized film was formed on Pt anode.

3.3. Degradation of 4-NP in divided cells

3.3.1. Decay of 4-NP in the divided cells

In order to investigate the difference between cathode reduction and electro-Fenton processes and the contribution of various degradation pathways in detail, 4-NP (0.2 mmol/L) is used as a representative nitrophenol to study the degradation in the divided cells. First, the adsorption of 4-NP by graphite electrode and the loss of 4-NP by volatilization and aeration were examined for 120 min in the same conditions as that for the electrochemical experiments, but electrolysis was not supplied. Results show that the removal of 4-NP by adsorption, volatilization and aeration can be neglected. The decay of 4-NP in cathode cell and anode cell are shown in Fig. 3.

As shown in Fig. 3, the removal of 4-NP in the cathode cell is much higher than in the anodic cell. In the cathode cell, when O_2 is swept by N_2, the possible decomposition pathway is the reduction of 4-NP on the cathode. Fig. 3(1) shows that 4-NP can be reduced with 98% after 120 min treatment. In the undivided cell in Section 3.1, O_2 is electro-generated on Pt anode by the electrolysis of H_2O and then reduced to H_2O_2 on the cathode [17]. H_2O_2 can oxidize 4-NP and compete with cathode reduction. So the effect of H_2O_2 oxidation was examined by the aeration of air in the cathode cell to simulate the electro-generation of O_2. Fig. 3(2) shows that aeration of air has no significant effect on the removal of 4-NP, which indicates that H_2O_2 oxidation has no sig-

nificant contribution to the removal of 4-NP in the present study. The addition of Fe^{2+} has no effect on the removal of 4-NP without O_2 (Fig. 3(3)), while the removal is enhanced greatly when both Fe^{2+} and O_2 are introduced (Fig. 3(4)). The combination of H_2O_2 and Fe^{2+} in the cathode cell, termed cathode Fenton, will produce hydroxyl radicals [4–8]. It can be inferred that hydroxyl radicals were formed in the system and have contribution to the degradation of 4-NP. On the other hand, the decomposition of 4-NP in the anodic cell is much slower than that in the cathode cell. The fact that the addition of Fe^{2+} has no effect on the removal of 4-NP in the anodic cell indicates no H_2O_2 is generated in the anodic cell by the produce of $S_2O_8{}^{2-}$ [24,25], which can oxidize H_2O to H_2O_2 directly. It has been verified in Section 3.2 that no polymerized film of 4-NP is formed on Pt anode. Consequently, the removal of 4-NP in the anodic cell (50% for 120 min) is owing to the direct anodic oxidation on Pt anode. It can be suggested that 4-NP is mainly decomposed by cathode reduction in the cathode reduction process in the undivided cell.

3.3.2. UV spectra change in divided cells

The difference of the processes involved in Section 3.3.1 is further discussed by the change of UV spectra. In Fig. 4(a), the sharp decrease of the peak around 400 nm reflects the quick decay of 4-NP and the destruction of $-NO_2$ group; the gradual increase of the peaks at 270 and 320 nm suggests the formation of intermediates. It is observed that the solution in the cathode cell turns light red gradually during electrolysis in the cathode cell and the samples of the later stage become brown when neutralized. This phenomenon is in good agreement with the characteristic of 4-aminophenol, which was reported to be the most possible intermediate accumulated from the reduction of 4-NP [23]. When O_2 and Fe^{2+} were introduced to the cathode cell (Fig. 4(b)), the peaks at 270 and 320 nm increase in the first 30 min and then decrease. Moreover, a new peak at 240 nm appears at 120 min. As a result, it can be supposed that 4-NP is first reduced to the unstable intermediate of 4-aminophenol in the cathode Fenton process, then 4-aminophenol is oxidized by hydroxyl radicals subsequently. In the anodic cell (Fig. 4(c)), the peak around 400 nm decreases gradually and the change in the wavelength below 350 is not obvious. The mechanism of the decomposition of 4-NP is different in the two cells.

Consequently, it can be proposed that cathode reduction predominates in the cathode reduction process in the undivided cell, while cathode reduction and hydroxyl oxidation competes in the electro-Fenton process. The detailed mechanism will be further discussed in the following.

3.4. Fate of 4-NP in cathode reduction and electro-Fenton processes

The fate of 4-NP in the cathode reduction and electro-Fenton processes was analyzed using 3.6 mmol/L 4-NP solution in the undivided cell. The decay of 4-NP and TOC are shown in Fig. 5.

It can be seen from Fig. 5 that both cathode reduction and electro-Fenton lead to more than 98% removal of 4-NP after 8 h treatment. In the first 4 h, the removal of 4-NP in electro-Fenton process is slightly higher than that in cathode reduction
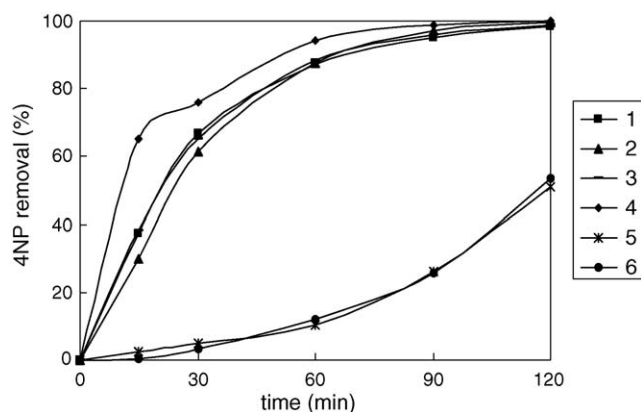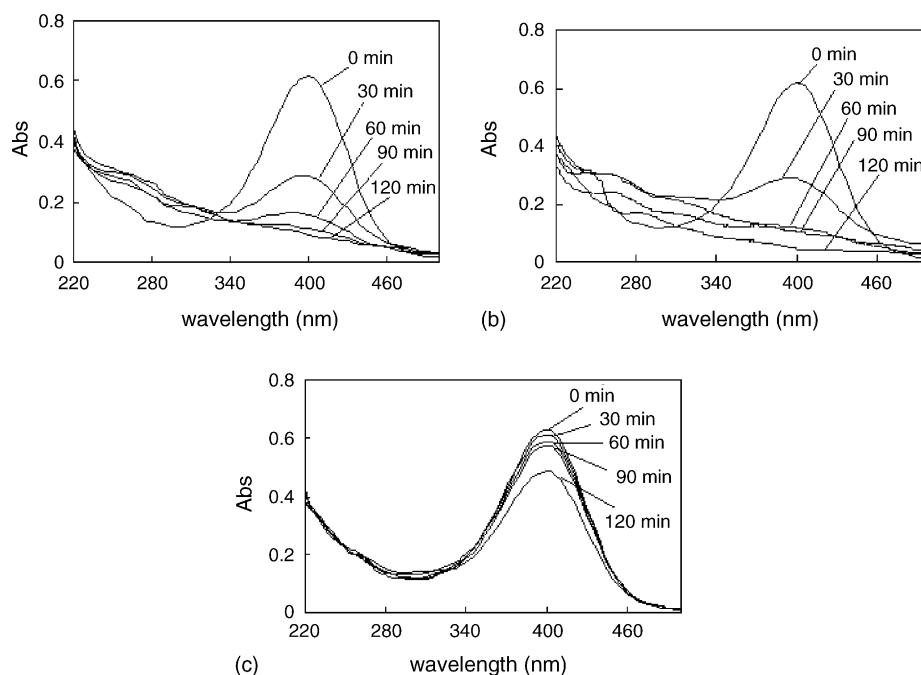

Fig. 3. Removal of 4-NP in divided cells. (1) sweeping O_2 by bubbling N_2 60 min before electrolysis in the cathode cell; (2) aeration of air during electrolysis in the cathode cell; (3) sweeping O_2 by bubbling N_2 60 min before electrolysis and addition of 0.5 mmol/L Fe^{2+} in the cathode cell; (4) aeration of air during electrolysis and addition of 0.5 mmol/L Fe^{2+} in the cathode cell; (5) in the anodic cell; (6) addition of 0.5 mmol/L Fe^{2+} in the anodic cell.

Fig. 4. UV spectra changes in the processes. (a) Sweeping O_2 by bubbling N_2 60 min before electrolysis in the cathode cell, conditions as for curve 1 in Fig. 3. (b) Aeration of air during electrolysis and addition of 0.5 mmol/L Fe^{2+} in the cathode cell, conditions as for curve 4 in Fig. 3. (c) In the anodic cell, conditions as for curve 5 in Fig. 3.

process. This is because of the oxidation power of hydroxyl radicals. The negligible difference between the decay of 4-NP in cathode reduction and electro-Fenton implies that the contribution of hydroxyl oxidation to the removal of high concentration of 4-NP is negligible. However, for the low concentration of 4-NP (0.2 mmol/L), the rate constant in electro-Fenton process (0.0428 min^{-1}) is much higher than that in cathode reduction process (0.0186 min^{-1}). It can be inferred that the contribution of hydroxyl oxidation is significant only in low concentration of 4-NP.

The TOC decay in both processes is not more than 13%, which implies that partial 4-NP is mineralized to CO_2 and H_2O. The decay of TOC in the cathode reduction and electro-Fenton processes is similar, suggesting the insignificant contribution of hydroxyl oxidation to the mineralization of 4-NP. Compared with the results obtained by Oturan et al. [4], where more

than 90% removal of TOC was achieved for the treatment of 1.0 mmol/L 4-NP (125 mL) with 800 coulomb electric quantity, the removal of TOC in this study (3.6 mmol/L 4-NP (200 mL) with 1440 C electric quantity calculated) is much smaller. This is mainly because of the use of different cathode materials, the reduction of O_2 to H_2O_2 on carbon felt cathode happens much more easily than on graphite cathode. As a result, cathode reduction predominates in the present study. This is different from that reported in the literature [4].

In order to explore the fate of nitrogen in 4-NP and provide further information on the degradation mechanism, nitrate and nitrite were measured by ion chromatograph. Negligible amount of nitrate or nitrite is detected in cathode reduction and electro-Fenton processes, which implies the release of –NO_2 or –NO
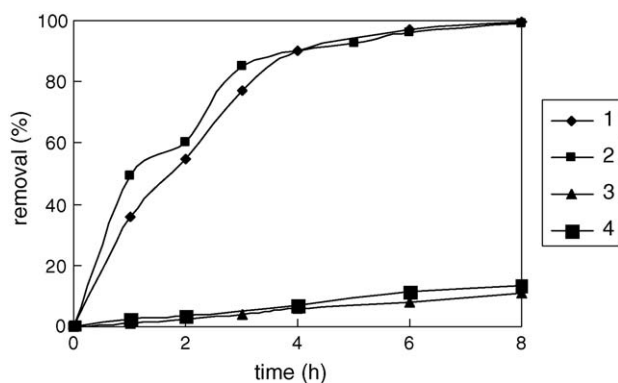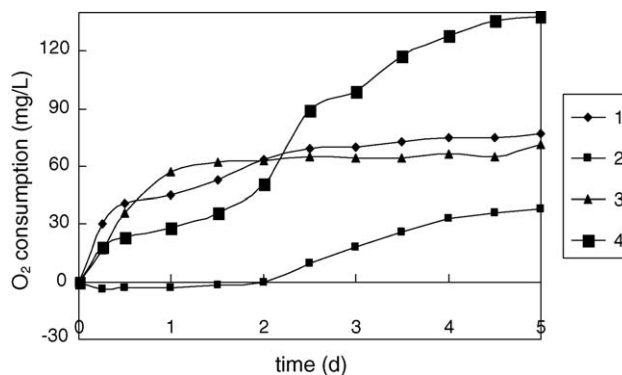

Fig. 5. Degradation of model compound 4-NP. (1) 4-NP removal in cathode reduction; (2) 4-NP removal in electro-Fenton; (3) TOC removal in cathode reduction; (4) TOC removal in electro-Fenton.

Fig. 6. Biodegradability test results: (1) O_2 consumption for the seed municipal sewage; (2) O_2 consumption for 3.6 mmol/L 4-NP solution and seed sewage; (3) O_2 consumption for cathode reduction treatment of 3.6 mmol/L 4-NP for 8 h and seed sewage; (4) O_2 consumption for electro-Fenton treatment of 3.6 mmol/L 4-NP for 8 h and seed sewage.
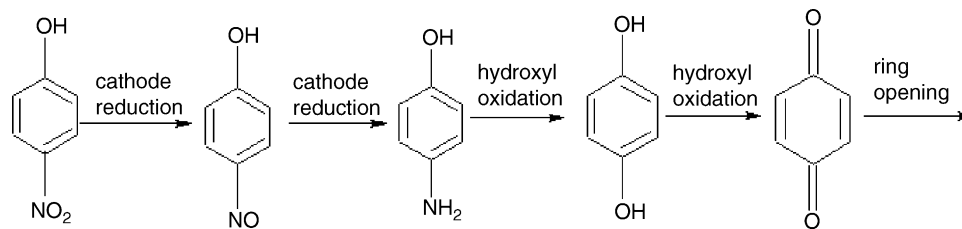
Fig. 7. Degradation pathway of 4-NP for electro-Fenton process.

from 4-NP and the intermediates produced is negligible. This result further confirms that cathode reduction predominates in the degradation of 4-NP with high concentration.

3.5. Biodegradability test

As known, nitrophenols are toxically refractory and inert to microorganisms [1,4]. So the biodegradability of the 4-NP wastewater (3.6 mmol/L) after treatment in the undivided cell was determined to examine the toxicity change by the treatment. From the microbial O_2 consumption curves in Fig. 6, it can be seen that both processes benefit the biodegradability of 4-NP wastewater. Municipal sewage, which contains large quantities of microorganism and some carbon source for microorganism, is used as the seed aqueous solution and the reference biodegradability. For original 4-NP solution (Fig. 6(2)), the microbial O_2 consumption is much lower than that of the reference seed aqueous solution (Fig. 6(1)), which indicates that 4-NP wastewater is toxic to microorganism. After 8 h cathode reduction treatment (Fig. 6(3)), the toxicity almost disappears, but the biodegradability is still bad, which suggests that the intermediates produced in the cathode reduction process has no toxicity but is difficult to biodegrade. However, after 8 h electro-Fenton treatment (Fig. 6(4)), the toxicity disappears completely and some intermediates can be biodegraded. As a result, it can be concluded that the cathode reduction process can only eliminate the toxicity of the 4-NP wastewater, while electro-Fenton process leads to an enhancement of biodegradability. Therefore, electro-Fenton method can be proposed as a pretreatment process for the toxic 4-NP wastewater.

3.6. Degradation pathway of 4-NP

The intermediates in the treatment of 4-NP by electro-Fenton process were identified by GC/MS analysis. The intermediates detected include hydroquinone and benzoquinone. 4-aminophenol is not detected because of its weak solubility in the solvent of CH_2Cl_2, but it should be present in the degradation path based on the former discussion and Refs. [11,23]. The main degradation pathway is proposed in Fig. 7. 4-NP is first reduced on cathode to 4-nitrosophenol, which is further reduced to 4-aminophenol. Then 4-aminophenol is oxidized to hydroquinone and benzoquinone by hydroxyl radicals. The intermediates can be further oxidized to ring opening compounds. Such a pathway is quite different from that proposed by Oturan et al. [4], where a dominant hydroxyl oxidation of 4-NP was found and no cathode reduction process was reported.

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