Electrochemical degradation of p-nitrophenol with different processes

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Abstract

The electrochemical degradation of p-nitrophenol (PNP) under different conditions was investigated. The electrochemical behavior of PNP and its reduction product p-aminophenol (PAP) on stainless steel cathode and Ti/Pt anode through cyclic voltammetry were observed. Electrochemical degradation process was performed in an undivided cell and 92% PNP was removed corresponding to a 22% total organic carbon removal. A divided cell was also used and it was found that PNP degradation was mainly attributed to cathodic reduction, while anodic oxidation was responsible for PNP removal due to the reaction with hydroxyl radicals and surface oxide generated on the anode. The sequential electrolytic processes, reduction-oxidation and oxidation-reduction, were compared in the divided cell. In the case of reduction-oxidation process, the total organic carbon removal reached 40%, but PNP removal was the same with the undivided cell. A black deposit was found in the effluent and identified by Fourier transform infrared spectroscopy as a polymer of PAP produced by the 1,4-addition reaction of quinoneimine. Intermediates left in the solution such as hydroquinone, p-benzoquinone and PAP were determined by high performance liquid chromatography. Whereas, the oxidation-reduction process proved unsatisfying.

Key words: degradation; cathodic reduction; anodic oxidation; sequential electrolysis

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Introduction

Nitro aromatic compounds (NACs) are widely used in the production of pesticides, paints, dyes and explosive materials (Shimazu et al., 2001; Canizares et al., 2004b; Gilbert and Sale, 2005). Owing to the significant toxicity to human, these compounds are considered as priority pollutants by the United States Environmental Protection Agency. Unfortunately, the biodegradation of NACs is difficult and requires long incubation time due to the strong electro withdrawing properties of –NO₂ group which confers a strong chemical stability to the aromatic ring and difficulty of being oxidized (Bhatti et al., 2002). As a result, it is important to develop effective methods to remove such toxic chemicals from liquid solution.

Electrochemical methods have been intensively investigated by either reductive or oxidative approaches for NACs wastewater treatment. The –NO₂ group of NACs can be easily reduced by cathodic reduction or zero valent iron technology through a six-electron reduction process, but the accumulation of intermediate products also poses concerns (Schmelling and Gray, 1996; Zhang et al., 2000; Rodgers and Bunce, 2001; Gilbert and Sale, 2005). The oxidative approaches, such as anodic oxidation (Brillas and Mur, 1998; Brillas and Casado, 2002; Yuan et al., 2006), have received increasing attention because the proposed degradation pathways are not as susceptible to the formation of toxic intermediate compounds. However, the mechanisms of oxidation approaches have not been well understood. Researchers have devoted to the investigation of the electrochemical mineralization of NACs via an undivided electrolytic cell posing limited concerns solely on the reactions at the anode (Canizares et al., 2004a; Borras and Laredo, 2004) or cathode (Yuan et al., 2006). As a result, the reactions of the other electrode have been neglected and the exact functions of anode and cathode during electrochemical reaction and the electrolysis in undivided cell have not been well studied. Considering the difficulties in achieving satisfying mineralization efficiency, reactions during electrolysis should be studied profoundly to improve mineralization, and correlative new technology is needed. Several authors have suggested the coupling of existing technologies utilizing both oxidative and reductive steps (Spanggord et al., 2000; Rodgers and Bunce, 2001; Wang and Qu, 2006; Gilbert and Sale, 2005) to overcome limitations of management strategies that involve solely oxidation or reduction, through sequential reduction-oxidation (a reduction step followed by an oxidation step) or oxidation-reduction (an oxidation step followed by a reduction step). However, it is not clear whether this coupling could improve mineralization efficiency and which sequence will result in an optimal...
overall transformation.

In this article, p-nitrophenol (PNP) was selected as the model substrate of NACs due to its relative simple chemical structure. The electrochemical degradation of PNP was performed in an undivided cell and a divided cell to elucidate the reactions and the concrete functions of each electrode during electrolysis. The sequential reduction-oxidation and oxidation-reduction processes were compared in divided cell. The intermediates of all electrolysis experiments were analyzed and mechanisms were proposed.

1 Materials and methods

1.1 Chemicals

p-Nitrophenol (CAS: 100-02-7), hydroquinone (CAS: 123-31-9), p-benzoquinone (CAS: 106-51-4), p-aminophenol (PAP) (CAS: 123-30-8) and 1,2,4-trihydroxybenzene (CAS: 533-73-3), which have been detected in other publications (Zhou et al., 2005; Yuan et al., 2006; Oturan et al., 2000), were used without further purification. Deionized water obtained from a Millipore Milli-Q system was used for the synthetic wastewater preparation and other solutions. Methanol (chromatogram grade, CAS: 67-56-1) and formic acid (chromatogram grade, CAS: 64-18-6) were supplied by TEDA for high performance liquid chromatography (HPLC) analysis. Bis-tris (chromatogram grade, CAS: 6976-37-0), p-hydroxybenzoic acid (chromatogram grade, CAS: 99-96-7) and boric acid (chromatogram grade, CAS: 10043-35-3) were used for ion chromatography (IC).

1.2 Procedures and equipment

1.2.1 Undivided cell

The undivided cell was designed with a capacity of 50 mL. In experiment, the PNP aqueous solution (100 mg/L) was stored in a glass mixing tank (250 mL) equipped with a magnetic stirrer, and circulated through the electrolytic cell by a peristaltic pump at a circulation rate of 50 mL/min. In experiment, the PNP aqueous solution (100 mg/L) was added to adjust pH to 2.0 and pH was kept constant by continuous addition of H2SO4 or NaOH (1.0 mol/L) to the electrolytic cell. Na2SO4 solution (1 g/L) was selected as the supporting electrolyte. A model WYJ601 DC power supply (Jonchan, China) was used for electrochemical experiment and a constant current density of 30 mA/cm2 was maintained. All experiments were performed at room temperature and the total electrolysis time was set to 300 min.

1.2.2 Divided cell

The divided cell was the same as the undivided one in both shapes and dimensions except for a Nafion 117 cation exchange membrane which was used to separate the anodic compartment from the cathodic compartment (Fig. 1). The divided cell was prepared to study the electrochemical reactions of anode and cathode separately, which could take place synchronously in the undivided cell, and it was also used for the experiment about sequential reduction-oxidation and oxidation-reduction processes. In the divided cell experiments, both anodic and cathodic electrolytes were stored in two glass mixing tanks (250 mL), separately. A brown glass tank was chosen for the cathodic electrolyte store to avoid the sunlight, and N2 purging was introduced to the brown tank for 30 min before and during electrolysis to displace dissolved oxygen. Two peristaltic pumps at a circulation rate of 25 mL/min were supplied for the two independent cycles to keep constant residence time compared with the undivided cell. For the sequential electrolysis processes experiment, the anode and cathode would be exchanged into the other compartment after regular intervals to realize reduction-oxidation and oxidation-reduction processes. All other conditions were the same as those in the undivided cell.

1.2.3 Cyclic voltammetry

Electrochemical measurements were performed using a conventional three-electrode cell in conjunction with a model 263 computer-controlled potentiostat/galvanostat (Princeton Applied Research, USA). For the cathodic behavior study of PNP, stainless steel (10 mm × 10 mm) was used as working electrode. For the anodic behavior study of PNP (100 mg/L, 1 g/L Na2SO4, pH 2.0) and PAP (100 mg/L, 1 g/L Na2SO4, pH 2.0), Ti/Pt (20 mm×10 mm) was chosen as a working electrode. A platinum plate was used as the counter electrode and a saturated calomel electrode was used as the reference electrode in all cyclic voltammetry studies. The solutions were deaerated by purging the solution with pure N2 for 30 min before the experiment.

1.3 Sample analysis

All samples were taken from the glass mixing tanks each hour, stored at 4°C, and then filtered by 0.22 µm filter membranes before chromatography and total organic

![Fig. 1 Schematic diagram of divided electrolytic cell. (a) anode; (b) cathode; (c) Nation 117 cation exchange membrane; (d) peristaltic pump.](https://example.com/f1.png)
carbon (TOC) analysis.

1.3.1 Chromatography
The progress of all reactions and aromatic intermediate products distribution including PNP was monitored by HPLC. Samples were compared with the retention time of standard materials and also by using standard materials as internal reference directly injected into samples. HPLC analyses were achieved by a model 1100 instrument (Agilent, USA) with a reverse phase SinoChrom ODS-BP C18 column (250 mm × 4.6 mm, 5 µm) at the flow rate of 1.0 mL/min and a column temperature of 40°C. The mobile phase consisted of methanol (A) and 0.2% formic acid aqueous solution (B) and eluted in gradient mode (0–5 min, A:B = 10:90, 5–15 min, A:B = 60:40). The volume of injection was 20 µL. The detection was performed by UV absorption at 280 nm.

The concentration of nitrate and nitrite ions produced when electrolysis was measured by a model SCL-10Asp IC (Shimadzu, Japan). The volume of injection was 100 µL. The mobile phase contained 1.105 g/L p-hydroxybenzoic acid, 0.6694 g/L Bis-tris and 3.0916 g/L boric acid with a flow rate of 1 mL/min.

1.3.2 Total organic carbon analysis
TOC analysis was carried out by a TOC-VCPH/TNM1 analyzer (Shimadzu, Japan). The carrier gas was pure oxygen at a rate of 12 L/hr.

1.3.3 Fourier-transform infrared
The infrared spectrum of polymer was obtained by a Prestige-21 Fourier-transform infrared spectrometer (FT-IR) (Shimadzu, Japan). The data were analyzed by the IR solution software provided with the spectrometer.

2 Results and discussion

2.1 Voltammetric study
The scan of Ti/Pt anode was studied in blank solution (pH 2.0, 1 g/L Na₂SO₄) at different scan rates (Fig. 2a).

In the anodic sweep, the peak around −0.2 V is identified as the hydrogen desorption. And the peak of 0.6 V is identified as the formation of surface oxide such as PtO on Ti/Pt anode. In the cathodic sweep, the peak around 0.4 V is the reduction of surface oxide and peaks around −0.1 V belong to hydrogen adsorption (Zhihui and Balbuena, 2007; Kucernak and Offer, 2008). As the scanning rate decreases, all peak intensities become weak. When the scanning rate decreases to 20 mV/sec, the oxide formation peak turns towards low potential and almost disappears. Meanwhile, the peak of reduction of surface oxide film switches to a higher potential.

The electrochemical behavior of PNP and PAP on Ti/Pt anode were also studied (Fig. 2b). The shoulder peak of surface oxide formation has switched to about 0.46 V in solution containing PNP and PAP. There is a peak around 1.00 V in the anodic sweep of PAP, which is considered as the oxidation reaction of PAP producing quinoneimine (Menezes and Maia, 2006). The higher peak at 1.10 V in the anodic sweep of PNP is assumed to be the reaction of PNP oxidation, which indicates that PNP is harder to be oxidized than PAP.

The electrochemical behavior of PNP on stainless steel cathode was investigated (Fig. 2c). There are two peaks at −0.83 V and a shoulder peak at −1.04 V in the cathodic sweep, and no peak has been found in the anodic sweep. The fact that PAP has been found in the effluent of cathodic reduction by HPLC analysis indicates that PNP could be reduced to PAP by cathodic reduction.
2.2 PNP degradation in undivided cell and electrode reaction study

The electrochemical degradation of PNP was achieved in an undivided cell and the contribution of various degradation pathways in a divided cell through anodic oxidation and cathodic reduction were studied (Fig. 3). The adsorption of PNP on the electrodes and the loss of PNP by volatilization were examined for 120 min in the same condition as that for the electrochemical experiments, but electrolysis was not supplied. Results showed that the removal of PNP by adsorption and volatilization could be neglected.

Undivided cell process could remove over 92% PNP and 22% TOC within 300 min, which was better than solely reduction or oxidation. Hydroquinone, p-benzoquinone and low concentration of PAP have been found in the effluent by HPLC. As shown in Table 1, the pseudo first-order model can describe the degradation of PNP well.

PNP degradation curve of reduction is very similar to undivided cell, which indicates that cathodic reduction reaction is the main PNP degradation pathway. High concentration of PAP, low concentrations of p-benzoquinone and hydroquinone were found in the solution, which indicates that PAP has been partially oxidized by air due to long reaction time. Almost 15% TOC is removed by reduction implying the organic compounds have been partially eliminated from solution in the form of the brown film on cathode surface. It has been reported that brown film, which was also found on the stainless steel cathode surface after PNP electrolysis (Canizares et al., 2004), is considered as the condensation of PAP formed in alkaline media. In the experiment, because of the electrolysis of water, hydrogen evolution led to the absence of hydrogen ions close to the cathode, resulting in a local increase in pH. Given the fact that nitrobenzene (NB) could be reduced to hydro-azobenzene or phenylhydroxylamine (Seshadri and Kelber, 1999; Zhang et al., 2000) in alkaline media, the substrate PNP, whose structure is similar to NB except for a –OH group on the para-position of –NO2, is also considered to follow the same mechanism, being reduced to similar hydro-azobenzene or phenylhydroxylamine. These products could adhere to the cathode surface in local alkaline media, and PAP produced by further reduction.

Anodic oxidation could remove about 51% PNP and 20% TOC from the solution within 300 min. The PNP degradation curve of oxidation, which presents a linear trend, indicating that it is controlled by the applied current density rather than the mass transport of the organics to the anode surface. The pseudo first-order rate constant of PNP degradation on anode is only 0.0021 min\(^{-1}\), implying PNP is hard to be oxidized by anodic oxidation solely. According to Comninellis’ theory (Foti et al., 1999; Iniesta et al., 2001; Di Giulio et al., 2007; Kapalka et al., 2008), Ti/Pt electrode belongs to electrochemical conversion electrodes, which means the concentration of physisorption hydroxyl radicals (Reaction (1)) is very low because physisorption hydroxyl radicals would change to chemisorption hydroxyl radicals by oxidizing Pt into PtO or other oxide (Reaction (2)). The cyclic voltammetry of Ti/Pt anode has shown that the formation of surface oxide occurs prior to the oxidation of organic compounds. As a result, the degradation of PNP by anodic oxidation is considered to proceed through reaction with hydroxyl radicals and surface oxide on the anode surface. Hydroxyl radicals could mineralize the organic compounds completely but the surface oxide could not (Reaction (3)). Excessive surface oxide could react with each other and release oxygen (Reaction (4)). Hydroquinone and p-benzoquinone have been identified as the main intermediates by HPLC in the effluent.

\[
\begin{align*}
\text{Pt} + \text{H}_2\text{O} & \rightarrow \text{Pt-OH}_{\text{ads}} + \text{H}^+ + e^- \\
\text{Pt-OH}_{\text{ads}} & \rightarrow \text{PtO} + \text{H}^+ + e^- \\
\chi\text{PtO} + \text{R}_{\text{aq}} & \rightarrow \text{RO}_x + \chi\text{Pt} \\
2\text{PtO} & \rightarrow 2\text{Pt} + \text{O}_2
\end{align*}
\]

The undivided cell process consists of cathodic reduction and anodic oxidation. However, it is not simple linear

![Fig. 3 PNP degradation (a) and total organic carbon (TOC) removal (b). Conditions: C_0 100 mg/L, pH 2.0, current density of electrode 30 mA/cm².](image-url)

Table 1 Pseudo first-order rate constant and correlation coefficient (R^2) of PNP degradation

<table>
<thead>
<tr>
<th>Electrolysis process</th>
<th>Rate constant (min(^{-1}))</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic oxidation</td>
<td>0.00210</td>
<td>0.984</td>
</tr>
<tr>
<td>Undivided cell</td>
<td>0.00909</td>
<td>0.998</td>
</tr>
<tr>
<td>Cathodic reduction</td>
<td>0.00637</td>
<td>0.991</td>
</tr>
</tbody>
</table>
correlation with the sum of cathodic reduction and anodic oxidation, since the kinetic constant of undivided cell process 0.00909 min$^{-1}$ was larger than the sum of anodic oxidation and cathodic reduction 0.00847 min$^{-1}$. The reason maybe that oxygen produced on the anode by water electrolysis reaction could transfer to the cathode surface, and then be reduced to H$_2$O$_2$ which could oxidize the substrate and intermediates in the solution. Meanwhile, the reductive product such as PAP, which could be transferred to anode surface and be oxidized by anode more easily, also resulted in the increase of TOC removal.

The possible degradation pathway of PNP is proposed (Fig. 4) based on the above findings. Hydroxyl radicals and Pt oxide have a strong electrophilic character, and –NO$_2$ group is a strong electron-withdrawing substituent. Therefore, –NO$_2$ group is attacked by hydroxyl radicals and Pt oxide, causing –NO$_2$ group to be detached from the aromatic ring and producing hydroquinone and p-benzoquinone. NO$_3^-$ was detected by IC without NO$_2^-$. Further oxidation of hydroquinone and p-benzoquinone results in ring opening products. PAP produced by cathodic reduction has been oxidized to quinoneimine which suffers hydrolysis to produce p-benzoquinone in acidic media and releases NH$_4^+$, which was found by nessler reagent and oxidized to NO$_3^-$.

### 2.3 Sequential electrolysis

For the sequential electrolysis experiments, the anode and cathode were exchanged into other compartments after regular intervals to realize reduction-oxidation and oxidation-reduction processes. Meanwhile, the reaction time of reduction and oxidation was controlled by electrode exchange. The ratio of reduction time/total time for reduction-oxidation process and oxidation time/total time for oxidation-reduction process were investigated with a total electrolysis time 300 min.

As shown in Fig. 5, long reduction time results in a higher removal efficiency of TOC and PNP. Sequential reduction-oxidation is prior to sequential oxidation-reduction. When reduction for 240 min and oxidation for 60 min, at which RT is 0.8, TOC removal achieves almost 40% TOC and 91% PNP is removed from solution (Fig. 5a), which is much better than electrolysis in undivided cell. A black deposit, which is assumed as polymer of PAP (PPAP), was found in the anodic compartment after reduction-oxidation process and it was not observed in other processes.

The IR spectra of the presented PPAP were obtained (Fig. 6). The peak in curve a at 3338 cm$^{-1}$ is attributed to N–H stretching vibrations and almost disappears in curve b, while the peak at 3280 cm$^{-1}$, assigned to the O–H stretching vibrations is replaced by a broad intense band around 3244 cm$^{-1}$ for PPAP. Those data indicate the presence of free –OH groups and the absence of free –NH$_2$ groups in the polymer. The peak at 1570 cm$^{-1}$ in curve b stands for the formation of a C≡N structure. In addition, no peak at 1635 cm$^{-1}$ reveals that there is no C=O group. The peak at 1261 cm$^{-1}$ is attributed to C–N stretching vibrations, while 1168 and 1103 cm$^{-1}$ are assigned to...
HSO$_4^-$ and SO$_4^{2-}$ ions, respectively, indicating the PPAP obtained is doped with HSO$_4^-$ and SO$_4^{2-}$ during the polymerization process. The peaks around 833 cm$^{-1}$ have been separated by IR solution software into two peaks, 833 cm$^{-1}$ and 810 cm$^{-1}$, which attribute to C–OH stretching vibrations. The C–OH stretching vibration peaks of o-, m- and p-aminophenols occur at 800, 822 and 825 cm$^{-1}$, respectively (Chen et al., 2008). Given the substrate of polymerization is p-substituted, 833 cm$^{-1}$ is considered as para-position and 810 cm$^{-1}$ as the ortho-position of the amino group. Based on the above discussion, the possible chemical structure of PPAP obtained is proposed (Fig. 7), of which A is an anion doped in PPAP.

The mechanism of electrochemical polymerization is proposed. PNP is firstly reduced to the cathode compartment, and the products are PAP and other compounds such as hydroquinone and p-benzoquinone due to PAP oxidation by air. Meanwhile, the brown film formed on the cathode surface. When the anode exchanged to the former cathode compartment in sequential reduction-oxidation process, PAP is oxidized to quinoneimine. Although quinoneimine could suffer hydrolysis to p-benzoquinone in acid condition, the quinoneimine molecular suffering hydrolysis, have been rapidly polymerized in the solution following the mechanism of 1, 4-addition reaction and produce PPAP.

3 Conclusions

In the present study, an effective method for electrochemical degradation processes of PNP has been developed. By which, 92% of PNP and corresponding to 22% total organic carbon (TOC) were removed within 300 min in undivided electrolytic cell. Cathodic reduction has been proved to be the main pathway of PNP degradation and could remove TOC by forming a brown film on cathode surface. The degradation of PNP is not oxidized by the anode directly, but by the surface oxide and hydroxyl radicals generated on the anode. Furthermore, a successful experiment about sequential electrolysis was carried out and the result suggested that sequential reduction-oxidation process could provide an effective alternative to traditional electrolysis in undivided cell. The TOC removal has been increased to 40%, although PNP removal keeps constant.

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References


