

Electrochemical reduction of nitrobenzene at carbon nanotube electrode

Yu-Ping Li^{a,b,*}, Hong-Bin Cao^a, Chen-Ming Liu^{a,b}, Yi Zhang^a

^a Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, P.O. Box 353, Beijing 100080, China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Received 18 July 2006; received in revised form 8 February 2007; accepted 8 February 2007

Available online 15 February 2007

Abstract

The electrochemical behaviors of nitrobenzene at a pyrolytic graphite electrode modified with carbon nanotubes (CNTs) were studied using cyclic voltammetry and constant-potential electrolysis technique, and the CNT-modified electrode was characterized with Fourier transform infrared spectroscopy (FTIR), high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) measurements. A CNT-modified packed-bed flow reactor was also constructed for electrocatalytic reduction of nitrobenzene. The results showed that CNTs exhibited high activity for nitrobenzene reduction to aniline and the electrochemical reduction of nitrobenzene at CNT-modified electrode followed the pathway of nitrobenzene → phenylhydroxylamine → aniline. CNTs had been functionalized with profuse carboxylic group and other oxygen-containing groups, became open with some lacuna on the wall, and were distributed symmetrically on the electrode with forming a three-dimensional layer, resulting in the high catalytic-activity for nitrobenzene reduction to aniline. The removal of nitrobenzene was over 95% with electrolysis for 50 min at -1.20 V in pH 5 solution using the CNT-modified packed-bed flow reactor, and no other product was obtained except aniline. The removal of nitrobenzene was over 95% with electrolysis for 80 min at -1.20 V in pH 7 solution and was 87% with electrolysis for 120 min in pH 9 solution. A little phenylhydroxylamine besides aniline was obtained during the initial electrolysis stage, and then all reduced to aniline. The average current efficiency at pH 5, 7 and 9 was 46, 51 and 63%, respectively. The electrolysis products were mineralized easily through aerobic biodegradation. © 2007 Elsevier B.V. All rights reserved.

Keywords: Nitrobenzene; Electrochemical reduction; Reduction mechanism; Carbon nanotube

1. Introduction

Nitrobenzene has been widely used in the industries for the production of aniline, aniline dyes, explosives, pesticides and drugs, and also as a solvent in products like paints, shoes and floor metal polishes [1]. As a toxic and suspected carcinogenic compound, nitrobenzene released to environment poses a great threat to human health. Even at low concentrations, it may present high risks to environment [2]. The strong electron affinity of nitro reduces the electron cloud density of benzene ring and thus makes nitrobenzene very stable. Therefore, nitrobenzene is listed as one of prior pollutants by many countries.

Nitroaromatic compounds are often difficult to donate electron due to the low electron cloud density in their benzene ring,

so the oxidation of nitroaromatic compounds is very difficult to achieve. Furthermore, the oxidation of nitrobenzene may produce some more toxic dead-end products like picolinic acid [3]. Therefore, reductive technologies attracted more and more attention recently [4]. The developed reductive technologies mainly comprise anaerobic reduction with microbial cultures, chemical reduction, catalytic hydrogenation reduction and electrochemical reduction. The researches on anaerobic reduction with microbial cultures emphasizes particularly on the separation and construction of highly effective strains [5]. Microbial reduction technology often needs the addition of biodegradable organic compounds for electron donor, and also these strains might not be able to endure high concentration of nitroaromatic compounds due to their high toxicity. Chemical reduction by zero-valent iron is one of the most widely used chemical reduction technologies for treatment of nitroaromatic compounds due to its low cost. The reactivity of zero-valent iron, with a standard potential of -0.42 V [6], is often limited in neutral medium for complete reduction of many nitroaromatic compounds whose reductive potential is often more negative than -0.700 V [7].

* Corresponding author at: Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, P.O. Box 353, Beijing 100080, China. Tel.: +86 10 62655828; fax: +86 10 62561822.

E-mail address: ypli@home.ipe.ac.cn (Y.-P. Li).

Furthermore, corrosion of zero-valent iron produces various kinds of ferric oxide, which forms a passivation layer at the surface of zero-valent iron, and consequently the passivation layer inhibits further reductive reaction. Catalytic hydrogenation reduction is seldom used in the treatment of wastewater but in the manufacture of aniline and *p*-aminophenol due to its high cost [8]. Electrochemical reduction has recently aroused increasing interest due to its cleaner process. However, the potential of nitrobenzene reduction to aniline is often negative than that of molecular hydrogen evolving at most electrodes, and thus electrolysis at the potential of nitrobenzene reduction to aniline often caused parallel electrolysis of water, resulting in lowering current efficiency as well. Consequently, researchers focused their efforts on seeking for novel cathodic materials for lowering the overpotential of nitrobenzene reduction to aniline [9,10].

The recent discovery of carbon nanotubes (CNTs) has attracted much attention because of their dimensions, structure-sensitive and subtle electronic properties [11]. These properties suggest that carbon nanotubes should have the ability to mediate electron transfer reactions when used as an electrode.

In this paper, electrochemical reduction of nitrobenzene on CNT-modified electrode was investigated. The reductive mechanism of nitrobenzene to aniline was discussed using cyclic voltammetry and constant-potential electrolysis techniques. The surface properties of CNT-modified electrode were also studied by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) measurements. A two-compartment flow reactor packed with CNT-modified electrodes was constructed for removal of nitrobenzene from wastewater, and current efficiency was also investigated.

2. Experimental

2.1. Materials

Multi-wall carbon nanotubes (CNTs) were obtained from the Chemical Engineering Department of Tsinghua University. Nitrosobenzene was purchased from Sigma Chemical Company (USA). Pyrolytic graphite (PG) was purchased from Shanghai Carbon Materials Company (China). All other chemicals were of analytical grade and purchased from Beijing Chemical Company (China). Aniline and nitrobenzene were purified by ambient atmospheric distillation and vacuum distillation, respectively. All solutions were prepared with Milli-Q water.

2.2. Preparation of CNT-modified electrode

CNTs were functionalized with carboxylic group as follows: a suspension of 75 mg CNTs in 35 mL concentrated nitric acid (68% AR grade) was stirred at 140 °C for 5 h. The flask contents were allowed to cool, filtered, and then the solid was washed extensively with water until no further change in filtrate pH. The black powder was then dried at 80 °C under vacuum overnight to yield 40 mg carboxylated CNTs.

1.5 mg of carboxylated CNTs was dispersed in 1 mL *N,N*-dimethylformamide (DMF) by ultrasonication for about 10 min

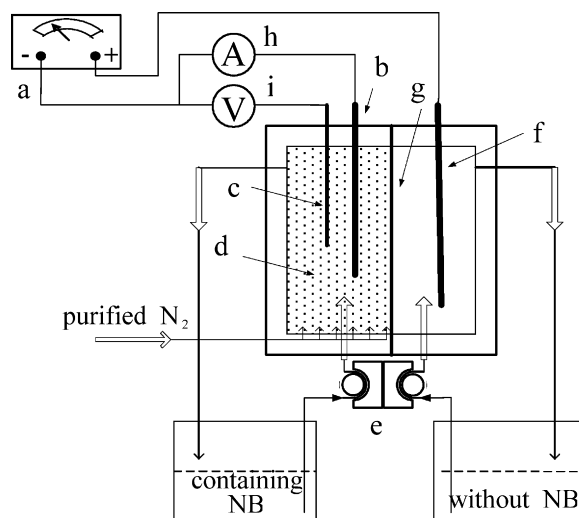


Fig. 1. Schematic diagram of packed-electrode reactor for wastewater treatment: (a) voltage-adjustable DC power; (b) current collector (pyrolytic graphite); (c) reference electrode (SCE); (d) electrodes matrix; (e) peristaltic pump; (f) anode; (g) cationic exchange membrane; (h) ampere meter; (i) voltage meter. NB: nitrobenzene.

to obtain a stable black suspension. A 5 μ L of CNTs dispersion was cast onto the surface of a polished pyrolytic graphite electrode (PGE) and a uniform CNTs film was formed after the DMF evaporated. Then CNT-modified electrode was prepared.

2.3. Construction of packed-bed flow reactor

The schematic diagram of the packed-bed flow reactor is shown in Fig. 1. The reactor was composed of two plexi-glass compartments separated by a cationic exchange membrane (Aldrich Nafion 450). The working electrode (cathode) compartment was packed with CNT-modified electrodes with a working volume of 25 mL. A PG electrode was inserted into the packed-bed to collect the current, a saturated calomel electrode (SCE) was positioned at the center of packed-bed as a reference electrode, and a large area of platinum plate was positioned at the center of the counter electrode (anode) compartment as a counter electrode. 0.1 M phosphate buffer (pH 7.0) containing 10 mM KCl was used as supporting electrolyte. The electrolyte in the counter electrode compartment was the same as that in the working electrode compartment except for the absence of nitrobenzene. The solution was purged with highly purified nitrogen before and during electrolysis.

2.4. Cyclic voltammetric (CV) measurement

Cyclic voltammetric measurement was performed on an IM6e electrochemical workstation (Zahner Instruments, Germany). The three-electrode system consisted of a platinum electrode as an auxiliary electrode, a SCE as a reference electrode, and the CNT-modified electrode as a working electrode (Fig. 2). All solution was purged with highly purified nitrogen for 20 min prior to cyclic voltammetric measurement and all experiments were carried out at 25 ± 1 °C.

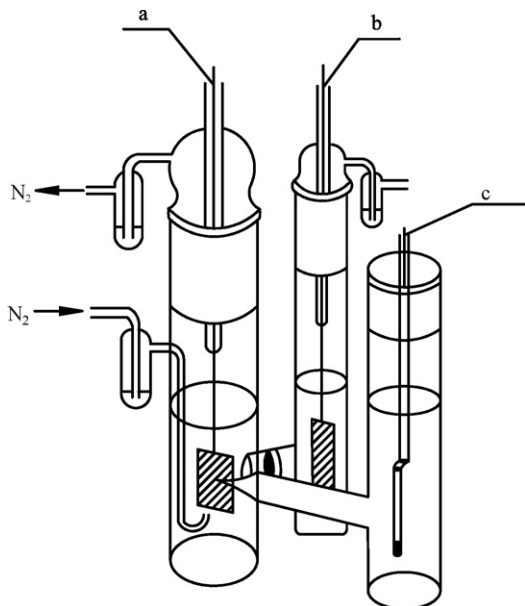


Fig. 2. Schematic diagram of the H-type cell consisting of three electrodes: (a) working electrode; (b) auxiliary electrode; (c) reference electrode.

2.5. FTIR, HRTEM and SEM measurements

FTIR spectroscopy was done with a Spectrum GX FTIR spectrometer (Perkin-Elmer, USA). CNTs were examined using KBr method.

HRTEM measurement was performed on an H-8100 transmission electron microscope (HITACHI, Japan). CNTs were sonicated for about 30 s and then placed on a 400-mesh copper grid with a carbon holey film before examined.

SEM image was done with a JSM-6700F cold field emission scanning electron microscope (JEOL, Japan). The CNT-modified electrode was cut into a small sheet, and then was examined directly.

2.6. Quantitative analysis

The concentrations of nitrobenzene and products in the course of electrolysis, were determined using an Agilent 1100 HPLC system (Agilent, USA) equipped with a ZORBAX Extend-C18 column. A variable wavelength detector (VWD) was used for the analysis, and the detection wavelength was 254 nm. The HPLC mobile phase was the mixture of water and methanol (1:1, v/v) at flow rate of 1.0 mL min⁻¹. The precision of the mass balance in the measurements was ca. 95–105% of the nominal value.

3. Results and discussion

3.1. Electrochemical behaviors of nitrobenzene on CNT-modified electrode

The electrochemical reduction of nitrobenzene produces a variety of products, including phenylhydroxylamine (PHA), aniline (AN), azoxybenzene, azobenzene, etc., which depend on

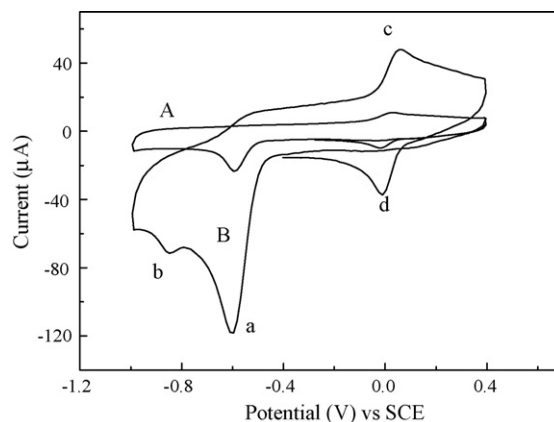


Fig. 3. Cyclic voltammograms of nitrobenzene on different electrodes (pH 5.0): (A) bare pyrolytic graphite electrode; (B) CNT-modified electrode.

the pH and electrode materials. Among these products, aniline exhibits the lowest toxicity and best biodegradable property. Therefore, the selective reduction of nitrobenzene to aniline is very important for electrochemical treatment.

Fig. 3 presented the cyclic voltammograms of 200 mg L⁻¹ nitrobenzene on a rare pyrolytic graphite electrode (curve A) and CNT-modified electrode (curve B), respectively. The reductive current of nitrobenzene on the rare PGE was very low, but it increased by a factor of six after the PGE was modified with CNT, indicating that CNTs possessed high activity for nitrobenzene reduction. As shown in Fig. 3, curve B, nitrobenzene started to be reduced at -0.40 V, and then two cathodic peaks were obtained at -0.60 V (peak (a)) and -0.90 V (peak (b)), respectively. An anodic peak at 0.2 V (peak (c)) was observed in the return cycle. When the potential sweep range was diminished from 0.40 to -0.70 V, peak (b) was disappeared, but both peak (a) and peak (c) were obtained, showing that peak (c) was paired with peak (a) instead of peak (b). In the second scan, a new cathodic peak (d) was observed at 0.1 V, attributing to the reduction of some product during the electrochemical reaction instead of the direct reduction of nitrobenzene. It was reported [12,13] that the active species of nitrobenzene reduction mainly comprised nitrosobenzene (NSB), phenylhydroxylamine (PHA), nitro or nitroso radical anion in alkaline media, etc. To demonstrate peak (a) and peak (c) are a pair redox of nitrosobenzene and phenylhydroxylamine, CV measurement of nitrosobenzene on CNT-modified electrode was performed (Fig. 4). For nitrosobenzene at CNT-modified electrode, a cathodic peak (d') at 0.05 V was observed. When the potential sweep continued negative shift, another cathodic peak (b') at -0.80 V could be obtained. In the return cycle, an anodic peak (c') at 0.20 V was observed, which was found to be paired with peak (d'). The main active-specie of nitrosobenzene reduction in basic media was PHA. Therefore, peak (d') might attribute to the reduction of NSB to PHA, and the oxidation of PHA to NSB in the return cycle generated peak (c'), namely that peak (c') and peak (d') are the PHA-NSB couple. Consequently, peak (c') and peak (d') were the PHA-NSB couple. Compared Fig. 3, curve B, with Fig. 4, it could be seen that the potential positions of peak (c) and peak (d) were approximately equal

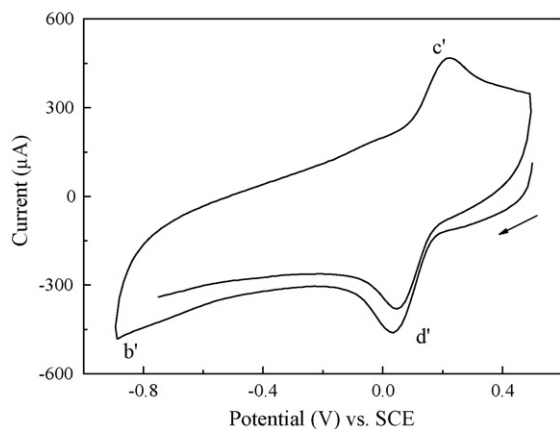
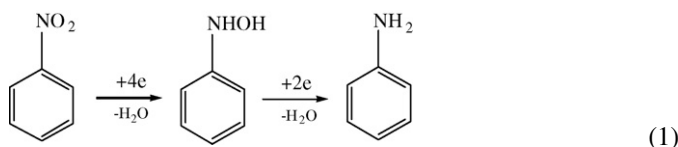


Fig. 4. Cyclic voltammograms of nitrosobenzene on CNT-modified electrode (pH 5.0).

to those of peak (c') and peak (d'), respectively, suggesting that the redox couples might be similar. Furthermore, the positions of peak (b) and peak (b') were near. These results showed that peak (c) and peak (d) attributed to the PHA-NSB couple, and peak (b) was generated by the reduction of PHA to aniline. Therefore, peak (a) in the first cycle at CNT-modified electrode is generated by the four-electron reduction of nitrobenzene to PHA, and then PHA continued to be reduced to aniline through a two-electron process, namely peak (b). In the return cycle, PHA, which was produced through nitrobenzene reduction (peak (a)), was oxidized to NSB (peak (c)). In the second cycle, the produced NSB was then reduced to PHA, generating the new peak (d). Therefore, the reductive pathway of nitrobenzene in the weakly acid solution can be described as follows:



As shown in Fig. 3, the peak of PHA reduction to aniline on CNT-modified electrode was located at ca. -0.8 V, prior to the potential where molecular hydrogen would evolve, and thus the process of nitrobenzene reduction to aniline might exhibit high current efficiency, showing the high activity of CNT for nitrobenzene reduction to AN. On the contrary, the peak of PHA reduction to aniline on the rare PGE was not observed (curve A). After 200 mg L^{-1} nitrobenzene was electrolyzed at constant-potential of -0.800 V for 30 min, aniline was obtained on the CNT-modified electrode with no molecular hydrogen evolving, but no aniline was detected on the rare PGE. When the electrolytic potential was shifted to -1.1 V, profuse molecular hydrogen evolved and aniline was obtained both on the CNT-modified electrode and the rare PGE. These results demonstrated that peak (b) attributed to PHA reduction to aniline, and CNT possessed the high activity for nitrobenzene reduction to aniline.

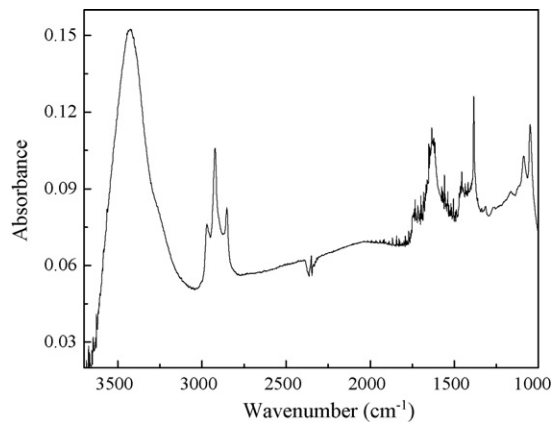


Fig. 5. The FTIR spectra of purified multi-wall carbon nanotubes.

3.2. Characterization of the CNT-modified electrode

Fig. 5 described the FTIR spectra of treated CNTs. There were obvious infrared absorbance peaks at 1740 , 1056 , 2900 , 3419 , 1390 and 1650 cm^{-1} , attributing to the stretching vibrations of C=O, C–OH, C–H and O–H, combined vibration of O–H deformation and C–O stretching vibration, and the vibration of hydrogen-bond in carboxylic, respectively. The results demonstrated that CNTs had been functionalized with carboxylic group and other oxygen-containing groups. These profuse oxygen-containing groups were the redox sites of CNTs [11], and thus made CNTs exhibit high activity for nitrobenzene reduction.

Fig. 6 presented TEM image of treated CNTs. CNTs became open after treated and some lacuna existed on the wall. The lacuna on the wall might become the reactive sites. The open CNTs could let nitrobenzene into CNTs and then the inner reactive sites of surface could also catalyze the reduction of nitrobenzene similar with the outer surface. These properties of CNTs promoted the electron transfer of nitrobenzene reduction.

As shown in Fig. 7, CNTs were distributed symmetrically on CNT-modified electrode, and enlaced each other, forming a three-dimensional layer. This three-dimensional electrode surface increased the surface area of the electrode significantly and then promoted the catalytic activity.

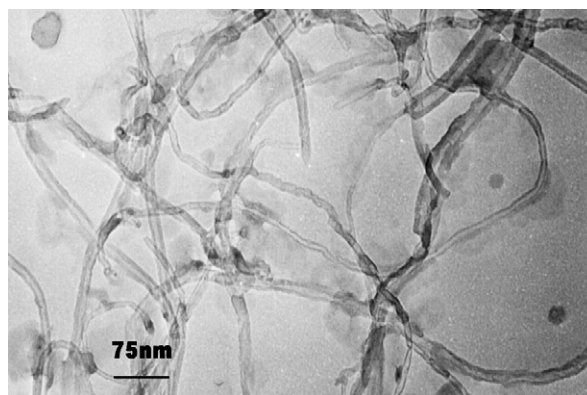


Fig. 6. The transmission electron microscopy image of purified multi-wall carbon nanotubes.

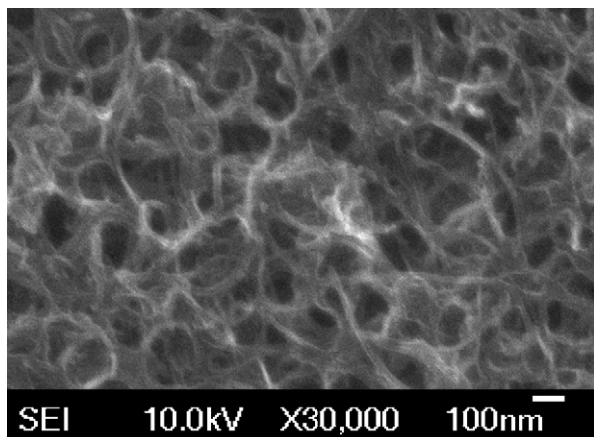


Fig. 7. The SEM image of CNT-modified electrode.

It was reported that CNTs possessed considerable capacity of adsorbing hydrogen [14]. This property may inhibit the evolving of molecular hydrogen and then lowered the parallel electrolysis of water during nitrobenzene reduction.

3.3. Nitrobenzene removal

A packed-bed flow reactor with CNT-modified electrode was constructed for nitrobenzene removal and the reactor worked at -1.2 V (versus SCE). As shown in Fig. 8, at pH 5.0, nitrobenzene was removed rapidly in the initial 30 min and the removal of nitrobenzene was over 95% with electrolysis for 50 min at -1.20 V. The yield of aniline was equivalent to the removal of nitrobenzene, indicating that aniline was the main product. As shown in Fig. 3, the peak of PHA reduction to aniline on CNT-modified electrode was located at ca. -0.8 V, and molecular hydrogen would evolve at potential more negative than -1.0 V, so the work potential of -1.2 V would lead to significant producing of AN and evolving of a little molecular hydrogen. The negative potential made the intermediate (PHA) reduced to aniline rapidly, resulting in that aniline was the main product. The real-time monitoring of electrolysis current showed that the initial current was up to 100 mA, and the current gradually went down with decrease of nitrobenzene concentration.

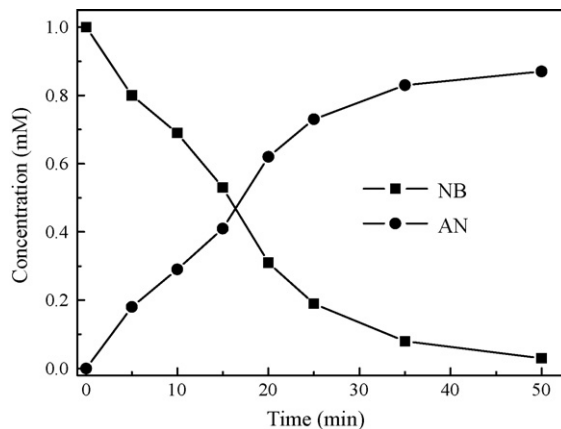


Fig. 8. Composition of the effluent from the packed-bed flow reactor for nitrobenzene removal (pH 5.0).

Fig. 9 presented composition of the effluent from the packed-bed flow reactor for nitrobenzene removal at pH 7 (curve a) and 9 (curve b). As shown in Fig. 9a, nitrobenzene was reduced rapidly in initial 60 min at pH 7 and the removal of nitrobenzene was over 95% with electrolysis for 80 min at -1.20 V. Compared with pH 5.0, the removal rate at pH 7.0 was lower, and a little PHA was obtained in the effluent during the initial electrolysis stage. Proton is necessary for the reduction of nitrobenzene and PHA, and then the peak of nitrobenzene reduction shifts to more negative potential with increase of pH, so electrolysis current and the removal rate of nitrobenzene go down. The reduction rate of PHA also decreases, and thus PHA becomes more stable at higher pH, resulting in the detection of PHA in the effluent during the initial electrolysis stage. The removal of nitrobenzene was 87% with electrolysis for 120 min at pH 9 (Fig. 9b). A little PHA was also obtained in the effluent during the initial electrolysis stage, but the amount was less than that at pH 7, demonstrating that PHA was more stable in neutral media as reported in reference [15].

The average current efficiency (CE_{avg}) in the period of $t=0 \sim \tau$ can be calculated as follows:

$$CE_{avg} = \frac{V(n_1 FC_{NSB} + n_2 FC_{PHA} + n_3 FC_{AN})}{Q} = \frac{V(n_1 FC_{NSB} + n_2 FC_{PHA} + n_3 FC_{AN})}{\int_{t=0}^{t=\tau} I dt} \quad (2)$$

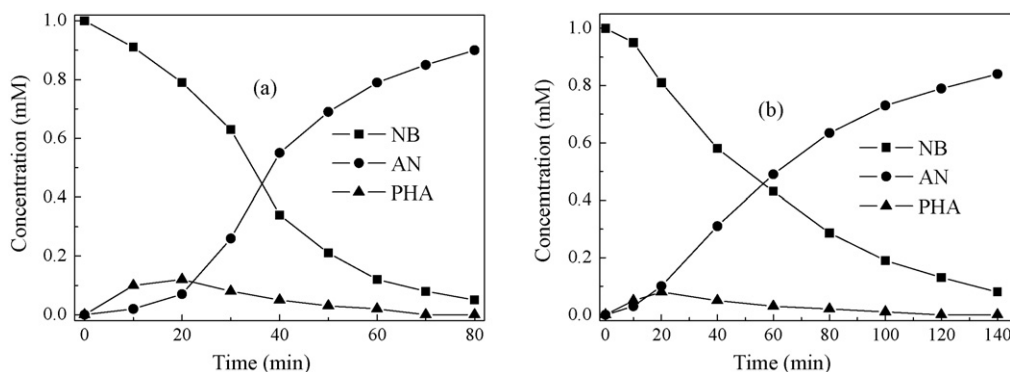


Fig. 9. Composition of the effluent from the packed-bed flow reactor for nitrobenzene removal: (a) pH 7.0; (b) pH 9.0.

Table 1
Effect of pH on current efficiency and nitrobenzene removal

pH	Nitrobenzene removal (%)	Current efficiency (%)	Electrolysis time (min)
5	95	46	50
7	95	51	80
9	93	63	1

where n_1 , n_2 and n_3 are the electron transfer numbers per 1 molecule of nitrobenzene reduction to NSB ($n_1=2$), PHA ($n_2=4$) and aniline ($n_3=6$), respectively, V the volume of total cathodic electrolyte (L), F the Faraday constant ($96,500 \text{ A s mol}^{-1}$), Q the total electric charge (A s), I the electrolysis current (A) and C_{NSB} , C_{PHA} and C_{AN} are the concentration (M) of NSB, PHA and aniline, respectively.

According to the real-time monitoring data of electrolysis current, the average current efficiency could be obtained by using Eq. (2), as shown in Table 1. The average current efficiency of nitrobenzene reduction to aniline at CNT-modified electrode was all over 45%, demonstrating the high activity of CNT. Nitrobenzene was reduced at the rapidest speed with the lowest average current efficiency at pH 5, while the average current efficiency was highest with lowest removal rate at pH 9. At pH 5, work potential of -1.2 V was negative than the potential of molecular hydrogen evolving, and the evolving of molecular hydrogen could be observed during the electrolysis period, resulting in lowering the current efficiency. Consequently, electrolysis at $\text{pH} < 5$ may presents lower current efficiency than that at pH 5. Electrolysis at pH 7 exhibits moderate removal rate and current efficiency. Furthermore, most of wastewater is at neutral pH and the addition of acid for adjusting pH may increase its cost. Therefore, electrolysis at pH 7 is suitable for wastewater treatment.

3.4. The biodegradation of electrolysis products

An aerobic biodegradation experiment was performed to verify the biodegradation property of electrolysis products. Some necessary microelement was added into the effluent, an aerobic culture was inoculated, and then the solution was cultured with shake flask. After cultured for 10 h, almost 100% of aniline was degraded and the removal of COD was up to 80%, indicating that the electrolysis products were mineralized easily through aerobic biodegradation.

4. Conclusions

The CNT-modified electrode acts as an efficient catalyst for electrochemical reduction of nitrobenzene to aniline and the electrochemical reduction of nitrobenzene follows the pathway of nitrobenzene \rightarrow phenylhydroxylamine \rightarrow aniline. CNTs had been functionalized with profuse carboxylic group and other oxygen-containing groups, became open with some lacuna

on the wall, and were distributed symmetrically on electrode with forming a three-dimensional layer, resulting in the high catalytic-activity. The removal of nitrobenzene was over 95% with electrolysis for 50 min at -1.20 V in pH 5 solution using the CNT-modified packed-bed flow reactor. The removal of nitrobenzene was over 95% with electrolysis for 80 min at -1.20 V in pH 7 solution and was 87% with electrolysis for 120 min in pH 9 solution. The average current efficiency at pH 5, 7 and 9 was 46, 51 and 63%, respectively. Aniline was the main electrolysis product and was mineralized easily through aerobic biodegradation.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant Nos. 30400011 and 20577051) and National High-Tech Research and Development Program of China (Grant No. 2004AA649340).

References

- [1] M. Latifoglu, M.D. Gurol, The effect of humic acids on nitrobenzene oxidation by ozonation and O_3/UV processes, *Water Res.* 37 (2003) 1879–1889.
- [2] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation of nitrobenzene using titanium dioxide and concentrated solar radiation: chemical effects and scaleup, *Water Res.* 37 (2003) 1223–1230.
- [3] S.F. Nishino, J.C. Spain, Degradation of nitrobenzene by a pseudomonas-pseudoalcaligenes, *Appl. Environ. Microbiol.* 59 (1993) 2520–2525.
- [4] E.K. Nefso, S.E. Burns, C.J. McGrathb, Degradation kinetics of TNT in the presence of six mineral surfaces and ferrous iron, *J. Hazard. Mater.* B123 (2005) 79–88.
- [5] R. Boopathy, C.F. Kulpa, Trinitrotoluene (TNT) as a sole nitrogen source for a sulfate-reducing bacterium *Desulfovibrio* sp. (B strain) isolated from an anaerobic digester, *Curr. Microbiol.* 25 (1992) 235–241.
- [6] I.F. Cheng, Q. Fernando, N. Korte, Electrochemical dechlorination of 4-chlorophenol to phenol, *Environ. Sci. Technol.* 31 (1997) 1074–1078.
- [7] M.C.F. Oliveira, Study of the hypophosphite effect on the electrochemical reduction of nitrobenzene on Ni, *Electrochim. Acta* 48 (2003) 1829–1835.
- [8] C.V. Rode, M.J. Vaidya, R. Jaganathan, R.V. Chaudhari, Hydrogenation of nitrobenzene to *p*-aminophenol in a four-phase reactor: reaction kinetics and mass transfer effects, *Chem. Eng. Sci.* 56 (2001) 1299–1304.
- [9] W.-Y. Xu, T.-Y. Gao, J.-H. Fan, Reduction of nitrobenzene by the catalyzed Fe–Cu process, *J. Hazard. Mater.* B123 (2005) 232–241.
- [10] C. Zhang, J. Yang, Z. Wu, Electroreduction of nitrobenzene on titanium electrode implanted with platinum, *Mater. Sci. Eng.* B68 (2000) 138–142.
- [11] P.J. Britto, K.S.V. Santhanam, P.M. Ajayan, Carbon nanotube electrode for oxidation of dopamine, *Bioelectrochem. Bioenerg.* 41 (1996) 121–125.
- [12] P. Gao, D. Gosztola, M.J. Weaver, Surface-enhanced Raman spectroscopy as a probe of electroorganic reaction pathway, *J. Phys. Chem.* 92 (1988) 7122–7130.
- [13] G. Kokkinidis, K. Juttner, The electrocatalytic influence of underpotential lead adsorbates on the reduction of nitrobenzene and nitrosobenzene on silver single crystal surfaces in methanolic solutions, *Electrochim. Acta* 26 (1981) 971–977.
- [14] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, Storage of hydrogen in single walled carbon nanotubes, *Nature* 386 (1997) 377–379.
- [15] A. Cyr, P. Huot, J.-F. Marcoux, G. Belot, E. Laviron, J. Lessard, The electrochemical reduction of nitrobenzene and azoxybenzene in neutral and basic aqueous methanolic solutions at polycrystalline copper and nickel electrodes, *Electrochim. Acta* 34 (1989) 439–445.