Accepted Manuscript

Title: Degradation of nitrobenzene by synchronistic oxidation and reduction in an internal circulation microelectrolysis reactor

Authors: Han Yanhe, Qi Mengmeng, Zhang Lei, Sang Yimin, Liu Meili, Zhao Tingting, Niu Junfeng, Zhang Shanqing

PII: S0304-3894(18)31055-0
DOI: <https://doi.org/10.1016/j.jhazmat.2018.11.036>
Reference: HAZMAT 19958

To appear in: *Journal of Hazardous Materials*

Received date: 30 May 2018
Revised date: 5 October 2018
Accepted date: 9 November 2018

Please cite this article as: Yanhe H, Mengmeng Q, Lei Z, Yimin S, Meili L, Tingting Z, Junfeng N, Shanqing Z, Degradation of nitrobenzene by synchronistic oxidation and reduction in an internal circulation microelectrolysis reactor, *Journal of Hazardous Materials* (2018), <https://doi.org/10.1016/j.jhazmat.2018.11.036>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Degradation of nitrobenzene by synchronistic oxidation and reduction in an internal circulation microelectrolysis reactor

Han Yanhe^{a,*}, Qi Mengmeng^a, Zhang Lei^a, Sang Yimin^a, Liu Meili^a, Zhao Tingting^a, Niu

Junfeng^{b,*}, Zhang Shanqing^c

^aDepartment of Environmental Engineering, Beijing Institute of Petrochemical Technology, 19

Qingyuan North Road, Daxing District, Beijing 102617, P.R. China

^bResearch Center for Eco-Environmental Engineering, Dongguan University of Technology,

Dongguan, Guangdong 523808, P.R. China

^cGriffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222, Australia

Corresponding author:

E-mail address: hanyanhe@bipt.edu.cn or hanyanhe@126.com (Y. Han), Tel./Fax:

+86-10-82192291; niujf@dgut.edu.cn (J. Niu), Tel./Fax: +86-769-22861848

Graphical abstract

HIGHLIGHTS

- Degradation of nitrobenzene by internal circulation microelectrolysis (ICE) is studied.
- Nitrobenzene was degraded by synchronistic oxidation and reduction in the ICE reactor.
- Effects of various parameters on nitrobenzene degradation are evaluated.
- Degradation intermediates of nitrobenzene are also identified.
- ICE technique can be suitable for the treatment of nitrobenzene in wastewater.

Abstract

The degradation of nitrobenzene by synchronistic oxidation and reduction was investigated using an internal circulation microelectrolysis (ICE) reactor with an active volume of 0.018 m³. Compared with a conventional fixed bed reactor with and without aeration, the ICE reactor exhibited a markedly higher nitrobenzene degradation efficiency. The effects of various operational parameters such as reaction time, aeration rate, initial nitrobenzene concentration, initial pH, and a volume ratio of iron and carbon (Fe/C) were also investigated. The optimal operating conditions (reaction time = 60 min, aeration rate = 5×10^{-4} m³/s, initial concentration of nitrobenzene = 300 mg/L, pH = 3.0, Fe/C = 1:1) gave removal efficiencies of nitrobenzene and chemical oxygen demand of 98.2% and 58%, respectively. The biodegradability index of the treated nitrobenzene solution was 0.45, which is 22 times that of the original solution. The reaction intermediates were identified through high-performance liquid chromatography, ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, gas chromatography-mass spectrometry, and ion chromatography. The primary intermediates were determined to be aniline, phenol,

and carboxylic acids, indicating that nitrobenzene was synchronously oxidized and reduced in the ICE reactor. Based on the identified intermediates, a possible pathway for nitrobenzene degradation in the ICE reactor is proposed.

Keywords: Internal circulation microelectrolysis reactor, nitrobenzene, iron–carbon, degradation pathway, synchronistic oxidation and reduction

1. Introduction

Nitrobenzene is an important chemical intermediate that is used widely in the pharmaceutical [1], dye [2], and petrochemical [3] industries. However, its production generates large quantities of nitrobenzene-contaminated wastewater [4]. Free nitrobenzene is hazardous to various organisms, including humans, and can lead to carcinogenesis, teratogenesis, and mutagenesis [5]. Further, it is not readily degraded by microorganisms [6], which encourages its accumulation in the environment [7]. Accordingly, it is a priority pollutant in many countries [8], making its removal from wastewater highly desirable [9–11].

Owing to the existence of a strong electron-withdrawing nitro group, nitrobenzene is refractory and relatively resistant to aerobic biodegradation and oxidation [1, 12]. Advanced oxidation processes such as photoelectrocatalysis [13], electrochemical processes [14], Fenton oxidation [15], and ozone oxidation [16] can rapidly oxidize nitrobenzene by using strongly oxidizing radicals (e.g., $\cdot\text{OH}$ radicals), but the high costs of these methods limit their applicability in the treatment of nitrobenzene-containing wastewater. Thus, an economical and efficient process must

be developed. Given the electrophilic nature of the nitro group, reduction processes have been developed to convert nitrobenzene into aniline, which can be completely oxidized with relative ease by a subsequent aerobic process [17, 18].

Before the biodegradation treatment of organic industrial wastewater containing high concentrations of hard-to-degrade nitrobenzene, an iron–carbon internal microelectrolysis (IE) process is usually performed to pretreat the wastewater. The basic principle of the IE process, in which iron chips and granular activated carbon are fed into a fixed bed (FB) reactor, is the microscopic galvanic cells produced by the iron and activated carbon in the wastewater solution containing acidic electrolytes. These cells induce the formation of various products on the electrode, such as ferric flocculants, active hydrogen, and $\cdot\text{OH}$ radicals [19]. These products have high activities, and undergo redox reactions with many components that are typically difficult to biodegrade. Moreover, because there is no need for extra power, the IE process is a low-energy-consumption and low-cost method that significantly improves the biodegradability [20].

Qin et al. [21] applied the IE process to degrade nitrobenzene wastewater. Using a 250 mL conical flask filled with 100 mL of nitrobenzene solution (concentration = 300 mg/L, initial pH = 3.0). Only 10.97% total organic carbon (TOC) removal efficiency was obtained, indicating that the mineralization rate was very low. In addition, the efficiency of the IE pretreatment decreases dramatically over time because of the hardening, blocking, and passivation of the iron–carbon mixture in the reactor [22, 23]. In an attempt to overcome such disadvantages, an IE process with

aeration in the FB reactor was developed [24]. However, because the iron–carbon mixture cannot be stirred by the dispersed air in the reactor, aeration only serves to delay the hardening and passivation of the iron–carbon mixture.

Therefore, an internal circulation microelectrolysis (ICE) reactor was developed by our research group [22]. This reactor gathers the dispersed air during the IE process into a central tube, which sucks the iron–carbon mixture into the central tube, and returns it to the upper part of the iron–carbon bed after being “washed”. The iron–carbon mixture is stirred by the internal cyclic flow, thus avoiding the hardening, blocking, and passivation of the iron–carbon mixture [22]. Moreover, the continuous aeration in the central tube provides an oxidizing atmosphere for the degradation of organic materials, and the oxygen consumption action of the iron and the hydrogen products generates a reducing environment in the outer annular space of the reactor. Therefore, the ICE reactor allows for synchronistic oxidation and reduction. Based on the properties of nitrobenzene and the ICE reactor, it was suggested that it would be possible to degrade nitrobenzene to a high degree by microelectrolysis in the ICE reactor.

The objective of this study was to investigate the feasibility of using the ICE technique for the treatment of nitrobenzene-containing wastewater. The performance of FB reactors with and without aeration was compared with that of the ICE reactor. Subsequently, the operational parameters, including reaction time, aeration rate, initial concentration of nitrobenzene, pH, and the volume ratio of iron and carbon (Fe/C), were optimized to achieve the highest nitrobenzene removal efficiency. Finally, the

mechanism underlying the degradation of nitrobenzene in the ICE reactor was explored, to provide a theoretical basis and technical guidance for the practical application of the ICE process.

2. Materials and methods

2.1. Materials

Nitrobenzene and other chemicals (e.g., HCl and NaOH) of analytical grade were obtained from Tianjin Chemical Industry Co. Ltd. (China). Chromatographic grade methanol was purchased from ANPEL Laboratory Technologies (China). Iron scraps were obtained from the metalworking facilities of our institution. To ensure circulation of the iron scraps in the ICE reactor, they were first passed through a sieve with a mesh size of 20 to ensure they were ≤ 0.85 mm in size. To eliminate the oil film and oxide layer on the scraps, which could affect the efficiency of microelectrolysis, they were soaked in a 10% NaOH solution for 120 min, dipped in a 5% HCl solution for 30 min, and finally rinsed with tap water until the pH was close to neutral. Granular activated carbon (GAC, 1–2 mm), purchased from Hebei Pengcheng Activated Carbon Co., Ltd. (China), was cleaned with deionized water. The cleaned GAC was submerged in a nitrobenzene solution until saturation was reached to remove the influence of absorption during the microelectrolysis degradation process.

2.2. ICE and FB reactors

The ICE reactor (shown in Fig. S1) has been described in detail in our previous work [22]. In brief, it consisted of a body and a central tube. Air was introduced into the central tube from below. The iron–carbon mixture was sprayed up the central tube

and agitated by the air bubbles, after which it fell back to the bed. The average density difference generates multiphase flow circulation inside and outside the central tube. The nitrobenzene solution, which was fed into the ICE reactor through an inlet pipe and uniformly distributed by a water distributor, was reduced outside and oxidized inside the central tube, against the flow. The treated solution was collected from an overflow-weir. Although iron is much heavier than activated carbon, the composition distribution of iron-carbon mixture can be kept uniformly rather than being separated in the ICE reactor after aeration stirring, validated by the images of the ICE reactor at the start and after running for 120 min (Fig. S2). This is beneficial to the degradation of nitrobenzene in the ICE reactor. For comparison, a FB reactor (shown in Fig. S3), similar to the ICE reactor but lacking the central tube, was also constructed and tested. The FB reactor was filled with an iron-carbon mixture of the same volume as that in the ICE reactor. The wastewater was pumped from below, flowing upward through the packed bed and out through the overflow-weir.

2.3. Experimental procedure

A 300 mg/L nitrobenzene solution with a pH of 3.0 was used to evaluate the FB and ICE reactors at room temperature (approximately 20 °C). The two reactors had the same effective volume of 0.018 m³, and the iron-carbon packed beds had an Fe/C volume ratio of 1:1 unless stated otherwise. The packing volume was 0.012 m³, with a density of 900–1100 kg/m³ and a height of approximately 0.45 m. In both cases, the aeration rate was 5×10^{-4} m³/s, and the pressure was 0.12 kg/cm², which was sufficient to ensure the circulation of iron scraps in the ICE reactor, thus achieving an

approximately uniform distribution of the iron–carbon mixture. After a certain reaction time, the pH of the effluents from the two reactors was adjusted to 8–9 using NaOH, and their concentrations were analyzed along with the chemical oxygen demand (COD), TOC, and biological oxygen demand (BOD). To optimize the operational parameters, a series of microelectrolysis experiments were performed using different reaction times, aeration rates, initial nitrobenzene concentrations, initial pH values, and Fe/C ratios. In order to explore the degradation mechanism of nitrobenzene in the ICE reactor, the reaction intermediates were identified using high-performance liquid chromatography (HPLC), ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS), and ion chromatography (IC).

2.4. Analytical methods

The concentration of nitrobenzene was determined using an HPLC system (Waters, 1525, U.S.A.) equipped with a UV detector (UV-2489) at 268 nm and a C18 reverse-phase column (150 mm × 4.6 mm, 5 μm). The flow rate of the mobile phase, which consisted of 70% methanol and 30% water, was set to 1.0 mL/min. The COD and BOD (for 5days) were measured as per the Chinese National Standard GB 11914-89 and HJ 505-2009, respectively. The TOC was determined using a TOC analyzer (Liqui TOC II, Elementar, Germany). The UV-vis spectra of the various samples were collected in the wavelength range of 190–400 nm.

GC-MS was performed to identify the reaction intermediates produced during the degradation of nitrobenzene. Chromatographic grade CH₂Cl₂ (20 mL) was used to

extract the sample from a 100 mL treated solution three times (acidic, neutral, and basic). The three samples were mixed, evaporated to approximately 5 mL, and dehydrated with anhydrous sodium sulfate. The residue was filtered through a 0.45 μm membrane, and then a 1.0 μL sample was injected into a GC-MS system (Agilent 7890A/5975C, U.S.A.) equipped with an HP-5MS capillary column (inner diameter 0.25 mm, length 30.0 m). The GC column was operated in a temperature-controlled mode, according to the work of Lai et al. [25]: 40 $^{\circ}\text{C}$ for 1 min, raised first to 100 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, then raised to 280 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, and held for 3 min. The solvent delay was 4 min and the total run time was 50 min. The mass range scanned was 20–700 m/z .

The carboxylic acids and inorganic ions present were identified using an IC system (Dionex Series DX 100, U.S.A.) equipped with a conductivity detector and a Dionex AG4A-SC column. A mixture of Na_2CO_3 (2.0 mmol/L) and NaHCO_3 (0.75 mmol/L) was used as the eluent. The flow rate was 1.0 mL/min. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the activated carbon samples were conducted using a thermal analyzer (Model Q50, TA instruments, U.S.A.) between room temperature and 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under a nitrogen flow of 50 mL/min.

3. Results and discussion

3.1. Comparison of degradation performance between ICE and FB reactors

ICE and FB reactors, each with an aeration rate of $5 \times 10^{-4} \text{ m}^3/\text{s}$, were employed in this study to investigate the degradation of nitrobenzene. Further, to identify how

aeration affects nitro group reduction, parallel experiments were performed in a FB reactor without aeration. The residual nitrobenzene concentration and TOC in solution after microelectrolysis using the ICE reactor and the FB reactor with and without aeration are shown in Fig. 1. It is well known that aeration can induce agitation, which is beneficial for the mass transfer and the degradation of nitrobenzene [26]. However, the degradation rate of nitrobenzene in the FB reactor with aeration was very low, and the degradation efficiency was less than 20%. In contrast, the degradation efficiency in the FB reactor without aeration for the same reaction time of 120 min was higher than 90%. Surprisingly, in the FB reactor without aeration, the extent of nitrobenzene mineralization was insignificant and much lower than that in the FB reactor with aeration. This result indicates that nitrobenzene was readily reduced during the microelectrolysis process but not easily oxidized, which is in keeping with previous reports [11, 27, 28].

Nevertheless, the degradation efficiency of nitrobenzene in the ICE reactor was as high as 98%, while the mineralization efficiency was approximately 50%, which is much higher than that in the FB reactor with aeration for the same degradation time. As the aeration rate was constant, differences in mass transfer could not cause this difference in degradation efficiency. The ICE reactor gathers almost all the air into the central tube, which has a volume of approximately 1% of the ICE reactor volume. Computational fluid dynamics [29] has revealed that, with an optimal ICE reactor structure, the gas holdup outside the central tube is very low. Therefore, dissolved oxygen is limited outside the central tube, and can easily be removed by the iron and

active hydrogen. Hence, the space outside the central tube is a reductive environment, inducing the reduction of nitrobenzene into aniline, which is oxidized more readily than nitrobenzene [30]. This results in a decrease of the TOC in the nitrobenzene solution.

It was concluded that the ICE reactor allows for both reduction and oxidation at the same time, inducing a high removal efficiency of nitrobenzene. Subsequently, the degradation of nitrobenzene in the ICE reactor was explored in greater detail.

3.2. Operational parameters

3.2.1. Reaction time

The effect of the ICE reaction time on nitrobenzene degradation was investigated. As the concentration of nitrobenzene in the test solution changed over time, Fig. 2 only shows the changes in the COD and BOD₅/COD values over time. The COD value decreased quickly, with a removal efficiency of 55% for a reaction time of 120 min. However, this decrease in the COD was inconsistent with the change in the nitrobenzene concentration, indicating that some of the removed nitrobenzene was transformed into intermediate products without being completely mineralized. The biodegradability of the nitrobenzene solution, which was evaluated based on the BOD₅/COD value, increased sharply from 0.02 to 0.45 at the beginning of the reaction, implying that the biodegradability was improved by a factor of 22. Therefore, the ICE technique can effectively enhance the biodegradability of nitrobenzene-containing wastewater. This result indicates that no toxic substances were formed during the degradation of nitrobenzene by the ICE process. To ensure a

high COD removal efficiency and improved biodegradability, a reaction time of 60 min was determined to be the most suitable for treating nitrobenzene in the ICE reactor. Hence, the reaction time was set to 60 min in further experiments.

3.2.2. Aeration rate

The amount of aeration influences not only the circulation performance of the iron-carbon mixture but also the size of the oxidizing part of the ICE reactor [22]. Therefore, the effect of the aeration rate on the removal efficiencies of nitrobenzene and COD from the test solution was investigated alongside the BOD₅/COD value, as shown in Fig. 3. The removal efficiency of nitrobenzene initially increased as the aeration rate increased from 3.3×10^{-4} to 5×10^{-4} m³/s, and then decreased between 5×10^{-4} and 8.3×10^{-4} m³/s, indicating that, while proper aeration is beneficial, excessive aeration has an adverse effect on the degradation of nitrobenzene in the ICE reactor. The removal efficiencies of COD and BOD₅/COD exhibited similar trends, with the optimal efficiencies observed at an aeration rate of 5×10^{-4} m³/s. However, the absolute variation in the COD values corresponding to the different aeration rates was much higher than that in the nitrobenzene concentration. This may be because lower aeration rates caused nitrobenzene to be reduced to intermediates rather than being completely mineralized into carbon dioxide and water [31]. At higher aeration rates, the increase in the amount of dissolved oxygen suggests nitrobenzene is not readily reduced, owing to the strong electron-withdrawing ability of the nitro group [32].

3.2.3. Initial concentration of nitrobenzene

Fig. 4 shows how the initial concentration of nitrobenzene in the test solution affects its degradation in the ICE reactor. The degradation efficiency increased as the initial concentration of nitrobenzene increased from 100 to 300 mg/L. Although a higher initial concentration of nitrobenzene resulted in more nitrobenzene molecules in the degraded solution, the calculated degradation efficiency increased. This behavior may occur because as the concentration increases, there are more nitrobenzene molecules to react with the reducing or oxidizing substances that are present in high concentrations on the surface layer of the solid reaction medium, resulting in a faster degradation rate. However, when the initial concentration of nitrobenzene was increased from 300 to 500 mg/L, the removal efficiencies of both nitrobenzene and COD decreased gradually. The degradation of nitrobenzene may be restricted by the limited number of reactive species at higher nitrobenzene concentrations. The BOD₅/COD value showed a similar trend. The highest BOD₅/COD value was observed at a nitrobenzene concentration of 300 mg/L. Hence, this concentration was considered optimal for nitrobenzene degradation under the conditions explored in this study.

3.2.4. Initial pH

The pH value significantly affects the efficiency of the microelectrolysis reaction [19]. Furthermore, the pH level of industrial wastewater fluctuates sharply [33]. Hence, the effect of pH was evaluated during the treatment of nitrobenzene in the ICE reactor, as shown in Fig. 5. The removal efficiencies of nitrobenzene (Fig. 5(a)) and COD (Fig. 5(b)) both decreased with an increase in pH. This trend can be explained

by the difference in reactive species. At low pH levels, O₂ on the carbon cathode is reduced during aeration to oxygen free radicals ($\cdot\text{O}$), reactive hydrogen ($[\text{H}]$), and hydrogen peroxide (H₂O₂), as shown in Eqs. (1) and (2) [34, 35], leading to the degradation of nitrobenzene and COD.

These reactive species can also transform biorefractory nitrobenzene into biodegradable intermediates, resulting in an improvement in the BOD₅/COD value, as shown in Fig. 5(b). However, under neutral or basic conditions, O₂ is changed only into OH⁻ (Eq. (3)); the oxidation potential (E^θ) decreases from +1.23 V to +0.41 V when the pH is increased from 2 to 8 [36].

This change reduces the biodegradability of the nitrobenzene solution [20]. Therefore, it was concluded that an acidic environment (e.g., pH 2–4) is more effective than an alkaline one (e.g., pH 8–10) for the degradation of nitrobenzene. Indeed, hydrogen is produced at pH values of <4, which is beneficial for the degradation of nitrobenzene. However, below pH 4.0, the corrosion rate increases linearly as the pH value decreases (Fig. S4), resulting in increased operation costs. In

consideration of these factors, the pH was kept at 3 during the following experiments.

3.2.5. Fe/C ratio

To compare the efficiencies of iron (Fe/C = 1:0), activated carbon (Fe/C = 0:1), and various iron–carbon mixtures (Fe/C = 2:1, 1:1, and 1:2) with respect to the degradation of nitrobenzene, their removal efficiencies toward nitrobenzene and COD, and the improvement in the BOD₅/COD value were investigated, as shown in Fig. 6. When activated carbon alone was used, nitrobenzene did not undergo noticeable degradation, suggesting that the amount of activated carbon adsorbed on nitrobenzene was saturated before the degradation reaction could take place. When iron alone was used, the extent of nitrobenzene degradation increased with reaction time. For the iron–carbon mixtures, an Fe/C ratio of 1:1 gave the highest rate constant of 0.080 min⁻¹, as shown in Fig. S5; the removal efficiency of nitrobenzene was 98.2% for a reaction time of 60 min. These results indicate that activated carbon accelerates the degradation reaction of nitrobenzene with iron, highlighting the fact that the microscopic galvanic cells that form between iron and activated carbon play a vital role in the ICE reactor. It can be seen from Fig. 6(b) that the COD removal efficiency and the biodegradability of the treated solution initially increased and then decreased with increasing Fe/C ratio. The optimal Fe/C ratio was determined to be 1:1, corresponding to a COD removal efficiency and BOD₅/COD value of 58% and 0.45, respectively. It is likely that the maximum number of microscopic galvanic cells are formed when iron and activated carbon are used in the same amounts [37].

3.3. Nitrobenzene degradation mechanism

Fig. 7 shows typical UV-vis spectra of the raw nitrobenzene solution and the solution treated for reaction times of 15, 30, 60, 90, and 120 min. The raw nitrobenzene solution exhibits an absorbance peak at approximately 268 nm, which is the characteristic peak of nitrobenzene [27]. However, this peak disappears in the treated solutions, which instead exhibit two typical absorbance peaks at 230 and 274 nm, indicating nitrobenzene degradation. To assign these spectral peaks, the UV-vis spectra of aniline and phenol were collected at pH 8–9, as shown in Fig. S6. It can be seen that the peak at 230 nm is characteristic of aniline, whereas the peak at 274 nm is contributed by phenol. These results suggest that nitrobenzene was reduced to aniline and phenol by the ICE treatment. However, these peaks gradually decreased in intensity and eventually disappeared as the reaction time increased, suggesting that aniline and phenol were also degraded.

To explore the underlying mechanism of nitrobenzene degradation in the ICE reactor, FTIR analyses were performed to monitor the reaction intermediates formed on the activated carbon, as shown in Fig. 8. Thus, the FTIR spectra of activated carbons with and without adsorbed nitrobenzene were measured and compared. The distinct peaks observed at approximately 1635, 2940, 3413, 3740, and 3849 cm^{-1} in the case of the raw activated carbon were attributable to the surface functional groups of activated carbon. For the samples with adsorbed nitrobenzene, a characteristic peak thought to be related to the symmetric stretching vibrations of the nitro group was observed at 1380 cm^{-1} . A further peak was observed at 2355 cm^{-1} , which was related to neither nitrobenzene [38, 39] nor activated carbon, indicating some aspect of

chemical bonding during adsorption. After being employed in the ICE reactor, the FTIR spectrum of the activated carbon sample exhibited two new bands at 1602 and 1622 cm^{-1} , which are related to the bending vibrations of the N–H bond in aniline, thus further confirming that nitrobenzene is reduced to aniline during the ICE process [40, 41].

The TGA and DTA results of the activated carbon samples are shown in Fig. 9. Each activated carbon exhibited an obvious weight loss below 100 °C owing to the evaporation of adsorbed water. The TGA profile of the activated carbon with adsorbed nitrobenzene displayed another notable weight loss between 150 and 300 °C corresponding to the evaporation of adsorbed nitrobenzene. However, this weight loss hardly occurred for the activated carbon that had been used in the ICE reactor, and the corresponding DTA peak was also very weak. This result indicates that adsorbed nitrobenzene was almost completely degraded by the ICE technique. Meanwhile, the many small peaks in the DTA curve can be attributed to the evaporation of the intermediate products of nitrobenzene degradation.

Reaction intermediates such as phenols, nitrophenols, organic acids, and inorganic ions are usually observed during the decomposition of nitrobenzene by advanced oxidation processes. Therefore, to explore the degradation pathway of nitrobenzene by the ICE process, the intermediate aromatic organics were analyzed using GC-MS and IC. Aniline and phenol were identified by GC-MS, whereas inorganic ions (e.g., nitrate and nitrite ions) and carboxylic acids were quantitatively detected by IC, as shown in Fig. 10. It was found that the concentrations of all the

carboxylic acids, such as oxalates, formates, and acetates, initially increased and then decreased with increasing reaction time. This observation indicates that nitrobenzene was decomposed into low-molecular-weight carboxylic acids, which were eventually mineralized by the ICE process. Ammonium, nitrate, and nitrite ions were also detected during the degradation of nitrobenzene. Similarly, their concentrations rose and then fell as the reaction time increased. The concentration of nitrite ions was much lower than that of nitrate ions, most likely owing to the instability of the former [42]. It was found that the total nitrogen content after a reaction time of 180 min was lower than that of the initial nitrobenzene solution. It may be that a small amount of nitrogen left the solution in the form of N_2 and/or was adsorbed by the iron-carbon mixture, leading to precipitate formation during the ICE process.

Therefore, the degradation of nitrobenzene can be expressed by the pathway shown in Fig. 11. Nitrobenzene is reduced to aniline by the active hydrogen species formed during microelectrolysis in the annular space of the ICE reactor (Eq. (S1) in Table S1) while also being oxidized into phenol by the hydroxyl radicals generated in the presence of oxygen within the central tube of the reactor. Aniline can be also oxidized into phenol [1, 43] and then further oxidized into hydroquinone (Eqs. (S2) and (S3) in Table S1, respectively). The aromatic ring of benzene opens, leading to the formation of carboxylic acids (Eqs. (S4) – (S7) in Table S1), which eventually leads to the complete mineralization of nitrobenzene by the reactive oxygen species generated during the ICE process (Eq. (S8) in Table S1). The amino group can be substituted or oxidized into ammonium, nitrite, and nitrate ions [42, 44, 45] (Eqs. (S9) and (S10) in

Table S1). Nitrate ions can be reduced to nitrite ions, and finally to nitrogen [46, 47] (Eqs. (S11) and (S12) in Table S1, respectively). Therefore, nitrobenzene can be completely mineralized by microelectrolysis in the ICE reactor.

4. Conclusions

In this study, it was demonstrated that nitrobenzene can be effectively degraded using the ICE technique. The nitrobenzene degradation efficiency of the ICE reactor was much higher than that of the FB reactor, both with and without aeration. The degradation efficiency was determined to be dependent on the reaction time, aeration rate, initial solution concentration, initial pH, and Fe/C ratio. The UV-vis spectrum of the treated nitrobenzene solution suggested that nitrobenzene is initially reduced to aniline and phenol. This pathway was confirmed by the results of HPLC, FTIR, and GC-MS analyses. Thus, nitrobenzene can be completely mineralized by the ICE technique, leading to the generation of ammonium, nitrite, and nitrate ions as well as carboxylic acids, whose concentrations decrease gradually with reaction time. Therefore, it can be concluded that nitrobenzene is synchronously reduced and oxidized in the ICE reactor, which is highly suited for the effective oxidation degradation of refractory organics with strong electron-withdrawing groups.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21677018) and the Joint Fund of the Beijing Municipal Natural Science Foundation and Beijing Municipal Education Commission (Grant No.

KZ201810017024).

Declaration of interests: none.

References

- [1] Z. Cai, J. Fu, P. Du, X. Zhao, X. Hao, W. Liu, D. Zhao, Reduction of nitrobenzene in aqueous and soil phases using carboxymethyl cellulose stabilized zero-valent iron nanoparticles, *Chem. Eng. J.* 332 (2018) 227-236.
- [2] V. Anand, V.C. Srivastava, Photocatalytic Degradation of Nitrobenzene and Azo Dye Using Zinc Oxide Nanoparticles Prepared by Electrochemical Method, *J. Sci. Ind. Res.* 75 (2016) 632-637.
- [3] Y.J. Dai, N. Terui, Y.B. Lin, S. Tanaka, K. Jin, Y. Hiram, M. Teduka, M.L. Zhang, X.D. Shen, B. Fugetsu, Determination of Nitrobenzene in Water and Ice Samples Collected from the Songhua River after an Explosion of a Petrochemical Plant and Investigation on Enclosing Behavior of Nitrobenzene into Ice, *Anal. Sci.* 26 (2010) 519-523.
- [4] E.R. Zhang, F. Wang, W.J. Zhai, K. Scott, X. Wang, G.W. Diao, Efficient removal of nitrobenzene and concomitant electricity production by single-chamber microbial fuel cells with activated carbon air-cathode, *Bioresour. Technol.* 229 (2017) 111-118.
- [5] K. Zasada, M. Karbownik-Lewinska, Comparison of potential protective effects of melatonin and propylthiouracil against lipid peroxidation caused by nitrobenzene in the thyroid gland, *Toxicol. Ind. Health* 31 (2015) 1195-1201.

- [6] G.F. Liu, B. Dong, J.T. Zhou, J. Wang, R.F. Jin, J.J. Li, Enhanced bioreduction of nitrobenzene by reduced graphene oxide materials: effects of surface modification and coexisting soluble electron shuttles, *Environ. Sci. Pollut. Res.* 24 (2017) 26874-26880.
- [7] W.K. Kirui, S.B. Wu, M. Lei, R.J. Dong, Nitrobenzene degradation pathways and their interaction with sulfur and nitrogen transformations in horizontal subsurface flow constructed wetlands, *Ecol. Eng.* 84 (2015) 77-83.
- [8] Z.G. Yan, Z.S. Zhang, H. Wang, F. Liang, J. Li, H.L. Liu, C. Sun, L.J. Liang, Z.T. Liu, Development of aquatic life criteria for nitrobenzene in China, *Environ. Pollut.* 162 (2012) 86-90.
- [9] Y.X. Zhang, X.B. Mao, S. Chen, J.H. Yao, C.a. Ma, Binary composite ionic liquids [bmim][BF₄] and [bmim][Ac] for electrochemical reduction of nitrobenzene, *Ionics* 20 (2014) 1703-1710.
- [10] L. Chen, W. Zhang, H. Chen, S.Q. Xia, The effect of Fe⁰/Fe²⁺/Fe³⁺ on nitrobenzene degradation in the anaerobic sludge, *J. Hazard. Mater.* 143 (2007) 57-64.
- [11] R. Zhang, J. Li, C. Liu, J. Shen, X. Sun, W. Han, L. Wang, Reduction of nitrobenzene using nanoscale zero-valent iron confined in channels of ordered mesoporous silica, *Colloids Surf. A* 425 (2013) 108-114.
- [12] Q. Ji, J. Li, Z. Xiong, B. Lai, Enhanced reactivity of microscale Fe/Cu bimetallic particles (mFe/Cu) with persulfate (PS) for p-nitrophenol (PNP) removal in aqueous solution, *Chemosphere* 172 (2017) 10-20.
- [13] Q.L. Ma, H.T. Wang, H.X. Zhang, X.W. Cheng, M.Z. Xie, Q.F. Cheng,

Fabrication of $\text{MnO}_2/\text{TiO}_2$ nano-tube arrays photoelectrode and its enhanced visible light photoelectrocatalytic performance and mechanism, *Sep. Purif. Technol.* 189 (2017) 193-203.

[14] A. Tokai, K. Okitsu, F. Hori, Y. Mizukoshi, Y. Nishimura, S. Seino, A. Iwase, One-pot preparation of Pd nanoparticles supported on graphene from Pd electrodes by discharge plasma in graphene suspension and its catalytic activity for hydrogenation of nitrobenzene, *Mater. Lett.* 199 (2017) 24-27.

[15] J.F. Bai, Y. Liu, X.H. Yin, H.T. Duan, J.H. Ma, Efficient removal of nitrobenzene by Fenton-like process with Co-Fe layered double hydroxide, *Appl. Surf. Sci.* 416 (2017) 45-50.

[16] A. Abdedayem, M. Guiza, F.J.R. Toledo, A. Ouederni, Nitrobenzene degradation in aqueous solution using ozone/cobalt supported activated carbon coupling process: A kinetic approach, *Sep. Purif. Technol.* 184 (2017) 308-318.

[17] Y. Zhang, X. Xie, W. Huang, S. Huang, Degradation of aniline by Fe^{2+} -activated persulfate oxidation at ambient temperature, *J. Cent. South Univ.* 20 (2013) 1010-1014.

[18] Z. Jing, S. Cao, T. Yu, J. Hu, Degradation Characteristics of Aniline with Ozonation and Subsequent Treatment Analysis, *J. Chem.* 2015 (2015) 1-6.

[19] M. Li, D. Zou, H. Zou, D. Fan, Degradation of nitrobenzene in simulated wastewater by iron-carbon micro-electrolysis packing, *Environ. Technol.* 32 (2011) 1761-1766.

[20] Z. Yang, Y. Ma, Y. Liu, Q. Li, Z. Zhou, Z. Ren, Degradation of organic pollutants

in near-neutral pH solution by Fe-C micro-electrolysis system, Chem. Eng. J. 315 (2017) 403-414.

[21] Y. Qin, L. Yu, S. Luo, W. Jiao, Y. Liu, Degradation of Nitrobenzene Wastewater via Iron/Carbon Micro-electrolysis Enhanced by Ultrasound Coupled with Hydrogen Peroxide, China. Pet. Process. Pe. 19 (2017) 72-81.

[22] Y. Han, H. Li, M. Liu, Y. Sang, C. Liang, J. Chen, Purification treatment of dyes wastewater with a novel micro-electrolysis reactor, Sep. Purif. Technol. 170 (2016) 241-247.

[23] S. Zhang, D. Wang, L. Zhou, X.W. Zhang, P.P. Fan, X. Quan, Intensified internal electrolysis for degradation of methylene blue as model compound induced by a novel hybrid material: Multi-walled carbon nanotubes immobilized on zero-valent iron plates (Fe-0-CNTs), Chem. Eng. J. 217 (2013) 99-107.

[24] X. Yang, Interior microelectrolysis oxidation of polyester wastewater and its treatment technology, J. Hazard. Mater. 169 (2009) 480-485.

[25] B. Lai, Y. Zhou, H. Qin, C. Wu, C. Pang, L. Yu, J. Xu, Pretreatment of wastewater from acrylonitrile-butadiene-styrene (ABS) resin manufacturing by microelectrolysis, Chem. Eng. J. 179 (2012) 1-7.

[26] K.P. Sang, H.C. Yang, Experimental investigation on mixed jet and mass transfer characteristics of horizontal aeration process, Int. J. Heat Mass Tran. 113 (2017) 544-555.

[27] S. Yang, D. Zheng, T. Ren, Y. Zhang, J. Xin, Zero-valent aluminum for reductive removal of aqueous pollutants over a wide pH range: Performance and mechanism

especially at near-neutral pH, Water Res. 123 (2017) 704-714.

[28] S. Chong, Y. Song, H. Zhao, G. Zhang, Enhanced degradation of nitrobenzene by combined ultrasonic irradiation and a zero-valent zinc catalyst, Desalin. Water Treat. 57 (2016) 23856-23863.

[29] L. Zhang, M. Wu, Y. Han, M. Liu, J. Niu, Structural parameter optimization for novel internal-loop iron-carbon micro-electrolysis reactors using computational fluid dynamics, Chin. J. Chem. Eng. (2018) <https://doi.org/10.1016/j.cjche.2018.08.001>.

[30] L. Tang, J. Tang, G. Zeng, G. Yang, X. Xie, Y. Zhou, Y. Pang, Y. Fang, J. Wang, W. Xiong, Rapid reductive degradation of aqueous p-nitrophenol using nanoscale zero-valent iron particles immobilized on mesoporous silica with enhanced antioxidation effect, Appl. Surf. Sci. 333 (2015) 220-228.

[31] J. Guo, L. Zhu, N. Sun, Y. Lan, Degradation of nitrobenzene by sodium persulfate activated with zero-valent zinc in the presence of low frequency ultrasound, J. Taiwan Inst. Chem. Eng. 78 (2017) 137-143.

[32] S.C. Jensen, S.B. Homan, E.A. Weiss, Photocatalytic Conversion of Nitrobenzene to Aniline through Sequential Proton-Coupled One-Electron Transfers from a Cadmium Sulfide Quantum Dot, J. Am. Chem. Soc. 138 (2016) 1591-1600.

[33] G. Allinson, F. Stagnitti, S. Colville, J. Hill, M. Coates, Growth of floating aquatic macrophytes in alkaline industrial wastewaters, J. Environ. Eng. 126 (2000) 1103-1107.

[34] X.A. Ning, W. Wen, Y. Zhang, R. Li, J. Sun, Y. Wang, Z. Yang, J. Liu, Enhanced dewaterability of textile dyeing sludge using micro-electrolysis pretreatment, J.

Environ. Manage. 161 (2015) 181-187.

[35] J. Zhang, S. Chen, X. Wang, Sustainable Treatment of Antibiotic Wastewater Using Combined Process of Microelectrolysis and Struvite Crystallization, *Water Air Soil Poll.* 226 (2015) 1-11.

[36] T. Li, T. Li, H. Xiong, D. Zou, Factors influencing hydroquinone degradation in aqueous solution using a modified microelectrolysis method, *Water Sci. Technol.* 71 (2015) 397-404.

[37] W. Jiao, Z. Feng, Y. Liu, H. Jiang, Degradation of nitrobenzene-containing wastewater by carbon nanotubes immobilized nanoscale zerovalent iron, *J. Nanopart. Res.* 18 (2016) 1-9.

[38] Y.P. Li, H.B. Cao, C.M. Liu, Y. Zhang, Electrochemical reduction of nitrobenzene at carbon nanotube electrode, *J. Hazard. Mater.* 148 (2007) 158-163.

[39] G. Richner, J.A. van Bokhoven, Y.M. Neuhold, M. Makosch, K. Hungerbuhler, In situ infrared monitoring of the solid/liquid catalyst interface during the three-phase hydrogenation of nitrobenzene over nanosized Au on TiO₂, *Phys. Chem. Chem. Phys.* 13 (2011) 12463-12471.

[40] F. Cases, F. Huerta, P. Garcés, E. Morallón, J.L. Vázquez, Voltammetric and in situ FTIRS study of the electrochemical oxidation of aniline from aqueous solutions buffered at pH 5, *J. Electroanal. Chem.* 501 (2001) 186-192.

[41] O.A. Anunziata, M.B. Gómez Costa, M.L. Martínez, Interaction of water and aniline adsorbed onto Na-AIMCM-41 and Na-ALSBA-15 catalysts as hosts materials, *Catal. Today* 133-135 (2008) 897-905.

- [42] Y. Liu, Aqueous p-chloronitrobenzene decomposition induced by contact glow discharge electrolysis, *J. Hazard. Mater.* 166 (2009) 1495-1499.
- [43] Z. Chen, Z. Wang, D. Wu, L. Ma, Electrochemical study of nitrobenzene reduction on galvanically replaced nanoscale Fe/Au particles, *J. Hazard. Mater.* 197 (2011) 424-429.
- [44] L. Jia-Tong, L. Yong-Sheng, S. Qing, H. Da-Qian, Z. Dan, J. Wen-Bao, The treatment of aniline in aqueous solutions by gamma irradiation, *J. Adv. Oxid. Technol.* 20 (2017) 1-11.
- [45] L. Carlos, D. Fabbri, A.L. Capparelli, A.B. Prevot, E. Pramauro, F.S. Einschlag, Intermediate distributions and primary yields of phenolic products in nitrobenzene degradation by Fenton's reagent, *Chemosphere* 72 (2008) 952-958.
- [46] Y. Su, A.S. Adeleye, Y. Huang, X. Sun, C. Dai, X. Zhou, Y. Zhang, A.A. Keller, Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and Au doped nZVI particles, *Water Res.* 63 (2014) 102-111.
- [47] S.B. Mortazavi, B. Ramavandi, G. Moussavi, Chemical reduction kinetics of nitrate in aqueous solution by Mg/Cu bimetallic particles, *Environ. Technol.* 32 (2011) 251-260.

Figure captions

Fig. 1. Percentage of (a) residual nitrobenzene concentration and (b) TOC in solution after microelectrolysis using ICE and FB reactors.

Fig. 2. Effect of the reaction time on the residual COD in solution and the BOD₅/COD value after microelectrolysis in the ICE reactor (initial concentration of nitrobenzene = 300 mg/L, Fe/C = 1:1, pH = 3.0, aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$).

Fig. 3. Effect of the aeration rate on (a) the residual concentration of nitrobenzene and (b) the COD removal efficiency and the BOD₅/COD value after microelectrolysis in the ICE reactor (initial concentration of nitrobenzene = 300 mg/L, Fe/C = 1:1, pH = 3.0, reaction time = 60 min).

Fig. 4. Effect of the initial concentration of nitrobenzene on (a) the residual concentration of nitrobenzene and (b) the COD removal efficiency and the BOD₅/COD value after microelectrolysis in the ICE reactor (reaction time = 60 min, aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$, Fe/C = 1:1, pH = 3.0).

Fig. 5. Effect of pH on (a) the residual concentration of nitrobenzene and (b) the COD removal efficiency and the BOD₅/COD value after microelectrolysis in the ICE reactor (reaction time = 60 min, aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$, initial concentration of nitrobenzene = 300 mg/L, Fe/C = 1:1).

Fig. 6. Effect of the Fe/C ratio on (a) the residual concentration of nitrobenzene and (b) the COD removal efficiency and the BOD₅/COD value after microelectrolysis

in the ICE reactor (reaction time = 60 min, aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$, initial concentration of nitrobenzene = 300 mg/L, pH = 3.0).

Fig. 7. UV-vis spectra of a nitrobenzene solution after being treated in the ICE reactor for different reaction times (aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$, initial concentration of nitrobenzene = 300 mg/L, pH = 3.0, Fe/C = 1:1).

Fig. 8. (a) FTIR spectra and (b) magnified versions of the spectra of raw and used activated carbons.

Fig. 9. TGA and DTA of raw and used activated carbon.

Fig. 10. Concentrations of intermediate ions at different reaction times (aeration rate = $5.0 \times 10^{-4} \text{ m}^3/\text{s}$, initial concentration of nitrobenzene = 300 mg/L, pH = 3.0, Fe/C = 1:1).

Fig. 11. Pathways for the degradation of nitrobenzene by the ICE technique.

Figures

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.