Reductive degradation of nitrobenzene in aqueous solution by zero-valent iron

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Abstract

The reductive degradation of nitrobenzene (NB) by zero-valent iron was investigated. Experimental results showed that the degradation of NB was influenced by pH and NB concentration. The optimum pH value was found to be 3.0 for the reductive degradation of NB in the tested pH ranges of 3.0–12.0. The formation rate of aniline, a major reductive product of NB, followed zero-order kinetics at various pH levels. Furthermore, GC/MS analysis showed that aniline, azobenzene and azoxybenzene were the reductive products of NB by zero-valent iron. With the analysis of the products with GC/MS and FTIR, possible reductive pathways of NB by zero-valent iron were suggested.
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1. Introduction

Nitrobenzene (NB), a carcinogenic pollutant, is widely used in the production of different types of products, such as dyes (Sarasa et al., 1998; Contreras et al., 2001), explosives and pesticides (Rodriguez et al., 2002). Even at low concentrations, NB may present high risks to environment (Bhatkhande et al., 2003). The electron-deficient character of the nitro-group prevents mineralization of NB by microorganisms (van der Zee et al., 2001). Therefore, conventional biological treatment processes are not effective for the treatment of NB-rich wastewaters (Nielsen and Christensen, 1994). During the last two decades, various advanced oxidation processes, such as ozonation and O_3/UV processes

(Latifoglu and Gurol, 2003), photocatalysis (Maldotti et al., 2000), photoassisted Fenton oxidation (Rodriguez et al., 2000), supercritical oxidation (Arslan-Alaton and Ferry, 2002) and other methods (Nomiya et al., 2001) have been applied for the degradation of NB-rich wastewaters. However, these methods are either expensive or ineffective for the treatment of NB-containing wastewaters.

In recent years, zero-valent iron has been intensively studied for its ability to reduce organic pollutants (Johnson et al., 1996; Cheng and Wu, 2000; Antoine, 2001; Ghauch, 2001) and nitrate (Huang et al., 1998). Elemental iron (Fe^0) and dissolved Fe^{2+} form a redox couple that has a standard reduction potential of -0.440 V (Cheng and Wu, 2000). Elemental iron has been regarded as a suitable donor of electrons for the in situ remediation of contaminated groundwater and soil (Cheng and Wu, 2000; Ghauch et al., 2001). Zero-valent iron has been used for the reduction of halogenated organic compounds (Johnson et al., 1996), nitroaromatic

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compounds (Agrawal and Tratnyek, 1996), pesticides (Antoine, 2001), and explosive-contaminated soil (Singh et al., 1998).

Despite extensive research and applications of Fe^0 for the remediation of light-contaminated ground water or soil, few studies have been conducted on high-polluted wastewaters by using elemental iron reduction. However, in several types of NB-containing industrial wastewaters, NB is often present at a concentration of several mMs (Sarasa et al., 1998; van der Zee et al., 2001; Rodriguez et al., 2002), much higher than that in groundwater. Information about the reductive degradation of NB at high concentrations in aqueous solutions by Fe^0 is still sparse, especially the identification of the reductive products and the elucidation of the degradation pathways. Therefore, in this study, the reductive degradation of NB at a level of several mMs was investigated in order to explore the feasibility of applying elemental iron reduction for NB-rich wastewater treatment. The effects of pH and NB concentration on the reductive degradation of NB were evaluated, and the formation kinetics of reductive products was determined. Furthermore, Fourier transform infrared spectroscopy (FTIR) and GC/MS measurements were carried out to identify the reductive products of NB and to elucidate the reduction pathways of NB by zero-valent iron.

2. Experimental

2.1. Chemicals

Nitrobenzene, aniline, hydrochloric acid, sodium hydroxide and ethyl acetate, all purchased from Shanghai Chemical Reagent Company, were of analytical reagent grade, and were used without further purification except that ethyl acetate was redistilled prior to use. Element iron particles were obtained from Hefei Iron Company, China. Double-distilled water was used throughout the experiment.

Zero-valent iron particles were prepared by sieving raw particles through a 20-mesh screen. Thereafter, they were washed with 10% NaOH solution for 20 min to remove lipids on the surface of particles, and later with 3% HCl solution for 30 min. Finally, the iron particles were washed with double-distilled water for 30 min to remove residual HCl and Fe^{2+}.

2.2. Reductive experiments

One hundred and fifty ml aqueous solution containing a known amount of NB and 5 g of pre-treated iron was placed in sealed 250-ml erlenmeyers. The pH of the NB solution was adjusted to required value with HCl (0.1 M) or NaOH (0.1 M) solutions. The test erlen-

meyers were shaken at 120 rpm using a horizontal vibrator (WHY-2, Guosheng Instrument Corp., Jiangsu) operated at 30 °C. At pre-determined time intervals, 15-ml samples were withdrawn from the erlenmeyer and were filtered through a 0.22 μm Millipore filter prior to analysis.

2.3. Analytical methods

The UV–VIS absorption spectra of NB solutions were monitored by a UV–VIS spectrophotometer (UV-2401PC, Shimadzu Co.). The measurement of NB and aniline was carried out using an HPLC (Model 1100, Agilent Co.) with a UV detector and a 5 μm × 4 mm × 250 mm Hypersil ODS column. The mobile phase was the methanol/water mixtures in the proportion of 70/30 (v/v).

Reductive products of NB were determined using FTIR (Magna-IR 750, Nicolet Instrument Co., USA), and an Agilent 6890 GC system coupled to a GCT-MS (Micromass Ltd., UK) through an electron impact interface. Prior to FTIR and GC/MS analysis, sample solutions were extracted with redistilled ethyl acetate. The extractions were merged and dried with anhydrous magnesium sulfate, then were concentrated under reduced pressure. Extractions of 0.2 μl were subjected to GC/MS determination. Chromatographic measurements were performed with a capillary column DB-5 (30 m × 0.25 mm × 0.25 μm). Ultra pure helium was used as the carrier gas with a flow rate of 1 ml min^{-1}.

3. Results and discussion

3.1. UV spectra of NB solutions

Fig. 1 illustrates the typical UV–VIS spectra of the raw NB solution, the treated samples after 0.3-, 1.6- and
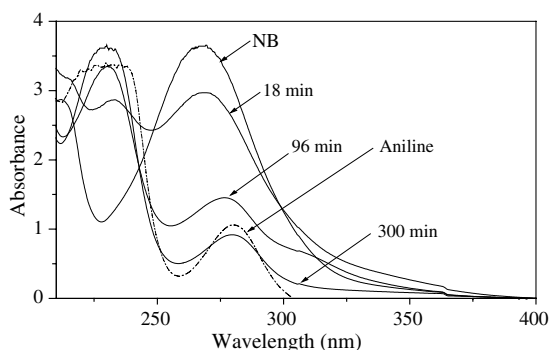

Fig. 1. UV absorption spectra of the raw NB, the treated samples and aniline. Initial NB concentration: 1.63 mM; aniline concentration: 1.00 mM; pH: 3.0.

5.0-h reaction, and the aniline solution. The characteristic absorbance band of NB is at 270 nm.

As shown in Fig. 1, the absorbance band at 270 nm decreased and shifted to a longer wavelength after 0.3-h reaction, whereas an absorbance band at 229 nm was formed. With increased reaction time to 1.6 and 5.0 h, the band at 270 nm decreased further, whereas the band at 229 nm increased with reaction time. The evolution of the absorbance spectra in Fig. 1 demonstrates the degradation of NB and the formation of reductive products. Since the characteristic absorption bands of aniline are at 229 and 280 nm, the absorbance spectra in Fig. 1 suggest that aniline was one of predominant reductive products of NB by zero-valent iron.

3.2. Effects of pH on NB degradation

Fig. 2 shows the influence of pH on the reduction of NB and the formation of aniline at an initial NB concentration of 1.63 mM. The mM NB removed decreased with increasing pH. For instance, after 45-min reaction, NB of 1.23 mM was removed at pH 3.0, while the corresponding value was 0.17 mM at pH 12.0. The mM aniline formed also decreased with the increase of pH, 0.71 mM at pH 3.0 and 0.08 mM at pH 12.0. This can be interpreted by the changes of the reduction potential of reaction, $Fe^0 - 2e = Fe^{2+}$, caused by the variation of pH. With the increase of hydrogen ion concentration, i.e., the decrease of pH, the Fe^{2+} concentration in solutions increased. According to the Nernst Equation, the reduction potential of reaction ($Fe^0 - 2e = Fe^{2+}$) increased. As a result, both the NB removed and aniline formed increased as the solution pH decreased.

3.3. Effects of NB concentration on NB degradation

The effects of the initial NB concentrations from 0.41 to 2.03 mM on the mM NB removed and the mM aniline formed are illustrated in Fig. 3. The mM NB re-
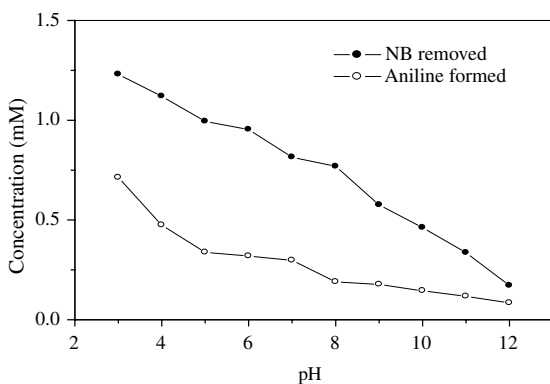

Fig. 2. Removed NB and formed aniline at various pH levels. Initial NB concentration: 1.63 mM; reaction time: 45 min.
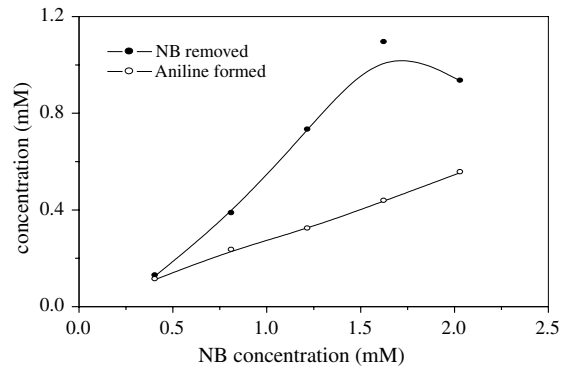

Fig. 3. Removed NB and formed aniline at various initial NB concentrations. pH: 4.0; reaction time: 45 min.

moved increased with increasing NB concentration, from 0.13 at 0.41 mM to 1.09 at 1.60 mM, but decreased with a further increase in initial NB concentration to 0.93 at 2.03 mM. On the other hand, the mM aniline formed increased with increasing NB concentration, as shown in Fig. 3. The reasons for the different changing patterns of NB and aniline are not clear, and should be explored in further studies.

3.4. Kinetic analysis of productive rate of aniline at various pH values

The reductive degradation of organics by zero-valent iron has been modeled using an empirical formula analogous to the Michaelis–Menten equation as follows (Johnson et al., 1996; Nam and Tratnyek, 2000):

$$-\frac{\mathrm{d}C_t}{\mathrm{d}t} = \frac{V_m C_t}{K_{1/2} + C_t} \tag{1}$$

where C_t (mM) is the NB concentration at reaction time t (min), V_m (mM min^{-1}) is the maximum reaction rate, and $K_{1/2}$ (mM), defined as C_t at $V_m/2$, reflects the affinity of the metal surface for the organic reactants (Nam and Tratnyek, 2000). Previous studies have demonstrated that $K_{1/2}$ is constant for a particular substrate, presumably because all iron tends to be coated with similar oxides (Johnson et al., 1996; Scherer et al., 1998), but V_m varies due to different concentrations of reactive sites (Scherer et al., 1998). However, in all the previous studies, this model has been employed to describe the reductive degradation rate of reactants (Johnson et al., 1996; Scherer et al., 1998; Nam and Tratnyek, 2000), not used to model the formation rate of reductive products. In the present work, aniline was found to be the predominant reductive product of NB. On the other hand, as shown in Fig. 4, aniline did not suffer significant degradation as it was exposed to Fe^0. This phenomenon was also observed by Hung et al. (2000).
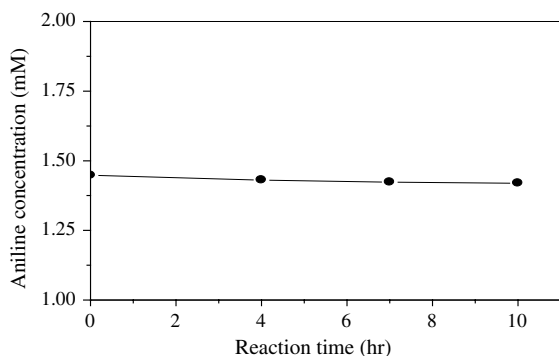
Fig. 4. Aniline degradation by Fe^0. Initial aniline concentration: 1.45 mM; pH: 3.0.

Eq. (1) was tested to find out whether it could be used to describe the aniline formation rate as following:

$$\frac{dC'_t}{dt} = \frac{V_m C_t}{K_{1/2} + C_t} \quad (2)$$

where C'_t (mM) is the aniline concentration at reaction time t.

If $C_t \gg K_{1/2}$, $K_{1/2} + C_t \approx C_t$, Eq. (2) is modified into the zero-order equation (Eq. (3)), and the apparent zero-order rate constant (k_{app}) equals to V_m.

$$\frac{dC'_t}{dt} = V_m \quad (3)$$

Eq. (3) was integrated and resulted in:

$$C'_t = V_m t \quad (4)$$

If plotting C'_t against t, a straight line could be obtained with a slope of V_m. The data in Table 1 are the results calculated from Eq. (4). The high values of the correlation coefficients in Table 1 suggest that the aniline formation was well described by zero-order kinetics. Table 1 shows that V_m decreased from 0.016 mM min^{-1} at pH 3.0–0.001 mM min^{-1} at pH 12.0. This clearly indicates that pH had a significant influence on V_m. Enhanced

Table 1
The maximum aniline formation rates (V_m) at various pH values (Initial NB concentration: 1.63 mM)

pH	V_m (mM min^{-1})	R
3.0	0.016	0.9883
4.0	0.012	0.9959
6.0	0.010	0.9895
7.0	0.010	0.9959
9.0	0.004	0.9970
10.0	0.004	0.9877
11.0	0.002	0.9985
12.0	0.001	0.9919

corrosion of the iron at lower pH values might be the reason for the observed pH dependence (Dombek et al., 2001). This warrants a further verification study.

3.5. FTIR analysis of the reductive products of NB

The FTIR spectra of NB and its reductive products were illustrated in Fig. 5. The asymmetrical stretching vibration (v_{as}, 1525 cm^{-1}) and symmetrical stretching vibration (v_s, 1348 cm^{-1}) of nitro-group were strong in the spectrum of raw NB (spectrum a), whereas those in spectra b (60-min reaction) and c (180-min reaction) were substantially weak, indicating the elimination of nitro-group of NB. On the other hand, the peaks at wavenumbers of 3432 and 3356 cm^{-1} in spectra b and c were much stronger than those in spectrum a. These two peaks are attributed to the asymmetrical stretching vibration (v_{as}) and symmetrical stretching vibration (v_s) of amido-group, respectively. This suggests that there was amido-group in the reductive products.

3.6. GC/MS analysis of the reduction products of NB

The complete reduction of nitrobenzene ($ArNO_2$) to aniline ($ArNH_2$) by Fe^0 involves six electrons, as proposed by Scherer et al. (2001), and can be written as:

$$ArNO_2 + 3Fe^0 + 6H^+ \rightarrow ArNH_2 + 3Fe^{2+} + 2H_2O \quad (5)$$

Eq. (5) represents the sum of several two-electron half-reactions: the oxidation of Fe^0 and the sequential reduction of $ArNO_2$ to nitrosobensene (ArNO), phenyl hydroxylamine (ArNHOH), and aniline:
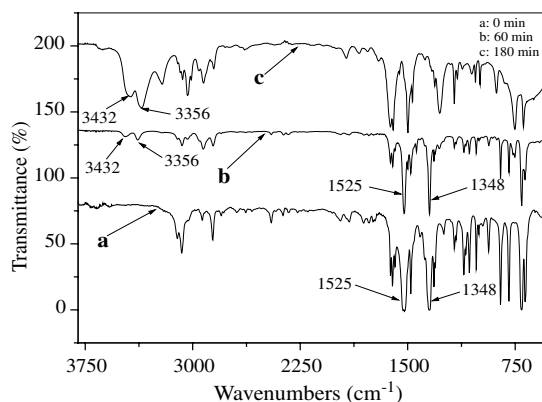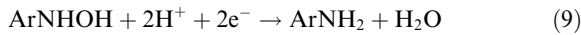
$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (6)$$

$$ArNO_2 + 2H^- + 2e^- \rightarrow ArNO + H_2O \quad (7)$$

$$ArNO + 2H^+ + 2e^- \rightarrow ArNHOH \quad (8)$$

Fig. 5. FTIR spectra of NB and its reductive products. Initial NB concentration: 1.63 mM; pH: 3.0; reaction time: 120 min.

$$ArNHOH + 2H^+ + 2e^- \rightarrow ArNH_2 + H_2O \qquad (9)$$

In order to further clarify the reductive pathways of NB by Fe^0, the sample after 120-min reaction was subjected to GC/MS determination. Fig. 6 shows the GC/MS spectra of the sample at pH of 3.0, while Fig. 7 shows the GC spectra of the sample at pH of 5.0 (MS spectra were not shown here). Comparison between Figs. 6 and 7 suggests the compositions of the degradation products at pH 3.0 were same as those at pH 5.0, although the relative abundances of the products were different. The peaks with retention times of 2.53 min (a), 6.65 min (b), 7.88 min (c) in Fig. 6, correspondingly to 2.55 min (a'), 6.67
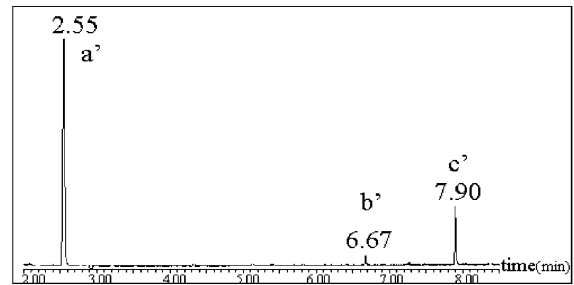

Fig. 7. GC spectra of the reductive products of NB by Fe^0. Initial NB concentration: 1.63 mM; pH: 5.0; reaction time: 120 min.
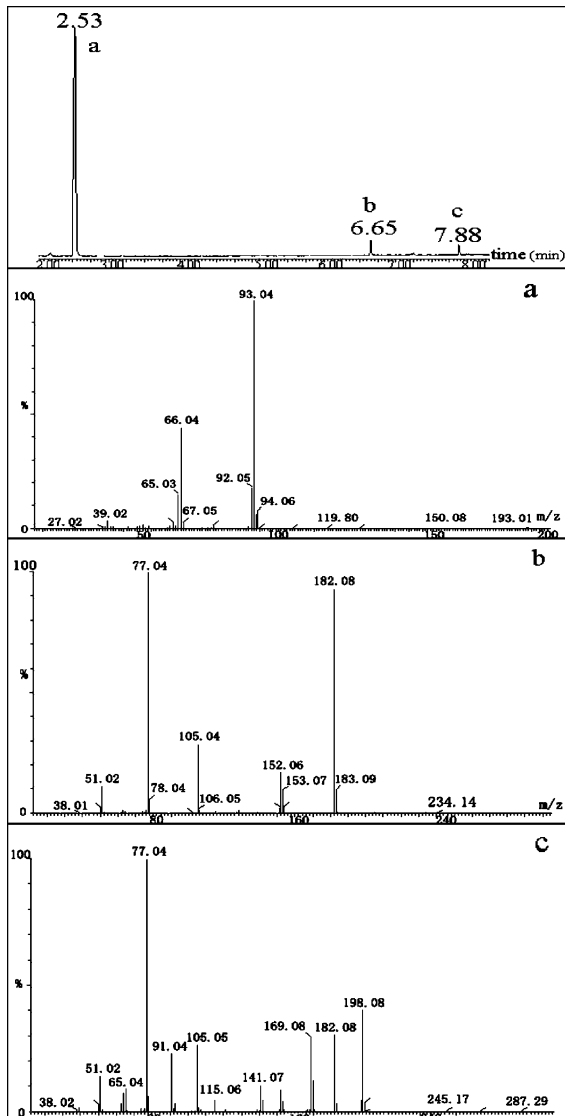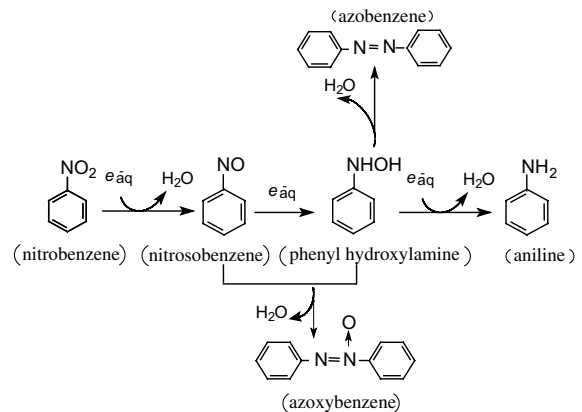

Fig. 8. Pathways of reductive degradation of NB by Fe^0.

min (b'), 7.90 min (c') in Fig. 7, were identified as aniline (m/z 93.0417), azobenzene (m/z 182.0797), and azoxybenzene (m/z 198.0772), respectively, by MS spectra.

With the product analysis by FTIR and GC/MS, possible reductive pathways of NB by zero-valent iron were proposed and illustrated in Fig. 8. Hydrated electrons released from the reaction ($Fe^0 - 2e = Fe^{2+}$) deoxidized NB to nitrosobenzene; via a further reduction, aniline was formed; the combination of reactive intermediates during the deoxidization processes produced azobenzene and azoxybenzene.

It is well known that the biodegradability of aniline is much higher than that of NB (Nielsen and Christensen, 1994). Therefore, after the reductive degradation by zero-valent iron, NB-laden wastewaters would be readily treated in a subsequent biological process.

4. Conclusions

This study demonstrated that the reductive degradation of NB by zero-valent iron was feasible. The optimum pH value was found to be 3.0 for the reductive

Fig. 6. GC/MS spectra of the reductive products of NB by Fe^0. Initial NB concentration: 1.63 mM; pH: 3.0; reaction time: 120 min.

degradation of NB in the tested pH ranges of 3.0–12.0. Both mM NB removed and mM aniline formed increased with the decrease of solution pH. The initial NB concentration had a significant effect on mM NB removed and mM aniline formed. Furthermore, the aniline formation rate was well described by zero-order kinetics at various pH levels, and the maximum reaction rate decreased as pH increased from 3.0 to 12.0. The GC/MS analysis shows that aniline, azobenzene, azoxybenzene were the main reductive products of NB by zero-valent iron. With the product analysis, the reductive pathways of NB by zero-valent iron were proposed.

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