Effective degradation of para-chloronitrobenzene through a sequential treatment using zero-valent iron reduction and Fenton oxidation

Chen Le, Junqian Liang, Jinhua Wu, Ping Li, Xiangde Wang, Nengwu Zhu, Pingxiao Wu and Bo Yang

ABSTRACT

In this study, zero-valent iron (ZVI) was used to pretreat para-chloronitrobenzene (p-CNB), and the major product was para-chloroaniline (p-CAN). By adding H2O2 directly, further p-CAN degradation can be attributed to Fenton oxidation because ferrous ions (Fe2+) released during the ZVI corrosion could be used as an activator for H2O2 decomposition. In the reduction process, the reduction efficiency of p-CNB as well as Fe2+ concentration increased with increasing iron dosage and decreasing solution pH. Under the optimal conditions, 25 mg L⁻¹ of p-CNB could be transformed in 3 h when initial solution pH was 3.0 and ZVI dosage was 2.0 g L⁻¹. A sufficient amount of Fe2+ (50.4 mg L⁻¹) was obtained after the above reaction to activate H2O2. In the Fenton process, the oxidation of p-CAN was also more effective in acidic conditions and it increased with increasing H2O2 concentration. The control experiments showed that the sequential treatment was more effective than Fenton oxidation alone in treating p-CNB wastewater since the removal rate of total organic carbon (TOC) was improved by about 34%. It suggested that the amino function group is more susceptible to oxidative radical attack than the nitro function group. Therefore, sequential treatment using zero-valent iron reduction followed by Fenton oxidation is a promising method for p-CNB degradation.

Key words | Fenton process, para-chloronitrobenzene, sequential treatment, zero-valent iron oxidation

INTRODUCTION

para-chloronitrobenzene (p-CNB) is widely used in the production of explosives, dyes, pharmaceuticals and other industrial chemicals (Guo et al. 2009). It has been reported that p-CNB is a toxic, mutagenic and non-biodegradable compound; and it can cause methemoglobinemia in humans. Besides, p-CNB has been proven to be an inherent immunotoxic effect on mice (Li et al. 1998). Disposal of p-CNB without any treatment poses a serious concern on the safety and health of humans and ecological receptors (Zhen et al. 2006). Therefore, in many countries, p-CNB has been listed as a priority contaminant because of its great potential risk. Concern about the p-CNB as a hazardous contaminant has led to varied technologies for the treatment of p-CNB wastewater (Lin et al. 2011).

Some advanced oxidation processes such ozonation, contact glow discharge electrolysis and heterogeneous catalytic oxidation have been applied for the treatment of p-CNB (Hofmann et al. 2005; Shen et al. 2008; Liu 2009). However, owing to the electron-withdrawing nature of chloro and nitro group on the benzene ring of p-CNB, the above oxidation methods are not effective for p-CNB degradation (Kuhlmann & Hegemann 1997). Moreover, when advanced oxidation process was used for p-CNB degradation directly, the major intermediates were nitroaromatic compounds (Shen et al. 2008; Liu 2009). The nitro function group still existed in these compounds and they were resistant to further degradation. Although some anaerobic microorganisms are able to reduce p-CNB to para-chloroaniline (p-CAN), additional organic cosubstrate was often required as electron donor in these processes, which might far exceed the stoichiometric requirements (Heijman et al. 1993; Mu et al. 2009). In addition, p-CAN is also a recalcitrant and toxic contaminant, and further treatment is required to completely mineralize p-CAN.
In recent years, zero-valent iron (ZVI) has been widely used in the treatment of nitro aromatics and azo dyes in wastewater for its inexpensive, reliable and innoxious properties (Stieber et al. 2008; Park et al. 2009; Moon et al. 2011). ZVI is an effective reductant (redox potential $E^0 = -0.44$ V) under anoxic condition. Azo dyes are reduced by ZVI to colorless aromatic amines (Lin et al. 2008). p-CNB can be transformed to p-CAN by ZVI as below (Agrawal & Tratnyek 1995):

$$p\text{-CNB} + 6\text{H}_2\text{O} + 3\text{Fe}(0) \rightarrow p\text{-CAN} + 3\text{Fe}^{2+} + 6\text{OH}^-$$

$$k = 0.0336 \text{ min}^{-1}$$

(1)

The reaction consists of a six-electron reduction of the $p$-CNB to the $p$-CAN through para-chloro-nitrosobenzene and para-chloro-hydroxylaminoanalogues (Schultz & Grundl 2000). One of the advantages of reaction (1) is that the resulting $p$-CAN is more susceptible to oxidative degradation than $p$-CNB because the electron withdrawing nitro function group is transformed to amino function group (Sánchez et al. 2002; Oh et al. 2003; Oh et al. 2010). In addition, $\text{Fe}^{2+}$ generated during the corrosion of iron can activate $\text{H}_2\text{O}_2$ to form hydroxyl radicals, which are effective oxidants for the degradation of organic pollutants to less harmful compounds, water and inorganic salts (Emami et al. 2010).

Based on the above consideration, we selected ZVI as the reduction reagent to transfer $p$-CNB to $p$-CAN. Then, Fenton oxidation process was applied for $p$-CAN degradation by adding $\text{H}_2\text{O}_2$ directly, in which the $\text{Fe}^{2+}$ generated from iron corrosion was utilized as the activator. In the reduction process, the effects of initial pH and iron dosage on $p$-CNB reduction were studied. In the Fenton process, the influences of solution pH and $\text{H}_2\text{O}_2$ concentration on $p$-CAN degradation were also explored.

**MATERIALS AND METHODS**

**Chemicals**

$p$-CNB and $p$-CAN were purchased from Aladdin-reagent Company (Shanghai, China). ZVI powder (97%, average grain size 0.05 mm), $\text{HCl}$, $\text{NaOH}$ and $\text{H}_2\text{O}_2$ were purchased from Guangzhou chemical reagent factory. The iron powder was used without any pretreatment. The $p$-CNB solution was prepared by dissolving required amount of $p$-CNB in deionized water and the initial pH value was adjusted to 7.0 by $\text{HCl}$ or $\text{NaOH}$. All the chemicals used in the experiments were of analytical grade.

**Experimental procedures**

$p$-CNB reduction experiments were conducted in 300 mL conical flasks containing 250 mL of 25 mg L$^{-1}$ $p$-CNB solution. After 0.25 g ZVI was added, the conical flask was capped with a rubber plug and agitated in an isothermal shaker (20 ± 1°C). The effects of initial solution pH and ZVI dosage on $p$-CNB reduction were investigated. The initial and final pH values were monitored. The ferrous ion concentration was also determined after the reaction.

Prior to the Fenton oxidation process, the iron powder was separated and the solution containing $p$-CAN was filtered through 0.45 μm membrane. The pH value of the solution was adjusted 3.0 by the addition of $\text{HCl}$ or $\text{NaOH}$. After that, $\text{H}_2\text{O}_2$ was added directly into the solution and then it was activated by $\text{Fe}^{2+}$ generated from iron corrosion. The sample solution was mixed with excessive sodium nitrite to quench the radical reaction and then analyzed with HPLC. Each experiment was run in duplicate, and average value was shown in this study.

**Analytical methods**

Both $p$-CNB and $p$-CAN were identified by a HPLC (Hitachi, L-2000), analysis parameters were as follows: the reversed-phase column of Luna 5u C18, the mobile phase of MeOH/$\text{H}_2\text{O}$ (50/50 v/v) with the flow rate of 1.0 mL min$^{-1}$, an injection valve fitted with 20 μL sample loop. The wavelength used in HPLC measurements was determined at 270 nm. The pH values were monitored by a pH meter (PHS-3C, Sanxin, China). The concentration of $\text{Fe}^{2+}$ was determined by the o-phenanthroline colorimetric method. Total organic carbon (TOC) concentration was measured by a TOC analyzer (Shimadzu TOC-5000).

**RESULTS AND DISCUSSION**

**Effect of iron dosage on $p$-CNB reduction**

The effect of iron dosage on $p$-CNB reduction was investigated as shown in Figure 1(a). The reduction rate of $p$-CNB increased with an increase of iron dosage. When iron dosage was 2.0 g L$^{-1}$, the $p$-CNB could be transformed.
The increase of iron dosage provided more active sites for the adsorption and reduction of target contaminants (Fang et al. 2011). Matheson and Tratnyek had reported similar results in which pollutant transformation by ZVI possessed a surface-mediated mechanism and the amount of iron was an important factor influencing the reaction rate (Matheson & Tratnyek 1994). However, increase of iron dosage from 2 to 4 g L$^{-1}$/C$\text{ Initial}$ did not remarkably improve the p-CN$\text{B}$ reduction. A possible explanation may be that iron reactivity increased nearly linearly with iron dosage, but it reached a plateau at higher iron dosage. The reaction rate was controlled by other factors such as mixing rate at this time (Cwiertny & Roberts 2005). The reduction of p-CN$\text{B}$ fit the pseudo-first-order kinetic model, $C = C_0 \exp(-kt)$, where $C$ is the p-CN$\text{B}$ concentration at time $t$, $C_0$ is the initial p-CN$\text{B}$ concentration, and $k$ is the observed rate constant of pseudo-first-order reaction. As shown in Table 1, $k$ under four different ZVI dosage (0.5, 1.0, 2.0 and 4.0 g L$^{-1}$) were determined as 0.0729, 0.2052, 0.824 and 1.0478 h$^{-1}$, respectively. Since p-CN$\text{B}$ was completely transformed in 6 h when iron dosage was 2 g L$^{-1}$, the initial iron dosage of 2 g L$^{-1}$ was selected for further experiments.

**Effect of initial pH on p-CN$\text{B}$ reduction**

The effect of initial pH on p-CN$\text{B}$ reduction was studied by changing the initial solution pH from 3.0 to 11.0. As shown in Figure 1(b), when initial pH value decreased from 11.0 to 3.0, the p-CN$\text{B}$ reduction rate increased from 0.5 to 99.5% within 3 h. It is apparent that the reduction process was
highly pH-dependent. As shown in Table 1, $k$ under five different initial pH values (3.0, 5.0, 7.0, 9.0 and 11.0) were determined as 1.7061, 1.0948, 0.824, 0.0802 and 0.0022 h$^{-1}$, respectively. This can be explained that the acid condition promoted the corrosion of iron and consequently accelerated the transformation of p-CN (Lin et al. 2008). Furthermore, lower pH may eliminate ferrous hydroxide and other protective layers accumulating on the surface of ZVI and generate more fresh active sites (Wang et al. 2006).

In the reduction process, p-CN can readily be reduced to p-CAN. This reduction of p-CN leads to less toxic aromatic amine. On molar basis, about 95, 92 and 90% p-CAN recovery were observed at initial pH values of 3, 5 and 7, respectively (data not shown). It indicated that p-CAN was the main product. The difference of p-CN recovery at initial pH 3, 5 and 7 was likely because some p-CN and p-CAN might be removed by adsorption onto the iron surface or co-precipitation with iron complexes at higher pH condition (Noubactep 2009).

As described in Table 1, in acidic and neutral condition, the solution pH increased to 6.7, 7.1 and 8.1 from initial pH 3.0, 5.0, and 7.0, respectively. It was likely due to the consumption of hydrogen ions during the reductive reaction of p-CN by ZVI. Shih et al. also reported that the pH values increased from 5.0 to 6.7 in 30 min for the reduction of decabrominated diphenyl ether using ZVI (Shih & Tai 2010). In alkaline condition, the solution pH only increased to 9.2 and 11.1 from initial pH 9.0 and 11.0, individually. Because the iron corrosion rate was low in alkaline condition, fewer hydroxyl ions were generated. Thus, the solution pH increased slightly after the reaction.

Besides, in acidic condition, more Fe$^{2+}$ released during iron corrosion, the final Fe$^{2+}$ concentration increased from 1.2 to 50.4 mg L$^{-1}$ when initial solution pH decreased from 11.0 to 3.0 (Table 1). Since a sufficient amount of Fe$^{2+}$ was required in the following Fenton process, the effluent of initial pH 3.0 was selected for further Fenton experiments.

**Effect of solution pH on p-CAN oxidation**

It is well established that the solution pH plays a significant role in Fenton process. As shown in Figure 2(a), when solution pH value decreased from 7.0 to 3.0, the oxidation rate of p-CAN increased from 36.6% to 100% within 7 min. The possible explanation is that when solution pH value was above 3.5, iron species could precipitate to form iron hydroxide (Fe(OH)$_3$) or hydrous ferric oxide (Fe$_2$O$_3$$\cdot$$n$H$_2$O), which have a relatively weak ability to activate H$_2$O$_2$ to produce hydroxyl radicals (Kang et al. 2002). In addition, H$_2$O$_2$ is stable in the pH range of 3–4, but it might decompose to produce O$_2$ instead of hydroxyl radicals when the pH increases (Chen et al. 2010). Based on the above results, pH 3.0 was selected as the optimum pH for further experiments.

**Effect of H$_2$O$_2$ concentration on p-CAN oxidation**

Figure 2(b) depicts the effect of initial H$_2$O$_2$ concentration on the p-CAN oxidation. When initial H$_2$O$_2$ concentration increased from 0.4 to 2 mM, the oxidation rate of p-CAN increased from 66.4 to 100% within 7 min. More hydroxyl radicals were available to oxidize p-CAN when H$_2$O$_2$ dosage enhanced. However, when H$_2$O$_2$ concentration exceeded 2 mM, no significant change of the oxidation efficiency was observed. It is probably because the high-concentration H$_2$O$_2$ may act as a hydroxyl radical scavenger.

![Figure 2](https://iwaponline.com/wst/article-pdf/64/10/2126/444088/2126.pdf)
Degradation of p-CN and p-CAN by Fenton process

Control experiments were conducted to evaluate the feasibility of applying a coupling process between ZVI reduction and Fenton oxidation to degrade p-CN. Fenton process was employed to treat the same concentration (0.159 mM) of p-CN and p-CAN, corresponding to 25 and 20.3 mg L⁻¹ for p-CN and p-CAN, respectively. The initial solution pH was adjusted to 3.0. And the initial concentrations of Fe²⁺ and H₂O₂ were 50 mg L⁻¹ and 2 mM, individually. As illustrated in Figure 3, the oxidation rate of p-CAN was faster than that of p-CN. p-CAN was completely degraded in 5 min, while 83.4% of p-CN was removed in 7 min. This is because the amino function group is more susceptible to oxidative radical attack than nitro function group (Oh et al. 2010). In addition, the removal rate of TOC for p-CAN was 75.7%, higher than that of p-CN (41.6% TOC removal). The relative low removal rate of TOC in p-CN solution may due to the formation of some recalcitrant intermediate products during the oxidation process. These products might be nitrophenols, dinitrophenols, chloronitrophenols and so on, they were resistible to the attack of hydroxyl radical because the electron-withdrawing nitro group still exist (Shen et al. 2008; Liu 2009). So converting the nitro group to amino group on p-CN molecule can promote the degradation efficiency of the subsequent Fenton reaction. Oh et al. also reported the similar result that the method of iron pretreatment improved the removal rate of TOC by approximately 20% and 60% in 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) wastewater, respectively (Oh et al. 2003).

CONCLUSIONS

Sequential treatment of p-CN (reductive transformation followed by oxidative degradation) was investigated in this study. ZVI was used for the pretreatment of p-CN and the major product was p-CAN. The acidic condition and higher iron dosage were favorable for p-CN reduction. After pretreatment with ZVI, H₂O₂ was added to mineralize p-CAN and the process follows Fenton oxidation, in which Fe²⁺ generated from iron corrosion was utilized as the activator. In the Fenton oxidation process, the degradation efficiency of p-CAN was also more effective in acidic condition; it increased with higher H₂O₂ concentration. In addition, the control experiments demonstrated that transformation of p-CN to p-CAN prior to Fenton process can improve the removal rate of TOC by about 34%. This study indicates that the sequential treatment using zero-valent iron reduction followed by Fenton oxidation is a promising method for removing p-CN in contaminated water.

ACKNOWLEDGEMENTS

The authors would like to thank National Natural Science Foundation of China (50708039), the National High-Tech Research and Development Program of China (863 Program; Grant 2009AA065302), the Fundamental Research Funds for the Central Universities (2009zzm0202, 2009zz0073, and 2009zz0048), Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP 20070561011) and Guangdong Provincial Natural Foundation for Science (05300188).
REFERENCES


First received 15 May 2011; accepted in revised form 3 August 2011