Effects of common dissolved anions on the reduction of para-chloronitrobenzene by zero-valent iron in groundwater

C. Le, J. H. Wu, S. B. Deng, P. Li, X. D. Wang, N. W. Zhu and P. X. Wu

ABSTRACT

Batch tests were conducted to evaluate the influences of several common dissolved anions in groundwater on the reduction of para-chloronitrobenzene (p-CNB) by zero-valent iron (ZVI). The results showed that p-CNB reduction was enhanced by both Cl\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}. HCO\textsubscript{3}\textsuperscript{-} could either improve or inhibit p-CNB reduction, depending on whether the mixing speed was intense enough to rapidly eliminate Fe–carbonate complex deposited on ZVI surface. Above a concentration of 100 mg L\textsuperscript{-1}, NO\textsubscript{3}\textsuperscript{-} increased the p-CNB reduction rate. The reduction rate by ClO\textsubscript{4}\textsuperscript{-} decreased because the ClO\textsubscript{4}\textsuperscript{-} competed with p-CNB for electrons. The p-CNB reduction was inhibited by PO\textsubscript{4}\textsuperscript{3-}, SiO\textsubscript{3}\textsuperscript{2-} and humic acid, in the order humic acid > PO\textsubscript{4}\textsuperscript{3-} > SiO\textsubscript{3}\textsuperscript{2-}, since these ions could form inner-sphere complexes on iron surface. The reaction even ceased when the ion concentrations were greater than 4, 0.5, and 30 mg L\textsuperscript{-1}, respectively. The results indicated that common dissolved anions in groundwater should be taken into account when ZVI is applied for contaminated groundwater remediation.

Key words | anions, para-chloronitrobenzene, reduction, zero-valent iron

INTRODUCTION

para-chloronitrobenzene (p-CNB) is widely used in the production of explosives, pesticides, dyes, pharmaceuticals and other industrial chemicals (Shen et al. 2008). It is considered to be more recalcitrant than other aromatics due to the electron-withdrawing character of chloro and nitro groups on the aromatic ring. Annually, a significant amount of p-CNB is released into groundwater owing to its wide application and improper disposal. Because of its high toxicity, chemical stability, and serious environmental risks, p-CNB has been listed as an environmental priority pollutant by US EPA and China SEPA (Guo et al. 2009).

In recent years, zero-valent iron (ZVI) has been extensively used in the treatment of chlorinated aromatics, chlorinated aliphatics, nitro aromatics, azo dyes, nitrate, and heavy metals for its inexpensive, reliable, and non-toxic properties (Chen et al. 2001; Stieber et al. 2008; Park et al. 2009). Permeable reactive barriers (PRB) using ZVI as a reactive medium for the treatment of contaminated groundwater have been proven to be a successful remediation technology. Reduction of p-CNB by ZVI is a surface-mediated process, in which ZVI donates two electrons accompanied by p-CNB reduction, and the reduction product is para-chloroaniline (p-CAN). Inorganic anions such as chloride, sulfate, carbonate, nitrate, perchlorate, phosphate and silicate occur frequently in groundwater or surface aqueous environment. Moreover, those anions and some natural organic matters (NOM) dissolved in groundwater may affect the reactivity of ZVI due to the effect of anions on the iron oxidation, electron transfer, and active site blocking (Su & Puls 2001; Xie & Shang 2007). However, these results are sometimes ambiguous or even contradictory to each other because of experimental differences. In addition, the concentrations of selected anions occasionally lack of representatives due to the variability of groundwater constitutions.

Based on the above consideration, several common dissolved anions in groundwater were selected to investigate the reduction performance of p-CNB by ZVI. To our knowledge, the p-CNB reduction using ZVI powders in the presence of common dissolved anions has not been systematically investigated. In this work, the effects of Cl\(^{-}\), SO\(^{2-}\), HCO\(_3\)^{−}, NO\(_3\)^{−}, ClO\(_3\), PO\(_4\)^{3-}, SiO\(_2\)^{3-} and humic acid on the reaction were studied. The focus of this study is to evaluate the impacts of anion types and anionic concentrations. The experimental results will be useful to the application of ZVI for the remediation of chloronitrobenzenes-contaminated groundwater.

**EXPERIMENTAL SECTION**

**Chemicals**

NaCl, Na\(_2\)SO\(_4\), NaHCO\(_3\), NaNO\(_3\), NaClO\(_4\), Na\(_2\)HPO\(_4\), Na\(_2\)SiO\(_3\), and iron powder (97%, average grain size 0.05 mm) were used. The p-CNB was provided by Aladdin reagent Company (Shanghai, China). All the chemicals used in the experiments were analytical grade except for humic acid which was chemically pure and obtained from Jufeng Chemical Technology Ltd. (Shanghai, China).

**Experimental procedures**

The iron powder was pretreated with 1N HCl washing for 30 min to remove oxides and impurities on the surface. The p-CNB solution was prepared by dissolving a corresponding amount of p-CNB in deionised water and the initial pH value was adjusted to 7.0 by HCl or NaOH. In order to simulate anaerobic conditions in groundwater, the deionised water was deoxygenated by nitrogen bubbling for 30 min prior to use. The stock solution of huminic acid (1,000 mg L\(^{-1}\)) was prepared by dissolving 1 g of humic acid powder into 1 L of deionised water. The final pH value of the solution was adjusted to 7.0. The solution was subsequently filtered with a 0.45 μm membrane and stored at 4°C before use.

The batch experiments were conducted in 550 mL conical flasks containing 500 mL of 25 mg L\(^{-1}\) p-CNB solution. After an anion with a corresponding concentration and 0.25 g ZVI were added, the conical flask was capped with a rubber plug and agitated at 120 rpm in an isothermal shaker (20 ± 1°C). During the process, 2.5 mL of solution sample was periodically withdrawn from the reactor with a glass syringe and then filtered with 0.45 μm membrane for immediate analysis. In addition, concentrations of NO\(_3\)^{−} in samples were determined at the beginning and the end of the NO\(_3\)^{−} effect experiment.

**Analytical methods**

p-CNB was identified by a HPLC (Hitachi, L-2000). Analysis parameters were as follows: column: reversed-phase column of Luna 5 μ C18; mobile phase: MeOH/H\(_2\)O (50/50 v/v); flow rate: 1.0 mL min\(^{-1}\); detector: UV at 270 nm; sample size: 20 μL. Nitrate was determined by the ultraviolet spectrophotometric method of phenol disulfonic acid (APHA 1999). The pH values were monitored by a pH meter (PHS-3C, Sanxin, China).

**RESULTS AND DISCUSSION**

**Effects of Cl\(^{-}\) and SO\(^{2-}\)**

The effects of Cl\(^{-}\) and SO\(^{2-}\) on p-CNB reduction are shown in Figure 1. p-CNB reduction rate significantly increased in the presence of Cl\(^{-}\) and SO\(^{2-}\). p-CNB reduction increased by 21.53% from 73.91% to 95.44% in 5 h when Cl\(^{-}\) concentration increased from 0 to 1,000 mg L\(^{-1}\). The increase of the p-CNB reduction can be attributed to the increase of either iron surface activity or its sorption capacity by the effect of Cl\(^{-}\) etching and pitting of the passive film generated during the reaction on iron surface (Devlin & Allin 2005). Above 1,000 (up to 10,000) mg L\(^{-1}\), increasing Cl\(^{-}\) concentration had little effect on the p-CNB reduction, most likely due to the saturation of active sites on iron surface.

As shown in Figure 1(b), similarly to Cl\(^{-}\), SO\(^{2-}\) also possessed a positive effect on p-CNB reduction. But SO\(^{2-}\) at low concentration was more favourable for p-CNB reduction; the reaction rate reached the maximum at 10 mg L\(^{-1}\) SO\(^{2-}\). The p-CNB reduction was inhibited when increasing SO\(^{2-}\) concentration from 10 to 10,000 mg L\(^{-1}\). Our results agree well with those from Devlin (Devlin & Allin 2005). The high reduction rate can be explained by the effective increase of active sites on iron surface with eliminating the surface ferrous hydroxides at low SO\(^{2-}\) concentration. The decrease of the p-CNB reduction rate at high SO\(^{2-}\) concentration was probably due to the inhibitory effect of sulfate green rust, which is generated in the process of iron corrosion (Su & Puls 2003):

\[
4Fe^{2+} + 2Fe^{3+} + SO_4^{2-} + 12H_2O \rightarrow Fe_6(OH)_{12}SO_4 + 12H^+ \tag{1}
\]

**Effect of HCO\(_3\)^{−}**

The effect of HCO\(_3\)^{−} on p-CNB reduction was investigated from 0 to 10,000 mg L\(^{-1}\). As shown in Figure 2(a), the
reduction efficiency of p-CNB increased gradually when HCO$_3^-$ concentration increased from 0 to 100 mg L$^{-1}$. The increase could be attributed to the effects of pH buffer and the acceleration of corrosion by bicarbonate, as shown in Equations (2) and (3) (Reardon 1995; Liu et al. 2009).

$$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (2)$$

$$\text{Fe} + 2\text{HCO}_3^- \rightarrow \text{Fe}^{2+} + 2\text{CO}_3^{2-} + \text{H}_2 \quad (3)$$

$$4\text{Fe}^{2+} + 2\text{Fe}^{3+} + \text{CO}_3^{2-} + 12\text{H}_2\text{O} \rightarrow \text{Fe}_6(\text{OH})_{12}\text{CO}_3 + 12\text{H}^+ \quad (4)$$

However, p-CNB reduction was apparently suppressed when HCO$_3^-$ concentration exceeded 100 mg L$^{-1}$. The p-CNB reduction declined from 97.31% to 80.13% in 3 h when HCO$_3^-$ concentration increased from 100 mg L$^{-1}$ to 10,000 mg L$^{-1}$, which was similar to the effect of SO$_4^{2-}$. It was probably because Fe–carbonate complex blocked the active sites on iron surface where electron transfer took place (Equations (3) and (4)).

In order to investigate the inhibitory effect of Fe–carbonate complex, five static experiments (0 rpm) were conducted. Figure 2(b) shows that the reduction efficiency of p-CNB decreased with the increase of initial HCO$_3^-$ concentration. No p-CNB reduction was observed when HCO$_3^-$ concentration reached 10,000 mg L$^{-1}$. Hence, it could be concluded that carbonate species could form precipitates and complexes which covered the iron surface and hence retarded the reductive reaction. In addition, static experiments were also conducted for sulfate, but the rate decrease was not observed (data not shown). It was probably because the Fe–carbonate complex was easier to generate than the Fe–sulfate complex. The result also suggested that the
inhibitory effect of Fe–carbonate complex partially depended on the mixing speed. The inhibitory effect was minimised if the mixing speed was fast enough to remove the precipitation which was bound to the ZVI surface. Considering the low mass transfer of groundwater remediation process, the adverse impacts of iron precipitations and complexes should be a rate-limiting factor.

As mentioned above, hydroxide ions released from iron corrosion can be neutralised by bicarbonate species. The bicarbonate species may also react as oxidants, providing cathodic reactions that accelerate the ZVI dissolution. However, the Fe–carbonate precipitations generated subsequently can passivate iron surface.

**Effects of NO\textsubscript{3} and ClO\textsubscript{4}\textsuperscript{-}**

NO\textsubscript{3} and ClO\textsubscript{4}\textsuperscript{-} are considered as ZVI-reducible anions for their electrons competitive properties. The effects of NO\textsubscript{3} and ClO\textsubscript{4}\textsuperscript{-} on p-CNB reduction are presented in Figure 3. As shown in Figure 3(a), ZVI-reducible effect of NO\textsubscript{3} was not observed. p-CNB reduction stayed the same with NO\textsubscript{3} at low concentration. It then increased with NO\textsubscript{3} and finally made a slight difference when NO\textsubscript{3} concentration presented between 600 and 1,000 mg L\textsuperscript{-1}. Additionally, NO\textsubscript{3} was degraded slightly after the reaction at various concentrations (data not shown). Our results differed from those in which a ZVI-reducible effect of NO\textsubscript{3} was observed in the reduction of TCB and TCE by ZVI (Liu et al. 2007; Lim & Zhu 2008). For example, Liu et al. reported that TCE dechlorination slowed down when NO\textsubscript{3} exceeded 186 mg L\textsuperscript{-1}, and the reduction process ceased when NO\textsubscript{3} presented at 310 mg L\textsuperscript{-1} (Liu et al. 2007). The discrepancies could be explained by the fact that the standard electrode potential of NO\textsubscript{3}/NO\textsubscript{2} (0.01 V) is much lower than that of p-CNB/p-CAN (between 0.5 and 1.5 V), so that the reduction rate of nitrate was much slower than that of p-CNB. Similar phenomena were also observed in the removal of arsenate and bromate by ZVI in the presence of NO\textsubscript{3} (Sun et al. 2006; Xie & Shang 2007).

In contrast, an inhibitory effect of ClO\textsubscript{4}\textsuperscript{-} was observed in Figure 3(b). The presence of ClO\textsubscript{4}\textsuperscript{-} dramatically decreased p-CNB reduction and the reaction almost ceased at a ClO\textsubscript{4}\textsuperscript{-} concentration of 50 mg L\textsuperscript{-1}. This is consistent with the results from Xie et al. (Xie & Shang 2007) that the reaction rate constants decreased by 17% when 1 mg L\textsuperscript{-1} ClO\textsubscript{4}\textsuperscript{-} was introduced in the bromate reduction by ZVI. The decrease of the p-CNB reduction is likely due to the electrons competitive effect of ClO\textsubscript{4}\textsuperscript{-} because the standard reduction potential of ClO\textsubscript{4}\textsuperscript{-}/Cl\textsuperscript{-} (1.287 V) is close to that of p-CNB/p-CAN (between 0.5 and 1.5 V).

**Effects of PO\textsubscript{4}\textsuperscript{3-}, SiO\textsubscript{2}\textsuperscript{3-} and humic acid**

As shown in Figure 4(a), p-CNB reduction efficiency decreased 39.63%, 64.51%, 94.37% in the presence of PO\textsubscript{4}\textsuperscript{3-} at 0.5, 1.0, 2 mg L\textsuperscript{-1}, respectively; the p-CNB reduction ceased at 4 mg L\textsuperscript{-1} PO\textsubscript{4}\textsuperscript{3-}. It implied that phosphate could form precipitation with iron oxides and the extent of precipitation increased with the increasing initial PO\textsubscript{4}\textsuperscript{3-} concentration. The adverse effect of Fe–phosphate precipitation was also observed in the trichlorobenzene dechlorination (Lim & Zhu 2008).

The effect of SiO\textsubscript{2}\textsuperscript{3-} on p-CNB reduction is depicted in Figure 4(b). The reduction efficiency of p-CNB decreased with SiO\textsubscript{2}\textsuperscript{3-} and no p-CNB could be removed at 0.5 mg L\textsuperscript{-1} SiO\textsubscript{2}\textsuperscript{3-}. A similar result was reported, that the addition of silica as low as 5.32 mg L\textsuperscript{-1} caused a 30% reduction in the reactivity of iron toward trichloroethane (Kohn et al. 2005). The adverse effect of silica on iron reactivity can be attributed...
to physical and chemical factors, including blocking the reactive sites and serving as anodic corrosion inhibitor (Kohn & Roberts 2006).

As shown in Figure 4(c), the reduction rate of p-CNB decreased in the presence of humic acid and the reaction ceased at 30 mg L\(^{-1}\) humic acid. It is consistent with the previous findings that the efficiency of ZVI to arsenate and 2,4,6-trinitrotoluene declined in the presence of NOM species (Grafe et al. 2001; Zhang et al. 2009). The inhibition could be attributed to complexes formed on iron oxides or on granular iron surface, occupying the active sites and decreasing the probability of formation of new adsorption sites. Unlike Fe-phosphate and Fe-silicate, Fe-humate complexes are considered to be more soluble for their lower inhibitory effect.

As mentioned above, the presence of PO\(_4^{3-}\), SiO\(_3^{2-}\) and humic acid may lead to the blocking of active sites on the ZVI surface and hence the decreasing of the ZVI reactivity. In the present study, the reductive reaction ceased when the concentrations of phosphate, silicate and humic acid reached 4, 0.5 and 30 mg L\(^{-1}\), respectively. Their inhibitory effects increased in the order humic acid < PO\(_4^{3-}\) < SiO\(_3^{2-}\). Consequently, there is a need to understand these three compounds, which might reduce the reactivity of a PRB.

CONCLUSIONS

The effects of several common dissolved anions in groundwater on the reduction of p-CNB by ZVI were investigated with batch experiments. The results demonstrated that Cl\(^-\) and SO\(_4^{2-}\) could eliminate ferrous hydroxide and significantly enhanced the reaction rate. HCO\(_3^-\) improved p-CNB reduction due to pH buffer and corrosion acceleration effects; but Fe-carbonate complex inhibited the reaction when mass transfer in aqueous solution was low. NO\(_3^-\) increased p-CNB reduction, while ClO\(_4^-\) competed with p-CNB for electrons and thereafter the reaction rate decreased. PO\(_4^{3-}\), SiO\(_3^{2-}\) and humic acid can form inner-sphere complexes and passivate reactive surface. Their inhibitory impacts increased in the order of humic acid < PO\(_4^{3-}\) < SiO\(_3^{2-}\). Therefore, the effects of common dissolved anions in groundwater should be taken into account when designing a PRB. Further column tests to elucidate these anions’ potential influences on PRB will be investigated in our future work.

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