



## Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron

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### Abstract

Nitrobenzene has been considered as a significant groundwater contaminant due to its wide usage in explosives, insecticides, herbicides, pharmaceuticals and dyes. Nitrobenzene is of environmental concern because of its toxicity. In the presence of zero-valent iron (ZVI), reduction of the nitro group is the dominant transformation process for nitrobenzene. A series of experiments were carried out to investigate the kinetics of nitrobenzene reduction by ZVI and the effects of pH and ZVI particle size on nitrobenzene removal in groundwater. The results indicated that nitrobenzene could be reduced to aniline by ZVI; the reduction of nitrobenzene by ZVI followed a pseudo first-order kinetics; the observed nitrobenzene reduction rate constant ( $k_{\text{obs}}$ ) was  $0.0006 \text{ min}^{-1}$  and the half-life of nitrobenzene ( $t_{1/2}$ ) was 115.5 min; the mass balance achieved 87.5% for nitrobenzene reduction by the 1 mm ZVI particle and the final removal efficiency was 80.98%. In addition, the pH and ZVI particle size were found to exhibit significant influences on the nitrobenzene reduction. The observed nitrobenzene reduction rate constant linearly decreased with increase pH and the data fitted on polynomial regression equation for the observed nitrobenzene reduction rate constant and ZVI particle size. Therefore, use of ZVI based permeable reactive barrier technology to remedy nitrobenzene contaminated groundwater was feasible.

**Key words:** zero-valent iron; nitrobenzene reduction; aniline formation; particle size

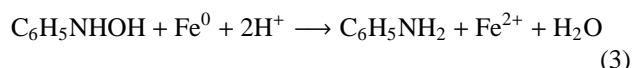
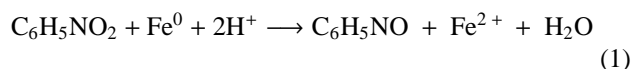
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### Introduction

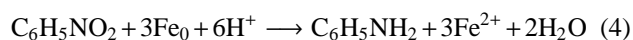
Permeable reactive barrier (PRB) technology has gained acceptance as an effective passive remediation strategy for treating organic and inorganic contaminants in groundwater. ZVI-based PRB technology has been investigated intensively in laboratory and pilot-scale or full-scale sites to remediate groundwater contaminated by reducible contaminants, such as heavy metals (Jeen et al., 2008; Lien and Wilkin, 2005; Morrison et al., 2002; Wilkin et al., 2005; Su and Puls, 2003; Alowitz and Scherer, 2002), chlorinated solvents (Oliver et al., 2000; Gandhi et al., 2002; Liu et al., 2006; Kenneke and McCutcheon, 2003), petroleum hydrocarbon (Guerin et al., 2002), dissolved nutrients (Alowitz and Scherer, 2002; Su and Puls, 2004; Cheng et al., 1997; Rodríguez-Maroto et al., 2009) and nitroaromatic compounds (Huang and Zhang, 2006a; Hung et al., 2000; Xu et al., 2008; Lavine et al., 2001; Agrawal and Tratnyek, 1996; Klausen et al., 2001). Among many targeted contaminants, as one of the most representative nitroaromatic compounds nitrobenzene has been investigated extensively (Huang and Zhang, 2006a; Hung et al., 2000; Xu et al., 2008; Mantha et al., 2001). It has been considered as a significant groundwater contaminant due

to its wide use in explosives, insecticides, herbicides, pharmaceuticals and dyes. Nitrobenzene is of environmental concern because of its toxicity.

In the presence of zero-valent iron (ZVI), reduction of the nitro group is the dominant transformation process for nitrobenzene. The reduction of nitrobenzene by ZVI yields aniline via nitrosobenzene and phenylhydroxylamine as intermediates according to the following Reactions (1)–(4) (Agrawal and Tratnyek, 1996; Mantha et al., 2001):



Formally, the overall reaction can be written as:



ZVI-based PRB has been studied to treat groundwater contaminated by nitrobenzene as well as other chlorinated organic compounds. Reduction of nitrobenzene by ZVI particles is a surface-mediated electron transfer process; the properties of surface coating will affect the reactivity of ZVI particles (Huang and Zhang, 2006a; Matheson and

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Tratnyek, 1994; Slater et al., 2005). ZVI as the ultimate electron donor is oxidized to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  accompanied by the reduction of nitrobenzene to aniline (Hung et al., 2000; Agrawal and Tratnyek, 1996). The reduction kinetics has often been reported to follow a pseudo first-order kinetics in term of the concentration of nitrobenzene (Mu et al., 2004; Bandstra et al., 2004; Jafarpour et al., 2005). The nitrobenzene reduction rate linearly increases with the concentration of iron surface area (Agrawal and Tratnyek, 1996). Reactions between ZVI and groundwater constituents can cause ZVI corrosion and subsequent secondary mineral precipitations contribute to reduction in performance of ZVI-based PRB in the long term (Suk et al., 2009). The composition of the solution can also influence the reactivity of ZVI particles. For instance, previous studies have shown that nitrate, sulfate, and bicarbonate are all corrosive to ZVI (Kamolpornwijit et al., 2003; Liang et al., 2005); ZVI particles are passivated by nitrite only at concentrations higher than 44 mmol/L (Mishra and Farrell, 2005; Huang and Zhang, 2006b).

The degradation rate and efficiency is dependent on the environmental conditions, such as pH, the concentration of  $\text{Fe}^{2+}$ , the morphologies of the minerals, and the presence of transitional metal ions (Liu et al., 2006). Previous studies have shown that dehalogenation by surface-bond  $\text{Fe}^{2+}$  happens faster when there is an oxide film on ZVI particles.  $\text{Fe}^{2+}$  reacts with the oxide surface and electrons are transferred between the adsorbed  $\text{Fe}^{2+}$  and the underlying  $\text{Fe}^{3+}$  oxide (Johnson et al., 1998). Nitrobenzene reduction is to a large extent dependent on pH (Mu et al., 2004); the presence of hard ions and carbonate in groundwater have great impact on the activity of ZVI particles due to their formation of precipitates on the ZVI surface that inhibits electron transfer and a diminished lifespan of the ZVI (Jeen et al., 2008; Suk et al., 2009; Lo et al., 2006; Wilkin et al., 2003). Passivating precipitates, such as magnetite and maghemite, can inhibit electron transfer by masking the reactive sites on the ZVI surface where electron transfer occurs resulting in a decreased reactivity of ZVI. Authigenic phases include amorphous iron hydroxides, green rust minerals, goethite, aragonite, calcite, siderite, mackinawite and elemental sulfur (Furukawa et al., 2002; Roh et al., 2000; Phillips et al., 2000).

In light of the findings from the previous studies, most PRB studies have investigated the ability of iron fillings or aqueous iron to remove nitrobenzene, the influences of ZVI type, microbial activity and composition of solution on the nitrobenzene removal efficiency or the reactivity of ZVI. However, there is no report about individual stepwise studies on effects of pH and ZVI particle size on the reactivity of ZVI to remove nitrobenzene from groundwater. The specific objectives of this study were: (1) to investigate the kinetics of nitrobenzene reduction by ZVI particles; (2) to evaluate the effects of pH and ZVI particle size on the kinetics of nitrobenzene reduction by ZVI particles; (3) to assess the feasibility of ZVI-based PRB technology used to remedy nitrobenzene polluted groundwater.

## 1 Materials and methods

### 1.1 Preparation of ZVI

The ZVI grains were hand-sieved to constrain grain size to 1–3 mm and then washed using 10% HCl (V/V) for 20 min to remove surface oxides and other coatings. The cleaned ZVI was washed three times with the bicarbonate buffer to remove residual acidity or chloride remaining after the acid treatment. This was followed by washing with  $\text{Na}_2\text{SO}_3$  solution to remove any remaining dissolved alkalinity. The pretreatment of the iron with HCl was to increase the metal surface area by etching and pitting through corrosion or mechanical abrasion during sonication. Cleaning the surface by dissolving and destroying the passivated oxide layer, increased the density of highly reactive “sites” which consist of steps, edges, and kinks (Agrawal and Tratnyek, 1996).

### 1.2 Experimental methods

#### 1.2.1 Nitrobenzene reduction with ZVI

Experiments on the reduction of nitrobenzene were carried out in closed 150 mL serum bottles. Two gram of 1 mm ZVI particle was put into a 100 mL solution containing 0.066 mmol/L nitrobenzene. The mixture was shaken at 50 r/min on a rotary shaker to ensure uniformity and promote reaction. A series of samples were taken for analysis of nitrobenzene and aniline at preselected time intervals over a range of 240 min.

#### 1.2.2 Effect of pH on nitrobenzene reduction

Experiments to investigate the effects of pH were conducted in 4 closed 150 mL serum bottles containing 2.0 g of prepared ZVI, 1 mm particle and the pH adjusted to 3, 5, 7 and 9. The mixtures were shaken at 50 r/min on a rotary shaker and a series of samples were taken for analysis of nitrobenzene and aniline at preselected time intervals over a range of 240 min.

#### 1.2.3 Effect of ZVI particle size on nitrobenzene reduction

The effect of particle size on reduction of nitrobenzene was investigated in four 150 mL serum bottles containing 2.0 g prepared ZVI with particle size of 0.1–0.5, 0.5–1, 1–2 and 2–5 mm respectively, and each was added with 100 mL solution of 0.145 mmol/L nitrobenzene and 0.015 mmol/L aniline. The bottles were shaken at 50 r/min on a rotary shaker and a series of samples were taken for analysis of nitrobenzene and aniline at preselected time intervals over a range of 240 min.

### 1.3 Analytical methods

The measurements of nitrobenzene and aniline concentration in aqueous were carried out with a model 6890 GC-MS (Agilent Technology Inc., USA). The pH and oxidation-reduction potential (ORP) were measured by pH 211 microprocessor (Hanna Instruments, USA).

## 2 Results and discussions

### 2.1 Kinetics of nitrobenzene reduction

Previous studies have shown that the degradation rate of nitrobenzene by ZVI particles could be described by a pseudo first-order kinetic model (Agrawal and Tratnyek, 1996; Mu et al., 2004; Bandstra et al., 2004; Jafarpour et al., 2005):

$$\frac{dC_{NB}}{dt} = -k_{obs}C_{NB} \quad (5)$$

where,  $C_{NB}$  is nitrobenzene concentration,  $k_{obs}$  ( $\text{min}^{-1}$ ) is the observed first-order rate constant. The integration of Eq. (5) results in Eq. (6):

$$C_{NB} = C_{NB}^0 e^{-k_{obs}t} \quad (6)$$

where,  $C_{NB}^0$  is the initial nitrobenzene concentration, and  $t$  is the residence time. Therefore,  $k_{obs}$  can be calculated from the regression of  $\ln C_{NB}$  versus residence time, and the half-life,  $t_{1/2}$ , of nitrobenzene can be calculated by Eq. (7).

$$t_{1/2} = \frac{-\ln 0.5}{k_{obs}} \quad (7)$$

Figure 1 describes the variation of  $\ln C_{NB}$  over residence time. A linear regression model on the data for  $\ln C_{NB}$  and time was given. The calculated  $K_{obs}$  and  $t_{1/2}$  is  $0.006 \text{ min}^{-1}$  and 115.5 min, respectively.

Figure 2 shows that the variations of pH and ORP over residence time. The result indicates that pH increased continuously over residence time. The increase rate remains high in the range 0–90 min; the average increase rate is  $0.0073 (\text{min} \cdot \text{L})^{-1}$ . After 90 min, it decreases to a constant rate of  $0.0011 (\text{min} \cdot \text{L})^{-1}$  on average. According to previous studies (Lavine et al., 2001; Agrawal and Tratnyek, 1996), the reduction of nitrobenzene could lead to an increase in pH which may be attributed to the ZVI corrosion accompanied by an increase in hydroxide ions. Under oxic conditions,  $\text{O}_2$  is the preferred oxidant resulting in a rapid corrosion according to Reaction (8). Further oxidation of  $\text{Fe}^{2+}$  by  $\text{O}_2$  leads to the formation of ferric hydroxides.

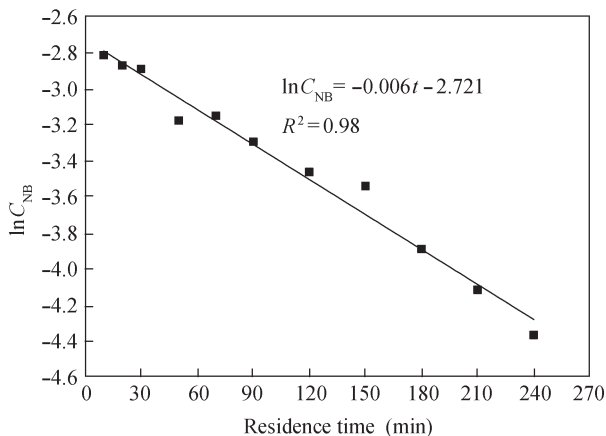
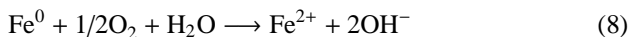


Fig. 1 Reduction of nitrobenzene by zero-valent iron (ZVI) over time.

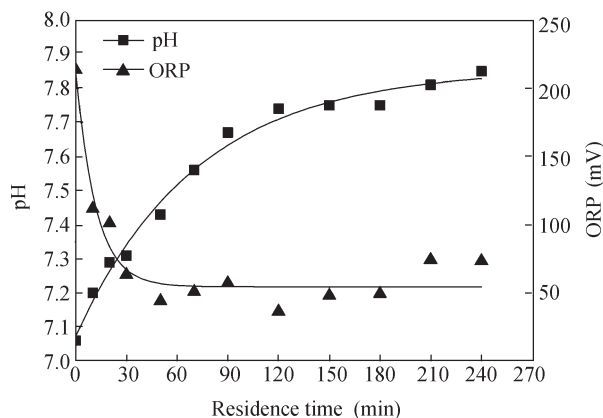
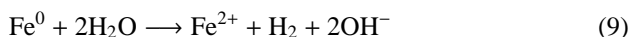


Fig. 2 Variations of pH and ORP over residence time.

Under anoxic conditions, water alone serves as the oxidant, and corrosion occurs according to Reaction (9).



Both Reactions (8) and (9) can result in an increase of pH. The pH increase favors the formation of iron hydroxide precipitates, which may form a surface layer on the ZVI particles that decreases the reactivity of ZVI.

Figure 2 suggests that the ORP dropped drastically from an initial value of 213.6 to 44.1 mV in 50 min indicating the reductive conditions in aqueous solution. This may be attributed to the higher corrosion rate of ZVI under the reductive conditions. However, the corrosion of ZVI and the increase of pH may cause precipitation of  $\text{Fe}(\text{OH})_2$ , which led to a slight increase in ORP after 50 min.

Figure 3 shows the kinetics of nitrobenzene reduction and aniline formation over residence time. The results indicate that the nitrobenzene concentration dropped from the initial 0.059 to 0.0127 mmol/L in 240 min while the concentration of aniline increased from 0.067 to 0.123 mmol/L in 240 min. The mass balance achieved 87.5% for nitrobenzene reduction by the ZVI particle. The results from this study were consistent with previous findings (Agrawal and Tratnyek, 1996; Klausen et al., 2001). The observed loss was due to the sorption of aniline onto the surface of the ZVI particles and not quantitatively determined intermediates, such as nitrosobenzene and

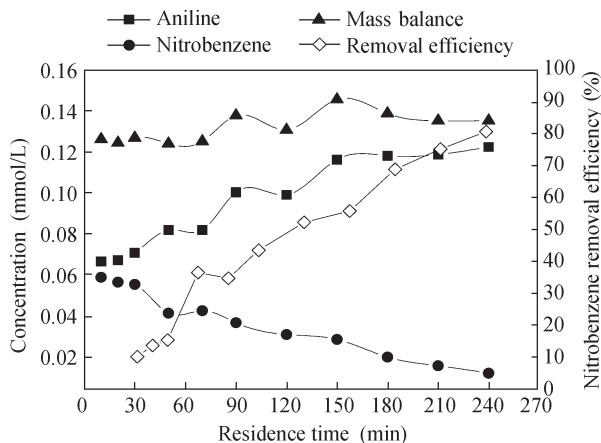


Fig. 3 Kinetics of nitrobenzene reduction to aniline.

phenylhydroxylamine. The sorption of aniline onto the surface of the ZVI particles was observed in independent experiments and similar observations have been reported previously (Klausen et al., 2001; Devlin et al., 1998; Bell et al., 2003). Although nitrosobenzene and phenylhydroxylamine were not quantitatively determined in this study, they were tentatively detected as uncalibrated peaks and concluded to be of very low concentration. The final removal efficiency of nitrobenzene was 80.98%.

## 2.2 Effect of pH

The  $H^+$  participation in the overall reaction (Reaction (4)) suggests that pH may influence the rate of nitrobenzene reduction. The results showed that pH has significant effect on the kinetics of nitrobenzene reduction (Fig. 4a).

Figure 4b shows that the values of first-order reduction rate constants for nitrobenzene reduction decrease with increase pH over residence time. The effect of pH on  $k_{obs}$  is apparently linear, and a regression line on the data for  $k_{obs}$  ( $\text{min}^{-1}$ ) and pH gives:

$$k_{obs} = -0.0028\text{pH} + 0.0278 \quad (r^2 = 0.95) \quad (10)$$

The slope of this line can be used for estimating the potential significance of pH variability on observed first-order nitrobenzene reduction rate constant. This finding is consistent with the findings of a previous study (Agrawal and Tratnyek, 1996). The final removal efficiency of nitrobenzene was 97.56%, 94.39%, 80.69% and 59.81% for pH 3, pH 5, pH 7 and pH 9 systems, respectively. The average rate of pH increase was 2.2, 1.4, 0.53 and 0.4  $\text{min}^{-1}$  when pH is 3, 5, 7 and 9, respectively. This indicates that the low pH condition was favorable to nitrobenzene reduction. Firstly, at the low pH conditions, rapid ZVI corrosion could occur. The direct involvement of  $H^+$  in the reactions (Reactions (1)–(4)) raises the possibility that protons may appear in one or more elementary steps that influence the reaction rate directly. Recent studies also indicated that aqueous  $Fe^{2+}$  could rejuvenate the otherwise passivated ZVI (Huang and Zhang, 2004, 2005, 2006a; Mishra and Farrell, 2005).  $Fe^{2+}$  could be released under

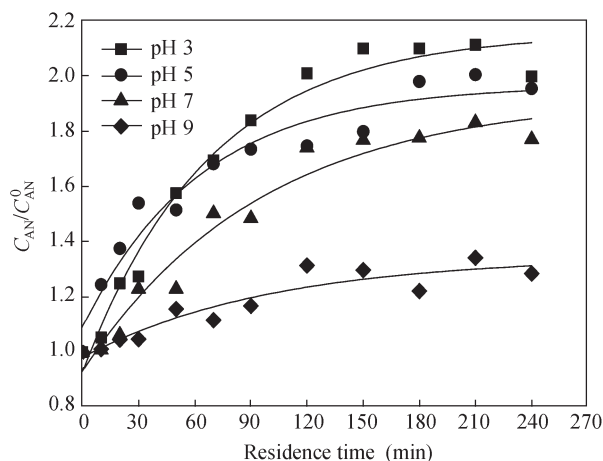


Fig. 5 Variation of aniline formation over time.

weak acidic conditions and thereafter may play a role in enhancing the reactivity (Huang and Zhang, 2004). Secondly, high pH favors the formation of iron hydroxide precipitates, which may eventually form a surface layer (or passive film) on the ZVI particle inhibiting its further dissolution thus limiting mass transport. Higher pH slows down the corrosion rate of ZVI, which in turn influences the rate of reduction since the kinetics of the redox process is controlled by the slower rate of the two reactions. Thirdly, a mass transport limitation is determined by the thickness of the Nernst layer between the passive film and the bulk electrolyte (Agrawal and Tratnyek, 1996). The actual reaction involves a series of electron and proton transfers, which occur on the surface of ZVI particles.

Figure 5 shows that the effect of pH on the variations of aniline concentration over residence time. It is evident that pH has significant influences on the formation of aniline. The rate constant for aniline formation is 0.015, 0.016, 0.011 and 0.01  $\text{min}^{-1}$  and aniline formation rate is  $3.0 \times 10^{-5}$ ,  $2.2 \times 10^{-5}$ ,  $1.4 \times 10^{-5}$  and  $0.7 \times 10^{-5}$   $\text{mmol}/(\text{L}\cdot\text{min})$  when pH is 3, 5, 7 and 9, respectively. It is clear that the lower the pH, the higher the aniline concentration. The rate of increase in aniline concentration dropped

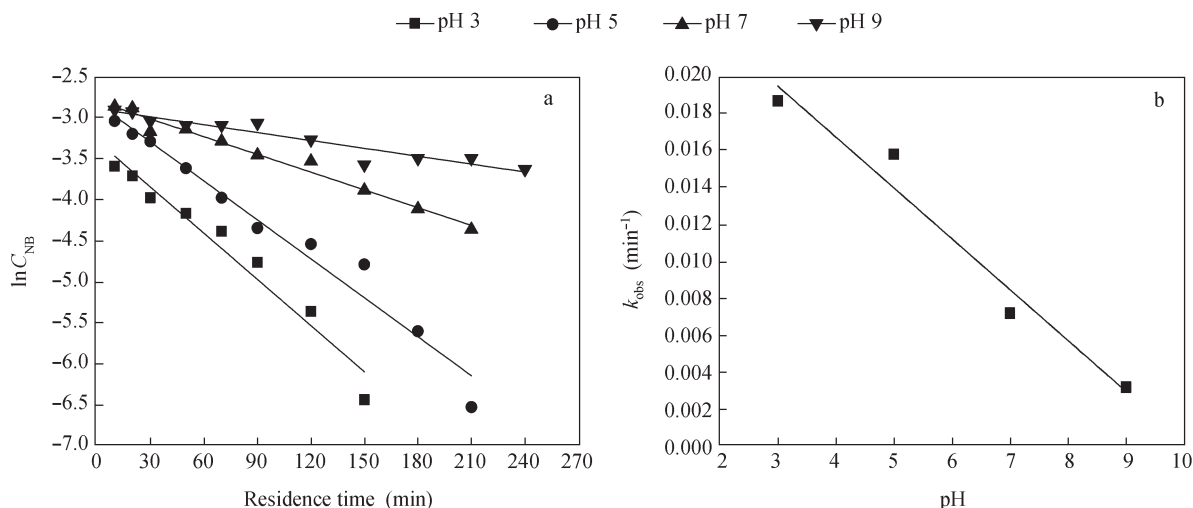


Fig. 4 Effect of pH on kinetics (a) and rate constant (b) of nitrobenzene reduction.

drastically after 180 min, which suggests that aniline can inhibit the nitrobenzene reduction while it is accumulated to a certain concentration. The protonation of the aniline formed probably prevents desorption of the product due to electrostatic attractions (Agrawal and Tratnyek, 1996). Changes in pH can also influence the adsorption of organic compounds on ZVI particles. At higher pH, aniline may inhibit the corrosion of ZVI particles and it may exhibit a greater adsorption towards ZVI, which in turn slows down the corrosion of ZVI, resulting in a lower reduction rate for organic compounds (Lavine et al., 2001; Agrawal and Tratnyek, 1996; Matheson and Tratnyek, 1994).

### 2.3 Effects of ZVI particle size

The surface area of ZVI particles has a significant effect on the dechlorination of halocarbon (Hung et al., 2000; Agrawal and Tratnyek, 1996; Matheson and Tratnyek, 1994). It was anticipated that the condition and size of ZVI surface area would also strongly influence the kinetics of nitrobenzene reduction. The direct role of ZVI particles as a reactant in nitrobenzene reduction reaction implies the involvement of reactive sites on the ZVI particles. In this study, remarkable differences in nitrobenzene reduction and aniline formation rates for the four different ZVI particle size systems were observed (Fig. 6a). For ZVI particle size less than 2 mm, the nitrobenzene reduction rate increased with ZVI particle size. The average reduction rates were  $9.1 \times 10^{-5}$ ,  $3.54 \times 10^{-4}$ ,  $1.82 \times 10^{-4}$ ,  $9.5 \times 10^{-5}$  mmol/(L·min) for 2–5, 1–2, 0.5–1, 0.1–0.5 mm ZVI particle systems, respectively. However, it was observed that there was a drop in nitrobenzene reduction in rates for ZVI particles greater than 2 mm. Reduction rate of nitrobenzene for the 2–5 mm ZVI particles dropped to  $9.1 \times 10^{-5}$  mmol/(L·min). The final removal efficiency of nitrobenzene was 74.04%, 91.77%, 100% and 74.35% for 2–5, 1–2, 0.5–1 and 0.1–0.5 mm ZVI particle systems, respectively.

The effect of ZVI particle size on the observed rate constant for nitrobenzene reduction is depicted in Fig. 6b. The results indicated that the observed reduction rate constants,  $k_{\text{obs}}$ , increased initially then decreased after a given particle size. The  $k_{\text{obs}}$  was 0.0061, 0.0099, 0.0152

and  $0.0052 \text{ min}^{-1}$  for 0.1–0.5, 0.5–1, 1–2 and 2–5 mm ZVI particles systems, respectively. Polynomial regression fitted on the  $k_{\text{obs}}$  ( $\text{min}^{-1}$ ) and ZVI particle size ( $S_{\text{ZVI}}$  mm) gives:

$$k_{\text{obs}} = 0.0144 \times S_{\text{ZVI}}^2 - 0.0038 \times S_{\text{ZVI}} + 0.0017 \quad (r^2 = 0.943) \quad (11)$$

The effect of ZVI particle size on the aniline formation over residence time is shown in Fig. 7. It was evident from the results that the particle size of ZVI has significant effect on the formation of aniline.

The experiment results show that the particle size of ZVI has significant effect on nitrobenzene reduction. In theory, the finer the ZVI particle, the higher the specific surface area and the faster nitrobenzene reduction rate. However in practice for finer particles is the contamination of iron surface by oxides coating may become a controlling factor and hence particle agglomeration should also be taken into account. Therefore, a compromise should be taken when choosing particles size of ZVI for nitrobenzene reduction.

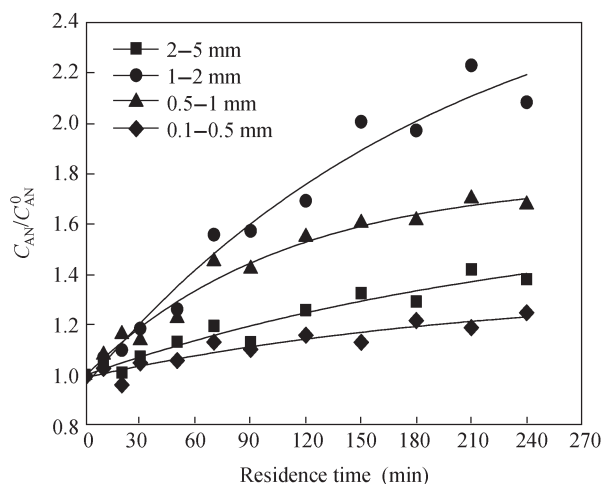


Fig. 7 Effect of ZVI particle size on aniline formation over time.

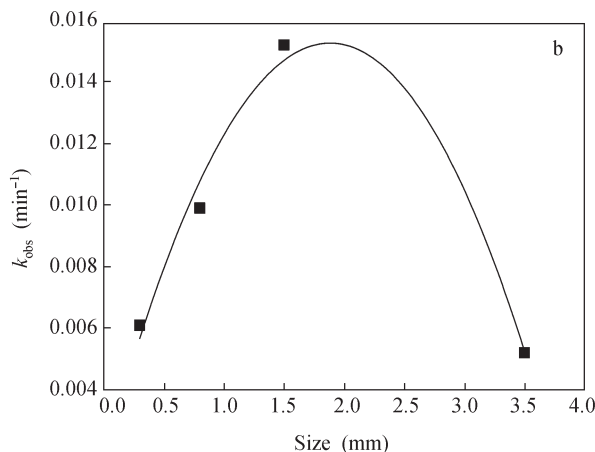
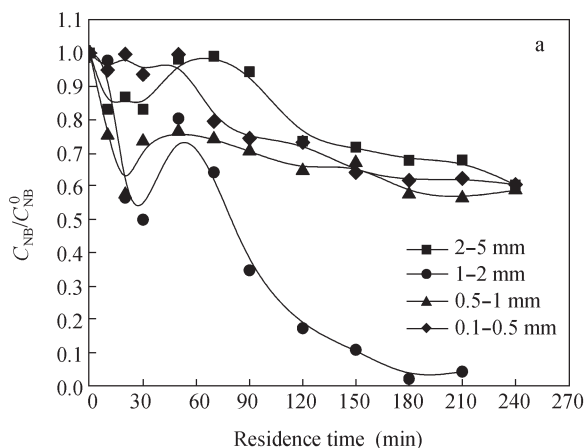


Fig. 6 Effect of ZVI particle size on kinetic (a) and  $k_{\text{obs}}$  (b) for nitrobenzene reduction.

### 3 Conclusions

This study investigated the kinetics of nitrobenzene reduction by ZVI particles and effects of pH and ZVI particle size on the nitrobenzene reduction rate and observed rate constant in laboratory. The results suggested that the reaction kinetics of nitrobenzene was follows a pseudo first-order kinetics. The half-life of nitrobenzene is 115.5 min. The observed nitrobenzene reduction rate constant linearly decreases with the increase of pH and the data for observed nitrobenzene reduction constant rate and ZVI particle size fitted on the polynomial regression equation. It is therefore feasible to use ZVI based PRB technology to remedy the limited amount of nitrobenzene polluted groundwater.

### Acknowledgments

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