Degradation of tetrachloromethane and tetrachloroethene by Ni/Fe bimetallic nanoparticles

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Abstract. The study investigated the potential of nanoscale Ni/Fe bimetallic particles reduction for carbon tetrachloride (CT) and tetrachloroethene (PCE). BET specific surface areas of the laboratory synthesized Ni/Fe (2% wt.) particle, with diameter on the order of 20-60 nm, was approximately 52.61 m²/g. Batch studies demonstrated that rapid transformations of PCE and CT were achieved with nanoscale Ni/Fe particles. The degradation process appeared to be pseudo-first-order. Values of the surface area normalized rate coefficients (K_{SA}) of PCE and CT for the reaction with nano Ni/Fe were 2.068 mL/(m²·h), 10.08 mL/(m²·h), respectively. This indicated that the degradation rate of CT was about 5 times larger than that of PCE under comparable environmental condition. Significant amounts of DCM were detected for the reaction with CT unlike the PCE transformation where ethane was the only end-product, amount to 103% of the initial PCE carbon. Both DCM (~15%) and methane (~27%) were the major end products for CT reaction. Based on the rapid rate of degradation and no or less chlorinated byproducts, the nanoscale particles technology offered great opportunities for both fundamental research and technological application for remediation of contaminated ground water.

Keywords: nanoscale Ni/Fe bimetallic particles; reaction rate constant K_{SA}; PCE; CT; dechlorination

1. Introduction

Because of many chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE) and carbon tetrachloride (CT), were known or potential threats to public health and the environment, so

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there was an urgent need to develop effective treatment methods. A survey of groundwater quality from east-northern area, China showed that TCE, followed by PCE, was detected. Approximately 44% of the total samples contained TCE, concentration of that above the drinking water standards issued by the US EPA, and the max concentration of TCE was almost 1000µg/L, 200 times greater than the standard [1].

Catalytic hydrodehalogenation with noble metal and direct reduction with zero-valent metal represent the two most widely studied processes. In the last two decades, Fe$^0$ permeable reactive barriers technology had received much interest as an alternative to pump and treat systems [2-5]. However, many challenges still exist for implementation of the zero-valent metal technology, such as slow reaction rate, accumulation of persistent byproducts, and progressive deactivation of the ZVI by the precipitated corrosion products [6-8]. To overcome these, various nanoscale bimetallic particles have been synthesized and used to improve the performance of the ZVI technology [5] [7-12]. Nanoscale metal particles, with diameter in the range 1~100 nm, were characterized by high surface area to volume ratio, high level of stepped surface, and high surface energy. There were also publications on the application of nano-iron to removal of heavy metals [13], transformation of nitrogen[14] or remediation of PCBs contaminated soils [15]. Nanoscale metal particles could be injected directly to contaminated soils, sediments, and aquifers for in situ remediation chlorinated hydrocarbons, instead of building permeable reactive barriers in the subsurface. The nanoscale particles could be anchored onto activated carbon and zeolite for ex situ treatment of contaminated waters and industrial effluents [7]. In the aqueous solution, the nanoscale iron particles could remain suspended under very gentle agitation. Bimetallic Pd/Fe particles have been shown to exhibit a high efficacy for the transformation of many chlorinated compounds. Among all the noble metal catalysts, Pd has been proved to be the best catalyst with high selectivity of C–Cl bond cleavage and resistance against catalyst deactivation. Hydrogen gas, metal hydride, and other small molecules such as formate, methanol and ethanol, can act as hydrogen donors in this reaction. It is well known that its cost for application in engineering is high because Pd is a noble metal. Less is known about the reaction kinetics and products formed during PCE or CT dechlorination by nano Ni/Fe particles. We presented low-cost nickel substitute for noble metal Pd, which removed PCE or CT using laboratory-synthesized nanoscale Ni/Fe. We present applications of the lab-synthesized nano-Ni/Fe for transformation of PCE and CT. The purpose of this study was aimed to measure the rate and extent of dechlorination and to characterize and quantify reaction intermediates and final products. Kinetic analysis was conducted by using pseudo-first-order rate equation and activity was expressed as both observed and surface-area-normalized rate constants.

2. Material and methods

2.1. Synthesis of nanoscale iron particles

FeCl$_3$·6H$_2$O was dissolved into 1L of 30% anhydrous ethanol, 70% deionized water (v/v). An appropriate amount of 1.0mol/L FeCl$_3$·6H$_2$O was placed in a conical flask, and purged with pure nitrogen for two hours. Synthesis of nanoscale iron particles was achieved by adding 1:1 volume ratio of NaBH$_4$ (1.6mol/L) dropwise to FeCl$_3$·6H$_2$O (1.0 mol/L). The solution was mixed vigorously on the
magnetic agitator under 22±1℃ for 5 minutes [16]. Fe³⁺ was reduced by borohydride according to the following reaction:

\[
4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow \text{Fe} \downarrow + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2
\]  

(1)

The nano-iron formed from the above reaction was rinsed with large volume of 0.5mol/L hydrochloric acid, de-oxygen water and ethanol for at least three times, respectively. Bimetals could be prepared by soaking freshly prepared nanoscale iron particles with ethanol solution containing 2% (wt.) NiCl₂. The mixture was stirred for 20 min and then filtered through a 0.2µm filter. The amount of Ni deposited on the nano-Fe surface can be got by analyzing the Ni²⁺ concentration in the solution before and after reaction:

\[
\text{Ni}^{2+} + \text{Fe} \rightarrow \text{Ni} + \text{Fe}^{2+}
\]  

(2)

Ni/Fe particles were washed three times with ethanol and dried at 105℃ for 4 h under a flow of N₂. Synthesizing nanoscale iron particles had average BET specific area of 52.61m²/g by nitrogen adsorption method (Autosorb-1 model SSA and porosity, USA). BET data were supplied by the laboratory of Analytical Chemistry in China University of Geosciences (Beijing). The micrographs (figure 1) showed that the synthetic particles were in the range of 20~60nm by S-4300F scan electron microscopy (SEM) at 30,000 magnification.

![SEM image of nano-Ni/Fe(2%)](image)

Figure 1. SEM image of nano-Ni/Fe(2%)  

2.2. Batch experiments

Batch experiments were conducted to test reactivity of the laboratory synthesized nanoscale particles for dechlorination of PCE. Take 0.4g freshly-made nano-Ni/Fe (2%) particles into 120-mL reaction bottle capped with a Teflon valve. The initial concentration \((C_0)\) of PCE was 15.83mg/L and volume was 50mL. The bottle was mixed on a rotary shaker at a speed of 170rpm at 20℃. Parallel experiments were also performed without metal particles (control sample). Analyses of organic mass in the control samples indicated that the total mass of parent chlorinated carbon in the batch bottles varied from 95 to 110% of the initial input when the experiment were completed. About 10% error of organic concentrations in the control samples was largely caused by volatilization of PCE or CT, and
the gas chromatograph (GC) analysis. Analytical working standards were prepared daily prior to analysis.

2.3. Methods of analysis

2.3.1. Chlorinated hydrocarbons

Periodically, 50µL of the aqueous solution was withdrawn by a 100-µL gas-tight syringe, and spiked quickly into a 10mL vial charged with 0.45mL purified water. Concentrations of chlorinated ethenes were measured by a HP 6890 GC equipped with a HP-5 capillary column (30m×0.25mm×0.25µm) and an electron capture detector (ECD). The carrier gas was ultra-pure nitrogen.

GC HP-6890: inlet 160°C, column flow 1.0 mL/min, oven 70°C, oven run time 10min, ECD 300°C. Headspace sampler: vial 50°C, loop 60°C, transline 70°C, vial equation time 10min, injection time 1min, shake time 5 min, carrier gas flow 30 mL/min [17].

2.3.2. Hydrocarbons products

Hydrocarbon products in the headspace ware qualitatively identified and quantified with GC analysis by comparing retention times and peak areas with standard gas samples(ethane, ethylene, acetylene and methane). The GC was equipped with a flame ionization detector and a HP-PLOT/Al2O3 capillary column (50m×0.53mm×15.0µm. Oven temperature was set at 100°C, injection port temperature at 150°C, and detector temperature at 160°C. The carrier gas was ultrapure nitrogen (99.999%).

2.3.3. Method detection limit (MDL)

The MDLs were got by experiments and calculation. Firstly prepared 7 samples with signal to noise ratio of 3, and analyzed these 7 samples to get their experimental concentration by calculation. The MDLs equal to 3 times the standard deviation value [18]. The results of MDLs were listed in Table 1.

| Compounds | MDL  |
|-----------|------|
| DCM       | 0.083|
| TCM       | 0.076|
| CT        | 0.022|
| TCE       | 0.041|
| PCE       | 0.021|
| DCE       | 0.083|
| VC        | 0.096|
| C2H6      | 0.48 |
| C2H4      | 0.48 |
| C2H2      | 2.4  |
| CH4       | 0.85 |
2.4. Chemicals

Five halogenated hydrocarbons dissolved in the methanol were purchased from the Institute of Reference Materials belonging to the Environmental Monitoring General Station of China, including 200µg/mL CF, 50µg/mL CT, 200µg/mL TCE, 100µg/mL PCE and 200µg/mL bromoform (BF). DCEs were from National Center for Reference Materials with a concentration of 0.93µg/mL. VC was from Chemistry Service, PA, USA. Standard gas samples were acquired from Beijing Hua Yuan gas Chemical Industry Co., Ltd. FeCl$_3$·6H$_2$O, NaBH$_4$, NiCl$_2$, HCl and anhydrous ethanol were analytical grade reagents.

3. Results and discussion

3.1. Degradation of PCE with nanoscale Ni/Fe bimetallic particles

Figure 2(a) showed the results of degradation of PCE by using nanoscale Ni/Fe bimetallic particles. The reaction kinetics of the degradation of PCE was modeled with a pseudo-first-order rate equation. Plots of the natural logarithm of concentrations of PCE versus time through linear regression analysis gave straight line results. Linear regression analyses were used to obtain observed first-order rate constants ($k_{obs}$). Disappearance of PCE reacting with nano-Ni/Fe was plotted in the form of ln($C/C_0$) as a function of time in figure 2(a) where $C_0$ was the initial concentration of PCE (15.83mg/L). Data presented in figure 2(a) indicated that the disappearance of PCE exhibited pseudo-first-order behavior ($R^2=0.9311$, n=6). PCE was rapidly degraded by nano-Ni/Fe. The observed first-order rate constant ($k_{obs}$) was 0.8487 h$^{-1}$. Half-life time ($t_{1/2} = \ln2/k_{obs}$) was 0.82h.

To better compare the reaction rates observed with different metal loading and particle size, it is useful to normalize the reactivity per unit metal surface area. The rate of dechlorination in a batch system can be described by the following equation (Johnson et al.1996):

\[
\frac{dC}{dt} = -k_{SA} P_a C. \tag{3}
\]

Where C=concentration of organic compound in the aqueous phase (mg/L). $t$=time (h). Specific surface area constant $P_a$=SSA×W/V (m$^2$/mL) where W was the weight of reactive materials and V the reaction solution volume. For a specific batch system, $k_{SA}$ and $P_a$ were constants. The above equation therefore represents a pseudo-first-order kinetics. The reaction rate constant and half-life time can be standardized by specific surface area constant $P_a$. In this experiment, $P_a$ was 0.4 m$^2$/mL, so $k_{obs}$ and $t_{1/2}$ was normalized per unit metal surface area. The surface-area-normalized rate coefficient ($K_{SA}=k_{obs}/P_a$) and the surface-area-normalized half-life time ($t_{50,N}=P_a t_{1/2}$) was 2.122mL/(m$^2$·h) and 0.33h, respectively.

Reaction of PCE with the nano Ni/Fe bimetallic particles were shown in figure 2(b). Concentrations in the figure were expressed as the molar ratio to initial organic concentrations. As shown in figure 2(b), 99% of PCE was reduced using nanoscale Ni/Fe particles within 6h. We observed the immediate appearance of ethane corresponding to the disappearance of PCE. Ethane concentrations increased steadily during the entire reaction time. No chlorinated intermediates or products such as TCE, DCEs and VC were detected above the detection limit. PCE was essentially reduced to ethane. Average yield of ethane from PCE was ~ 103% after 6h. Only trace levels of ethene (~6%) appeared briefly in the headspace. It may be much ethane or hydrogen adhering to the surface of nanoscale Ni/Fe particles.
prevented PCE from arriving at the reactive situation, so that reactive rate was reduced rapidly. On the other hand, nanoscale Ni/Fe reactivity was decreased over time, probably due to the precipitation on the surface of Ni/Fe.

Figure 2. Reactions of nanoscale Ni/Fe bimetallic particles with PCE. Initial organic concentration was 15.83mg/L, and metal to solution ratio was 0.4g/50mL.

The concentration of Ni^{2+} ion in solution, determined by ICP-MS, was less than 10µg/L when the reaction completed, which suggested that Ni likely served as catalyst within a bimetallic system. At present, there are different opinions on mechanisms of the dechlorination in a bimetallic system. Zhang et al. [5] and Mallat et al.[19]) thought that presence of the noble metal on the surface of iron certainly creates many galvanic cells thus promoting the electron release reactions of iron corrosion. Quan et al.[20]) studied the characteristics on the degradation of TCM, CT and TCE in water using different bimetallic systems (Cu/Fe, Zn/Fe, Pd/Fe, Ni/Fe). The results showed hydrogenation catalyst such as Pd and Ni acted as important function during the transfer of H_{2}. In addition, Pd and Ni as transition metal had vacant orbits, which could form transition compounds with the p electron pair or π bond of chlorine atom in chlorinated hydrocarbons, and decreased the reactive energy.

3.2. Degradation of CT with nanoscale Ni/Fe bimetallic particles

Figure 3(a) showed the results of degradation of CT by using nanoscale Ni/Fe bimetallic particles. Rapid transformations of CT were achieved with nanoscale Ni/Fe bimetallic particles. CT was reduced below detection limits within 60 min. Disappearance of CT reacting with nano-Ni/Fe was plotted in the form of ln(C/C_0) as a function of time in figure 3(a) where C_0 was the initial concentration of CT (26.28mg/L). Plots of the natural logarithm of concentrations of CT versus time through linear regression analysis gave straight line results. Data presented in figure 3(a) indicated that the disappearance of CT exhibited pseudo-first-order behavior (R^2=0.996, n=5). The observed first-order rate constant (k_{obs}) was 4.242h^{-1}. Half-life time (t_{1/2} = ln2/k_{obs}) was 0.16h. The surface-area-normalized rate coefficient (K_{SA}=k_{obs}/P_a) and the surface-area-normalized half-life time (t_{50,N}=P_a×t_{1/2}) was 10.60 mL/( m^2·h) and 0.07h, respectively.

The rate of CT dechlorination observed in this experiment was comparable to the results for PCE.
Observed rate constants of CT and PCE were 4.242 and 0.8487 (h\(^{-1}\)), respectively. This indicated that the degradation rate of CT was 5 times larger than PCE.

![Graph](a) \( \ln(C/C_0) = -4.242t \) \( R^2 = 0.996 \), \( t_{50,N} = 0.07h \)

Figure 3. Reactions of nanoscale Ni/Fe bimetallic particles with CT. Initial organic concentration was 26.28mg/L, and metal to solution ratio was 0.4g/50mL.

Figure 3(b) showed the time course of the product formation when degrading CT by nanoscale Ni/Fe particles. CT in the amount of 0.426mM (26.28mg/L) was completely reduced within 1h while CF, DCM and methane were produced. CF emerged very quickly and peaked (25%) around 0.5h. Complete reduction of CF was achieved around 4h. On the other hand, concentrations of DCM increased continuously to about 15% of the initial CT carbon after 1h and remained essentially constant after that. Methane accumulated with a final yield around 27%. Both DCM (~15%) and methane (~27%) were the major end products for CT reaction.

4. Conclusions

In summary, nanoscale Ni/Fe particles had indicated distinct dechlorination for PCE and CT. The degradation process appeared to be pseudo-first-order. Many advantages of nanoscale Ni/Fe bimetallic particles for treatment of PCE or CT include: 1) due to high specific surface area and high surface reactivity, the nanoscale Ni/Fe particles were observed to suspend in the aqueous solution, which favored to increase the dechlorination rate. Freshly synthesized nanoscale Ni/Fe bimetal for PCE exhibited higher activity. 2) Due to the presence of catalyst Ni on the surface of iron, increased reactivity per unit surface area, and reduced the yield of chlorinated by-product. The reduction of PCE with nanoscale Ni/Fe particles would then completely dechlorinated to non-chlorinated products. 3) cost-effectiveness. However, before this technology can be fully optimized for environmental applications, further study is needed. Considered the low cost of nickel (relative to palladium) and its high activity, Ni/Fe could be a promising reactive reagent for remediation of groundwater contaminated with halogenated carbon. Nevertheless, a better understanding of the kinetics and mechanisms of the rate-limiting process is required to take full advantage of this new treatment technology. The dechlorination of CT with Fe as electron donor was not sequential. Reductive
dechlorination of alkyl chlorides is probably initiated by a one-electron transfer, producing an alkyl radical and liberating a chloride ion [21]. The alkyl radical can rapidly uptake a second electron and a proton from solution [22].

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