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Enhanced dechlorination of tetrachloroethylene by polyethylene glycol-coated zerovalent silicon in the presence of nickel ions

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ABSTRACT

In this study, the combined effect of polyethylene glycol (PEG) and nickel ions on the dechlorination of tetrachloroethylene (PCE) by zerovalent silicon (Si(0)) under anoxic conditions was investigated. PEG was first coated onto the surface of Si(0) to form PEG-coated Si(0) (Si_{PEG}) and the concentration effect of Ni(II) ions at 0.001–2 mM on the dechlorination of PCE by Si_{PEG} was evaluated and optimized. Results of X-ray photoelectron spectroscopy and electron probe microanalysis showed that addition of PEG can not only inhibit the formation of SiO_2 but also change the distribution pattern of SiO_2 from homogeneous distribution to discrete and localized dispersion, resulting in the enhancement of dechlorination efficiency and rat of PCE by Si(0). The dechlorination of PCE by Si_{PEG} followed pseudo-first-order kinetics and the pseudo-first-order rate constant (k_{obs}) for PCE dechlorination was $0.36 \pm 0.02\ h^{-1}$. Addition of Ni(II) exhibited the synergistic effect on the enhanced dechlorination of PCE by Si_{PEG}, and the maximum k_{obs} for PCE dechlorination was $0.79 \pm 0.02\ h^{-1}$, which corresponded to 220–335 times higher than that by Si(0) alone. Hydrogenolysis and hydrodechlorination occurred simultaneously for PCE dechlorination by bimetallic Ni/Si_{PEG} system in the presence of Ni(II) ions, and the product distribution was highly dependent on the mass loading of Ni ions. The surface coverage of Ni onto Si_{PEG} was used to well describe the synergistic effect of Ni(II) and Si_{PEG} on the enhanced dechlorination of PCE by Si(0) under anoxic conditions.

1. Introduction

Zerovalent iron (ZVI) has been widely used as a reductive material for the dechlorination of chlorinated hydrocarbons such as tetrachloroethylene (PCE) and trichloroethylene (TCE) in aquatic environments [1–3]. The dechlorination of PCE and TCE by ZVI is a surface-mediated reaction and is largely controlled by the available surface sites [4–6]. However, the formation of iron oxides on the surface of ZVI decreases the dechlorination efficiency and rate of chlorinated hydrocarbons [7]. In addition, the use of sodium borohydride as the reducing agent to produce nanoscale ZVI may generate and release boron/boron oxide nanoparticles, which can deposit on environmental media and be toxic to organisms [8,9]. Recently, zerovalent silicon (Si(0)) has been demonstrated as a promising material for dechlorination of PCE and carbon tetrachloride [10–12]. Silicon is the second most abundant element in the earth's crust and the cost-benefit is comparable to that of ZVI. A previous study has shown that the reaction rate of PCE dechlorination by Si(0) was 1.5–2.4 times higher than that by ZVI [12]. However, TCE was the major product for PCE dechlorination by Si(0). The addition of second catalytic metal ions can increase the dechlorination rate as well as change the distribution of end products [13–16]. Lee and Doong [11] have recently reported that the reaction mechanism for PCE dechlorination changed from reductive dechlorination to hydrodechlorination in the presence of bimetallic Ni/Si. In addition, the dechlorination rate of PCE by bimetallic Ni/Si increased 15 times when compared with Si(0) alone, clearly showing the superior reactivity of Ni/Si toward PCE dechlorination.

In addition to the second catalytic metal ions, the increase in electron transfer from the reductive metal to chlorinated hydrocarbons in the presence of electron mediators such as surfactants and humid acid is another strategy for the enhancement of dechlorination efficiency [17,18]. Cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate, and Tween 80 are commonly used surfactant in ZVI system [19–21]. Alessi and Li [21] reported that the rate constant for PCE dechlorination increased by factors of 4–19 after adding CTAB to the ZVI system. Our previous study has indicated that polyethylene glycol (PEG) and CTAB could significantly increase the dechlorination efficiency and rate of PCE removal by Si(0) and the reaction rate enhanced by PEG was 1.7 times higher than that by CTAB [10]. Different from the enhanced solubilization of PCE by CTAB, addition of PEG can prevent the formation of silicon dioxide (SiO_2) on Si(0) surface, and further enhances the reaction rate of PCE dechlorination by a factor of

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106 at pH 8.3 ± 0.2. However, the reaction mechanism for PCE dechlorination by Si(0) in the presence of PEG remains unclear.

PEG is a bi-functional amphiphilic polymer with reactive hydroxyl groups on both ends with the advantages of high water solubility, non-toxicity, low cost, and environmental friendliness. Our previous study has indicated that the surface modification with PEG is a simple method to enhance the reactivity of Si(0) toward chlorinated compound dechlorination [10]. In addition, PEG can serve as a cross-linker to immobilize the nanoscale zerovalent metals onto the support and as a chelating agent for adsorption of metal ions [22,23]. Similar to the ZVI, Si(0) is a strong reducing material which can reduce the catalytic metal ions such as Ni^{2+} and Cu^{2+} into the reduced species to form bimetallic Cu/Si and Ni/Si systems for the increase in dechlorination rate of chlorinated hydrocarbon [11,24]. This gives a great impetus to understand the combined effect of nickel ions and PEG on the enhanced dechlorination of PCE by Si(0). However, the synergistic effect of nickel ions and PEG on the dechlorination of PCE by Si(0) has been rarely reported.

In this study, the synergistic effect of nickel ions and PEG on the dechlorination efficiency and rate of PCE by Si(0) was investigated under anoxic conditions. PEG was first coated onto the surface of Si(0) to form PEG-coated Si(0) (Si_{PEG}) and the concentration effect of Ni(II) ions on the dechlorination of PCE by Si_{PEG} was evaluated and optimized. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were utilized to characterize the change in morphology and metal species on the surface of Si(0) before and after the addition of PEG and nickel ions. In addition, the product distribution as well as reaction mechanism for PCE dechlorination by Si_{PEG} in the presence of various mass loadings of Ni(II) was determined.

2. Materials and methods

2.1. Chemicals

Tetrachloroethylene (PCE) (>99.8%, GC grade), trichloroethylene (TCE) (>99.8%, GC grade), and PEG (MW 2000–35,000) were purchased from Sigma–Aldrich Co. (Milwaukee, WI). Tris(hydroxymethyl) aminomethane (Tris buffer) (reagent grade), and zerovalent silicon (>99.5% purity, <100 μm) were purchased from Merck Co. (Darmstadt, Germany). All other chemicals were of analytical grade and were used as received without further purification. Solutions were prepared with high-purity deoxygenated deionized water (Millipore, 18.3 MΩ cm) using a vacuum and N_2 (>99.99%) purging system.

2.2. Preparation of PEG pre-coated silicon (Si_{PEG})

The PEG pre-coated Si(0) was prepared according to our previous work with minor modification [10]. Briefly, 0.5 g of HF-washed Si(0) and 17.5 μg of PEG with various molecular weights ranging from 2000 to 35,000 was added into a 60-mL serum bottle for preparation of Si_{PEG}. After adding 25 mL of anoxic bidistilled deionized water (DI H_2O) and equilibration for 3 h under stirring, the Si_{PEG} was harvested by centrifugation at 6944×g for 5 min and dried by a gentle flow of N_2 gas. Fig. S1 shows the SEM images of HF-washed and PEG-coated Si(0). A smooth surface of fresh Si(0) was observed after washing with HF. However, some white spots were observed onto the surface of Si_{PEG}, presumably attributed to the formation of SiO_2 during the coating of PEG onto Si(0). The XPS spectrum of Si_{PEG} (Fig. S2) showed peaks at 99.4 and 104 eV, which can be assigned as Si(0) and SiO_2, respectively. This means that parts of the silicon surface were oxidized to silica during the preparation step of Si_{PEG}. In addition, the molecular weight as well as carbon length of PEG has little influence on the enhancement of dechlorination efficiency and rate of PCE when the added amounts of PEG are the same (Fig. S3). Therefore, PEG-35000 was selected as the model compound for further experiments.

2.3. Dechlorination experiments.

Experiments were conducted in batch-fed modes using serum bottles sealed with Teflon-lined rubber septa and aluminum crimp caps. In addition, all the serum bottles were initially stored in the anaerobic glove box to maintain the anoxic conditions. 60 mL serum bottles were filled with 0.05 g Si_{PEG}. After being capped with Teflon-lined rubber septa with aluminum crimp caps (The Wheaton Co., NJ), the sealed serum bottles could maintain the anaerobic conditions. Since all the anoxic solutions were prepared using vacuum and N_2-pruging system outside the glove box, serum bottles were transported outside the glove box, and then filled with 25 mL of deoxygenated buffer solutions by 25 mL N_2-purged syringe under anoxic conditions. 50 mM Tris buffer solution was used to control the pH at 8.3 ± 0.1. The stock solution of PCE dissolved in deoxygenated methanol was introduced into the Si_{PEG} system to get a final concentration of 60 μM. In addition, stock solutions of Ni(II) were added into the serum bottles to obtain the final concentrations of 0.001–2 mM. The total volume of the liquid phase was 25 mL, resulting in a 35-mL headspace left for headspace analysis. The bottles were incubated with an orbital shaker at 120 rpm and at 25 ± 1 °C in the dark to well-suspend the Si_{PEG} and bimetallic Ni-Si_{PEG} particles and to minimize the mass transfer limitation in the batch experiments [10–12]. The XPS spectrum of bimetallic Ni/Si_{PEG} particles shown in Fig. S4 clearly indicated two peaks located at 852.7 and 869.9 eV, which corresponded to $2p_{2/3}$ and $2p_{1/2}$ of Ni(0). Parallel experiments were also carried out without the addition of zerovalent silicon. All the experiments were run in duplicate or triplicate.

It is known that the dechlorination of chlorinated hydrocarbons by zerovalent metals is a surface-mediated reaction, and Langmuir-Hinshelwood kinetic model can be used to elucidate the reaction kinetics on the Si_{PEG} surface:

$$r = \frac{dC}{dt} = k_{app}\frac{K_L S_t C}{1 + K_L C} \quad (1)$$

where C is the aqueous concentration of PCE, k_{app} is the limiting-step rate constant of reaction at maximum coverage under the given conditions, S_t is the abundance of reactive sites, and K_L is the Langmuir adsorption coefficient of PCE on reactive sites. Zhu et al. [18] used Langmuir–Hinshelwood kinetic model to elucidate the reaction kinetics of trichlorobenzene on the amphiphile-modified Pd/Fe surface, and found a reasonable consistence between the changes of the pseudo-first-order rate constants (k_{obs}) and $k_L S_t$ with changing amphiphile concentrations. When the concentration C is low and $K_L C \ll 1$, Eq (1) can be simplified to the pseudo-first-order kinetics.

2.4. Analytical methods

The headspace analytical technique was used for the determination of chlorinated hydrocarbons and non-chlorinated hydrocarbons. The concentrations of PCE and the byproducts in the headspace of the test bottles were monitored by withdrawing 40 μL of gas in the headspace using a 50-μL gas-tight syringe. The headspace sample was immediately injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD) and a flame ionization detector (FID) (PerkinElmer, Autosystem, Norwark, CT). A 60-m VOCOL fused-silica megabore capillary column (0.545 mm × 3.0 μm, Supelco Co.) was used to separate the organic compounds. The column was connected to the FID