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Impact of size and sorption on degradation of trichloroethylene and polychlorinated biphenyls by nano-scale zerovalent iron

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HIGHLIGHTS

- nZVIs were synthesized using a layer-by-layer or poly(acrylic acid) stabilization approach.
- These nZVIs were used to degrade TCE and PCB.
- nZVI coatings impacted reactivity by altering pollutants/particle interactions.
- Smaller nZVI particle size led to greater reactivity.

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ABSTRACT

Nano-scale zerovalent iron (nZVI) has been studied in recent years for environmental remediation applications such as the degradation of chlorinated organic contaminants. To overcome limitations related to the transport of nZVI, it is becoming common to add a polymer stabilizer to limit aggregation and enhance the particle reactivity. Another method investigated to enhance particle reactivity has been to limit particle size through novel synthesis techniques. However, the relative impacts of particle size and interactions of the chemicals with the coatings are not yet well understood. The purpose of this study was to investigate the mechanisms of particle size and polymer coating or polyelectrolyte multilayer (PEM) synthesis conditions on degradation of two common chlorinated contaminants: trichloroethylene (TCE) and polychlorinated biphenyls (PCBs). This was accomplished using two different synthesis techniques, a layer-by-layer approach at different pH values or iron reduction in the presence of varying concentrations of poly(acrylic acid). nZVI produced by both techniques yielded higher degradation rates than a traditional approach. The mechanistic investigation indicated that hydrophobicity and sorption to the multilayer impacts the availability of the hydrophobic compound to the nZVI and that particle size also had a large role with smaller particles having stronger dechlorination rates.

1. Introduction

Many environmental sites are contaminated with chlorinated organic pollutants through historical and continuous releases. Two of the most common compounds causing such contamination are trichloroethylene (TCE) and polychlorinated biphenyls (PCBs). TCE has been used as a degreasing agent and has been released into the environment through related applications such as by dry cleaners and military bases. It can form dense nonaqueous phase liquids (DNAPLs) in the environment making it challenging to remediate and leading to long-term releases into groundwater. PCBs were also widely used in previous years for commercial applications as dielectric and coolant fluids such as with electric transformers and capacitors. However, they were subsequently found to have highly toxic effects on humans and environmental organisms. They are resistant to natural abiotic/biotic degradation and thus remain in the environment for extended periods in the absence of remediation.

One approach that has been investigated for the remediation of both of these compounds in recent years is nano-scale zerovalent iron (nZVI) [1–9]. nZVI has been shown to have increased surface area per mass basis and higher reactivity than larger iron particles [5,6]. For example, nZVI has been shown to degrade PCBs without

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elevating the treatment-zone temperature even though larger iron particles cannot degrade PCBs at ambient conditions [5,6]. The addition of another metal to produce a bimetallic catalyst such as Fe/Pd or Fe/Ni can usually further increase the degradation rates. nZVI has also been researched for the remediation of areas impacted by arsenic [10–12] and cadmium [13].

Nevertheless, there have been limitations to the application of nZVI such as its tendency to agglomerate in the absence of stabilizing polymers [2,4] and its limited mobility in subsurface systems without added polymers [14–18]. Thus, usage of surface coatings has recently been researched to facilitate the transport of nZVI [14–18]. While coatings have been added after nZVI synthesis to minimize aggregation [4], they have also been used in the synthesis of nZVI to produce smaller and more monodisperse particles [7,8]. These particles have been shown to substantially increase the rates of the contaminant degradation, but the mechanisms are not yet fully understood. There could be several possibilities. For example, the changed micro-environment in the nanoparticle/surface coating may alter relative hydrophobicity that in turn impacts the pollutants/particle interactions.

The purpose of this study was to test a matrix of experimental conditions to better understand the mechanisms of nZVI-mediated contaminant degradation. Very small (<10 nm) nZVI particles were produced using two different synthesis methods: a layer-by-layer (LbL) and a slurry synthesis method. These particles were used to degrade two common organic pollutants with different hydrophobicities (TCE and PCB) in the absence and presence of Pd to form a bimetallic catalyst with enhanced reactivity. A range of nanoparticle synthesis conditions were used to test the impact of pH and stabilizer concentration. The LbL synthesis method was reported in our previous study [8], which has subsequently been researched for various environmental applications [19–22]. The slurry synthesis method described here is novel and is expected to facilitate NP transport in subsurface environments.

2. Experimental

2.1. Materials

The following materials were utilized in this study. Poly(allylamine hydrochloride) (PAH) (Mw = 70,000) and palladium(II) acetate trimer (99.98% Pd on metal mass basis, Pd was 47% minimum of total mass) were purchased from Alfa Aesar (Ward Hill, MA). Poly(acrylic acid) (PAA) (MW = 90,000, 25% solids in water) was purchased from Polysciences (Warrington, PA), while $FeSO_4{\cdot}7H_2O$, and $NaBH_4$ were from Fisher (Morris Plains, NJ). Glass beads (150–212 μm) was purchased from Sigma–Aldrich (St. Louis, MO). Trichloroethylene (99+%) was from Acros Organics (Pittsburgh, PA). 2,2′,4,4′-Tetrachlorobiphenyl (PCB-47) was from Promochem (Wesel, Germany). Carbon-coated copper grids used in the transmission electron microscopy analysis were from Ted Pella Inc. (Redding, CA). All solutions and rinsing procedures used distilled deionized water (>18 MΩ cm) produced by a Milli-Q ultrapure water system (Millipore).

2.2. ZVI nanoparticle synthesis

ZVI nanoparticles were prepared either using an LbL or slurry approach. The LbL method was identical to that described in a previous report [8]. Briefly, polyelectrolyte multilayers comprising PAA and PAH were assembled either on glass beads previously treated by the RCA procedure [23]. PAA and PAH solutions were adjusted to the desired pH (2.5, 3.5, or 4.5) by slowly adding either 1 mol/L HCl or NaOH. Samples used in the sorption experiment were also prepared without controlling the initial pH. The pH of the synthesis solutions in which the pH was initially controlled changed by 0.2 units or less during the synthesis procedure. Glass beads were immersed in 10 mmol/L (by repeating unit) PAH or PAA solution for 5 min followed by three 2 min immersions into water as rinsing steps. The immersion/rinsing steps were repeated to make fifteen bilayers formed by alternating immersions in PAH and PAA. To form the ZVI nanoparticles, the support substrate with polyelectrolyte multilayer (PEM) was then immersed for 30 min in $FeSO_4$ solution that was adjusted to the same pH at which the PEM was assembled, a step that allowed ferrous cations to complex with available free carboxyl groups on PAA through ion exchange. The PEM was then rinsed. The substrates were then immersed in 10-mmol/L $NaBH_4$ solution to reduce ferrous to Fe^0 nanoparticles. The ion exchange and reduction processes were repeated for nine cycles. The samples were stored in anhydrous ethanol until use. For nZVI support materials prepared at pH values of 2.5, 3.5, and 4.5, iron loadings were previously determined to be 2.25 mg/g, 3.59 mg/g, and 3.32 mg/g, respectively [8]. Previous characterization using transmission electron microscopy with energy dispersive X-ray spectroscopy and electron energy loss spectroscopy, and X-ray photoelectron spectroscopy confirmed that zero-valent iron nanoparticles were formed with an oxide coating [8]. The average sizes of nZVI nanoparticles synthesized at pH values of 2.5, 3.5, and 4.5 were 2.87 nm, 2.28 nm, and 1.51 nm, respectively [8].

For experiments using ZVI in slurry form, the ZVI-nanoparticles were formed in situ by reducing a defined solution volume of ferrous ions dispersed with different levels of PAA (0.1%, 0.2%, and 0.4% with respect to the volume of solution, attaining solution pH values of 3.6, 3.4, and 3.0 before reduction, respectively) with the aid of excess sodium borohydride. The ZVI slurry formed was centrifuged, the supernatant discarded, and the solids rinsed with helium-purged de-ionized water for immediate use in reaction studies or characterization. Solutions of nanoparticles prepared using the slurry method were added to carbon-coated copper grids and examined using transmission electron microscopy (TEM) with a FEI Titan Analytical TEM operated at 300 kV. Images were recorded from at least two different grid squares for each sample, and the size of 200 particles was measured manually using Digital Micrograph. For experiments with palladium added to increase the reactivity of the iron nanoparticles, palladium was added at a concentration of 0.50% of the iron loading observed for the specific experimental condition.

2.3. Sorption to PEM assessment

Both TCE and PCB-47 were assessed for sorption to the polyelectrolyte multilayer (PEM). PEM obtained with 15 cycles of PAH/PAA on glass beads were added to 40 mL centrifugal borosilicate tubes. Sorption was tested in vials filled to minimize headspace. PCB-47 was tested at concentrations (45 μg/L, 15 μg/L, and 5 μg/L) below its solubility limit (54 μg/L), and TCE was tested at a concentration of 10 mg/L. Except for the unbuffered condition for which the pH was not controlled, a 10 mmol/L phosphate buffer was used to maintain the pH at the prescribed value. Because the concentration of the phosphate buffer was larger than the other components in the system, the pH was not monitored during the sorption experiments. The solution pH was maintained at values of 2.5, 3.5 and 4.5, and these mixtures were then allowed to equilibrate for 24 h. Aliquots of the supernatant were then collected from each vial and analyzed using gas chromatography–mass spectrometry (GC–MS) as described below. The remaining solution was then discarded, and the glass beads containing the PEM were rinsed three times with de-ionized water. Acetone or isooctane was then added to each vial containing the glass beads to desorb TCE and PCB-47, respectively. The vials were bath sonicated, and the solvent tested according