



# Degradation of TCE, PCE, and 1,2–DCE DNAPLs in contaminated groundwater using polyethylenimine-modified zero-valent iron nanoparticles

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## ABSTRACT

Remediation of dense non-aqueous phase liquid (DNAPL), which consists primarily of chlorinated solvents, is considered a top priority in the field of groundwater decontamination. Downward migration of DNAPL can lead to formation of impermeable strata due to low solubility and high density. Remediation is therefore one of the most complex technical challenges faced by environmental engineers. In the present work, remediation of trichloroethylene (TCE), perchloroethene (PCE), and 1,2-dichloroethene (1,2-DCE) DNAPL-contaminated groundwater was studied by a reductive reaction with polyethylenimine (PEI) surface-modified zero-valent iron nanoparticles (PEI–nZVI). Compared with fresh nZVI, PEI–nZVI exhibited smaller spherical particles of 20–80 nm and a greater surface area of 53.4 m<sup>2</sup>/g. Furthermore, slow desorption of the PEI indicated its potential application as a protective shell layer for efficient delivery of active nZVI to the water/DNAPL interface. Laboratory batch remediation results indicate that both nZVI and PEI–nZVI can remove 99% of TCE, PCE, and 1,2-DCE. The rate of reaction for fresh nZVI was higher in the early stage. Comparatively, PEI–nZVI had a higher removal rate and efficiency after 2 h. The kinetic studies also revealed that the removal rate for 1,2-DCE was greater than that for TCE and PCE. Additionally, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy studies indicated that the nZVI and PEI–nZVI have two central Fe atoms coordinated by primarily Fe–O and Fe–Fe with bond distances of 1.87 Å and 3.05 Å, respectively. Furthermore, after the reductive reaction, nZVI and PEI–nZVI were oxidized to Fe<sub>3</sub>O<sub>4</sub>, and bond distance values for the reacted samples were 1.94 Å and 1.96 Å, respectively.

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## 1. Introduction

Chlorinated volatile organic compounds (CVOCs), such as TCE, PCE, and 1,2–DCE, that have low aqueous solubility and a greater density than water are known as DNAPLs (Baker et al., 2016; Chen and Wu, 2017; Pérez-de-Mora et al., 2014) and are widely used in the cleaning, extraction, foam, spray, and solvent manufacturing industries. The DNAPL contaminants are a type of recalcitrant compounds prevalent at contaminated sites (Dong et al., 2016; He et al., 2015). These DNAPL compounds have a stable chemical structure and are degraded very slowly in environmental systems

(Fu et al., 2014; Hiortdahl and Borden, 2013; Tang et al., 2015). Due to low solubility and high density, they can be quickly deposited as an impermeable layer at the bottom of an aquifer. Contaminated zones can serve as a persistent source of groundwater pollution, posing grave risks to humans and ecosystems (Heron et al., 2016; Orozco et al., 2015; Power et al., 2014). Over time, DNAPL sources dissolve in groundwater and form plumes, leading to the closure of downgradient water supply wells and creating vapor intrusion issues in buildings located above the plume (Baker et al., 2016). Conventional remediation strategies such as pump and treat involve excavation and plume management via either advanced oxidation processes to degrade the chlorinated compounds or air stripping to transfer contaminants to other media, both of which pose high operational costs (Parker et al., 2012; Trellu et al., 2016; Wang et al., 2012). Therefore, *in-situ* remediation techniques for

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the treatment of DNAPL bring substantial economic benefits by allowing soil or groundwater to be treated without being excavated and transported (Baker et al., 2016; Hiortdahl and Borden, 2013; Obiri-Nyarko et al., 2014; Sheng et al., 2016; West and Kueper, 2012).

Over the last two decades, many laboratory and field studies have demonstrated that through the emplacement of permeable reactive barriers (PRB), zero-valent iron nanoparticles (nZVI) can effectively transform chlorinated contaminants at much faster rates than other *in-situ* technologies (Baker et al., 2016; Fu et al., 2014). Nevertheless, PRB treatment still relies on dissolution of DNAPLs and transport of the dissolved chlorinated solvents to the PRB, which poses long-term monitoring and remediation costs (Ma et al., 2015; Quinn et al., 2005; Su et al., 2013; Wang et al., 2015). In order to overcome the limitations of PRB, the viable approach is improving the dissolution of pooled DNAPLs using surfactant solutions (Ma et al., 2017; Wang et al., 2012). Alternatively, reactive agents such as nZVI can be transported to the DNAPL sources (Goswami et al., 2017; Huang et al., 2016; Ma et al., 2017).

Zero-valent iron nanoparticles have increasingly gained attention from researchers and practitioners recently due to its highly reactivity, cost effectiveness, and potential to treat a various range of contaminants (Mukherjee et al., 2016). Zero-valent iron nanoparticles exhibit greater degradation rates, because it has a greater surface area and reactivity from faster corrosion (Goswami et al., 2017; He et al., 2015; Oprčkal et al., 2017).

Numerous studies confirmed nZVI powder can degrade a wide range of contaminants, even more than that of granular form. It is attributed to their extremely high specific surface areas, resulting in high reaction rates by orders of magnitude than those of millimetric iron (Ghosh et al., 2017; Lien and Zhang, 2001). Moreover, nano-scale zero-valent iron is well known as an electron-source material for the *in-situ* remediation of contaminants in groundwater. However, nZVI is high susceptible to forming large aggregates that is ascribed to the magnetic properties and speedy oxidation of metallic iron. Thus, these new-formed aggregates with less surface active sites and reaction rate, restricting the stability and mobility of nZVI in subsurface environment (Huo et al., 2017; Kim et al., 2014; Phenrat et al., 2007; Sun et al., 2007; Teng et al., 2017; Tosco et al., 2014). Owing to these limitations, there is a need to evade aggregation and oxidation by developing cost-effective applications of nZVI. For an effective utilization of *in-situ* DNAPLs remediation, nZVI should remain long-time suspended in slurry for the efficient injection into the contaminated site (Comba et al., 2011; He and Zhao, 2005). Furthermore, efficient delivery of nZVI to the water/DNAPL interface without flocculation and oxidation is the key for achieving maximum efficiency (Dong and Lo, 2013; Lin et al., 2013; Lubphoo et al., 2016; Tang et al., 2015). Surface modification of nZVI with a protective polymer layer keeps nZVI separated from dissolved oxygen and hydrogen while creating an affinity for the water/DNAPL interface, therefore enhancing the destruction of chlorinated DNAPL in source zones (Golshirazi et al., 2017; Noubactep et al., 2012). On the other hand, the disadvantages of nZVI such as facile aggregation/oxidation, poor mobility, and low stability can be solved by coating PEI on the surfaces of nZVI particles, forming PEI–nZVI composite material (Bennett et al., 2010; Ghosh et al., 2017; Goswami et al., 2017; He et al., 2010; Henn and Waddill, 2006; Oprčkal et al., 2017). Comparison of nZVI, composite PEI–nZVI can be fast injected into the source of contamination through subsoil. Apart from PEI, there are another polymeric materials can well-suspended the nZVI in water (Comba et al., 2011; He and Zhao, 2005). However, PEI exhibits remarkable content of functional groups, good water solubility, and chemical stability for a great affinity with metals. Polyelectrolyte character and larger macromolecular size of PEI make them very useful in

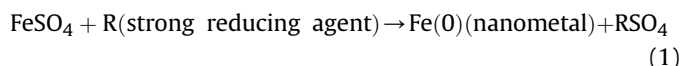
sequestering metal ions from dilute solutions (Chaufer and Deratani, 1988; Kobayashi et al., 1987). In addition, PEI offers good hydrophilicity, high rate, and capacity of adsorption for contaminants (Chen et al., 2010). Kim et al. (2017) have confirmed that the triphenylphosphine (TPP)-coated nZVI also enhanced the stability of nZVI, and inhibited the agglomeration/sedimentation of nZVI. Furthermore, the reactivity of nZVI is controlled by the nature of the ligand and coating procedure. For instance, high concentrations of sodium dodecyl sulfate and alcohols (Huo et al., 2017; Loraine, 2001; Wang et al., 2012) decrease nZVI reactivity, while Triton X-a00 (Loraine, 2001) and biodegradable vegetable oil (Quinn et al., 2005) can enhance TCE reduction. Furthermore, surface modification reduces nZVI activity due to uncontrolled sequestering of DNAPLs in mobile micelles (Dong and Lo, 2013; Fu et al., 2014; Noubactep et al., 2012; Wang et al., 2015).

Therefore, the present work aimed to study the treatment of TCE, PCE, and 1,2-DCE contaminated wastewater using PEI–nZVI. In this context, the effects of different concentrations and time scales on the degradation of contaminants were evaluated. The removal rate and efficiency of PEI–nZVI was compared with those of fresh nZVI. Furthermore, X-ray photoelectron spectroscopy (XPS) and X-ray Absorption near edge spectroscopy (XANES) was also used to determine the corrosion products and the mechanisms of DNAPL reduction on nZVI and PEI–nZVI surfaces.

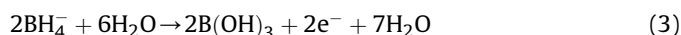
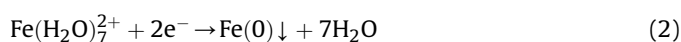
## 2. Materials and methods

### 2.1. Preparation of nZVI and PEI–nZVI

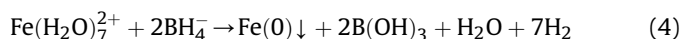
The zero-valent iron nanoparticles were prepared using a well-known chemical reduction method that employs sodium borohydride as a reducing agent. Ponder et al. (2000), first proposed the use of NaBH<sub>4</sub>, a strong reducing agent for Fe (0) precipitation. The reaction can be described as:



The reaction of a ferrous sulfate aqueous solution with this strong reducing agent takes place in two steps:



By merging the two half-reactions, the complete reaction becomes:



Following this method, 10 g of FeSO<sub>4</sub>·7H<sub>2</sub>O were dissolved in 100 mL of 30% ethanol, and 70% deionized (DI) water. The pH value was adjusted to 6.8 with 3.8 N NaOH<sub>(aq)</sub>. After the addition of 1.8 g NaBH<sub>4</sub> powder, the mixture was stirred for 20 min, and the residues were then washed several times with ethanol. The resulting nZVI were vacuum-dried overnight. The PEI solution was prepared by dissolving an appropriate amount of the polymer into DI water followed by sonication for 2 h. Upon mixing the polymer solution with the resulting particles, the resultant mixture was sonicated for 1 h and then dried in an oven at 80 °C for 12 h.

### 2.2. Characterization of nZVI and PEI–nZVI

The morphology and microstructure of the nZVI were determined by FE–SEM/EDS (Hitachi, S–4700 Type II) and TEM (Hitachi, H–7500) with a resolution of 0.1 nm. The crystal structure of nZVI

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