# Effect of anions and humic acid on the performance of nanoscale zero-valent iron particles coated with polyacrylic acid

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## HIGHLIGHTS

- Polyacrylic acid (PAA) coating impeded the Fe(0) core oxidation by humic acid.
- PAA-coated NZVI showed 2.3-fold greater TCE degradation capacity than uncoated NZVI.
- At a very low molar ratio of anions/NZVI, a reactivity increase of NZVI was observed.
- A hydrodechlorination pathway for TCE was observed in the absence of metallic catalysts.

## ARTICLE INFO

## ABSTRACT

Effects of anions ($NO_3^-$, $HCO_3^-$, $Cl^-$, $SO_4^{2-}$) and humic acid on the reactivity and core/shell chemistries of polyacrylic acid-coated nanoscale zero-valent iron (PAA-NZVI) and inorganically modified NZVI (INORG-NZVI) particles were investigated. The reactivity tests under various ion concentrations (0.2–30 mN) revealed the existence of a favorable molar ratio of anion/NZVI that increased the reactivity of NZVI particles. The presence of a relatively small amount of humic acid (0.5 mg $L^{-1}$) substantially decreased the INORG-NZVI reactivity by 76%, whereas the reactivity of PAA-NZVI decreased only by 12%. The XRD and TEM results supported the role of the PAA coating of PAA-NZVI in impeding the oxidation of the Fe(0) core by groundwater solutes. This protective role provided by the organic coating also resulted in a 2.3-fold increase in the trichloroethylene (TCE) reduction capacity of PAA-NZVI compared to that of INORG-NZVI in the presence of anions/humic acid. Ethylene and ethane were simultaneously produced as the major reduction products of TCE in both NZVI systems, suggesting that a hydrodechlorination occurred without the aid of metallic catalysts. The PAA coating, originally designed to improve the mobility of NZVI, enhanced TCE degradation performances of NZVI in the presence of anions and humic acid.

## 1. Introduction

The redox reactivity of zero-valent iron (ZVI) is of interest in the environmental remediation of contaminated soil and groundwater. Since the late 1990s, nanoscale ZVI (NZVI) particles have attracted research interest because of their higher reduction and sorption capabilities stemming from their very small particle sizes. Significant advances have been made with respect to the NZVI-mediated treatment of various contaminants, including chlorinated ethylenes (trichloroethylene; TCE) and methane derivatives (carbon tetra-chloride), nitrogen compounds (nitrates), heavy metals (As, Cd),

dyes (AB24), and emerging contaminants (polybromodiphenyl ether, antibiotics) (Matheson and Tratnyek, 1994; Wang and Zhang, 1997; Kanel et al., 2005; Yang and Lee, 2005; Lin et al., 2008; Ghauch et al., 2009; Boparai et al., 2011; Qiu et al., 2011). However, further research should be conducted on the fate and toxicity of NZVI that would be injected to the subsurface for the purpose of remediation.

Recently, polyacrylic acid (PAA)-modified NZVI particles (NANOFER 25S, NANO IRON s.r.o., Czech Republic) have been commercially introduced and successfully used for the remediation of contaminated soil and groundwater in Europe (Mueller and Nowack, 2010). This commercially available NZVI is produced by the hydrogen reduction of natural ferrihydrite (Filip et al., 2007); further modification with PAA stabilizes the NZVI particles by

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forming a negatively charged surface, and enhances its mobility in the subsurface environment (Schrick et al., 2004). Extensive studies have been conducted for enhancing the mobility of NZVI particles using various surfactants and polyelectrolytes, including PAA (Wielant et al., 2007; Johnson et al., 2009; Phenrat et al., 2009; Raychoudhury et al., 2010; Chen et al., 2011). However, investigations into changes in the characteristics and reactivities of surface-modified NZVI particles when reacted with various groundwater solutes such as anions and natural organic matters (NOMs) have not been actively pursued, despite the importance of the potential effects of surface coatings on the reactivity of NZVI particles. This fundamental knowledge on the potential roles of organic coatings will further aid in extending the application of NZVI particles to site remediation.

Numerous studies have been conducted on the effects of anions ($NO_3^-$, $Cl^-$, $SO_4^{2-}$, and $HCO_3^-$) and NOMs on the reactivity of micro-sized ZVI materials. Nitrate has been reported to noticeably decrease the reactivities of ZVI particle by competing with other contaminants for reactive sites on the ZVI particle surface (Farrell et al., 2000; Alowitz and Scherer, 2002). However, the effects of other anions are not clearly understood because of the two contrasting reaction mechanisms taking place on the iron surface. First, anions such as $HCO_3^-$, $Cl^-$, and $SO_4^{2-}$ are reported to increase the reactivity of iron particles by accelerating the Fe(0) dissolution and removing the passivating iron oxide layers from the ZVI surface; second, other anions are known to decrease the reactivity by forming iron precipitates, thereby blocking the reactive sites on the iron particles (Johnson et al., 1998; Klausen et al., 2001; Agrawal et al., 2002; Su and Puls, 2004; Liu et al., 2007). However, iron precipitates do not necessarily decrease the reactivity. For instance, Klausen et al. (2003) have reported the formation of a green rust that provided a redox-active phase for reductively dechlorinating contaminants and Noubactep (2008) and Ghauch et al. (2010) reported removal of organic contaminants. Iron corrosion products were also reported to remove organic contaminants by adsorption.

Previous studies on NOMs in the NZVI area have focused mostly on the colloidal effects of NOMs in enhancing the mobility of NZVI particles in the subsurface, rather than on the effects on the reactivity of the NZVI particles themselves (Wielant et al., 2007; Johnson et al., 2009; Chen et al., 2011; Tratnyek et al., 2011). The organic functional groups comprising NOMs, such as carboxyl acids, hydroxyls, phenolics, and amines, could interact with the coatings/surfaces of NZVI particles, thus potentially influencing their reactivities.

Therefore, experimental studies were performed to further elucidate the effects of the anions and NOM on the reactivity, degradation capacity and core/shell chemistries of PAA-NZVI. The kinetics of TCE reduction by PAA-NZVI was investigated using batch reactors containing individual and mixed solutes ($NO_3^-$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$, and humic acid). For comparison, an inorganically modified NZVI (INORG-NZVI) was also tested under the same experimental conditions. The TEM and XRD analyses were performed on the NZVI particles to investigate the changes in their morphological and mineralogical characteristics during TCE reduction. Finally, the TCE degradation capacities of PAA-NZVI and INORG-NZVI were evaluated and the degradation products were analyzed.

## 2. Materials and methods

### 2.1. Iron nanoparticles and chemicals

Two types of commercial NZVI particles were purchased from NANO IRON s.r.o (Czech Republic); namely NANOFER 25 particles, which contain an inorganic coating for reactivity enhancement (INORG-NZVI), and NANOFER 25S particles, which are modified by PAA to enhance their mobilities (PAA-NZVI). The particles were stored in an anaerobic chamber (SHEL Lab Bactron 1.5, USA). The characteristics of the inorganic coating in NANOFER 25 have not yet been reported. However, according to a previous study (Klimkova et al., 2011), the organic coating of NANOFER 25S is PAA, which is used to stabilize the NZVI particles. The weight ratio of PAA/NZVI is 1/10.

All experiments were conducted using deionized/deoxygenated (DI/DO) water. The anions used ($Cl^-$, $HCO_3^-$, $NO_3^-$, and $SO_4^{2-}$) were obtained as sodium salts such as NaCl, $NaHCO_3$ (Junsei Chemical, Japan), $NaNO_3$, and $Na_2SO_4$ (Kanto Chemical, Japan). Humic acid (sodium salt, Aldrich Chemistry) was used as an NOM surrogate. The other chemicals used were TCE (99%, Acros Organics), 1,1-dichloroethylene (1,1-DCE; 99.5%, Fluka), *cis*-DCE (97%, Acros Organics), *trans*-DCE (99.7%, Acros Organics), vinyl chloride (VC; 2.0 mg mL$^{-1}$ in methanol, Supelco), 1% ethylene in nitrogen (Matheson Tri-Gas), 1% acetylene in nitrogen (Matheson Tri-Gas), 1% ethane in nitrogen (Matheson Tri-Gas), hexane (99% HPLC grade, J.T. Baker), and methanol (99% HPLC grade, J.T. Baker).

### 2.2. Background solutions containing anions and/or humic acid

The concentrations of the anions and humic acid were based on those observed at a TCE-contaminated groundwater site in Wonju, South Korea. TCE was found at a maximum concentration of 0.1 mM. The average concentrations of the anions at the site were 1.95 mN (69.1 mg L$^{-1}$) $Cl^-$, 1.14 mN (69.4 mg L$^{-1}$) $HCO_3^-$, 0.15 mN (9.3 mg L$^{-1}$) $NO_3^-$, and 0.44 mN (21.3 mg L$^{-1}$) $SO_4^{2-}$. The average dissolved organic carbon (DOC) concentration at the site was 2.5 mg L$^{-1}$. The concentration of the anions in the kinetic experiments varied between 0 and 30 mN and that of humic acid between 0 and 25 mg L$^{-1}$, which was designed to cover the site concentrations as well as to investigate the effects of those solutes at various concentrations. Synthetic groundwater in this study denotes a solution containing the four aforementioned anions and humic acid in the field average concentrations.

### 2.3. Kinetic experiments

Batch degradation experiments were carried out in clear borosilicate glass vials (nominal volume of 20 mL) equipped with a mininert valve (24 mm, VICI, USA) that was designed to minimize the oxygen intrusion. All experiments were conducted in an anaerobic chamber using DI/DO water. Batch reactors contained 20 mL of the aqueous solution, with minimal headspace volumes (0.3–0.6 mL). This allowed for 2–4% of the headspace partitioning of TCE, which was considered insignificant. The dosage of the NZVI particles was 5 g L$^{-1}$ for most of the experiments; dosages of 2.5, 5, and 25 g L$^{-1}$ were used for experiments examining the effect of the NZVI dosage on TCE degradation.

To initiate the experiments, an aliquot of a TCE stock solution was introduced to vials containing an aqueous solution and NZVI particles to yield a TCE concentration of 0.1 mM. The vials were then placed on an end-over-end rotator at 30 rpm in the anaerobic chamber at room temperature (22.5 ± 1.0 °C). At each sampling event, an aqueous sample (50 μL) was withdrawn and transferred to a 2 mL gas chromatograph (GC) vial filled with hexane (1 mL) for solvent extraction to analyze the TCE content and degradation products (DCEs, VC, acetylene, ethylene, and ethane). To test the degradation capacity of NZVI particles, an aliquot of the TCE stock solution with a concentration of 500 mM was added to the reactors at the end of each TCE degradation cycle in order to restore the initial TCE concentration of 0.1 mM. The vials were then placed