

Synthesis of iron nanoparticles with poly(1-vinylpyrrolidone-co-vinyl acetate) and its application to nitrate reduction

Nara Lee ^{1a}, Kyunghoon Choi ¹, Basil Uthuppu ², Mogens H. Jakobsen ²,
Yuhoon Hwang ³, Mette M. Broholm ³ and Woojin Lee ^{*1}

¹ Department of Civil and Environmental Engineering, Korea Advanced Institute for Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

² Department of Micro- and Nanotechnology, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

³ Department of Environmental Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

(Received December 14, 2013, Revised March 14, 2014, Accepted March 25, 2014)

Abstract. This study aimed to synthesize dispersed and reactive nanoscale zero-valent iron (nZVI) with poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA), nontoxic and biodegradable stabilizer. The nZVI used for the experiments was prepared by reduction of ferric solution in the presence of PVP/VA with specific weight ratios to iron contents. Colloidal stability was investigated based on the rate of sedimentation, hydrodynamic radius and zeta potential measurement. The characteristic time, which demonstrated dispersivity of particles resisting aggregation, increased from 21.2 min (bare nZVI) to 97.8 min with increasing amount of PVP/VA (the ratios of 2). For the most stable nZVI coated by PVP/VA, its reactivity was examined by nitrate reduction in a closed batch system. The pseudo-first-order kinetic rate constants for the nitrate reduction by the nanoparticles with PVP/VA ratios of 0 and 2 were 0.1633 and 0.1395 min⁻¹ respectively. A nitrogen mass balance, established by quantitative analysis of aqueous nitrogen species, showed that the addition of PVP/VA to nZVI can change the reduction capacity of the nanoparticles.

Keywords: Poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA); nanoscale zero-valent iron (nZVI); colloidal stability; nitrate reduction

1. Introduction

Nanoscale zero-valent irons (nZVIs) have been studied and developed as one of the most promising materials for soil and groundwater remediation (Elliott and Zhang 2001). Intensive efforts have been made to synthesize and manipulate iron nanoparticles with high reactivity and specific functions. For example, methods for reduction of ferrous and ferric solutions by sodium

*Corresponding author, Professor, E-mail: woojin_lee@kaist.ac.kr

^a Ph. D. Student, E-mail: nr56@kaist.ac.kr

borohydride have been thoroughly investigated to achieve nZVI with higher surface area (Wang and Zhang 1997, Lien and Zhang 2001, Liu *et al.* 2005). To degrade a variety of pollutants rapidly to innocuous products, additional enhancers such as palladium (Zhang *et al.* 1998) and vitamin B₁₂ (Amir and Lee 2011) have been applied to enhance reducing power and sorption capacity of nZVI.

Although nZVI has been certainly known to degrade a variety of contaminants, numerous in situ application studies have been reported that deterioration of reactivity caused by the aggregation of the nanoparticles made their application to the subsurface environments difficult (Saleh *et al.* 2007). A pilot-scale study showed that nZVIs were injected and transported only a few meters from injection area (Schrick *et al.* 2004). Therefore, aggregation property should be controlled although the reducing agents such as nZVI have been successfully degraded target contaminants under subsurface conditions (Cao *et al.* 2005). Due to relatively high ionic strength and density of iron, iron nanoparticles tend to agglomerate together so that they have limited mobility in soil below ground surface (Schrick *et al.* 2004, Noubactep *et al.* 2012). Not only stability, also the reactivity of synthesized iron nanoparticles was important for remediation of soil and groundwater contaminated with several contaminants including chlorinated solvents, dyes and heavy metals. (Sun *et al.* 2006, Phenrat *et al.* 2009, Hotze *et al.* 2010). It is necessary to deliver the particles retaining their reactivity to where they needed to be placed. For this purpose, various nanomaterials have been manipulated by adopting surface coating materials such as surfactants, polymers, polyelectrolytes to enhance their colloidal stability or give functionality (Hotze *et al.* 2010). Surface of ZVI nanoparticles can be modified by adding such materials to inhibit aggregation, decrease adhesion to solid porous media, and increase mobility in the subsurface (He *et al.* 2009). Some surfactants, adsorbed or covalently bonded on iron surface, prevented agglomeration effectively by increasing electrostatic repulsion (Zhang *et al.* 2011). However, it was achieved only when sufficient amount of surfactants was applied to make a complete micelle and the molecules of surfactants could be easily detached from the surface of particles (Crane and Scott 2012). As a more advanced technology modifying nZVI surface has been developed, a wide spectrum of polymers which can be adsorbed more stronger than surfactants to provide the targeted delivery has been well accepted and applied, including carboxymethyl cellulose (He and Zhao 2007), guar gum (Tiraferri *et al.* 2008), polyacrylic acid (Cirtiu *et al.* 2011) and polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (Sun *et al.* 2007).

Poly(1-vinylpyrrolidone-co-vinyl acetate) (PVA/VA), one of the widely used non-ionic amphiphilic copolymers, is soluble in both hydrophilic liquids such as water and hydrophobic solvents and chemically stable. Biodegradable PVP/VA film with good plasticity and elasticity can be formed in water as well as organic solvents (Bühler 2008). Using this property, it has been applied to gold colloids (Mirescu and Prübe 2006) and platinum nanocatalysts (Mayer and Mark 1996), but not tried for iron nanoparticles up to date.

The objective of this research is to investigate on the effect of the coated polymer on the stability and reactivity of surface modified nZVI for the application to in situ remediation technology. We selected nitrate as a representative groundwater contaminant because it is one of major pollutants in groundwater and has been known to be hazardous to human health (methemoglobinemia and blue baby syndrome) and result in formation of carcinogenic nitrosamine in the human body (Jung *et al.* 2012). In this work, PVP/VA as a surface modifier was investigated for its dispersivity to make nZVIs stable and reactive and it was compared to that in untreated nZVI. Optimal amount of PVP/VA was evaluated by changing the molar ratio of concentration of PVP/VA to that of Fe²⁺ during synthesis of coated nZVIs. With the various ratios of PVP/VA and iron, nitrate reduction was examined as well.

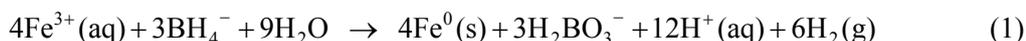
2. Materials and methods

2.1 Chemicals

Ferric chloride (FeCl_3 , $\geq 99.0\%$), sodium borohydride (NaBH_4 , $\geq 98.0\%$), ethanol (99.9%) and PVP/VA (e.g., Kollidon® VA 64, copovidone and copolyvidone, 98%) were obtained from Sigma-Aldrich. Sodium carbonate (Na_2CO_3 , $\geq 99.5\%$), sodium bicarbonate (NaHCO_3 , $\geq 99.5\%$), nitric acid (HNO_3 , 70%), sodium nitrate (NaNO_3 , $\geq 99.0\%$), sodium nitrite (NaNO_2 , = 99.5%) and ammonium chloride (NH_4Cl , $\geq 99.5\%$) were used to prepare eluent, stock and standard solution for ion chromatograph analysis. Milli-Q water (18 $\text{M}\Omega\cdot\text{cm}$) was deoxygenated by nitrogen purging for 4 hours prior to use (Lee *et al.* 2000, Choi and Lee 2008). Unless otherwise stated, every chemical was used as received without further treatment.

2.2 Synthesis of iron nanoparticles

The synthesis method for bare iron nanoparticle (1 g Fe/L) was adapted from He *et al.* (2007). We used FeCl_3 as precursor because it has been reported that the nZVI made from FeCl_3 showed the same uniform shape and size with that made from hydrated ferrous originated particle, which has good stability and reactivity (Greenlee and Hooker 2012). In brief, 0.29047 g (~1.8 mM) of ferric chloride was dissolved with 70 mL of deaerated deionized water (DDIW) and 25 mL of ethanol in 250 mL Schlenk flasks equipped with tunable mechanical stirrer (250 rpm) and nitrogen purging line to completely mix each component and maintain anaerobic condition during whole procedures. An appropriate amount (0.26 g (~6.9 mM)) of sodium borohydride was dissolved with DDIW (5 mL) and then added into the flask dropwise at a constant flow rate of 10 mL/min using a peristaltic pump. The reduction reaction is expressed as follows (Hwang *et al.* 2011)



The mixture was stirred for 30 min regarded as the end point of hydrogen gas generation. Then supernatant with excess dissolved salt was removed via centrifugation (4500 rpm ($2739 \times g$) for 10 min) and the solid was re-suspended by replaced DDIW. This was performed one more time. DDIW was used again the last washing step.

For the preparation of PVP/VA coated nZVIs, we applied pre-grafting method (Sun *et al.* 2007) rather than post-grafting, which was known as more advantageous synthesis way to give high stability. PVP/VA was added to Fe^{3+} precursor solution and mixed under nitrogen purging condition for 30 min before titrating sodium borohydride. The concentrations of solutions were determined based on Eq. (1) and Table 1. Previous research results reported that iron molecules were attached on the polymer chains and then reduced to Fe^0 particles in the chain structure (Cirtiu *et al.* 2011). Other procedures were identical to the preparation step for bare nZVI synthesis.

2.3 Physical stability characterization

2.3.1 Sedimentation analysis for stability examination

Colloidal stability of iron nano particles has been defined as the tendency to disperse in solvent against to aggregation during specific time period (Dobias 1993). The dispersion stability of nZVIs was assessed by measuring the absorbance of suspended solution at 508 nm by UV-Vis

Table 1 Conditions for bare and PVP/VA coated nZVI synthesis in aqueous solution

Fe concentration (g/L)		1	
[Fe ²⁺]:[BH ₄ ⁻] (mol:mol)		1:4	
PVP/VA concentration (g/L)	0	1	2
[PVP/VA]:[Fe] (w:w)	0	1	2

spectrophotometer (Cary50, Agilent Technologies Inc.) for 90 min (Saleh *et al.* 2007, 2008). Diluted sample solutions (0.25 g Fe /L) were transferred into a 1 cm cuvette, capped to prevent further oxidation, and shaken by hand gently prior to sedimentation measurement. In the previous work by Phenrat *et al.* (2006), they suggested interpretation equation if the sedimentation behaviour was measured by UV-Vis spectrometer as the function of the absorbance and time.

$$I_t = I_0 e^{-t/\tau}$$

$$I_0, I_t : \text{the absorbance at initial time and time } t \quad (2)$$

$$\tau : \text{the characteristic time based on Stokes' law}$$

2.3.2 Particle size and zeta potential

The particle size of bare and PVP/VA coated nZVIs was analyzed by dynamic laser light scattering (DLS, Malvern Zetasizer NanoZS, Malvern Instruments Ltd). It measures the diffusion of particles moving under Brownian motion and converts into size distribution based on Stokes-Einstein relationship. A 1 cm cuvette with the same samples used in sedimentation analysis was used for DLS analysis. For zeta potential analysis, samples were poured into the folded capillary cell with the electrodes. The mobility of charged iron particles under an electric field which related to zeta potential was measured as the velocity by laser Doppler micro-electrophoresis. All samples were measured in triplicate.

2.4 Nitrate reduction by coated nZVI

Nitrate reduction experiment was performed in a 50 mL glass serum bottle as a batch reactor with bare nZVI and PVP/VA coated nZVI with higher stability. 15 mL of freshly synthesized nZVI solutions was transferred to the bottle and 13.5 mL of DDIW was added. The initial pH of nZVI slurry was 8.09 ± 0.2 . The reactor was capped with PTFE/silicon septum and aluminum crimp seal and 1.5 mL of nitrate stock solution (1000 mg NO₃⁻-N/L) was injected by syringe. Initial concentrations of nitrate and iron were 50 mg NO₃⁻-N/L and 500 mg Fe/L, respectively, and the reaction could be expressed by following equation



The reactors were placed on an orbital shaker (100 rpm) for mixing. At each sampling time, 2 mL of each sample was taken by a syringe for analysis. The sample was immediately filtered by 0.2 μm syringe membrane filter. 1 mL of the filtrate was used to measure concentration of nitrate, nitrite and ammonium by ion chromatograph (IC, 883 Basic IC Plus, Metrohm). IC was equipped with Anion SUPP 4 Column (Metrohm) and Metrosep C4 column (Metrohm) for anion and cation

analysis. Sodium bicarbonate (1.8 mM), sodium carbonate (1.7 mM) and nitric acid (1.7 mM) solutions were used as mobile phases for each analysis at a flow rate of 1 mL/min.

3. Results and discussion

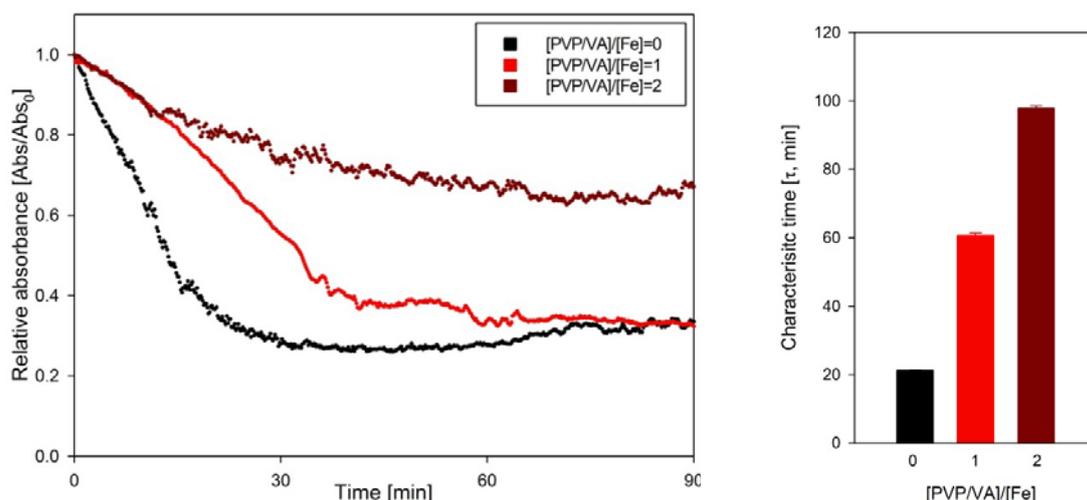
3.1 Effect of PVP/VA on particle stability

3.1.1 Sedimentation of PVP/VA coated nZVI

Fig. 1(a) shows the sedimentation profile of PVP/VA coated nZVI with different [PVP/VA]/[Fe] weight ratios. The optical absorbance of the suspensions was normalized and plotted over time and decreasing tendencies were observed due to settling of particles. According to Eq. (2), bare nZVI without PVP/VA coating showed the highest relative absorbance decay (74 % in 90 min). About after 30 min, almost every particle was settled down.

The addition of PVP/VA during synthesis of nZVI exhibited a positive effect by enhancing the stability of particle, [PVP/VA]/[Fe] with ratio of 2 shows more stable property than that with less ratio. Sample with the ratio of 1 in [PVP/VA]/[Fe] showed nearly similar relative absorbance to that of bare nZVI at 90 min. However, the tendency of [PVP/VA]/[Fe] with ratio of 1 for settling down to the bottom of cuvette was slower than that of bare nZVI. The coated nZVI with a ratio of 2 showed considerably high dispersion state throughout the experiment.

The characteristic time, τ , was calculated to compare sedimentation behaviour in the early stage of settling movement shown by each ratio of [PVP/VA]/[Fe] using Eq. (2) from 0 to 30 min. Because the bare nZVI particles settled down most rapidly, the characteristic time was the lowest among the tested sample as 21.2 min. The time for PVP/VA coated nZVIs with ratio of 1 and 2 were 60.7 and 97.8 min, respectively. As illustrated in Fig. 1(b), characteristic time increased as the amount of PVP/VA added to nZVI increased.



(a) Sedimentation curves at different ratios of [PVP/VA]/[Fe]

(b) Calculated characteristic time

Fig. 1 Sedimentation profiles of PVP/VA coated nZVI with different [PVP/VA]/[Fe] ratios

3.1.2 Particle size and zeta potential of PVP/VA coated Nzvi

The size of the fractal aggregates formed in the concentrated slurry was estimated using the characteristic time (Fig. 1(b)) which is correlated with the hydrodynamic radius based on Stokes' law

$$\tau = \frac{9\eta(\beta - p_f)}{2g^2(\rho_s - \rho_l)^2 R_H^2} \quad (4)$$

where η is the solvent viscosity, β is a function of the permeability of the aggregate, ρ_s and ρ_l are densities of solid and liquid, g is the gravity acceleration, p_f is the fluid pressure and R_H is the hydrodynamic radius (Phenrat *et al.* 2006). The factors, excepting R_H , can be considered as constant values. Therefore, increasing tendency of characteristic time indicates that the size of colloidal particles decreased based on Eq. (4) (Tirafferri *et al.* 2008, Hwang *et al.* 2011, Kocur *et al.* 2013, Lee *et al.* 2014).

However, the patterns of particle size shown by DLS were totally different from that by sedimentation analysis. Increasing the concentration of PVP/VA from 0 to 2 g/L while keeping the concentration of Fe constant (1 g/L) resulted in an overall increase (120.2, 215.0, 345.6 nm) of the particle sizes (Fig. 2(a)). The hydrodynamic radius can refer to the Stokes-Einstein radius and the radius can be affected by the extent on collection of subparticles based on a common study for polymer mixture (Strobl 1996). Therefore, R_H can be the radius of the collected volume of subparticles if the particles can be rotated in all directions and form a sphere. On this basis, size of particles in long chain structure with PVP/VA molecules might be measured exaggeratedly. Cirtiu *et al.* (2011) proposed a mechanism to explain the influence of the chelating polymer on the size of iron nanoparticles. They explained that the increase in the size of iron nanoparticles resulted from a higher precursor concentration within the polymer in unit volume compared to that of bare nZVI. The same experimental result showing the effect of polymeric manipulation on the size of nanoparticles was reported in the study using gold nanoparticles (Shimmin *et al.* 2004). Therefore,

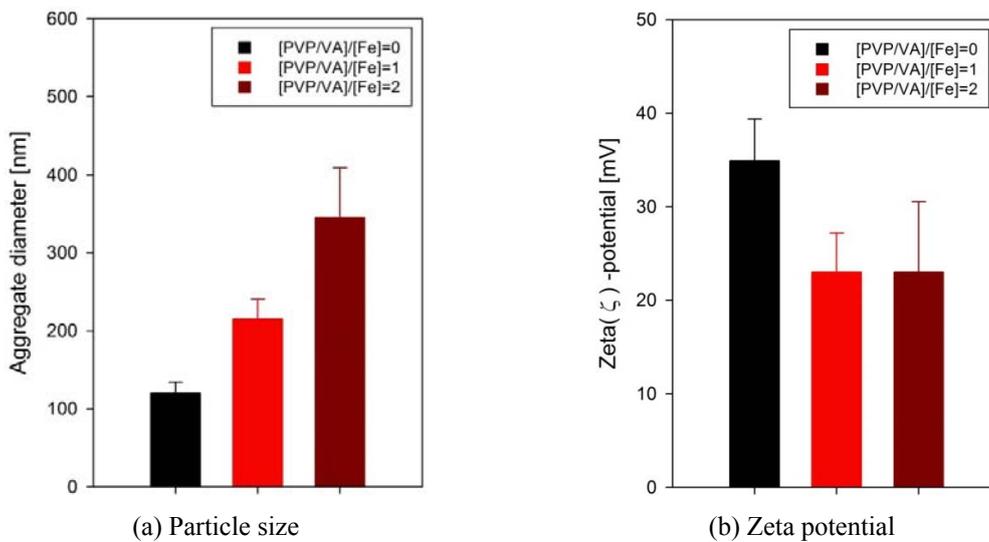


Fig. 2 Particle size and zeta potential of nZVIs coated with different concentration of [PVP/VA]

the size of PVP/VA coated nZVIs measured by DLS in this study might be also increased with increasing the PVP/VA amount due probably to aggregation by unintended consequence.

Zeta potential of each coated nZVI was measured to investigate the extent of the electrostatic interactions between suspended particles in the slurries. Fig. 2(b) shows the measured zeta potential values at different PVP/VA concentration ratios of 0 to 2. The zeta potential of bare nZVI was 34.9 mV and those of PVP/VA coated nZVIs were 23.0 mV with different standard deviations.

Stabilization effect on zeta potential has been known to increase with increasing the amount of stabilizers (Sun *et al.* 2007, Cirtiu *et al.* 2011). Therefore, the enhanced colloidal stability of PVP/VA coated nZVI could not be explained by the electrostatic repulsion. It might be interpreted by the steric repulsion which can prevent the aggregation of polymers with nanoparticles on their chain structure. Furthermore, Sun *et al.* (2007) reported that negatively charged particles have enhanced mobility in aquifer materials which is negatively charged in general. Although the surface of PVP/VA coated nZVIs was not charged negatively, adding PVP/VA to nZVI might make the surface charge of the particles lower than that of bare nZVI.

3.2 Effect of PVP/VA added to nZVI on the reductive degradation of nitrate

It has been reported that the impact on reactivity of nZVI with stabilizer was negative specifically for the nZVI prepared by post-grafting method (Saleh *et al.* 2007, Hwang *et al.* 2014). To cope with this limitation, pre-grafting technique using PVP/VA was applied to synthesize the polymeric nZVI.

Relativity of prepared bare nZVI and nZVI coated by PVP/VA with ratio of 2 which showed was evaluated by reductive degradation of nitrate in batch system. Theoretically, 31.4 mg/L of $\text{NO}_3\text{-N}$ can be reduced by 500 mg/L of nZVI based on Eq. (3) (Hwang *et al.* 2011), but less amount of nitrate was reacted with iron in actual circumstance. It has been known that the nitrate reduction by nZVI follow pseudo-first-order kinetics, and the observed degradation kinetic rate constant can be calculated from the following equation C_t , C_u and C_0 stand for the nitrate

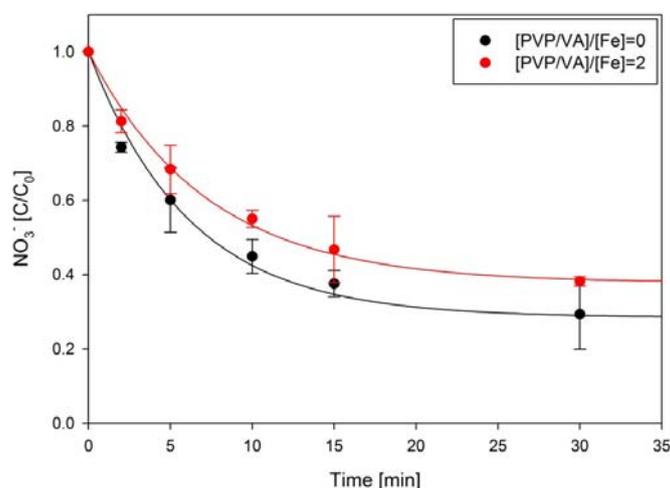


Fig. 3 Nitrate reduction profiles by nZVI coated with [PVP/VA]/[Fe] at ratios of 0 and 2. The curves were obtained by fitting to the pseudo-first-order kinetic

Table 2 Nitrate removal and by-product selectivity in PVP/VA coated nZVI system

[PVP/VA]/[Fe]	K_{NO_3} (min^{-1})	R^2	NO_3^- removal (%)	NO_2^- production (%)	NH_4^+ production (%)
0	0.1633	0.9898	73.2	1.8	70.8
2	0.1395	0.9954	62.1	1.8	60.5

concentration at specific time, initial state and final state with unreacted compounds, and k is the observed rate constant (h^{-1}).

$$C_t = C_u + (C_0 - C_u)e^{-kt} \quad (5)$$

As shown in Fig. 3 and Table 2, bare and PVP/VA stabilized nZVIs transformed nitrate into nitrite and ammonium at different reaction rates. Uncoated sample showed faster reduction rate (0.1633 min^{-1}) and NO_3^- removal (73.2%) compared to PVP/VA coated nZVI sample (0.1395 min^{-1} and 62.1 %) in PVP/VA coated nZVI samples. After 30 min, nitrate concentration reached a plateau, showing that the reaction was not proceeded any further. Therefore, it is clear that NO_3^- can be removed equivalently to the reduction capacity of nZVI under iron limiting condition (Tanboonchuy *et al.* 2012). The difference of nitrate removal in between bare nZVI and PVP/VA coated nZVI (ratio of 2) was 11.1%, showing that coating by stabilizer can reduce the reactivity of nZVI. This was due to the decreased reactive sites resulted from nZVI surface coated by PVP/VA (Wang *et al.* 2010).

4. Conclusions

PVP/VA coated nZVI was synthesized by the reduction of ferric solution and pre-grafting method, showing that, stable nZVI coated by PVP/VA can be produced. Effects of different concentration of PVP/VA on the characterization of nZVI and reductive degradation of nitrate were evaluated. Among samples, the most stable nZVI was the [PVP/VA]/[Fe] with a ratio of 2 based on the results from sedimentation behavior showing the shortest characteristic time (97.8 min). On the other hand, particle size of the coated nZVIs increased as the amount of the PVP/VA added to the nZVI increased. This might result from exaggeratedly measured result by long chain shaped structure of PVP/VA adsorbed by nZVI particles. Additionally, the positive zeta potentials of nZVI coated with different PVP/VA ratios decreased as the amount of stabilizer increased. This was due probably to the increased inhibition of aggregation by steric repulsion resulted from chin-like structure of the polymer.

Reactivity of PVP/VA coated nZVI was lower than that of bare nZVI. This can be explained by the decreased reactive sites on synthesized nZVI surface due to the ineffective surface coating. Although both nitrate removals and reaction rate constants have decreased after adding PVP/VA polymer to nZVI, this study showed that PVP/VA coated nZVI can be applied as one of the possible reducing agent at subsurface environment based on the high stability.

Acknowledgments

This research was financially supported by Korea Minister of Ministry of Land, Infrastructure

and Transport (MOLIT) as 「U-City Master and Doctor Course Grant Program」 and Korean National Research Foundation (NRF) funded by the Korean Ministry of Education (2012-C1AAA001-M1A2A2026588). Also this work was supported by the Korea Ministry of the Environment as ‘The GAIA project’.

References

- Amir, A. and Lee, W. (2011), “Enhanced reductive dechlorination of tetrachloroethene by nano-sized zero valent iron with vitamin B₁₂”, *Chem. Eng. J.*, **170**(2), 492-497.
- Barke, M.B. and Luebke, R.A. (1981), “*Stable protective seed coating*”, U.S. Patent No. 4,272,417. Washington, DC: U.S. Patent and Trademark Office.
- Bühler, V. (2008), “*Kollidon*”, BASF SE, Ludwigshafen, Germany.
- Cao, J., Elliott, D. and Zhang, W.-x. (2005), “Perchlorate reduction by nanoscale iron particles”, *J. Nanoparticle Res.*, **7**(4-5), 499-506.
- Cirtiu, C.M., Raychoudhury, T., Ghoshal, S. and Moores, A. (2011), “Systematic comparison of the size, surface characteristics and colloidal stability of zero valent iron nanoparticles pre-and post-grafted with common polymers”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **390**(1), 95-104.
- Choi, J. and Lee, W. (2008), “Enhanced degradation of tetrachloroethylene by green rusts with platinum”, *Environ. Sci. Tech.*, **42**(9), 3356-3362.
- Crane, R.A. and Scott, T.B. (2012), “Nanoscale zero-valent iron: future prospects for an emerging water treatment technology”, *J. Hazard. Mater.*, **211-212**, 112-125.
- Dobias, B. (1993), *Coagulation and Flocculation: Theory and Applications*, CRC Press, Boca Raton, FL, USA.
- Elliott, D.W. and Zhang, W.-X. (2001), “Field assessment of nanoscale bimetallic particles for groundwater treatment”, *Environ. Sci. Tech.*, **35**(24), 4922-4926.
- Greenlee, L.F. and Hooker, S.A. (2012), “Development of stabilized zero valent iron nanoparticles”, *Desalination Water Treat.*, **37**(1-3), 114-121.
- He, F. and Zhao, D. (2007), “Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers”, *Environ. Sci. Tech.*, **41**(17), 6216-6221.
- He, F., Zhang, M., Qian, T. and Zhao, D. (2009), “Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: Column experiments and modeling”, *J. Colloid Interface Sci.*, **334**(1), 96-102.
- Hotze, E.M., Phenrat, T. and Lowry, G.V. (2010), “Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment”, *J. Environ. Quality*, **39**(6), 1909-1924.
- Hwang, Y.-H., Kim, D.-G. and Shin, H.-S. (2011), “Effects of synthesis conditions on the characteristics and reactivity of nano scale zero valent iron”, *Appl. Catalysis B: Environmental*, **105**(1), 144-150.
- Hwang, Y., Lee, Y.C., Mines, P.D., Huh, Y.S. and Andersen, H.R. (2014), “Nanoscale zero-valent iron (nZVI) synthesis in a Mg-aminoclay solution exhibits increased stability and reactivity for reductive decontamination”, *Appl. Catal. B: Environ.*, **147**, 748-755.
- Jung, J., Bae, S. and Lee, W. (2012), “Nitrate reduction by maghemite supported Cu-Pd bimetallic catalyst”, *Applied Catalysis B: Environmental*, **127**, 148-158.
- Kocur, C.M., O’Carroll, D.M. and Sleep, B.E. (2013), “Impact of nZVI stability on mobility in porous media”, *Journal of contaminant hydrology*, **145**, 17-25.
- Lee, W., Batchelor, B., Schlautman, M.A. (2000), “Reductive capacity of soils for chromium”, *Environ. Tech.*, **21**(8), 953-963.
- Lee, Y.-C., Lee, K., Hwang, Y., Andersen, H.R., Kim, B., Lee, S.Y., Choi, M.-H., Park, J.-Y., Han, Y.-K. and Oh, Y.-K. (2014), “Aminoclay-templated nanoscale zero-valent iron (nZVI) synthesis for efficient harvesting of oleaginous microalga, *Chlorella* sp. KR-1”, *RSC Advances*, **4**(8), 4122-4127.
- Lien, H.-L. and Zhang, W.-X. (2001), “Nanoscale iron particles for complete reduction of chlorinated

- ethenes”, *Colloids Surfaces A: Physicochem. Eng. Aspects*, **191**(1-2), 97-105.
- Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S. and Lowry, G.V. (2005), “TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties”, *Environ. Sci. Tech.*, **39**(5), 1338-1345.
- Mayer, A.B. and Mark, J.E. (1996), “Polymer-protected, colloidal platinum nanocatalysts”, *Polymer Bulletin*, **37**(5), 683-690.
- Mirescu, A. and Prüße, U. (2006), “Selective glucose oxidation on gold colloids”, *Catalysis Commun.*, **7**(1), 11-17.
- Noubactep, C., Caré, S. and Crane, R. (2012), “Nanoscale metallic iron for environmental remediation: prospects and limitations”, *Water Air Soil Pollut.*, **223**(3), 1363-1382.
- Phenrat, T., Saleh, N., Sirk, K., Tilton, R.D. and Lowry, G.V. (2006), “Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions”, *Environ. Sci. Tech.*, **41**(1), 284-290.
- Phenrat, T., Liu, Y., Tilton, R.D. and Lowry, G.V. (2009), “Adsorbed polyelectrolyte coatings decrease Fe⁰ nanoparticle reactivity with TCE in water: conceptual model and mechanisms”, *Environ. Sci. Tech.*, **43**(5), 1507-1514.
- Porter, S.C. (1981), “Tablet coating”, *Drug Cosmetic Industry*, **128**(5), 46-93.
- Saleh, N., Sirk, K., Liu, Y., Phenrat, T., Dufour, B., Matyjaszewski, K., Tilton, R.D. and Lowry, G.V. (2007), “Surface modifications enhance nanoiron transport and NAPL targeting in saturated porous media”, *Environ. Eng. Sci.*, **24**(1), 45-57.
- Saleh, N., Kim, H.-J., Phenrat, T., Matyjaszewski, K., Tilton, R.D. and Lowry, G.V. (2008), “Ionic strength and composition affect the mobility of surface-modified Fe⁰ nanoparticles in water-saturated sand columns”, *Environ. Sci. Tech.*, **42**(9), 3349-3355.
- Schrick, B., Hydutsky, B.W., Blough, J.L. and Mallouk, T.E. (2004), “Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater”, *Chem. Mater.*, **16** (11), 2187-2193.
- Shimmin, R.G., Schoch, A.B. and Braun, P.V. (2004), “Polymer size and concentration effects on the size of gold nanoparticles capped by polymeric thiols”, *Langmuir*, **20**(13), 5613-5620.
- Strobl, G.R. (1996), *The Physics of Polymers Concepts for Understanding Their Structures and Behavior*, Springer-Verlag, New York, USA.
- Sun, Y.-P., Li, X.-Q., Zhang, W.-X. and Wang, H.P. (2007), “A method for the preparation of stable dispersion of zero-valent iron nanoparticles”, *Colloids Surfaces A: Physicochem. Eng. Aspects*, **308**(1), 60-66.
- Sun, Y.-P., Li, X.-Q., Li, J., Cao, J., Zhang, W.-X. and Wang, H.P. (2006), “Characterization of zero-valent iron nanoparticles”, *Adv. Colloid Interface Sci.*, **120**(1-3), 47-56.
- Tanboonchuy, V., Grisdanurak, N. and Liao, C.-H. (2012), “Nitrate probe for quantifying reducing power of nanoscale zero-valent iron”, *Sustain. Environ. Res.*, **22**(3), 185-191.
- Tiraferri, A., Chen, K.L., Sethi, R. and Elimelech, M. (2008), “Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum”, *J. Colloid Interface Sci.*, **324**(1-2), 71-79.
- Wang, C.-B. and Zhang, W.-X. (1997), “Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs”, *Environ. Sci. Tech.*, **31**(7), 2154-2156.
- Wang, W., Zhou, M., Jin, Z. and Li, T. (2010), “Reactivity characteristics of poly(methyl methacrylate) coated nanoscale iron particles for trichloroethylene remediation”, *J. Hazard. Mater.*, **173**(1), 724-730.
- Zhang, W.-X., Wang, C.-B. and Lien, H.-L. (1998), “Treatment of chlorinated organic contaminants with nanoscale bimetallic particles”, *Catalysis Today*, **40**(4), 387-395.
- Zhou, H., Han, J., Baig, S.A. and Xu, X. (2011), “Dechlorination of 2, 4-dichlorophenoxyacetic acid by sodium carboxymethyl cellulose-stabilized Pd/Fe nanoparticles”, *J. Hazard. Mater.*, **198**, 7-12.
- Zhang, M., He, F., Zhao, D. and Hao, X. (2011), “Degradation of soil-sorbed trichloroethylene by stabilized zero valent iron nanoparticles: effects of sorption, surfactants, and natural organic matter”, *Water Res.*, **45**(7), 2401-2414.