DTU Library

Mg-aminoclay as stabilizer for synthesizing highly stable and reactive nZVI for decontamination

Hwang, Yuhoon; Lee, Young-Chul; Mines, Paul D.; Huh, Y. S.; Andersen, Henrik Rasmus

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Hwang, Y., Lee, Y-C., Mines, P. D., Huh, Y. S., & Andersen, H. R. (2014). *Mg-aminoclay as stabilizer for synthesizing highly stable and reactive nZVI for decontamination*. Abstract from 2014 IWA World Water Congress & Exhibition, Lisbon, Portugal.

Mg-aminoclay as stabilizer for synthesizing highly stable and reactive nZVI for decontamination

Yuhoon Hwang*, Young-Chul Lee,***, P.D. Mines*, Y.S. Huh***, H.R. Andersen***

* Department of Environmental Engineering, Technical University of Denmark, Miljøvej, B113, DK-2800 Kgs. Lyngby, Denmark (yuoh@env.dtu.dk)
** Department of Civil and Environmental Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
*** Department of Biological Engineering, College of Engineering, Inha University, Incheon 402-751, Republic of Korea

Abstract: Despite the large surface area and superior reactivity of nZVI, its limited stability is a major obstacle for in situ subsurface remediation. In this study, Mg-aminoclay (MgAC) was applied for the first time as a stabilizer in nZVI synthesis. With increased doses of Mg-aminoclay, nZVI particle growth was inhibited and thin sheathed grape-like nZVI particles with higher crystallinity were produced. The coated nZVI were smaller and non-aggregating, and it can reduced nitrate 350-fold faster than uncoated. The higher stability of MgAC coated nZVI was achieved by electrostatic repulsion from the positively charged MgAC coating. Moreover, the proper washing strategy is essential to keep stability and reactivity during preparation and transport.

Keywords: aging effect; colloidal stability; Mg-aminoclay (MgAC); nanoscale zero-valent iron (nZVI)

Introduction

Though nano zero valent iron (nZVI) has emerged as one of the most effective technologies for soil and groundwater remediation, loss of stability and reactivity during transport by rapid aggregation is the major obstacle for practical application (He and Zhao, 2007). Thus, particle stabilization has been achieved by attaching stabilizer molecules onto the nanoparticles (Sakulchaicharoen et al., 2010).

Recently, organo-functionalized clays, especially aminosilanes employed clay (aminoclay), have been markedly developed and applied in environmental fields (Lee et al., 2011). Previously, metal nanoparticles such as Pt, Pd, Ag, and Au, were successfully synthesized in the presence of Mg-aminoclay (MgAC) (Datta et al., 2007). Taking into consideration MgAC function, MgAC can be expected to positively alter the nZVI properties, and namely, enhance their stability and reactivity.

Here, we report the studies of MgAC templated nZVI synthesis and discuss its feasibility for environmental clean-up. Moreover, the proper washing and storage procedure was discussed to increase of feasibility for practical application.

Material and Methods

MgAC was prepared using methods stated in previous study (Lee et al., 2011). MgAC coated nZVI was prepared by the chemical reduction of ferrous ion in the MgAC solution using sodium borohydride as reductant. The prepared MgAC coated nZVI was characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR).

The stability of MgAC coated nZVI was determined by sedimentation analysis, particle size measured by dynamic light scattering (DLS), and zeta potential. The reactivity was analyzed by reactive iron content and nitrate reduction kinetic.

The effect of washing and storage on aging of MgAC coated nZVI was investigated by different washing-storage procedures. The change of stability and reactivity during aging was measured by same procedure as described above.

Results and Conclusions

The particle stability could be enhanced by increasing applied amount of MgAC (Table 1, Fig 1(a)). As MgAC loading increased, nZVI particle growth was inhibited and thin sheathed grape-like nZVI particles with a higher degree of crystallinity were produced (Fig 2). The higher stability of MgAC coated nZVI was obtained by electrostatic repulsion by the positively charged MgAC coating.

Table 1 Characteristics of MgAC coated nZVI under different MgAC/Fe weight ratio

MgAC/Fe (w/w)	Characteristic time[a] (τ, min)	Particle size (d.nm)	Zeta potential (mV)	Observed kinetic constant[b] (h^{-1})	Fe(0) normalized kinetic constant[b] (h^{-1} mg $Fe(0)^{-1}$)
0	6.71	5130	14.5	1.17	0.124
1	17.0	1850	14.6	5.22	0.753
5	19.7	1710	15.1	15.5	4.07
7.5	65.3	508	21.5	34.5	15.3
10	73.1	404	22.9	26.5	17.7
20	83.8	186	25.3	42.0	43.8

[a] obtained from sedimentation curve ($I_t = I_0 e^{-t/\tau}$)
[b] obtained from nitrate reduction curve ($C_t = C_0 e^{-kt}$)

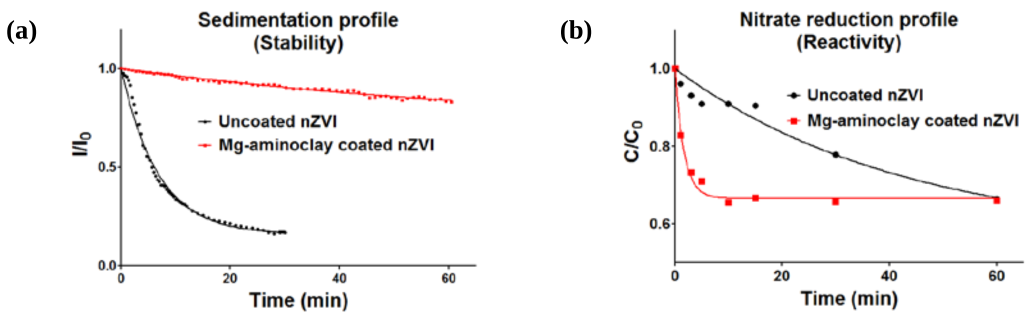

Figure 1 Enhancement of particle stability and reactivity by Mg-aminoclay coating under MgAC:Fe weight ratio of 7.5, (a) stability, (b) reactivity

The MgAC coated nZVI exhibited higher tendency to react with target contaminants (Fig 1 (b)). The higher reaction rate toward nitrate, observed (1.17-42.0 h^{-1}) and Fe(0) normalized (0.124-43.8 h^{-1}·mg-$Fe(0)^{-1}$), directly verified advantages of stabilization, which can increase the overall reaction speed. The stabilized MgAC coated nZVI, therefore, showed the high feasibility to apply in the field of subsurface remediation, which can have high mobility and short required remediation time.

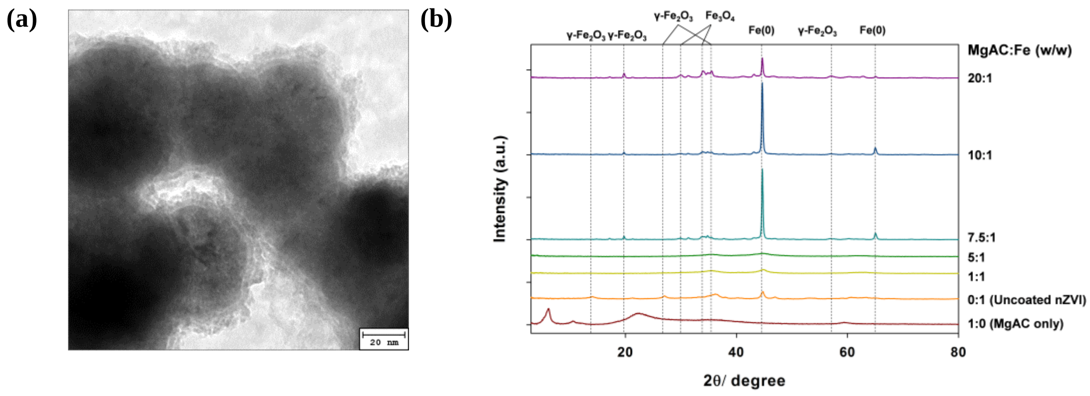

Figure 2 Properties of MgAC coated nZVI, (a) TEM images (MgAC:Fe = 7.5), (b) XRD spectra

Moreover, effect of washing on aging of MgAC coated nZVI was investigated. Even though the initial particle size was similar, the particle size greatly increased during 1 week of aging when unattached MgAC was removed by pre-storage washing (Fig 3 (a)). The high aggregation tendency of pre-washed nZVI was due to break-down and loss of surface coating during washing. On the other hand, washing step is essential to keep reactivity by removal of residual inorganic ions in synthesis mixture which can increase iron corrosion rate (Fig 3 (b)). Based on this finding, stabilizer solution (MgAC) was applied again after pre-storage washing, and it exhibited both of high stability as pre-storage washing and high reactivity as post-storage washing. Here, it is found that the proper washing procedure is mightily important to provide lasting stability and reactivity during preparation and transport.

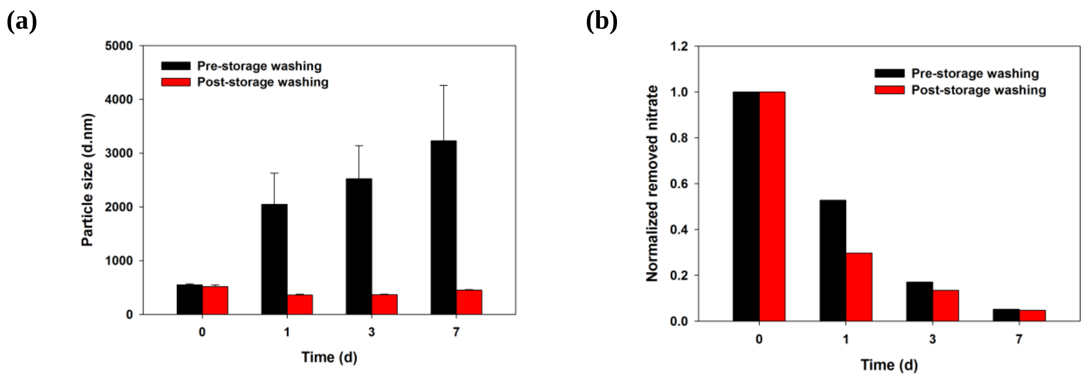

Figure 3 Effect of washing strategy on aging of MgAC coated nZVI, (a) particle size, (b) normalized nitrate reduction capacity

References

Datta, K.K.R., Eswaramoorthy, M. and Rao, C.N.R. (2007), Water-solubilized aminoclay-metal nanoparticle composites and their novel properties. *J. Mater. Chem.* **17**(7), 613-615.

He, F. and Zhao, D. (2005), Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. *Environ. Sci. Technol.* **39**(9), 3314-3320.

Lee, Y.C., Kim, E.J., Ko, D.A. and Yang, J.W. (2011), Water-soluble organo-building blocks of aminoclay as a soil-flushing agent for heavy metal contaminated soil. *J. Hazard. Mater.* **196**, 101-108.

Sakulchaicharoen, N., O'Carroll, D.M. and Herrera, J.E. (2010), Enhanced stability and dechlorination activity of pre-synthesis stabilized nanoscale FePd particles. *J. Contam. Hydrol.* **118**(3-4), 117-127.