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Enhancement of Nanoscale Zero-Valent Iron Stability in Aqueous Solution Via Metal Hydroxide Coating

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Abstract: Concerns have been increased regarding the behavior of nanoscale zero-valent iron (nZVI) in subsurface environmental remediation applications. In this study, the iron particles were coated by magnesium hydroxide ($Mg(OH)_2$) shell in order to improve their suspension stability in aqueous solutions. Sedimentation tests were conducted for different ratios of the coating material to evaluate the enhancement of particles stability and to determine the optimum coating ratio. Results of sedimentation tests showed that, the coated iron particles $Mg(OH)_2$ -CnZVI exhibited better stability performance than that of bare nZVI (BnZVI). Additionally, optical absorbance results depicted that Mg/Fe coating ratios of 0.8 and 1 showed less aggregation potential than that of the other coating ratios and BnZVI as well. Moreover, beside the enhanced stability, the addition of the nonmagnetic coating layer protected the nZVI core from the rapid corrosion. Further studies should be conducted to investigate the sustainability of the coated nZVI reactivity.

Keywords: Nanoscale zero-valent iron; Magnesium hydroxide ($Mg(OH)_2$) shell; Encapsulation; Suspension stability.

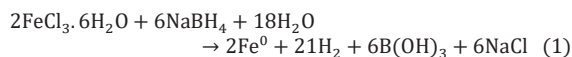
1. INTRODUCTION

The global concern has been significantly increasing along the last decade on nanoscale zero-valent iron (nZVI) applications in the fields of environmental remediation and water treatment (1). The high surface area to volume ratio as well as the unique core-shell structure of these particles provide the potential to be an efficient adsorbents for several soluble contaminants in water (2, 3). However, nZVI particles tend to agglomerate in aqueous solutions to form larger clusters due to the strong magnetic attraction between the particles (4). Furthermore, the limiting mobility in addition to the conditional suspension stability affect the feasibility of nZVI in subsurface treatment applications. Therefore, the main aim of this study is to improve the suspension stability of the nZVI particles using a modified encapsulation technique via one-layer coating of magnesium hydroxide ($Mg(OH)_2$) nonmagnetic shell.

2. MATERIALS & METHODS

2.1 Synthesis of bare nanoscale zero-valent iron

Bare nanoscale zero-valent iron (BnZVI) was synthesized through the reduction of ferric chloride ($FeCl_3$) by sodium borohydride ($NaBH_4$) according to the following equation (5):



In order to prepare synthesis solutions to produce 1g BnZVI, 2.2g of sodium borohydride and 5g of ferric chloride were dissolved in 100 mL and 200 mL deoxygenated deionized water (DDIW) respectively. Reductant solution was then fed in a dropwise pumping rate of 20 mL/min into a four-neck flask that was kept in a water bath at 30 ± 0.5 °C and contained the precursor solution. The mixing process of the former solutions was achieved by a vigorous stirring at 400 rpm along with a continuous nitrogen flow providing anaerobic environment during aging time of 5 min. The resultant black precipitates were then vacuum filtrated through a 0.45 μ m paper membrane followed by three times

washing using DDIW.

2.2 Synthesis of coated nZVI

The coating process that was used to prepare coated nanoscale zero-valent iron (CnZVI) was based on the precipitation of $Mg(OH)_2$ shell on the surface of the nano iron particles (6). Firstly, 100 mL dispersed BnZVI/ethanol solution of 1g- Fe^0 /L was kept in 500 mL flask. Furthermore, stock solution of Mg^{2+} ionic concentration 1 g/L was prepared by dissolving the appropriate amount of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) in ethanol. Secondly, varied volumes of Mg/ethanol solution was injected into the BnZVI slurry at 2 rpm injection rate in order to target different Mg/Fe coating ratios (0.2, 0.4, 0.6, 0.8, and 1). Then, varied volume of NaOH/ethanol solution (NaOH concentration: 3.3 g/L) was injected into the mixture in order to maintain molar ratio (OH/Mg: 2) (Eq. 2). The mixture solution was ultrasonicated during the whole injection processes with a continuous nitrogen purging and kept at 30 ± 0.5 °C for one hour aging time. The resultant $Mg(OH)_2$ -CnZVI was then vacuum filtrated through a 0.45 μ m paper membrane followed by washing three times with ethanol.



2.3 Sedimentation test

Sedimentation test was conducted for the synthesized samples in order to investigate the suspension stability of the particles in aqueous solution. Hence, 50 mL of $NaHCO_3$ (2.5 mM) solution was used to disperse 0.25 g of BnZVI/CnZVI for one hour using ultrasonication. Then, particles settlement through the solution was visually observed in 50 mL transparent glass cylinder for 180 min. Moreover, 1 mL and 5 mL samples were withdrawn at the top of solution inside the cylinder after 180 min settlement for total iron and solid iron concentrations analysis respectively.

2.4 Optical absorbance test

Optical absorbance was examined for the synthesized samples at predetermined time intervals. 10 mg of

BnZVI/CnZVI was ultrasonicated in 10 mL dispersing solution of NaHCO_3 (2.5 mM) for 30 min. In order to record the change of the optical absorbance (I_t) with time, the dispersed solution with concentration of 1 g/L BnZVI/EnZVI was monitored in 10 mL cuvette at 508 nm wavelength using Spectrophotometer DR3900 (Hach Co., US).

3. RESULTS & DISCUSSION

3.1 Sedimentation test

The relative suspended iron concentration was plotted as a function of Mg/Fe mass ratio (Fig. 1). It is apparent from the iron concentration displayed data that suspension stability of nZVI particles is significantly dependent on Mg coating ratio, which was consistent with the visually observed photos. Consequently, the Increase in Mg/Fe mass ratio resulted in the enhancement of the nZVI stability. However, the results implied that the difference in stability performance was slight between the highest coating ratios (Mg/Fe: 0.8 and 1). Unlike the other ratios, almost 90 % of the particles were still suspended in the solution for the two former coating ratios even after 180 min of settlement time. Furthermore, the end-pH values were recorded for the synthesis solutions as it is displayed in (Fig. 2). The results showed an obvious increase in pH values corresponding to the increase in Mg coating ratio, which is attributed to the increase in injected volume of NaOH/ethanol solution ($\text{pH} = 12.8 \pm 0.5$) during the synthesis in order to maintain (OH/Mg) molar ratio of 2.

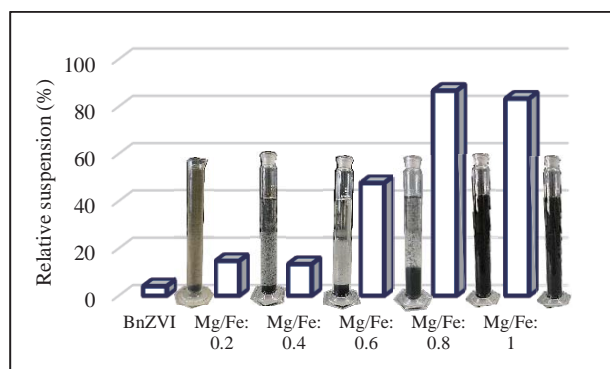


Fig. 1. Relative suspended iron concentration after 180 min settlement time.

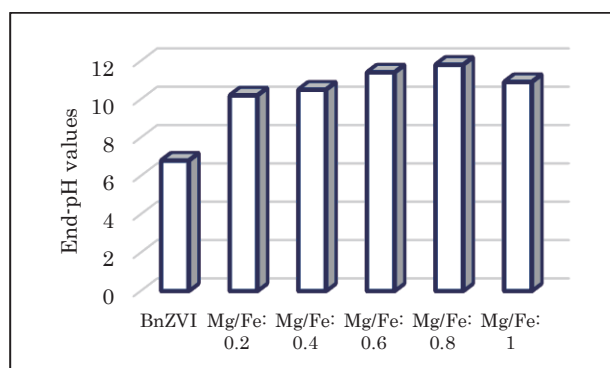


Fig. 2. End-pH values of synthesis solutions.

3.2 Optical absorbance test

Sedimentation curves in (Fig. 3) were obtained by plotting the normalized absorbance ratio (I_t/I_0) with respect to time, where I_t is the optical absorbance as a function of time (t), and I_0 is the initial optical absorbance

at zero time ($t = 0$). Without the coating shell of $\text{Mg}(\text{OH})_2$, BnZVI was settled within almost 30 min. Gradual decrease in I_t/I_0 value was observed for $\text{Mg}(\text{OH})_2$ -CnZVI. Whereas, the steep decrease in case of BnZVI is attributed to the rapid settlement of the particles. It is clear that, I_t/I_0 value tended to decrease gradually along with the increase of Mg coating ratio, indicating that the more Magnesium coating dosage, the less aggregated the particles become.

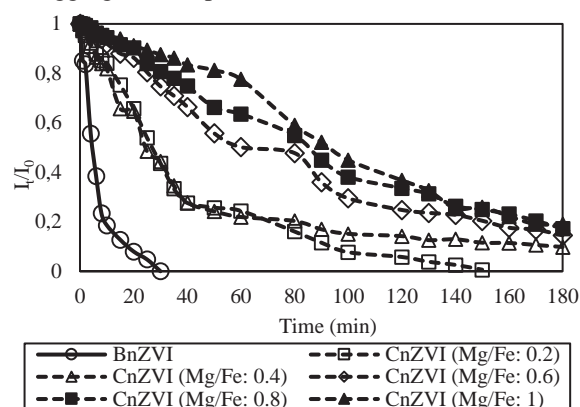


Fig. 3. Sedimentation curves of $\text{Mg}(\text{OH})_2$ -CnZVI.

4. CONCLUSIONS

In this study, nZVI was successfully coated with a nonmagnetic $\text{Mg}(\text{OH})_2$ shell that resulted in improved suspension stability in aqueous solution. The low cost of such used encapsulating approach could be a promising technique for reactive nanoparticles modification. Moreover, sedimentation test results confirmed that $\text{Mg}(\text{OH})_2$ -CnZVI had a multiple functional effect on particles stability in suspension as well as the considerable protection of core rapid corrosion. Finally, further researches should be performed to examine the sustainability of the current coated particles reactivity towards soluble contaminants.

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