Stimulating effect of magnesium hydroxide on aqueous characteristics of iron nanocomposites

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ABSTRACT

Nanoscale zero-valent iron (nFe0) tends to aggregate, which dramatically affects its aqueous characteristics and thereby its potential in water treatment applications. Hence, the main aim of this study is to overcome such drawback of nFe0 by a new modification approach. Iron nanoparticles were modified by magnesium hydroxide (Mg(OH)2) addition with different mass ratios in order to form a nanocomposite with superior aqueous characteristics. The optimization process of the iron–magnesium nanocomposite (nFe0-Mg) was conducted through different approaches including settlement tests, morphology and crystallinity investigations and particle size estimation. The addition of Mg(OH)2 to nFe0 with a Mg/Fe coating ratio of 100% resulted in stimulated stability of the particles in aqueous suspension with around 95% enhancement in the suspension efficiency compared to that of nFe0. Results showed that the average particle size and degree of crystallinity of nFe0-Mg(Mg/Fe:100%) decreased by 46.7% and increased by 16.8%, respectively, comparing with that of nFe0. Additionally, the iron core of the synthesized nFe0 was adequately protected from aqueous corrosion with lower iron oxides leachates after the optimal modification with Mg(OH)2. Furthermore, Mg(OH)2 coating resulted in a stimulated adsorption reactivity of the composite towards phosphorus (P) with around 3.13% promotion in the removal efficiency comparing to that of nFe0.

Key words | aqueous characteristics, crystallinity, iron nanocomposites, magnesium hydroxide

INTRODUCTION

Nanotechnology has emerged recently in several environmental remediation aspects owing to the excellent functional characteristics of the nanomaterials (Ghasemzadeh et al. 2014; Zhao et al. 2016; Maamoun et al. 2020). Nanoscale zero valent iron (nFe0) has been one of the most commonly used nanomaterials in water treatment applications during the last two decades. Owing to its particular core-shell structure in addition to the dual redox potential, nFe0 has the ability to react with most of the soluble contaminants in water in addition to the dual redox potential (O’Carroll et al. 2013; Wen et al. 2014; Eljamal et al. 2019). Furthermore, it has a high performance as an efficient adsorbent comparing with other adsorbents because of the relatively large surface/volume ratio of the nanoparticles (Maamoun et al. 2017, 2018a; Nunez Garcia et al. 2020). Despite all the formerly mentioned features, nFe0 particles have some serious drawbacks in terms of the aqueous characteristics when it comes to the real water treatment applications, including the tendency of aggregation and the rapid settlement due to the strong magnetic attraction force between the particles (Tosco et al. 2014; Eljamal et al. 2018b; Li et al. 2020). Therefore, several modifying techniques for the nFe0-based materials were applied to avoid such drawbacks, such as using supporting materials as substrate for iron nanoparticles (Zhang et al. 2011; Tomašević et al. 2014; Khalil et al. 2017), in addition to nanoscale zero valent iron stabilization (Jiemvarangkul et al. 2011; Raychoudhury et al. 2012).

Hence, the main objective of this study is the modification of nFe0 by magnesium hydroxide (Mg(OH)2) addition with different coating ratios in order to form an iron–magnesium nanocomposite (nFe0-Mg) with superior aqueous characteristics. Morphology and crystallinity properties of the synthesized particles were investigated using transmission electron microscopy (TEM) and X-ray diffraction (XRD) analyses respectively. Moreover, aqueous stability in suspension was examined through a set of settlement experiments based on the spectrophotometric absorbance principle. The presented optimized nFe0-Mg showed an improved potential in...
terms of morphological properties, aqueous suspension stability, reactivity and longevity effect.

MATERIALS AND METHODS

Chemicals

For the preparation of nFe₀, ferric chloride hexahydrate (FeCl₃·6H₂O, >99.0%, Junsei Chemical Co., Japan) and sodium borohydride (NaBH₄, >98.0%, Sigma-Aldrich Inc., USA) were used. Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, >99.0%, Sigma-Aldrich Inc., USA) was used to synthesize the iron–magnesium nanocomposites. nFe₀ synthesis and coating solutions were prepared using deoxygenated deionized water (DDIW, 18.2 MΩ·cm, Milli-Q filter) and ethanol (C₂H₅OH, >99.5%, Wako Co., Japan) respectively. For pH adjustment, sodium hydroxide (NaOH, >97.0%, Wako Co., Japan) and hydrochloric acid (HCl, 30.0%, Wako Co., Japan) were employed. Phosphorus solutions were prepared using potassium dihydrogen phosphate (KH₂PO₄, 99.5%, Wako Co., Japan) to be used in reactivity experiments. All chemicals were used directly without further purification.

Materials synthesis

Preparation of nFe₀

Chemical reduction methodology was considered to synthesize the nanoscale zero valent iron (nFe₀) particles, using ferric chloride and sodium borohydride as precursor and reductant respectively, following this reaction equation (Yuvakkumar et al. 2011; Almeelbi & Bezbarauh 2012):

$$2\text{FeCl}_3 + 6\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{Fe}^0 + 6\text{B(OH)}_3 + 21\text{H}_2 + 6\text{NaCl} \quad (1)$$

One hundred millilitres of the reductant solution (22 g/L) was injected dropwise at 20 mL/min into a four-neck flask containing 200 mL of the ferric solution (25 g/L). The synthesis solutions were mechanically mixed (400 rpm) and kept in a water bath at 30 °C during the whole injection time in addition to another 5 min as aging time for a complete reduction. Nitrogen bubbling was provided to prevent any interruption of the process by the oxidation. Synthesized particles were collected using a vacuum filtration system after washing several times with DDIW.

Synthesis of nFe₀-Mg

The iron–magnesium nanocomposite was synthesized by the hydrothermal precipitation of Mg(OH)₂ onto the nFe₀ surface within an alkaline medium (NaOH) (Hu et al. 2018; Maamoun et al. 2018b). Concentrations of the Mg/ethanol and NaOH/ethanol solutions were controlled in order to keep the OH⁻/Mg²⁺ molar ratio to be 2. Moreover, different Mg/Fe mass coating ratios were considered through varying the added volumes of magnesium and hydroxide solutions. The whole coating process was conducted under ultrasonication at 50 °C and the final composite product was separated by vacuum filtration.

Characterization & analysis

Crystalline structure of nFe₀ and nFe₀-Mg composites was examined using an X-ray diffractometer (TTR, Rigaku Inc., Japan). Measurements were conducted using Cu Kα radiation at 40 kV/200 mA (λ = 1.5418 Å) and scanning rate of 2°/min from 3° to 90° (Eljamal et al. 2016). The degree of crystallinity (DOC) was estimated from the XRD patterns as follows (Aggarwal & Tilley 1955; Sami et al. 2010):

$$\text{DOC} (%) = \frac{\text{Area of crystalline peaks}}{\text{Area of (crystalline + amorphous) peaks}} \times 100 \quad (2)$$

Furthermore, morphology characteristics of the synthesized materials were investigated using TEM. Average particle size was estimated from the TEM images considering around 80–90 particles using imaging software (ImageJ, NIH) (Schneider et al. 2012). Phosphorus (P) concentration was analysed using a UV-Vis spectrophotometer (DR3900, Hach Co., USA), considering the US Environmental Protection Agency (USEPA) PhosVer 3-ascorbic acid method at 880 nm wavelength. Whereas, samples were analysed for nitrate (NO₃⁻) concentration considering the dimethylphenol method (colorimetrically at 345 nm), using the formerly mentioned device.

Stability tests

In order to investigate the suspension stability of the synthesized nFe₀-Mg composites within aqueous solutions, an optical absorbance test was conducted by dispersing
0.01 g of the materials in 10 mL of 2.5 mM sodium hydrocarbonate (NaHCO₃, >99.7%, Sigma-Aldrich Inc., USA). Using an optical cuvette, the settlement of the suspension was recorded at 508 nm wavelength using a UV-Vis spectrophotometer (DR3900, Hach Co., USA).

**Reactivity tests**

The reactivity of the synthesized nFe⁰-Mg particles was investigated towards P and nitrate NO₃ through a set of batch experiments. The tests were conducted using 50 mL solution volume of 50 mg/L P or 200 mg/L NO₃ as initial concentration. The introduced sorbent dosage which was added was 50 mg of nFe⁰ or nFe⁰-Mg nanoparticles. Periodical sampling was performed using a 0.22 μm polyethersulfone syringe filter for P and NO₃ analysis. The leaching of iron oxides, ferrous (II) and ferric (III), was investigated over a 1-week batch experiment to examine the reactive longevity of the nFe⁰-Mg composites within aqueous solutions. The standardized determination methods for ferrous and total iron concentrations were 1,10-phenanthroline (Ferrous reagents) and USEPA FerroVer iron (FerroVer reagents) methods, respectively, using a UV-Vis spectrophotometer (DR3900, Hach Co., USA) (Pyenson & Tracy 1945; Tang & Chen 1996). Ferric concentration was directly estimated as: (Fe(III) = total-Fe – Fe(II)).

**RESULTS AND DISCUSSION**

**Characterization**

**Crystallinity**

XRD results, shown in Figure 1, depicted obvious peaks of brucite (Mg(OH)₂) in the iron–magnesium composites which confirmed the formation of the magnesium hydroxide coating around the nFe⁰ core. Moreover, no peaks related to the presence of iron oxides, indicating the functional effect of the magnesium hydroxide shell in the protection of the nFe⁰ core from oxidation. The peak of α-Fe⁰ became broader by the increase of the Mg/Fe coating, which could be related to the semi-amorphous nature of the brucite shell on the surface of nFe⁰ particles. The degree of crystallinity results, presented in Table 1, implied that the higher the Mg/Fe coating ratio from 20% to 100%, the higher the crystallinity of the composite. The poor crystallinity of nFe⁰ has been previously reported whereas there is lack in the reported literature on the crystallinity investigation of the nFe⁰-Mg(OH)₂ composites (El Ghandoor et al. 2012; Ruiz-Torres et al. 2019). However, the reported work in this regard confirmed the semi-crystalline nature of the composite due to the presence of both crystalline and less crystalline peaks of muskovite and brucite, respectively (Maamoun et al. 2020).

**Morphology characteristics**

Results of TEM investigation are displayed in Figure 2. TEM images obviously depicted aggregated clusters of bare nFe⁰ with average estimated particle size of 92.4 nm. On the other hand, particles agglomeration slightly decreased for the nFe⁰-Mg composites with finer size comparing to that of bare nFe⁰. The increase of the Mg/Fe coating ratio resulted in smaller size of the particles as presented in Table 1, where nFe⁰-Mg(Mg/Fe:100%) exhibited an average

![Figure 1 | X-ray diffractograms of nFe³ and iron-magnesium nanocomposites.](image)

![Figure 2 | TEM images of bare nFe⁰ and nFe⁰-Mg composites.](image)
particle size decrease of 46.7% comparing with that of bare nFe⁰. In general, the achieved finer size of the nFe⁰ composites provides a great potential towards higher specific surface area, which is a crucial factor in the water treatment applications.

**Settlement investigation**

The addition of Mg(OH)₂ to nFe⁰ with a Mg/Fe coating ratio of 100% resulted in stimulated stability of the particles in aqueous suspension with lower settlement rate (SR) than that of unmodified iron particles. As shown in Figure 3, the increase in the Mg/Fe coating ratio resulted in a higher SE up to around 88% for the fully coated nFe⁰-Mg particles.

The normalized absorbance intensity (Iₙ) was considered as an indicator of the suspension stability of the suspension over 3 hrs settlement time, where (Iₙ = Iₜ/I₀) is a function of absorbance intensity at specific time (Iₜ) and initial intensity (I₀). Sedimentation curves were obtained by plotting Iₙ with respect to time as displayed in Figure 4. For nFe⁰-Mg composites, the value of the normalized intensity tended to decrease gradually along with the increase in Mg/Fe coating ratio, whereas rapid settlement occurred for bare nFe⁰ with full settlement within 30 minutes. Additionally, the suspension stability of the composites

![Figure 2](image1.png)  
**Figure 2** | TEM images at 100 nm resolution of (a) nFe⁰ and nFe⁰-Mg composites, with Mg/Fe coating ratios of (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100%.

![Figure 3](image2.png)  
**Figure 3** | Suspension efficiencies and settlement rates of nFe⁰ and iron–magnesium nanocomposites.

![Figure 4](image3.png)  
**Figure 4** | Normalized absorbance intensity vs. time for nFe⁰ and iron–magnesium nanocomposites suspensions.
was enhanced with the increase of the Mg/Fe coating ratio. Moreover, $nFe^0$-$Mg (Mg/Fe:100\%)$ was found to be the optimal coating ratio in terms of suspension stability in aqueous solution, which was consistent with the visual observation.

**Reactivity effect**

Phosphorus and nitrate were considered as the indicator for the reactivity influence of the synthesized materials towards adsorption and reduction mechanisms, respectively. Removal efficiency of the synthesized iron-magnesium nanocomposites towards phosphorus and nitrate was calculated as a function of initial ($C_0$) and final ($C_f$) concentrations, corresponding to different Mg/Fe coating ratios using the following formula:

\[
\text{Removal efficiency} \, (\%) = \frac{(C_0 - C_f)}{C_0} \times 100
\]

(3)

As shown in Figure 5(a), the $nFe^0$-$Mg$ particles showed comparable removal efficiencies to that of bare $nFe^0$. The stimulating effect of the Mg/Fe coating ratio on the phosphorus removal efficiency was clearly observed, where Mg/Fe ratio of 100% was corresponding to the highest value of the removal efficiency. Moreover, phosphorus removal by $nFe^0 (Mg/Fe:100\%)$ and $nFe^0 (Mg/Fe:80\%)$ was 3.13% and 2.23% respectively higher than that of bare $nFe^0$. This enhanced effect in reactivity of the iron–magnesium composites could be attributed to the contribution of the formed magnesium hydroxide shell around the iron core in the phosphorus adsorption. Additionally, as was previously reported, the neutral pH conditions provide a positive surface charge to the Mg(OH)$_2$, leading to a better electrostatic attraction of the aqueous phosphate ($PO_4^{3-}$) species onto the adsorbent surface (Schott 1984). The reactivity of the $nFe^0$-$Mg$ composite towards NO$_3^-$ is presented in Figure 5(b). It can be clearly observed that the nitrate removal of the coated iron nanocomposites was comparable to that of $nFe^0$. The lowest coating ratio (Mg/Fe:20%) showed the highest removal efficiency of around 98%, with a slight enhancement (around 0.7%) over that of $nFe^0$. It can be clearly observed that with increasing the coating ratio, the reduction potential of the composite towards nitrate slightly decreased. Consistent with a previously reported study (Maamoun et al. 2020), the prolonged dissolution of the Mg(OH)$_2$ coating could possibly affect the reduction potential of the $nFe^0$ core. Nevertheless, the lowest removal efficiency corresponding to the highest coating ratio (Mg/Fe:100%) showed great removal performance, with a slight decrease, only 4.5%, comparing to that of $nFe^0$. Such results confirmed that even if the coating has a slightly negative effect on the reduction mechanism, the great enhancement in the aqueous characteristics of the current composite along with the promoted adsorption reactivity makes it a promising candidate for real applications.

The leaching of iron oxides, ferrous (II) and ferric (III), was considered as an indicator to investigate the reactive longevity of the $nFe^0$-$Mg$ composites within aqueous solutions over a 1-week experiment. Ferrous aqueous concentration is representative of the iron dissolution, where the higher the concentration, the more the dissolution and the less the precipitation (Eljamal et al. 2018a). As shown in Figure 6, iron dissolution occurred rapidly (within the first hour) for $nFe^0$, represented by maximum ferrous concentration of 2.42 mg/L, followed by a declining trend corresponding to a rise in ferric concentration, whereas iron oxides precipitation was dominant during the rest of the days. For $nFe^0$-$Mg$ (Mg/Fe:100%), iron dissolution started after 12 hrs due to the high coating ratio and it was competing with precipitation during the rest of the
Iron–magnesium nanocomposite with enhanced aqueous characteristics was successfully synthesized. Coating nFe₀ with a shell of Mg(OH)₂ led to an increased performance in different aspects of the aqueous characteristics of the particles. The increase of the Mg/Fe coating ratio up to 100% resulted in a smaller average particle size by 46.7% comparing with that of bare nFe₀. An anti-aggregation effect was achieved corresponding to the smaller average particle size of the nFe₀-Mg particles, which was confirmed by the TEM morphological observation. Moreover, the degree of crystallinity was enhanced for the nFe₀-Mg composites as the Mg/Fe coating ratio increased from 20% to 100%, the higher the crystallinity of the composite. The 3 hrs settlement investigation of the modified nFe₀ exhibited higher stability in aqueous suspension comparing with the rapid settlement of bare nFe₀. The increase in the Mg/Fe coating ratio led to stimulated stability of the particles in aqueous suspension with lower settlement rate than that of unmodified iron particles, where Mg/Fe ratio of 100% showed around 95% enhancement in the suspension efficiency. Furthermore, phosphorus removal efficiency was improved by 2–3% for the nFe₀-Mg composites compared to that of nFe₀. In contrast, it was clearly observed that with increasing the Mg/Fe coating ratio up to 100%, the reduction potential of the composite towards nitrate slightly decreased by around 4.5%, comparing to that of nFe₀. Additionally, the iron core of the synthesized nFe₀ was adequately protected from aqueous corrosion after the optimal modification with Mg(OH)₂, corresponding to leachates with lower iron oxides, indicating the enhanced reactive longevity of the modified composites. The current work suggests that the achieved enhanced features of the proposed iron-based nanocomposites could lead to great potential applicability towards sustainable effectiveness in water treatment applications.

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