Synthesis and Characterization of Zero-Valent Iron Nanoparticles

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Synthesis and Characterization of Zero-Valent Iron Nanoparticles

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Abstract. Nanoparticles, particles of size 10^{-9} have a high potential as water, waste water and air pollution treatment. In this research, nanoscale iron particles were synthesized by reduction of Fe_2SO_4 7 H_2O by $NaBH_4$ at low temperature to avoid oxidation during the process. Characterization of the particles based on particle size, material structure, surface morphology and the composition of forming element was done by transmission electron microscopy (TEM), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectometry (EDS), respectively. Surface area and magnetic character was measured by BET surface area and vibrating sample magnetometry (VSM), respectively. Morfological observation showed that structured core-shell of size < 44 nm and shell of size ~ 3 nm with saturated magnetization value ~ 132 emu g^{-1} has been formed.

Introduction

Nanotechnology is an engineering and art of manipulating matter at nanoscale [1]. Nanoparticles, i.e. particles of size 10^{-9} has a high potential as water, waste water and air pollution treatment [2]. Important characteristics of the nanoparticle are particle size, structure, density and surface intrinsic reactivity. Iron nanoparticle technology represents perhaps one of the first generation nanoscale environmental technologies [3]. Several field test have demonstrated the promising prospective for in situ remediation [4,5].

Nanoscale zero- valent iron particles can be prepared in aqueous solution via reduction of ferric iron (Fe(III)) or ferrous iron (II) with sodium borohydride [4,5]. The particles produced by this method are referred to as Fe (B). It is also possible to heat pentacarbonyl to 200-250 ^{o}C . At this temperature it will disassociate into nano zero- valent iron and carbon monoxide [5,6].

In this study, synthesizing of the s zero-valent iron nanoparticles was done following the method suggested by [3,7]. However, this research was performed at different ratio of ethanol and deionized (DI) water (v/v), mixing speed of 650 rpm and low temperature (+ 10 ^{o}C)., Synthesizing under this condition is expected to results in homogenous fine particles the core-shell structure, hence; greater surface contact and, therefore; its potential to react and reduce the zero-valent iron will increase. The use of temperature at low temperatures and stirring at 650 rpm speed is expected to slow down the oxidation at the time of formation of zero-valent iron nanoparticles and produce zero-valent iron that reaches the optimum size, <50 nm and homogeneous. Synthesis performed [7] using Fe_2SO_4 reduced by reducing agent $NaBH_4$ at room temperature to give a zero-valent iron nanoparticles size of 10-100 nm, which has not reached the optimum size of zero-valent iron nanoparticles [9].The resulting zero-valent iron nanoparticles is characterized based on its morphology, phase and magnetic properties.

Materials and method

The chemicals used in this study such as $FeSO_4 7H_2O$, sodium borohydride ($NaBH_4$), ethanol were of analytical grade. The N_2 gas utilized in this research is of Ultra High Purity (UHP) grade.

Synthesis zero-valent iron nanoparticles. For the synthesis of nanoscale zero-valent iron, 20 g of $Fe_2SO_4.7\ H_2O$ was dissolved in a 3:2 (v/v) deionized water/ethanol mixture (300 ml (DI) water + 200 ml ethanol) and completely dissolved by stirring for 10 minutes at 650 rpm. Prior to the test, deionized (DI) water was purged with purified N_2 gas for 15 min to remove dissolved oxygen. After that, 2 g of $NaBH_4$ was added to 50 ml of deionized water. The borohydride solution is poured in a burette and added drop-by-drop to aqueous iron salt at 5 ml/min and vigorously mixed by a propeller revolving at 650 rpm. All process was performed in N_2 environment while the outside of the reaction container was cooled down with ice cubes to prevent oxidation of zero-valent iron nanoparticles. During this process, the solution slowly turned to black color. The black colored particles washed by N_2 saturated deionized water and at least three times by 99 % absolute ethanol. Finally, the synthesized zero-valent nanoparticles were dried in a desiccator. The dried particles were used for further characterization.

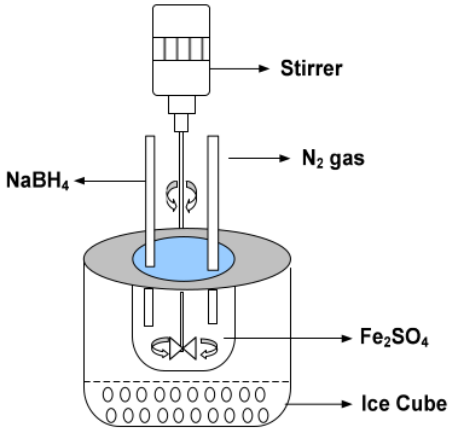

Fig. 1 Schematic diagram for iron nanoparticles synthesis.

Results and Discussion

In this study, zero-valent iron nanoparticles (6 – 40 nm) have been synthesised by the method of Fe_2SO_4 reduction using $NaBH_4$ as a reducing agent at low temperature. Effect of low temperature on the synthesis of zero-valent iron provide qualified optimum size. Research by the same method and using room temperature [7] generates a zero-valent iron nanoparticles of 10-100 nm, while [9] get zero-valent iron nanoparticles of 50 -100 nm. Effect of stirring speed on the synthesized process also contributed to the size of the zero-valent iron nanoparticles produced. A systematiccharacterisation of zero-valent iron nanoparticles has been performed using XRD, TEM, SEM-EDS, VSM and BET studies.

The XRD patterns of zero-valent iron nanoparticles is shown in Figure 2. The main reaction at zero-valent iron phase i.e. 2 peaks at 2 theta angle at 45^o and 65.3^o with crystal plane of 110 and 220, respectively [3]. Peak which indicates Fe_3O_4 layer looks at an angle 2 theta 40.49^o, respectively. An iron oxide layer that is perhaps formed through the drying step in the workup. TEM image of iron nanoparticles is shown in Figure 3. The resulting structure matches the structural model with core shell zero valent iron [2,3]. The core is made of metallic iron while the shell consists mostly of iron oxides, such as Fe_3O_4 and hydroxides formed from the oxidation of zero-valent iron. In general, the core with size <44 nm is formed with a flat and smooth shell ~ 3 nm thick on the surface. In addition to having smaller particle sizes, the effect of low temperature and stirring speed during Fe_2SO_4

reduction with NaBH4 reductant more homogeneous core surfaces in size and color distribution that indicated incomplete formation of the phase.

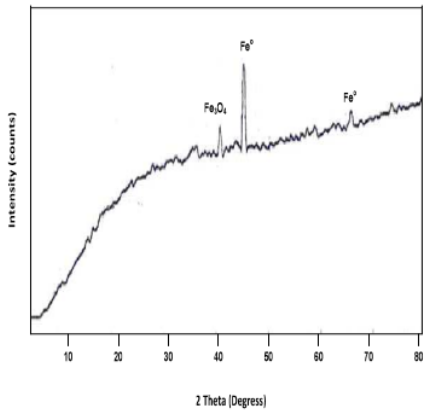

Fig. 2. XRD pattern zero-valent iron.

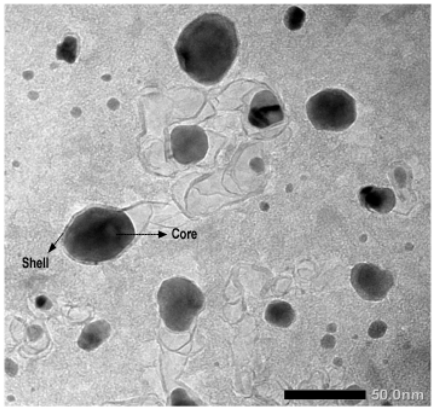

Fig.3. TEM images of zero-valent iron.

Surface morphologies of zero- valent iron were carried out by SEM analysis and the result is shown in Figure 4. The micrograph shows that zero- valent iron particles did not appear as discrete particles but formed much larger dendritic flocks. The aggregation is attributed due to the Van Der Waals forces and magnetic interactions among the particles [10].

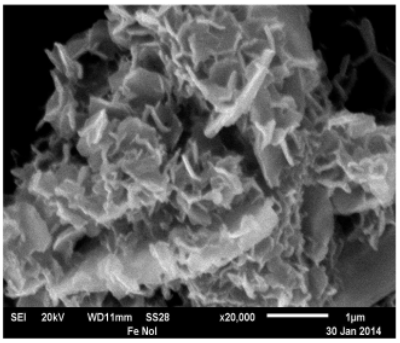

Fig. 4. SEM of zero-valent iron.

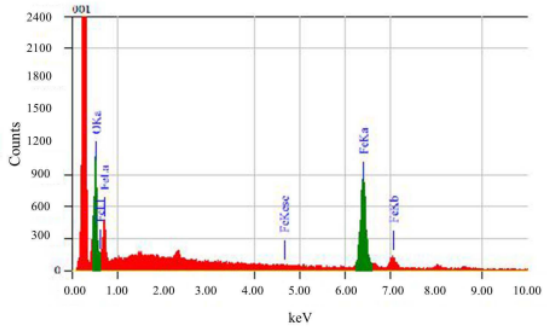

Fig. 5. EDS of zero-valent iron.

EDS micrograph explains the surface atomic distribution and chemical composition of zero- valent iron nanoparticles. In this analysis, zero-valent iron from synthesis confirmed the presence of elemental iron signal (Figure 5). Strong signal from the iron atoms are observed 66.01 % and signal from O 33,99 %. Similar results were reported in literature [10] i.e. 72.11 % from the iron and weaker signal from N (7.23 %) and O (20.66 %).

Further identification on the formation of nanoparticles magnetic was done by characterization of magnetic characteristics of material. Figure 6 shows the hysteresis curve of nanoparticles from the measurement by Vibrating sample magnetometer at room temperature. Magnetization value at zero-valent iron nanoparticles is ~132 emu g^{-1}, which is similar with the magnetization value reported in literature, i.e. ~ 130 emu g^{-1} [11]. This high magnetization values cause the aggregate particles as revealed in the SEM image. Surface area of zero valent iron nanoparticles was analyzed by data isotherm adsorption BET (Brunner Emmet Teller) using Nova instrument based on absorption of adsorbent on N_2 gas. The BET surface area values is 17.2 m^2 g^{-1} for zero-valent iron particles as

shown in Figure 7, which is comparable to some BET surface area reported in literature i.e. 14.5 $m^2 g^{-1}$[3] and 25 $m^2 g^{-1}$[8] .

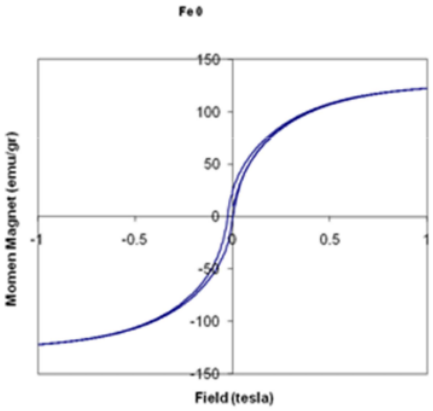

Fig. 6. Hysteretic curve of zero-valent iron.

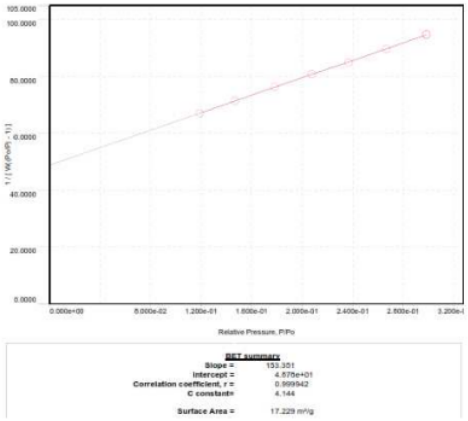

Fig. 7. BET surface area plot of zero-valent iron.

Conclusion

Zero-valent iron nanoparticles (6-40 nm) was synthesized by $FeSO_4.7H_2O$ reduction using $NaBH_4$ as a reducing agent at low temperature and high mixing speed (650 rpm). Effect of low temperature causes the optimum size of the resulting particle is less than 50 nm while its maximum value magnetization is ~ 132 emu g^{-1}. The formation of a homogeneous structure visible by TEM image of a shell layer surrounding the core so that a more homogeneous size distribution, with the resulting particle size between 6 and 40 nm and shell of size ~ 3 nm.

References

[1] W. Zhang, Nanoscale iron particles for environmental remediation: An overview, J. Nanoparticle Researh. 5 (2003) 323-332.
[2] X. Li, D.W. Elliot and W. Zhang, Zero-Valent iron nanoparticles for abatement of environmental pollutans: Materials and enginer.spects, J.Critical Reviews in Solid State and Mat. 31(2006) 111-122.
[3] Y. Sun, X. Li, J. Cao, W. Zhang, and H.P. Wang, Chracterization of zero-valet iron nanoparticles, J. Advance in Colloidal and Interface Science 120. (2006) 47-56.
[4] D.W. Elliot, W. Zhang, Applications of iron nanoparticles for groundwater remediation, J. Remediation (2006) 7-19.
[5] N.C. Muller, B. Nowack, Nano zero valent iron – The solution for water and soil remediation?, Observatory Nano (2010).
[6] S.M.Ponder, J.G. Darab, and T.E. Mallouk, Remediation of Cr (VI) and Pb (II) aqueous solutions using supported, nanoscale zero valent iron, J. Environ. Sci. Technol. 34 (2000) 2564-2589.
[7] H. Choi, A.B.M. Glasuddin, and S.R. Kanel, Method of synthesizing air-stable zero-valent iron nanoparticles at room temperature and applications, United States Patent Application (2008).
[8] R. Yuvakkumar, V. Elango, V. Rajendra and N. Kannan, Preparation and characterization of zero valent iron nanoparticles, J. Digest of nanomaterials and biostructure, 6 (2011) 1771-1776.
[9] U.S. EPA Workshop on nanotechnology for site remediation (2005)
[10] S. Murugan and P. Paulpandian, Synergistic antibacterial evaluation of commercial antibiotics combine with nanoiron against human pathogens, Int.J.Pharm.Sci. Rev. Res 18 (2013) 183-190.
[11] G.T.J, Sulungbudi, Mujamilah and A. Handayani, Sin. Nanoparticles magnetic coreshell. Fe/oksida , J. Indonesian of Material Science, 3 (2012) 182-187.

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