

Removal of Arsenic (III) from Contaminated Water by Synthetic Nano Size Zerovalent Iron

A. R. Rahmani, H. R. Ghaffari, and M. T. Samadi

Abstract—The present work was conducted for Arsenic (III) removal, which one of the most poisonous groundwater pollutants, by synthetic nano size zerovalent iron (nZVI). Batch experiments were performed to investigate the influence of As (III), nZVI concentration, pH of solution and contact time on the efficiency of As (III) removal. nZVI was synthesized by reduction of ferric chloride by sodium borohydride. SEM and XRD were used to determine particle size and characterization of produced nanoparticles. Up to 99.9% removal efficiency for arsenic (III) was obtained by nZVI dosage of 1 g/L at time equal to 10 min. and pH=7. It could be concluded that the removal efficiency were enhanced with increasing of ZVI dosage and reaction time, but decreased with increasing of arsenic concentration and pH for nano sized ZVI. nZVI presented an outstanding ability to remove As (III) due to not only a high surface area and low particle size but also to high inherent activity.

Keywords—Arsenic removal, aqueous solution, zero valent iron.

I. INTRODUCTION

ARSENIC (As), one of the common constituent of earth crust, is a carcinogenic and toxic contaminant of groundwater and surface water resources [1-4]. High levels of arsenic can cause acute toxic effects on human health including gastrointestinal symptom, disturbance of cardiovascular and nervous system function, pigmentation, depigmentation, keratosis, skin cancer, teratogenicity, reproduction disorder and death [1]. The major pathway to human exposure by arsenic is drinking of polluted groundwater [3]. In order to minimize the health effect of arsenic, the U.S.EPA, World Health Organization (WHO) and the European Commission (E.C.) have set Maximum Contamination Level (MCL) of 10 µg/L As in drinking water [1-3]. Arsenic is introduced into environment through both natural and anthropogenic activity. In the sources and is associated with the ores of metal like copper, lead and gold [1, 3, 4]. In natural water, the inorganic forms of arsenic such as arsenite species (arsenious acid, H_3AsO_3) and negatively charged arsenate (H_2AsO_4 and HAsO_4) are prevail [1, 3, 4]. Many different technologies have been developed to remove arsenic from drinking water in order to comply with the new MCL. The common method for remove of arsenic from water is physical-chemical treatment including precipitation,

adsorption, ion exchange, membrane filtration and also microbial transformation [1, 3].

Recently zero-valent iron (ZVI) has become one of the most common adsorbent for rapid removal of As (III) and As(V) from subsurface environment [1, 4, 5]. The use of ZVI as a remediation agent in groundwater treatment started in early 1990s when granular ZVI was first employed in permeable reactive barrier (PRBs) systems [6]. Considerably the reactivity of ZVI has recently been improved by the development of smaller sized, i.e. nanoscale zero-valent iron (nZVI) [1]. The researches has shown that nanoscale iron particle is very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as perchlorate, brominated methane, Cr(VI), Pb(II), TCE, humic acid, nitrate, biosolids, copper and zinc [7-15].

For that reason and in view of highly efficiency of nZVI, the aim of this work was synthesis of nanoparticles zero valent iron in As (III) removal from aqueous solutions. Also the effects of As (III), nZVI concentration, pH and contact time on the As (III) removal efficiency were evaluated.

II. MATERIALS AND METHODS

A. Chemicals

All chemical reagents that used in this study (NaBH_4 , NaAsO_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, HCl , NaCl , Morpholin, CHCl_3 , AgSCSN (C_2H_5)₂, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Pb}(\text{CHCOO})_2 \cdot 3\text{H}_2\text{O}$, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ and CH_3COOH) was obtained from Merck (Germany). The solutions were prepared by dissolving the adequate quantities of the compounds in deionized water. Arsenic solutions were arranged by dissolving the NaAsO_2 in deionized water and determined in 520 nm by UV/VIS spectrophotometer (Shimadzu-1700, Japan). 1 M HCl or NaOH was used to adjustment of pH and controlled by pH meter (Suntex model sp-701). Water was purified with a water distiller (Fater Electronic model 2104).

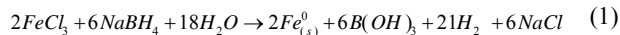
B. Preparation of Nanoparticle Zero Valent Iron (nZVI)

Nano sized was produced by reduction of ferric iron in the presence of sodium borohydride. These particles were prepared freshly each day by adding 0.16 M NaBH_4 aqueous solution drop wise to a 0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution at ambient temperature and under atmospheric conditions [16]. The preparation of solutions involved the following steps: sodium borohydride (NaBH_4 , 0.6053 g) solids were dissolved in 100 mL of 0.1 M NaOH solution (0.16 M NaBH_4 in 0.1 M NaOH solution), and then 2.7030 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved into 100-mL pure water (0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). NaBH_4 solution can

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be made either in water or NaOH solution, although NaBH_4 is unstable in water and can quickly result in a loss of reduction power. Addition of the NaBH_4 to the FeCl_3 solution in the presence of vigorous magnetic stirring resulted in the rapid formation of fine black precipitates as the ferric iron reduced to Fe^0 and precipitated according to the following reaction:



The particles were washed 3 to 4 times with a 4-10 M HCl (pH 4) solution and stored as a 5-mg Fe/mL concentrate at pH 4 and kept in a refrigerator at $<4^\circ\text{C}$. The characterizations of solid-phase nZVI were carried out using XRD (Philips X'Pert) and SEM (Philips XL30).

C. Batch Experiment by Nano Sized ZVI

Batch experiments were performed with 100 ml beaker covered with aluminum foil. The beaker was mixed by magnetic stirrer (150 rpm) at room temperature. After given period of time the sample centrifuged at 3000 rpm for 15 min. Then the solution filtered through 0.45 μm membrane filter and analyzed for arsenic by Silver Diethyldithiocarbamate method (SDDC) (17). The effect of various parameters such as contact time (2, 5, 10 and 15 min), pH (4, 7 and 11), nZVI mass (0.1, 0.25, 0.5 and 1 g/L) and initial arsenic concentration (1, 3, 5, 10, 15, 20, 25 and 30 mg/L) were studied in term of their effect on reaction processes.

III. RESULT AND DISCUSSION

A. Characterization of Fe^0 Nanoparticles

The pristine samples collected from different crops synthesis of nZVI and were tested for characterization. Our result was similar to those reported in the literatures [1, 2]. The SEM micrograph of the Fe^0 nanoparticles is shown in Fig. 1 (a-b). Synthetic nZVI particle was in the size range of 10-100 nm as measured by SEM. This micrograph showed that the Fe^0 nanoparticles do not appear as discrete particles but form much larger dendritic flocs whose size could reaches micron scale. The aggregation is attributed to the magnetic forces among the Fe particles. Similar phenomenon was observed by other researchers [9]. X-Ray diffraction of nZVI surface composition is shown on Fig. 2 and indicated that surface species of prepared nZVI is Fe^0 (14.06) and FeOOH (26.9, 36.29, 38.03, and 46.7).

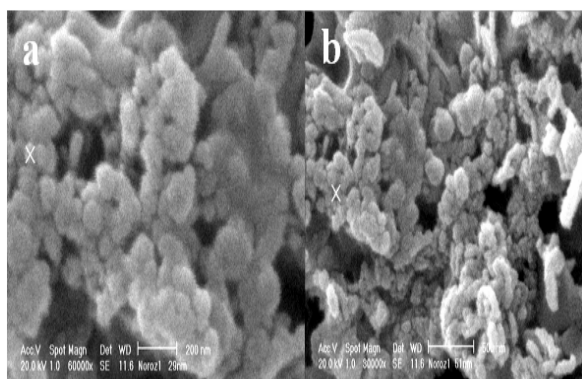


Fig. 1 SEM image of synthesized nZVI

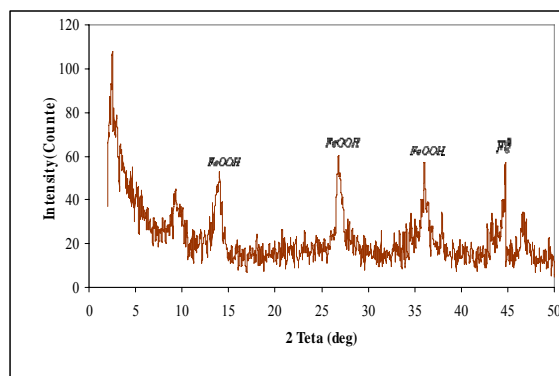


Fig. 2 X-Ray diffraction analysis of synthesized nZVI

B. Effect of pH

The pH is one of the important factors in the As (III) removal using nanoparticle zero-valent iron. For investigation effect of pH, 10 mg/L As (III) was adsorbed on 1 g/L nZVI at various pH ranges (4, 7 and 11) and 2-15 min. contact time. It was determined that As (III) can be removed by nZVI at different pH values. As shown in Fig. 3, the As (III) removal efficiency increased significantly with decreasing pH. The removal efficiency in detention time of 10 min and pH range 4-11 was 92-99.9%. Also, results of pH effect (4, 7, and 11) on adsorption of As (III) (10 mg/L) at different nZVI dosage (0.1, 0.25, 0.5, and 1 g/L) and contact time equal to 10 min is shown in Fig. 4. In 1 g/L nZVI dosage, 100 % adsorption of As (III) at pH 4 was decreased to 98 % at pH 7 and 92% at pH 11. The pH dependent behavior can be explained by ionization of both the adsorbate and the adsorbent causing repulsion at the surface and decreasing the net As (III) adsorption [1, 2]. Below pH 9.2, H_3AsO_3 is the predominant species and presumably the major species being adsorbed. When the pH is above 9.2, H_2AsO_3^- is the predominant As species while the nZVI corrosion product surfaces are also negative ($\text{Fe}(\text{III})\text{-O}$) causing electrostatic repulsion. A similar pH dependence trend in As adsorption amorphous iron oxide, synthetic goethite, and magnetite has been observed [1]. Other reason for this phenomena is accelerated corrosion of Fe^0 in acid condition [1, 2, 18]. Also when the ferrous ions dissolved from the iron surface collided with hydroxyl ions in alkaline solution, producing ferrous hydroxide precipitation on the iron surface occupying the reactive sites to hinder the reaction. This means that acidic condition is the better for this process [18].

C. Effect of nZVI Dosage

Adsorption studies of As (III) onto nZVI were performed using 10 mg/L As (III) treated with varying nZVI solid concentrations (0.1, 0.25, 0.5, 1 g/L) in contact time of 10 min. Fig. 4 shows that the increases of Fe^0 concentration greatly enhanced the removal efficiency. In detention time of 10 min and pH 7 all As (III) was removed when the Fe^0 mass concentration was 1 g/L, but only 52.1% was removed when the Fe^0 mass concentration was 0.1 g/L. Therefore the more nZVI particles are able to provide more iron surface-active sites for collision with As (III) molecules to accelerate the As (III) removal efficiencies [9, 12, 18]. The higher As (III) removal with time elapse is due to the superior surface area of

nZVI particles demanding a much lower dose than that of micro scale iron [18].

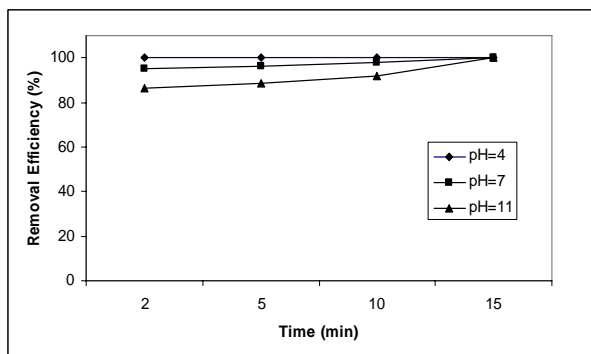


Fig. 3 Adsorption efficiency of As (III) on nZVI as a function of pH and time. Reaction conditions: 10 mg/L As (III) adsorbed on 1.0 g/L nZVI

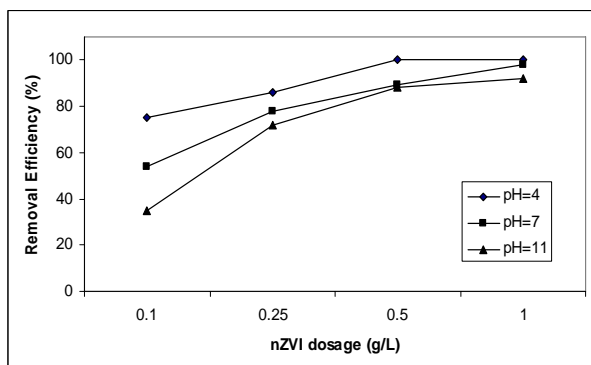


Fig. 4 Adsorption efficiency of As (III) on nZVI as a function of pH and nZVI dosage. Reaction conditions: 10 mg/L As (III), reaction time 10 min.

D. Effect of nZVI Dosage

Adsorption studies of As (III) onto nZVI were performed using 10 mg/L As (III) treated with varying nZVI solid concentrations (0.1, 0.25, 0.5, 1 g/L) in contact time of 10 min. Fig. 4 shows that the increases of Fe^0 concentration greatly enhanced the removal efficiency. In detention time of 10 min and pH 7 all As (III) was removed when the Fe^0 mass concentration was 1 g/L, but only 52.1% was removed when the Fe^0 mass concentration was 0.1 g/L.

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E. Effect of Contact Time

Adsorption of As(III) on nZVI as a function of time and nZVI dosage at pH 7 is shown in Fig. 5. As shown in this figure the removal efficiency increased with elapse of contact time. For a 10 mg/L initial As (III) concentration and nZVI dosage of 0.1 g/L, a residual of about 86% was found after the first 2 min, promptly increased to about 59% after 5 min, and about 48% and 35% at 10 and 15 min respectively. For 1 g/L

nZVI, removal efficiency was 96.5-100% at contact time range of 2-15 min.

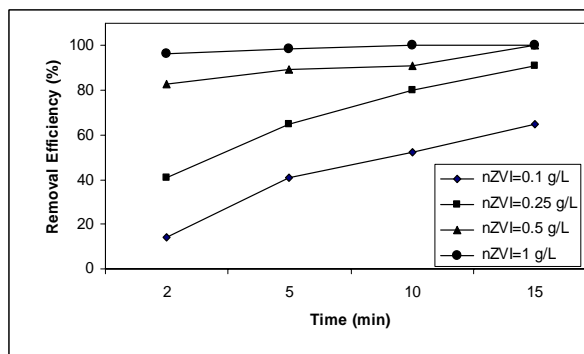


Fig. 5 Adsorption efficiency of As (III) on nZVI as a function of time and nZVI dosage. Reaction conditions: 10 mg/L As (III), pH 7

F. Effect of initial As (III) Concentration

In the batch experiment with nZVI, the As (III) adsorption efficiency steadily decreased linearly from 100 to 88.3% when the initial concentration increased from 1 to 30 mg/L, as shown in Fig. 6.

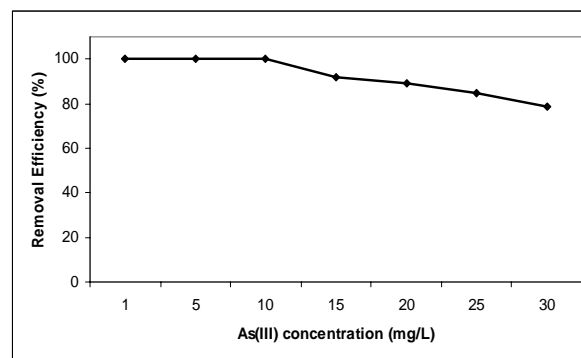


Fig. 6 Adsorption efficiency of As(III) on nZVI as a function of As (III) concentration. Reaction conditions: pH 7, 1.0 g/L nZVI and reaction time 10 min

IV. CONCLUSION

The results of present work showed rapid reaction between nZVI and arsenic. Nanoparticle zero-valent iron could remove arsenic from aqueous solution at very short time (minute scale) over a wide range of pH.

In processes, nZVI, efficiency decrease by increasing pH and arsenic concentration in solution. In addition removal efficiency has direct relation with contact time and dosage of nZVI. Due to the low amount of iron used, the mass of produced sludge in the process was significantly low; so, the flocs may be removed by magnetic techniques, often more efficient and faster than centrifugation or filtration.

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REFERENCES

- [1] S.R. Kanel, B. Manning, L. Charlet and H. Choi, "Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron" *Environ. Sci. Technol.* 2005, 39, pp.1291-1298.
- [2] S.R. Kanel, J.M. Greneche and H. Choi "Arsenic(V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a colloidal Reactive Barrier Material" *Environ. Sci. Technol.* 2006, 40, pp.2045-2050.
- [3] T. Konstantina, P. Nikolaos, V. Nikolaos, K. Nikolaos and E. Pavlos, "Arsenic removal from geothermal water with zero-valent iron–Effect of temperature", phosphate and nitrate", *Water Research Journal.* 2006, 40(12), pp.2375-2386.
- [4] T. Konstantina, P. Elpida and P.N. Nikolaos, "Modeling of arsenic immobilization by zero valent iron", *European Journal of Soil Biology*, 2007, 43, pp.356-367.
- [5] B. Sunback, D. Mark and P. Georg, "Xiaoguang, M. Chemical reaction between arsenic and zero-valent iron", *Water Research Journal*, 2005, 39(5), pp.763-7700.
- [6] L. Xiao-qin, D.W. Elliott and Z. Wei-xian, "Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects". *Critical Reviews in Solid State and Materials Sciences*, 2006, 31, pp.111-122.
- [7] V. Plagantz, M. Ebert and A. Dahmke, "Remediation of groundwater chlorinated and brominated hydrocarbons, benzen and chromate by sequential treatment using ZVI and GAC" *Environ Geol.* 2006, 49: pp.684–695
- [8] C. Shiao-Shing, C. Chih-Yu, L. Chi-Wang, C. Pao-Hsuan and C. Yu-Min, "Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process" *journal of Hazardous Materials.* 2007, 142, pp.362-367.
- [9] N. Shao-feng, L. Yong, X. Xin-hua and L. Zhang-hua, "Removal of hexavalent chromium from aqueous solution by iron nanoparticles", *Journal of Zhejiang University Science-B*, 2005, 6(10), pp.1022-1027.
- [10] X. Yinhui and Z. Dongye, "Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles" *Water Research Journal*, 2007, 41, pp.2101-2108.
- [11] Abul B.M. Giasuddin, R.K. Sushil and C. Heechul, "Adsorption of Humic Acid onto Nanoscale Zero valent Iron and Its Effect on Arsenic Removal" *Environ. Sci. Technol*, 2007, 41, pp.2022-2027.
- [12] C.C. Gordon and H.L. Yang, Lee, "Chemical reduction of nitrate by nanosized iron: kinetics and pathways" *Water Research Journal*, 2005, 39, pp.884-894.
- [13] C. Shiao-Shing, H. Hong-Der and L. Chi-Wang, "A new method to produce nanoscale iron for nitrate removal" *Journal of Nanoparticle Research*, 2005, 6: pp.639-647.
- [14] L. Xiao-qin, G.B. Derick and Z. Wei-xian, "Stabilization of biosolids with nanoscale zero-valent iron (nZVI)" *Journal of nanoparticle research*, 2007, 9, pp.233–243.
- [15] R. Rangisivek and M.R. Jekel, "Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibrium, processes and implications for storm water runoff treatment" *Water Research Journal*, 2005, 39, pp.4153–4163.
- [16] J. Sung Hee and I. Francis Cheng, "Nanotechnology for Environmental Remediation" Springer Science+Business Media, Inc, USA, 2006.
- [17] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*. 19th Ed.: APHA, Washington DC, 1998.
- [18] H.Y. Shu, M.C. Chang, H.H. Yu and W.H. Chen, "Reduction of an azo dye Acid Black 24 solution using synthesized nanoscale zero valent iron particles", *Journal of Colloid and Interface Science*, 2007, 314, pp.89-97.