

行政院國家科學委員會補助專題研究計畫成果報告

Fe^0/CO_2 程序串聯流體化床反應槽新穎技術處理含砷地下水

Arsenic-contaminated groundwater treatment by innovative technology of the Fe^0/CO_2 process and fluidized bed reaction tank in series

計畫類別：☒ 個別型 ☐ 整合型

計畫編號：**NSC 97-2221-E-041 -010 -MY3**

執行期間：**97 年 08 月 01 日至 100 年 07 月 31 日**

執行機構及系所：嘉南藥理科技大學

計畫主持人：**廖志祥** 教授(環境資源管理系)

共同主持人：**林啟燦** 副教授(海洋環境工程系)；**林健榮** 副教授(環境工程與科學系(所))

計畫參與人員：

1. Visanu Tanboonchuy , Ph.D. student (February 11, 2009), Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Klong-Luang, Pathumthani, 12120, THAILAND.
2. ERICKSON CABUHAT ROQUE, Ph.D. student (April 16, 2009), Department of Chemical Engineering, University of the Philippines, Diliman, Quezon City 1101, Philippines.
3. PIYANATE NAKSEEDDEE, Ph.D. student (May 1, 2010), International Postgraduate Programs in Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok, THAILAND
4. Thanatorn Yoadsomsuay , Ph.D. student (October 24, 2010), International Postgraduate Programs in Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok, THAILAND
5. 魏煜倫(環境工程與科學系/2007 碩士生)、王信惟(環境工程與科學系/2008 碩士生)、盧正修(環境工程與科學系/2009 碩士生)

成果報告類型(依經費核定清單規定繳交)：☐ 精簡報告 ☒ 完整報告

本計畫除繳交成果報告外，另須繳交以下出國心得報告：

- ☐ 赴國外出差或研習心得報告
☐ 赴大陸地區出差或研習心得報告
☒ 出席國際學術會議心得報告 (第三年)
☐ 國際合作研究計畫國外研究報告。

處理方式：除列管計畫及下列情形者外，得立即公開查詢

- ☐ 涉及專利或其他智慧財產權， ☐ 一年 ☒ 二年後可公開查詢

中 華 民 國 100 年 10 月 31 日

目 錄

中文摘要

英文摘要

報告內容/參考文獻

計畫成果自評

可供推廣之研發成果資料表

附錄

摘要

本計畫執行期程為2008.8.1-2011.7.31，研究目標為針對含砷之飲用水對人體健康所造成之危害，提出 Fe^0/CO_2 新穎處理技術。主要研究內容包括：奈米鐵材料及水質之影響效應、砷去除反應動力、技術應用潛力。

針對上述研究項目，本案所達成之研究成果（詳次頁著作清單），截至本報告書撰稿日(2011.10)為止，計有國際期刊論文2篇刊登(IF分別為4.144及2.411)、1篇修正中(IF分別為4.144)、1篇審查中、1篇準備投寄中；國際研討會論文計有9篇（分別發表於日本、台灣、泰國、越南、印尼、馬來西亞等國家）；3件博士生論文著作、1件碩士生論文著作。

觀諸上述研究品質/數量及高階人才培訓，本研究計畫案已然達成預期目標。另外，有關本研究案重要之發現與結論，將以主題式方式，編輯各期刊及研討會論文分篇呈現於本報告中。未來筆者將著力於本研究成果之擴散與推廣，包括專利申請與技轉等方面。

關鍵字：砷污染、砷酸鹽、亞砷酸鹽、二氧化碳、烏腳病、氧化鐵覆膜石英砂、砂濾、零價鐵。

本研究案衍生著作清單

說明：

● 標示☑者列入本報告之分項內容

● 本案3年期之目標包括：“A”-材料選擇；“B”-背景水質；“C”-反應動力；“D”-應用潛力

期刊論文 (2+1+1+1 篇)

1. ☑ **B/C/D** Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. (2011). *Impact of selected solution factors on arsenate and arsenite removal by nanoiron particles*. **Environ. Sci. Pollut. Res.** 18: 857-864. (Impact Factor **2.411**).
2. ☑ **C/D** Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. (2011). *Gas-bubbled nano zero-valent iron process for high concentration arsenate removal*. **J. Haz. Mat.** 186: 2123–2128. (Impact Factor **4.144**)
3. ☑ **B/C/D** Tanboonchuy V., Grisdanurak N., Liao C.H. *Background species effect on aqueous arsenic removal by nano zero-valent iron using fractional factorial design*. **J. Haz. Mat.** (2011). **Minor revision**.
4. ☑ **A** Tanboonchuy V., Grisdanurak N., Liao C.H. *Nitrate probe for quantifying reducing power of nanoscale zero-valent iron*. **Sustainable Environment Research** (2011). **Under review**.
5. ☐ **B/C/D** Tanboonchuy V., Grisdanurak N., Liao C.H. (2011) *Novel process for arsenic removal by nanoiron coupled with gases bubbling system*. **To be submitted to ES&T**.

研討會論文 (9 篇)

1. ☐ Piyanate Nakseedee, Jia-Chin Hsu, Nurak Grisdanurak, Chih-Hsiang Liao* (2011). *Arsenic Removal by Cu/Fe Bimetal in the Gas Bubbling System*. **International Conference on Environmental Quality Concern, Control and Conservation**, May 20-21, 2011, National Kaohsiung Marine University, Taiwan, Taiwan.
2. ☐ Thanatorn Yoadsomsuay, Nurak Grisdanurak, Chih-Hsiang Liao* (2011). *Arsenic Disappearance in the Presence of Nanoscale Zero-Valent Iron*. **International Conference on Environmental Quality Concern, Control and Conservation**, May 20-21, 2011, National Kaohsiung Marine University, Taiwan, Taiwan.
3. ☑ Tanboonchuy V., Grisdanurak N., Liao C.H. *A novel method for quantifying reducing capacity of nanoiron particles*. **International Conference on Nanotechnology – Research and Commercialisation (ICONT2011)** Sabah, MALASIA. 6-9 June, 2011.
4. ☑ Tanboonchuy V., Grisdanurak N., Liao C.H. *Arsenic Removal by Nanoiron in the Gas-bubbled Aqueous Solution*. 2011 **International Conference on Environmental Science and Engineering (ICESE 2011)**. Bali Island, INDONESIA. 1-3 April, 2011.

5. ☒ Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. *Arsenate removal by nano zero-valent iron in the gas bubbling system*. 2010 International Conference on Applied Chemistry and Chemical Engineering (ICACCE 2010). Tokyo, JAPAN. 26-28 May, 2010.
6. ☒ Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. *Influence of selected anions on arsenic removal by nano-zero valent iron*. 2010 International Conference on Environmental Quality Concern, Control and Conservation (EQC³ 2010). Tainan, TAIWAN. 22-23 May, 2010.
7. ☒ Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. *Arsenic removal by nano zero-valent iron: effect of initial concentration and dissolved oxygen*. 2010 Asian-Pacific Regional Conference on Practical Environmental Technologies (APRC 2010). Ubonratchathani, THAILAND. 22-27 March, 2010.
8. ☒ Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. *Nanoiron technology for arsenic-contaminated groundwater treatment*. 2009 Asian-Pacific Regional Conference on Practical Environmental Technologies (APRC 2009). Hanoi, VIETNAM. 7-8 August, 2009.
9. ☒ Tanboonchuy V., Hsu J.C., Grisdanurak N., Liao C.H. *Test of reducing power of nano zero-valent iron particles using nitrate as a chemical probe*. The 6th Conference on Environmental Protection and Nanotechnology (EPTN 2009). Kaohsiung, TAIWAN. 22 May, 2009.

博/碩士論文(4 件)

- ☐ Visanu Tanboonchuy (February 2012). *Arsenic removal by combination of nanoiron/gas bubbling and fluidized sand bed processes*. Department of Chemical Engineering, Faculty of Engineering, Thammasat University, THAILAND. 註：預計 2012 年 2 月進行口試。
- ☐ 王信惟，*Fe⁰/CO₂ 串聯流體化床反應系統之水力特性試驗*。嘉南藥理科技大學環境工程與科學系(2010)。
- ☐ Piyanate Nakseedee (2012-2013). *Arsenic removal by gas-bubbled nano bimetals*. International Postgraduate Programs in Environmental and Hazardous Waste Management, Chulalongkorn University, THAILAND. 註：本案所衍之生研究題材
- ☐ Thanatorn Yoadsomsuay (2012-2013). *Arsenic removal by organics-modified nanoiron particles*. International Postgraduate Programs in Environmental and Hazardous Waste Management, Chulalongkorn University, THAILAND. 註：本案所衍之生研究題材

Abstract

This project was conducted over the period of August 1, 2008-July 31, 2011. The goal was to use the innovative process of Fe^0/CO_2 for the treatment of arsenic-contaminated drinking water, which is harmful to humans. The work implemented involves nanoiron material and water quality effects, arsenic removal kinetics, and potential for field application of this process.

Based on the above research items, the achievements of this project include: 2 international journal publications with IF=4.144 and 2.411, respectively; 1 manuscript in revision (IF = 4.144); 1 manuscript in reviewing; 1 manuscript in submission; 9 conference paper publications; 3 doctoral dissertations; and 1 Master thesis.

In view of research quality and quantity and graduate student cultivation, the goal of this project appears to meet the set standard. Concerning the important findings and conclusions of this research project, they will be presented thematically and edited in the format of journal/conference papers in series. In the future, we will place our efforts to disseminate the outcomes of this research project through patent application and technology transfer.

Keywords: Arsenic contamination; arsenate; arsenite; blackfoot disease; carbon dioxide; iron-oxide coated sand (IOCS); sand filter; Zero-valent iron.

報告內容

Environ. Sci. Pollut. Res. (2011), 18: 857-864.

Impact of selected solution factors on arsenate and arsenite removal by nanoiron particles

Visanu Tanboonchuy^a, Jia-Chin Hsu^b, Nurak Grisdanurak^{a, c}, Chih-Hsiang Liao^{d, *}

^aDepartment of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND.

^bDepartment of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

^cNational Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Pathumthani, THAILAND.

^dDepartment of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

Corresponding author: Prof. Chih-Hsiang Liao

*Email: chliao@mail.chna.edu.tw

Telephone no.: +886-6-266-3230

Fax no.: +886-6-366-3756

Abstract

Nano-scale zero-valent iron (NZVI) was used for the removal of arsenite (As(III)) and arsenate (As(V)) in aqueous solution. Batch experiments were conducted to investigate the effects of initial pH, initial arsenic concentration, dissolved oxygen (DO), and ratio of As(III)/As(V) on arsenic removal. Consequently, the sorption performance of arsenic was highly influenced by the initial pH; it was observed that the arsenic removal increased with decreasing pH. Arsenic removal rates of both As(V) and As(III) were lower in the system with lower DO. The rate of As(III) removal decreased with the increase of its initial concentration. In contrast, the removal rate of As(V) still remained significantly high as its initial concentration increased. The effect of As(III)/As(V) ratio was also investigated, and the results showed that the total arsenic was removed faster than solution containing As(III) or As(V) alone. In addition, the mixture with higher fraction of As(V) resulted in higher arsenic removal.

Keywords: arsenic; arsenate; arsenite; nanoiron particles; zero-valent iron

1. Introduction

Arsenic is a contaminant of concern in groundwater. It is well-known that arsenic is stable in several oxidation states, such as the As(III), mainly found in reducing condition, and As(V), stable in oxidizing state. Both are the most common forms of arsenic in natural waters (Smedley and Kinniburgh 2001). Consuming water with high level of arsenic can cause skin, lung, bladder or kidney cancers and black foot diseases (Mohan and Pittman Jr 2007). Thus, the search for technologies that focus on arsenic removal in groundwater still continues. Some of the technologies that are now being used for the removal of arsenic from groundwater include precipitation, coagulation and filtration, reverse osmosis, electrodialysis, and ion exchange (Triszcz et al. 2009). However, the technologies mentioned above are effective mostly for As(V) removal, and a pre-oxidation step is required to transform As(III) to As(V) (Lackovic et al. 2000).

Adsorption process by using zero-valent iron (ZVI) is a promising alternative for arsenic removal because this sorption media was used to remove both As(V) and As(III) simultaneously, without pre-oxidation step (Sun et al. 2006) and such process does not require the use of additional chemical reagents. Lackovic et al. (2000) first reported arsenic removal by using ZVI in 2000. They reported that ZVI has a high capacity for arsenic remediation. Afterwards, there were many reports about arsenic removal by ZVI. Bang et al. (2005) used iron filings, which were pretreated by acid to remove the oxide layer, for arsenic removal in a batch system. They revealed that the removal rate of As(V) under oxic condition was faster than anoxic condition and the removal rate was higher at pH 4 than at pH 7. Sun et al. (2006) performed experiments by using packed column of iron chippings, which were obtained from industrial waste and screened to less than 20 mesh. Their results show that As(III) was removed more rapidly than As(V) under anaerobic condition, but the reverse phenomenon was observed under aerobic condition. Melitas et al. (2002) demonstrated the effectiveness of packed column of iron fillings for As(V) removal. They concluded that the performance of As(V) removal depends not only on the adsorptive sites of iron oxide generated from reaction, but also on the ability of As(V) reaching those adsorptive sites. However, the problem associated with the use of ZVI is that the reaction time required for the complete removal of arsenic is in days (Jegadeesan et al. 2005). Based on the method of nano-scale zero-valent iron (NZVI) synthesis developed by Lehigh University research group in 1995 (Glavee et al. 1995), it was found that NZVI possesses higher capacity for arsenic removal than micro-scale zero-valent iron (MZVI) (Kanel et al. 2006; Giasuddin et al. 2007).

In natural groundwater the ratio of As(III) and As(V) can vary significantly, depending on condition of *in situ* oxidation state of water (Sasaki et al. 2009). There is a lack of documents reporting on treatment of arsenic with different ratios of As(III) and As(V). Thus, this study investigated such aspect of arsenic removal. In addition, the effects of solution pH, initial arsenic concentration, and DO on the rates of arsenic removal by NZVI were studied as well.

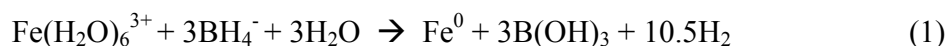
2. Materials and Methods

2.1. Materials

The chemicals of reagent grade used in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Merck), and NaBH_4 (> 96%; Merck). Both the As(III) and As(V) stock solution were prepared from NaAsO_2 (Fluka) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (J.T. Baker), respectively. H_2SO_4 and NaOH were used for adjusting the initial solution pH. All chemical solutions were prepared with deionized water (18.2 M Ω Mill-Q).

2.2. NZVI synthesis

The NZVI was synthesized according to Glavee et al. (1995). 40 mL of 0.25 M NaBH_4 were added into 40 mL of 0.045 M FeCl_3 aqueous solution. The mixture was agitated by a revolving propeller. The reaction for NZVI formation is shown in Equation (1).



The NZVI particles formed were separated from the liquid solution using a magnet. Immediately, it was then used in the treatment system. Concerning the NZVI particles characterization, it was dried by freezing dryer for 24 hr under the N_2 -purged environment. The dried NZVI was characterized first by TEM (JEL-2010, Japan) for its particle size. As for the pH with zero charge point, denoted as pH_{pzc} , was determined by using zeta-meter system 3.0+ (Meditop Co., Thailand). Table 1 shows the properties of the synthesized NZVI.

Table 1. Characterization of NZVI synthesized in this study

Parameter	Value
pH_{pzc}	7.8
particle size	
95% of the particles	< 90 nm
average of particle size	56 nm

2.3. Reaction system

The NZVI was used in the arsenic treatment system right after it was synthesized. A NZVI dosage of 0.023 g/L was maintained throughout all experiments. As described in earlier study (Anotai et al. 2010), the reactor with liquid volume of 4.4 L was designed to combine the two chambers for both reactants reaction and particles settling in one unit. The external-circulating pump was connected at outlet of the reactor to form a recirculation mode for arsenate removal (see Figure 1). 5 mL of the liquid sample treated were taken at each time point and filtered by using a 0.45 μm membrane filter to remove the solids particles from solution before analyses of the residual arsenic concentrations. All samples were stored at 4°C and analyzed within a period of 5 days.

2.4. Analytical methods

The solution pH and ORP were measured by pH and ORP meter (Suntex TS1), while the

dissolved oxygen was measured by DO meter (Oxi 330i). The total arsenic, (As(V) and As(III)), was determined by inductively coupled argon plasma and atomic emission spectroscopy (ICP-AES) using Thermo Scientific Model iCAP 6000 series (Thermo Scientific, USA). Determination of individual arsenic species was conducted by using an anion-exchange cartridge, DSC-SAX 500 mg (Supelco) (Kom et al. 2004). As the arsenic-bearing water samples pass through the cartridge, the As(V) will be retained inside, while the As(III) will be carried out, rendering the separation of As(V) and As(III) from each other. The eluent is then analyzed for the As(III) concentration by ICP. Finally, the As(V) concentration is obtained by subtracting the measured As(III) concentration from the total arsenic concentration.

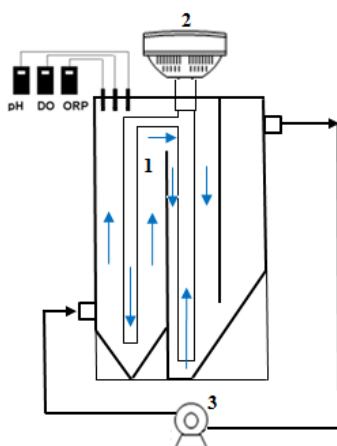


Fig. 1. Experimental setup for arsenic removal by nanoiron particles: 1. Reactor; 2. Internal-circulating pump; 3. External-circulating pump.

3. Results and discussion

3.1. Effect of initial pH

The initial arsenic concentration (C_0) applied was 1000 $\mu\text{g/L}$, while the initial pH's of the solution studied were 4.0, 7.0 and 9.0. As presented in Figure 2, the adsorption reaction of As(III) reached equilibrium at times of 10, 15, and 30 min for pH 4, 7, and 9, respectively, whereas As(V) reached equilibrium at times of 7, 20, and 40 min for the corresponding pH's. The percentage removal at equilibrium for pH 4 was around 81% of the initial arsenic concentration for As(III), and it was 99% for As(V). When the initial solution pH was raised to pH 7, the removal percentage at equilibrium for As(V) decreased to 95%; on the contrary, it increased to 88% for As(III). However, with pH 9, significant reduction in the adsorbed As(III), and As(V) was observed, the removal percentages of which at equilibrium were 65% and 85%, respectively. The results demonstrate that the adsorption performance of arsenic is highly influenced by initial solution pH, as also evidenced by other similar researches (Borah et al. 2009).

Arsenic can exist in different forms, depending on the pH condition. According to this study, the pH_{pzc} for NZVI synthesized was 7.8, while the available literature data of pH_{pzc} for iron oxides was 8.0 (Li et al. 2006). Also, the pK_a values reported for As(III) are listed as follows: $\text{pK}_1 = 9.22$, $\text{pK}_2 = 12.13$, and $\text{pK}_3 = 12.7$; and for As(V), they are: $\text{pK}_1 = 2.2$, $\text{pK}_2 = 6.97$, and $\text{pK}_3 = 11.53$ (Raven et al. 1998). In

the range of pH 2-7, the dominant form of As(V) is H_2AsO_4^- , a negatively charged ion, whereas the adsorbent surface shows positive charge. The opposite charges of the ion and the adsorbent surface will lead to the enhancement of the arsenic removal through electrostatic attraction force. For the basic pH condition (7-12), the dominant form of As(V) is HAsO_4^{2-} , whereas the adsorbent surface becomes negatively charged, thus the electrostatic repulsion force resulted in decreased adsorption of As(V). Similarly, under conditions of pH 4-7, the dominant form for As(III) is H_3AsO_3 ; its neutral charge still resulted in attraction with positively charged adsorbent. However, for the basic pH condition, the dominant forms of As(III) are with the negative charges, H_2AsO_3^- and HAsO_3^{2-} , and the adsorbent surface is also negatively charged, hence, the adsorption efficiency was decreased.

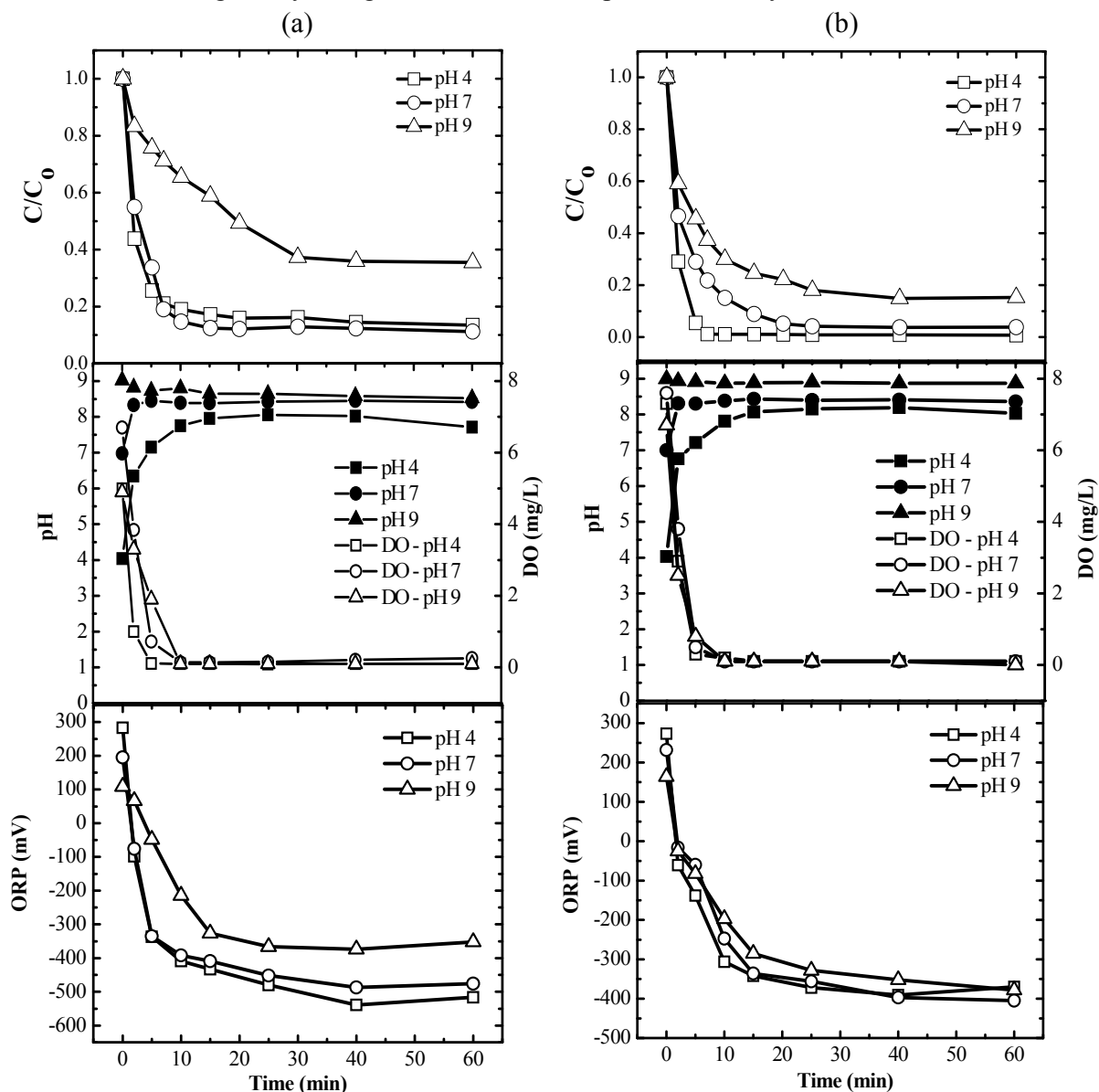


Fig. 2. Effect of initial solution pH on (a) As(III) and (b) As(V) removal: NZVI dosage = 0.023 g/L, initial As concentration = 1000 $\mu\text{g/L}$.

To understand the NZVI behavior more in the solution, the pH, DO and ORP profiles were further illustrated in Figure 2. The results show that the final solution pH were increased for both As(III) and As(V) when the initial pH were 4 and 7. However, in the case of initial pH 9, the pH value dropped slightly to 8.5-8.7. The pH was observed to increase in the presence of Fe⁰ due to the reaction of NZVI with water and dissolved oxygen, which resulted in the formation of hydroxide and the consumption of DO in solution. The reactions are presented by Equations (2) and (3) (Ruangchainikom et al. 2006).



The Fe²⁺ present in the aqueous solution can be oxidized by oxygen into Fe³⁺, which will result in producing corrosion products of different iron (hydr)oxides such as Fe₃O₄, Fe₂O₃, FeOOH, Fe(OH)₂, and Fe(OH)₃, depending on the solution conditions (Triszcz et al. 2009; Giasuddin et al. 2007; Kanel et al. 2005; Huang and Zhang 2005). According to Figure 2, the ORP value decreased rapidly from positive values to negative ones. Such phenomenon occurs due to electrons being released from the reductant. In only 5 min of reaction, the ORP values have dropped down to the very negative range, indicating that the solution exhibited a state of reducing environment in the presence of NZVI (Ruangchainikom et al. 2006).

Table 2. NZVI capacity for arsenic removal under various pH conditions

pH	q _e (mg /g)	
	As(III)	As(V)
4	38.48	43.63
7	39.52	42.33
9	28.01	37.51

Note: The solution volume is 4.4 L, mass of the NZVI is 0.1 g, and the initial arsenic concentration is 1 mg/L

In view of NZVI capacity for arsenic removal under various pH conditions, the data presented in Figure 2 were further analyzed according to Equation (4) (Borah et al. 2009):

$$m (q_e - q_o) = V (C_o - C_e) \quad (4)$$

Where *m* is the mass of the NZVI (g); *q_o* and *q_e* are the arsenic removed by the NZVI (mg/g) at initial and equilibrium conditions, respectively; *C_o* and *C_e* are the initial and equilibrium concentrations of arsenic in solution (mg/L); *V* is the solution volume (L). The NZVI capacities to remove As(III) and As(V) under various pH conditions were calculated and presented in Table 2. As depicted in Table 2, higher NZVI capacities (*q_e*) for As(III) and As(V) were observed at lower pH 4 and 7, when compared

to that at pH 9. With pH 4 and 7, it is noticed here that the NZVI capacities were not significantly different from each other.

Table 2 Speciation of Fe⁰ in an aqueous system

Reaction	Equation	Reference
Primary reactions of NZVI oxidation		
$\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$	(6)	[35]
$2\text{Fe}^0 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$	(7)	[35]
Secondary reactions		
$4\text{Fe}^{2+} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^-$	(8)	[36]
$\text{Fe}^0 + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$	(9)	[36]
Formation of iron (hydr)oxides		
$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_{2\downarrow}$	(10)	[38]
$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_{3\downarrow} + 3\text{H}^+$	(11)	[36]
$6\text{Fe}(\text{OH})_{2\downarrow} + \text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_{4\downarrow} + 6\text{H}_2\text{O}$	(12)	[18]
$\text{Fe}(\text{OH})_{3\downarrow} + 3\text{H}^+ \rightarrow \text{FeOOH}_{\downarrow} + \text{H}_2\text{O}$	(13)	[25]
$\text{FeOOH}_{\downarrow} + \text{Fe}^{2+} \rightarrow \text{Fe}_3\text{O}_{4\downarrow} + 2\text{H}^+$	(14)	[37]
$8\text{FeOOH}_{\downarrow} + \text{Fe}^0 \rightarrow 3\text{Fe}_3\text{O}_{4\downarrow} + 4\text{H}_2\text{O}$	(15)	[37]

3.2. Effect of initial arsenic concentration

To investigate the effect of initial arsenic concentration, experiments were performed by varying arsenic concentrations from 1000 to 2500 µg/L, and the initial solution pH was adjusted to 4. Figure 3 shows that As(III) removal decreases as the initial concentration of arsenic increases. However, this behavior is not followed by As(V). Initial arsenic concentration imposed no significant effect on As(V) removal. As described earlier, the reason for the difference of adsorption profiles between As(III) and As(V) was related to electrostatic attraction significantly.

In view of adsorption model, the Langmuir and Freundlich isotherms are used in this study to describe the behavior of arsenic adsorption in the NZVI reaction system. The relevant formulas were listed in Equations (5) and (6) (Guo et al. 2007), respectively.

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where q_m is the maximum adsorption capacity (mg/g), b is a constant related to the adsorption energy (L/mg), K_F is the Freundlich constant denoting the sorption capacity of adsorbent (mg/g), n is the adsorption intensity parameter, and other parameters was defined in Section 3.1.

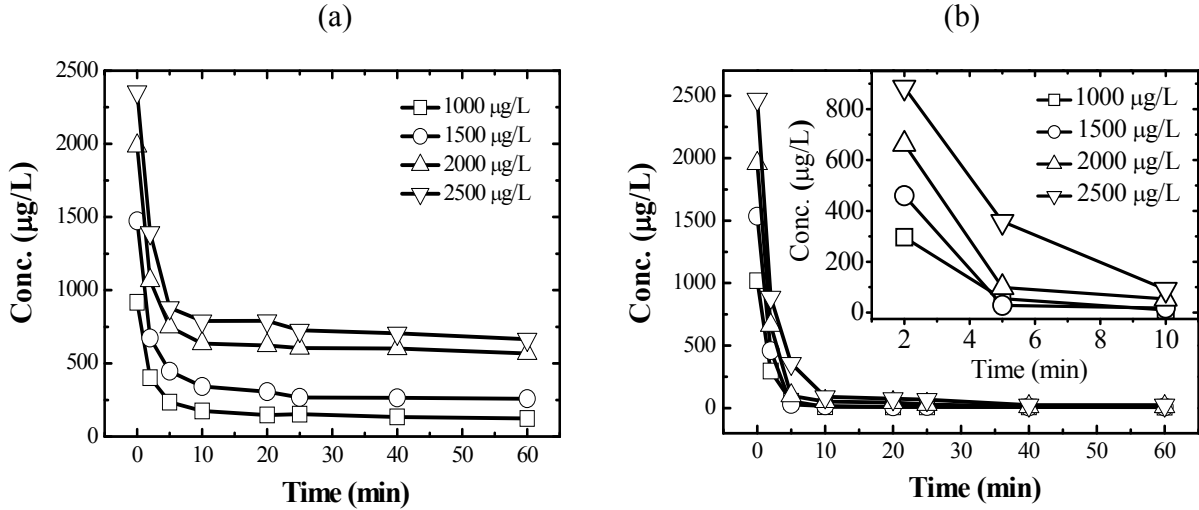


Fig. 3. Effect of initial concentration of (a) As(III) and (b) As(V) on arsenic removal: NZVI dosage = 0.023 g/L, initial solution pH = 4.

As a result of data fitting, model parameters are depicted in Table 3. Based on the correlation coefficient, R^2 , the Langmuir isotherm model for As(III) and As(V) has R^2 values of 0.99 and 0.96, respectively, slightly higher than those of the Freundlich isotherm model. Thus, it appears that the Langmuir model can better describe arsenic adsorption in the studied system. Note that the Langmuir isotherm assumes the site energy for adsorption being equal for all surface sites and each site binding only one molecule, i.e., mono layer (Montgomery 1985). As for adsorption capacity, both isotherm models show higher capacity for arsenate than for arsenite.

According to the literature, the essential characteristics of Langmuir isotherm can be disclosed by the dimensionless constant, called separation factor (R_L) (Qadeer 2005; ALzaydien 2009), as depicted in Equation (7).

$$R_L = \frac{1}{1 + b[As]_o} \quad (7)$$

Table 3. Isotherm parameters for arsenic adsorption

Isotherm/parameters	As(III)	As(V)
Langmuir		
q_m (mg/g)	102	118
b (L/mg)	2.39	42.5
R^2	0.99	0.96
Freundlich		
K_F (mg/g)	76.9	205.6
$1/n$	0.52	0.32
R^2	0.98	0.92

The R_L values can be related to the equilibrium isotherm as follows: $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, and $R_L = 0$ irreversible. All calculated R_L values are between 0 and 1, indicating favorable sorption has occurred in the reaction system. This can be further evidenced by the Freundlich model parameter, $(1/n)$, the values (0.52; 0.32) of which fall within the range of 0.1-1. Similarly, the studied system is strongly favorable for arsenic adsorption (Namasivayam and Ranganathan 1995).

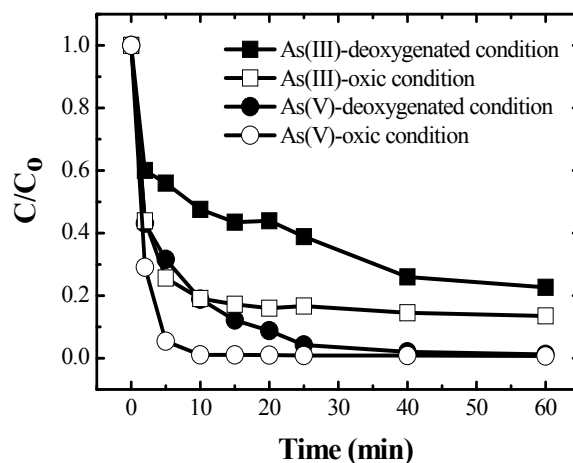


Fig. 4. Comparison of As(III) and As(V) removal under oxic and deoxygenated conditions: NZVI dosage = 0.023 g/L, initial arsenic concentration = 1000 µg/L.

3.3. Effect of dissolved oxygen

To reveal the role of oxygen in the reaction solution, experiments were designed to explore arsenic removal under oxic and deoxygenated conditions. Prior to reaction, the solution was bubbled with nitrogen gas for 30 min to strip out oxygen from the solution until the DO value was less than 0.5

mg/L, deoxygenated condition. Afterwards, the nitrogen gas remained continuously supplied into the reaction solution. The effect of DO in arsenic removal is shown in Figure 4. The As(III) removed was more than 80% after 10 min of reaction when the solution was under oxic condition, while 52% was removed under deoxygenated condition. For As(V), 99% and 76% were removed after 7 min of reaction under oxic and deoxygenated conditions, respectively. This indicates that arsenic removal can be enhanced in the presence of oxygen because arsenic can form inner- and/or outer-sphere complexes with the oxygen-induced iron corrosion products such as iron (hydr)oxides, according to several recent spectroscopic studies (Bang et al. 2005; Sunbaek et al. 2005; Mayo et al. 2007; Mishra and Farrell 2005; Zhang et al. 2004). Thus, the presence of DO will enhance the rate of iron corrosion and subsequently improve the arsenic adsorption as well.

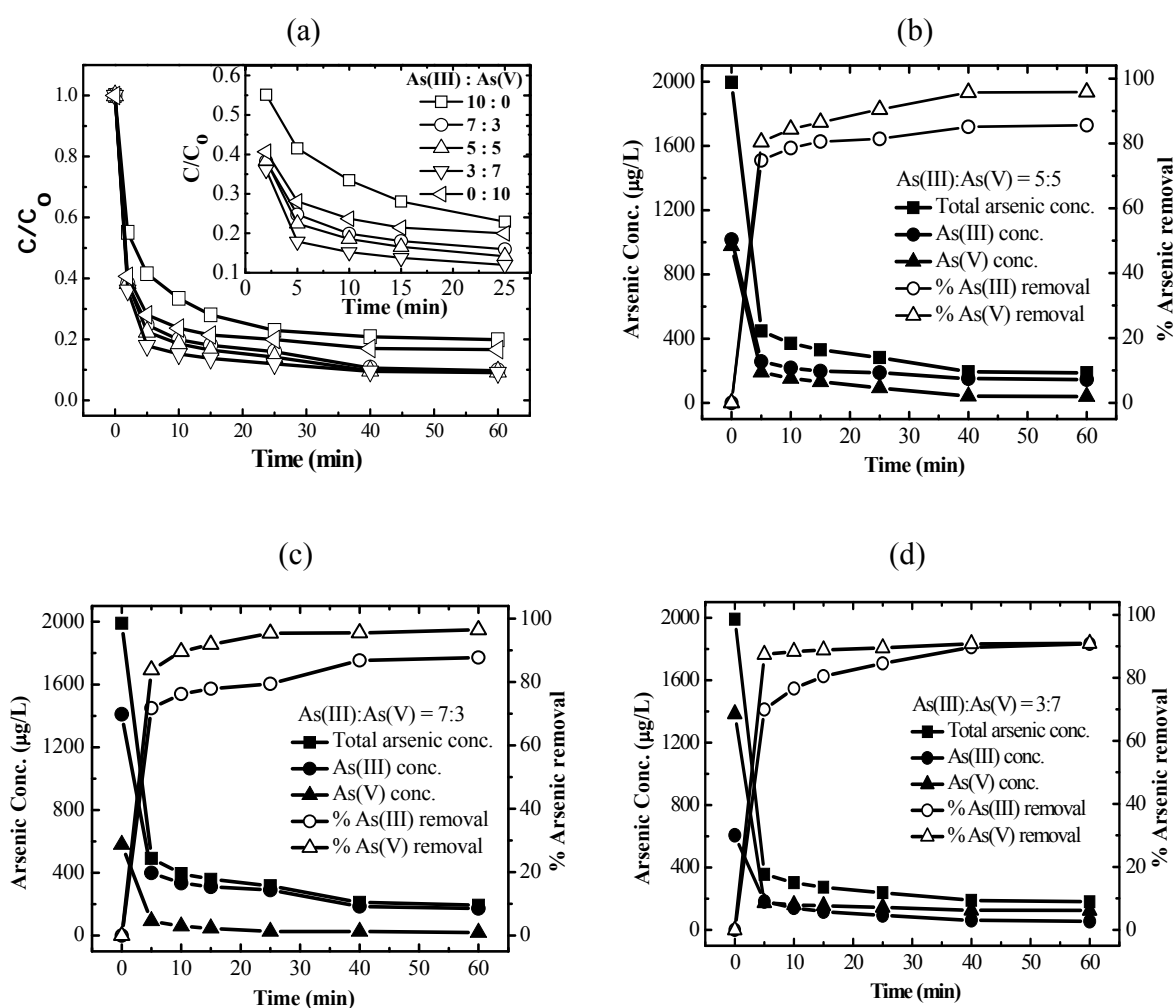


Fig. 5. (a) Total arsenic removal at different ratios of As(III) versus As(V), and the individual profiles of remaining concentration and percentage removal at their ratios of (b) 5:5, (c) 7:3, and (d) 3:7. NZVI dosage = 0.023 g/L, initial arsenic concentration = 2000 μg/L, initial pH = 7.

3.4. Effect of ratio of As(III) versus As(V)

For field application, the impact of different ratios of As(III)/As(V) on arsenic removal is important. To provide such information, different mass ratios of As(III)/As(V), 3:7, 5:5, and 7:3, were explored. Control experiments with As(III) or As(V) alone in the solution were also investigated. The initial pH was controlled at 7. As shown in Figure 5(a), the total arsenic removal was higher when the solution contains higher As(V). Interestingly, if both As(III) and As(V) are present, the total arsenic removal is enhanced, as compared to the case when the As(III) alone or As(V) alone is present. It is expected that the solution containing As(V) alone should be the one with the highest arsenic removal since As(V) is removed more easily than As(III). As shown in Figure 5(a), the total arsenic removal from the highest to the lowest is in the following sequence with respect to As(III)/As(V) ratios of 3:7, 5:5, 7:3, As(V) alone, and As(III) alone. This implies that co-existence of arsenic creates a favorable condition for arsenic removal by NZVI. As is well-known, the mechanism of arsenic removal by NZVI involves not only adsorption but also co-precipitation and precipitation (Lackovic et al. 2000; Tyrovola et al. 2007). During the formation of ferric (hydr)oxides, some researchers reported that As(III) was removed by co-precipitation with a lesser degree than As(V) (Waychunas et al. 1995; Hering et al. 1997; Manceau 1995). As evidenced from Figure 5(b)-(d), the removal percentage of As(V) is always higher than As(III) in all cases of different ratios of As(III) versus As(V). Based on such results, the mechanism of arsenic removal in co-existence of both species was proposed, as shown in Figure 6. Through its co-precipitation with ferrous or ferric ion, the As(V) may help create new adsorptive sites, which in turn enhance the adsorption of As(III). Therefore, the higher the ratio of As(V) contained in solution, the higher the total arsenic removal. However, comprehensive investigation needs to be conducted to verify the above adsorption mechanism.

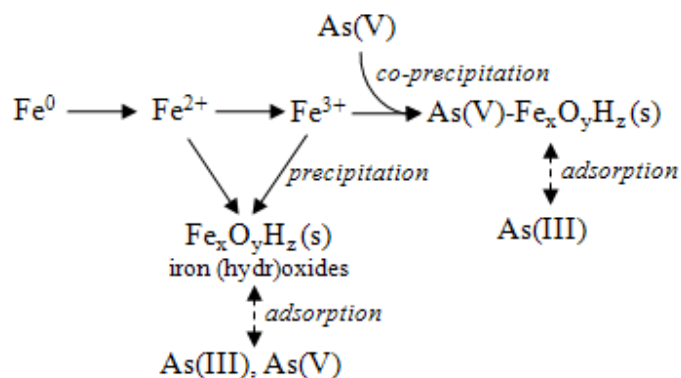


Fig. 6. Proposed mechanism of arsenic adsorption in the co-existence of As(III) and As(V)

4. Conclusions

This study was conducted to investigate performance of NZVI as adsorptive media in removing arsenic from aqueous solutions. The effects of different parameters such as initial solution pH, DO, initial arsenic concentration, and As(III)/As(V) ratio were studied. Arsenic in the form of As(V) can be

removed easier than As(III) for the studied pH values. Concerning the DO effect, the presence of oxygen will help remove arsenic through oxygen-induced corrosion products of iron. In the case of initial concentration, the increase in As(V) did not greatly affect its removal rate, whereas the performance of As(III) removal decreased with the increase of its initial concentration. The presence of both As(III) and As(V) results in better removal of total arsenic than the presence of As(V) or As(III) alone. This study also reveals that the higher the mass fraction of As(V) present, the higher the amount of total arsenic can be removed.

Acknowledgements

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program. Appreciation goes to Dr. Ma. Lourdes P. Dalida, University of the Philippines, Diliman for her valuable comments and polishing of this paper.

References

- Alzaydien AS (2009) Adsorption of Methylene Blue from Aqueous Solution onto a Low-Cost Natural Jordanian Tripoli. *American J of Environ Sci* 5:197-208
- Anotai J, Liao CH, Ruangchanikom C (2010) Nitrate removal by Fe^0/CO_2 process using an innovative continuous flow reactor. *J Environ Eng Manage* 20:77-84
- Bang S, Johnson MD, Korfiatis GP, Meng X (2005) Chemical reactions between arsenic and zero-valent iron in water. *Water Res* 39:763-770
- Borah D, Satokawa S, Kato S, Kojima T (2009) Sorption of As(V) from aqueous solution using acid modified carbon black. *J Hazard Mater* 162:1269-1277
- Glavee GN, Klabunde KJ, Sorensen CM, Hadjipanayis GC (1995) Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe_2B powders. *Inorg Chem* 34:28-35
- Guo H, Stuben D, Berner Z (2007) Adsorption of arsenic(III) and arsenic(V) from groundwater using natural siderite as the adsorbent. *J Colloid and Inter Sci* 315:47-53
- Hering JG, Chen PY, Wilkie JA, Elimelech M (1997) Arsenic removal from drinking water during coagulation. *J Environ Eng* 123:800-807
- Huang YH, and Zhang TC (2005) Effects of dissolved oxygen on formation of corrosion products and concomitant oxygen and nitrate reduction in zero-valent iron systems with or without aqueous Fe^{2+} . *Water Res* 39:1751-1760

- Jegadeesan G, Mondal K, Lalvani SB (2005) Arsenate remediation using nanosized modified zerovalent iron particles. *Environ Progress* 24:289-296
- Kanel SR, Greneche JM, Choi H (2006) Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. *Environ Sci Technol* 40:2045-2050
- Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environ Sci Technol* 39:1291-1298
- Kom I, Kim J, Kim KW (2004) Arsenic speciation and sorption kinetics in the As-hematite-humic acid system. *Colloids Surf A* 234:43-50
- Lackovic JA, Nikolaidis NP, Dobbs GM (2000) Inorganic arsenic removal by zero-valent iron. *Environ Eng Sci* 17:29-40
- Li X, Elliott DW, Zhang W (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. *Solid State and Mater Sci* 31:111-122
- Manceau A (1995) The mechanism of anion adsorption on iron oxides: Evidence for the bonding of arsenate tetrahedra on free $\text{Fe}(\text{O}, \text{OH})_6$ edges. *Geochim Cosmochim Acta* 59:3647-3653
- Mayo JT, Yavuz C, Yean S, Cong L, Shipley H, Yu W, Falkner J, Kan A, Tomson M, Colvin VL (2007) The effect of nanocrystalline magnetite size on arsenic removal. *Sci Technol Adv Mater* 8:71-75
- Melitas N, Wang J, Conklin M, O'Day P, Farrell J (2002) Understanding soluble arsenate removal kinetics by zero-valent iron media. *Environ Sci Technol* 36:2074-2081
- Mishra D, and Farrell J (2005) Evaluation of mixed valent iron oxides as reactive adsorbents for arsenic removal. *Environ Sci Technol* 39:9689-9694
- Mohan D, and Pittman CU Jr (2007) Arsenic removal from water/wastewater using adsorbents - A critical review. *J Hazard Mater* 142:1-53
- Montgomery JM (1985) *Water Treatment: Principles and Design*, 2nd edn. John Wiley and Sons, pp 1275
- Namasivayam C, and Ranganathan K (1995) Removal of Pb(II) by adsorption onto waste Fe(III)/Cr(III) hydroxide from aqueous solution and radiator manufacturing industry wastewater. *Ind Eng Chem Res* 34:869-873
- Qadeer R (2005) Adsorption of neodymium ions on activated charcoal from aqueous solutions. *J of Radioanalytical and Nuclear Chemis* 265: 377- 381
- Raven KP, Jain A, Loeppert RH (1998) Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ Sci Technol* 32:344-349
- Ruangchainikom C, Liao CH, Anotai J, Lee MT (2006) Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and of CO_2 - bubbled system. *Water Res* 40:195-204
- Sasaki K, Nakano H, Wilopo W, Miura Y, Hirajima T (2009) Sorption and speciation of arsenic by zero-valent iron. *Colloids Surf A* 347:8-17
- Smedley PL, and Kinniburgh DG (2001) A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17:517-568
- Sunbaek B, Mark DJ, George PK, Meng X (2005) Chemical reactions between arsenic and zero-valent iron in water. *Water Res* 39:763-770
- Sun H, Wang L, Zhang R, Sui J, Xu G (2006) Treatment of groundwater polluted by arsenic compounds

- by zero valent iron. J Hazard Mater B129:297-303
- Triszczy JM, Porta A, Einschlag FSG (2009) Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal. Chem Eng J 150:431-439
- Tyrovola K, Peroulaki E, Nikolaidis NP (2007) Modeling of arsenic immobilization by zero valent iron. European J Soil Biology 43:356-367
- Waychunas GA, Davis JA, Fuller CG (1995) Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results and topological factors in predicting sorbate geometry, and evidence for monodentate complexes. Geochim Cosmochim Acta 59:3655-3661
- Zhang W, Singh P, Paling E, Delides S (2004) Arsenic removal from contaminated water by natural iron ores. Miner Eng 17:517-524

Gas-bubbled nano zero-valent iron process for high concentration arsenate removal

Visanu Tanboonchuy ¹, Jia-Chin Hsu ², Nurak Grisdanurak ^{1,3}, Chih-Hsiang Liao ^{4*}

¹*Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND.*

²*Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.*

³*National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Pathumthani, THAILAND.*

⁴*Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.*

* Corresponding author's email: chliao@mail.chna.edu.tw

Telephone no.: +886-6-266-3230

Fax no.: +886-6-366-3756

Abstract

In this study, batch experiments were performed to investigate a novel process for high concentration arsenate removal in the presence of air and/or CO₂ bubbling. The pretreatment step, CO₂ bubbling at 300 mL/min for 5 min, was taken to adjust the solution pH to an acidic environment, followed by air bubbling at 300 mL/min for 10 min to increase dissolved oxygen in the solution. In the treatment period, the nano-scale zero-valent iron was applied to remove aqueous arsenate of 3000 µg/L, while the treatment system was continuously bubbled by 300 mL/min of air. Such a process resulted in outstanding performance in arsenate removal. Furthermore, in the field groundwater application, the arsenate removal rate for the proposed process was 5 times faster than the rate measured when the system was pretreated by acidic chemical species only.

Keywords: Arsenic; arsenate; nano-scale iron; gas bubbling

1. Introduction

Hazardous arsenic exists in natural waters mostly in the forms of arsenite (As(III)) and arsenate (As(V)) in reducing and oxidizing environments respectively [1]. Arsenic is typically associated with iron oxide under oxic conditions and with pyrite minerals under anoxic ones [2]. Arsenic may be released into the environment from natural sources (e.g., oxidative weathering and geochemical reaction) as well as from anthropogenic activities (e.g., discharge of industrial waste containing arsenic, mining operations, and use of arsenical pesticides) [3-5]. The presence of arsenic compounds in groundwater is a serious human health problem because consumption of water with high levels of

arsenic causes skin, lung, bladder, kidney cancers and black foot disease [1]. As has been reported, countries affected by highly arsenic-contaminated groundwater include Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [6, 7]. To mitigate the health impact of arsenic, the USEPA has defined the maximum allowable level of arsenic in drinking water as 10 µg/L [8].

Several researchers have reported that arsenic can be removed by adsorption into a variety of iron (hydr)oxides, such as hematite (Fe₂O₃) [9], goethite (FeO(OH)), magnetite (Fe₃O₄), amorphous iron oxide (HFO) [10], and mixed valent iron oxides [11]. In addition, there was a report about arsenic removal by zero-valent iron (ZVI), which has a high capacity for arsenic remediation, including both As(III) and As(V) [8, 12-14]. However, the problem associated with the use of ZVI is that the reaction time required for the complete removal of arsenic is in days [15]. Based on the method of nano-scale ZVI (NZVI) synthesis developed by Glavee et al. [16] and Kanel et al. [17, 18] who investigated the As(III) and As(V) removal by NZVI, the researchers found that arsenic was rapidly adsorbed in minutes and a pseudo first order reaction was observed. In addition, their results show that arsenic removal by NZVI is more effective in an acidic environment.

In summary, the As(V) can be better removed by iron oxides under acidic conditions than under base conditions, according to the surveyed literature [13, 14, 17, 18]. However, utilizing acidic chemicals to adjust the solution pH will result in undesirable species, which in turn will cause deterioration of the treated water quality. According to an earlier study [19], the above concern can be resolved by CO₂ bubbling, which adjusts the solution pH to an acidic condition through hydrogen ions generated from carbonated water, as described below:



In addition, it has been reported that a high amount of NZVI is required for As(V) removal in field groundwater [17] because of the competition between arsenic species and background species, or because of the inadequate amount of the dissolved oxygen (DO) required for iron oxidation in the field groundwater. With such an understanding in mind, air bubbling was employed and tested in this study.

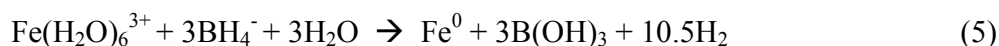
So far, there have rarely been studies about the use of combination of ZVI and gas bubbling for targeted contaminant removal. Hsu et al. [20] used micro-scale ZVI (MZVI) and CO₂ bubbling for nitrate removal from groundwater. They reported that solution pH dropped to 3.2 with CO₂ bubbling (500 mL/min) within 10 min and nitrate levels were reduced by 85% in the presence of MZVI (2 g/L). Ruangchainikom et al. [21] investigated the effects of water characteristics on nitrate reduction by a combination of MZVI and CO₂ bubbling. Li et al. [22] studied nitrate removal by means of a fluidized ZVI reactor under high-pressure CO₂ gas. To date, no articles have described the use of CO₂ and/or air bubbling in the NZVI process for arsenic removal. Thus, the main objective of this study is to propose a novel process for As(V) removal by NZVI, without the addition of acidic chemicals. First, experiments

were performed to investigate the effect of initial pH and the effect of DO on As(V) removal. Second, this study screened various scenarios of experiments to select the most favorable one for As(V) removal by means of the proposed gas-bubbled NZVI process. Finally, field groundwater spiked with As(V) was used to test the potential of the proposed process.

2. Materials and Methods

2.1. NZVI synthesis

The NZVI used in this study was synthesized according to Glavee et al. [16]. 0.25 M of NaBH₄ (> 96%, Merck) was added to 0.045 M of FeCl₃·6H₂O (> 99%, Merck) aqueous solution. Then, the mixture was agitated by a revolving propeller. Finally, ferric iron was reduced into zero-valent iron (Fe⁰) by borohydride, as shown in Reaction (5):



The morphology of the NZVI thus synthesized is characterized by the use of Transmission Electron Microscopy (TEM) (JEL-2010, Japan), and Scanning Electron Microscopy (SEM) with energy-dispersive X-ray (EDX) analyses. The Brunauer-Emmett-Teller (BET) N₂ method was used to measure the specific surface area of synthesized particles. The point of zero charge, denoted as pH_{pzc}, was determined by using zeta-meter system 3.0+ (Meditop Co., Thailand).

2.2. Experimental system

The NZVI was applied immediately right after its synthesis in the treatment of As(V) prepared from Na₂HAsO₄·7H₂O (J.T. Baker). As described in an earlier study [23], the reactor consists of two chambers, the first for mixing solutions and for reactions, and the second for settling solids. This two-in-one reactor was operated as a batch process by directing the effluent stream to the inlet of the reactor, i.e., a re-circulated mode for As(V) removal.

The experiments with gas-bubbled NZVI were designed to optimize process performance in order to create the most favorable conditions for As(V) treatment. The details of various gas-bubbled scenarios tested (Scenarios 1-5) are explained in Table 1. For the field groundwater test, experiments were conducted for As(V) removal performance evaluation by using Scenarios 1 and 5. Note that field groundwater used in this study was pumped from a groundwater site at Chia Nan University of Pharmacy and Science, Taiwan. The field groundwater was further spiked with As(V) to obtain an initial As(V) concentration of 3000 ppb.

Gases of CO₂ (99.5%), Air (O₂ 21%, N₂ 79%), and N₂ (99.99%) used in this study were purchased from a local supplier (Tainan, Taiwan). In addition, residual arsenic levels were determined by inductively coupled argon plasma (ICP) (Thermo Scientific Model iCAP 6000 series) while the solution pH and DO were measured by the pH meter (Suntex TS1) and the DO meter (Oxi 330i), respectively.

3. Results and Discussion

3.1. Characterization of NZVI

Figure 1(a) shows that the morphology of NZVI has two distinct layers. The inside core represents the Fe^0 itself, while the outer layer covering the Fe^0 is iron oxide(s). This is in agreement with the report by Kanel et al. (2006) [17]. They used high-resolution TEM to investigate the morphology of pristine NZVI and found that the outer layer of iron oxide had thickness of 10 nm, and the inside core of Fe^0 was 20 nm of diameter. This is evidenced by the EDX profile, which demonstrates that the major components are O, Cl, and Fe, with the following weight % ratio: 1.58: 1.74: 96.68, according to Figure 1(b). Note that the Cl originated from the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution when the NZVI was synthesized. The histogram in Figure 1(c) shows that more than 95% of the particles were smaller than 90 nm and the average particle size was 56 nm, based on a count of 100 particles. Figure 1(d) shows that the measured solution pH_{pzc} for the lab-synthesized NZVI fell to around 7.8. Additionally, the NZVI was further characterized by the BET method resulting in a specific surface area measurement of $7.67 \text{ m}^2/\text{g}$.

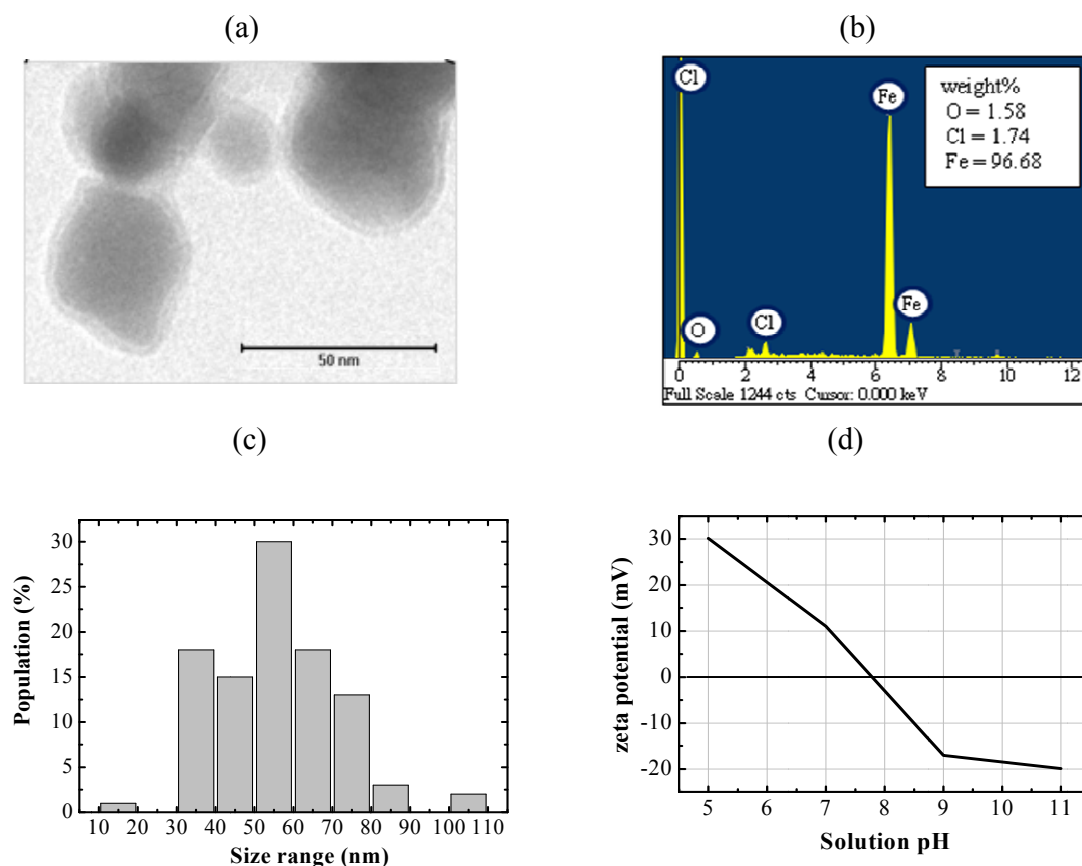


Fig. 1. Characterization of NZVI synthesized: (a) TEM image, (b) EDX profile, (c) particle size distribution histogram, and (d) zeta potential versus pH.

3.2. Effect of pH and DO

As shown in Figure 2, the sorption performance of As(V) was highly influenced by the initial pH: it was observed that As(V) removal increased with decreases in pH. Such a phenomenon can be elucidated from the speciation of arsenic in solution. The arsenic species may exist in several forms, depending on the pH condition. According to the literature, the pK_a values of As(V) are as follows: $pK_1 = 2.2$, $pK_2 = 6.97$, and $pK_3 = 11.53$ [24]. The point of zero charge for pristine NZVI is at pH 7.8, and it is at pH 8.0 for iron oxides [25]. Thus, the dominant form of As(V) within the range of pH 2-7 is $H_2AsO_4^-$, whereas the adsorbent surface shows a positive charge under acidic pH conditions. As understood, the opposite charges of adsorbate and adsorbent will enhance arsenic removal through electrostatic attraction [26]. For base pH conditions (7-12), the dominant form of As(V) is $HAsO_4^{2-}$. On the other hand, the adsorbent surface will be negatively charged under alkaline conditions, which will lead to electrostatic repulsion and thus a smaller level of As(V) adsorption

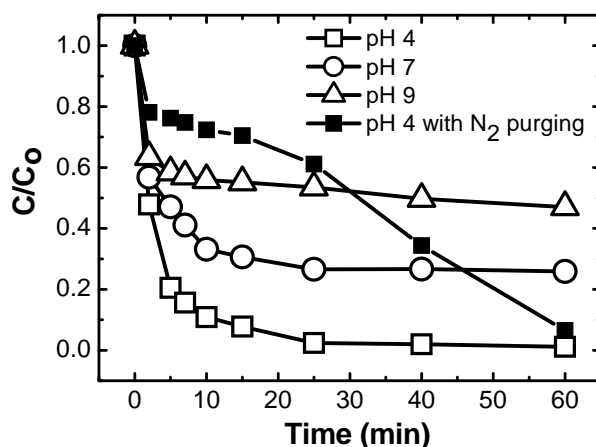


Fig. 2. Effect of initial pH and DO on As(V) removal. The initial solution pH was adjusted by NaOH and H_2SO_4 , and the initial As(V) concentration and NZVI dosage were 3000 ppb and 0.023 g/L, respectively.

Experiments were also conducted to investigate the effect of DO on As(V) removal at pH 4. First, the solution was bubbled with N_2 for 30 min to strip out oxygen until the DO value fell within the anoxic range, which was less than 0.5 mg/L in this study. Then, N_2 was continuously supplied throughout the reaction period. The results indicate that the As(V) was more completely removed under oxic conditions than under anoxic conditions (N_2 purging), given that the initial solution pH was controlled at 4. This may be a result of the iron corrosion products formed in the presence of DO, as depicted in Table 2. The Fe^0 will be rapidly oxidized into the primary product Fe^{2+} , according to Equations (6) and (7). In turn, the Fe^{2+} will be further oxidized into Fe^{3+} , as shown in Equation (8). Next, with DO, both Fe^{2+} and Fe^{3+} will result in several forms of iron (hydr)oxides such as Fe_3O_4 , Fe_2O_3 , $FeO(OH)$, $Fe(OH)_2$, and $Fe(OH)_3$. These iron (hydr)oxides may further combine with the As(V) through inner- and/or outer-sphere complexes, according to several recent spectroscopic studies [11-13].

In addition, Fe^{3+} (oxy)hydroxides are more likely to be formed than Fe^{2+} (oxy)hydroxides. The formed Fe^{3+} can result in coagulation of Fe^{3+} (hydr)oxides and thus can enhance As(V) removal [27-30]. In brief, a high DO level will enhance the rate of iron oxidation and ultimately improve As(V) adsorption as well.

Table 1 Description of various scenarios for a gas-bubbled NZVI process

Scenario	Pre-treatment	Treatment
1	pH adjusted to 4 by H_2SO_4 or NaOH	No gas bubbling
2	pH adjusted to 7 by H_2SO_4 or NaOH	No gas bubbling
3	pH adjusted to 7 by H_2SO_4 or NaOH	Air bubbling of 300 mL/min
4	pH adjusted to around 4 by CO_2 bubbling of 300 mL/min for 5 min	Air bubbling of 300 mL/min
5	pH adjusted to around 4 by CO_2 bubbling of 300 mL/min for 5 min; oxygen supply by air bubbling of 300 mL/min for 10 min	Air bubbling of 300 mL/min

3.3. Gas-bubbled nano-iron process

According to Table 1, five scenarios of gas-bubbled nano-iron process were proposed in order to maximize As(V) removal. Scenarios 1 and 2 were performed with the initial pH levels adjusted to 4 and 7, respectively, without any gas bubbling. As has been discussed in detail in Section 3.2, an acidic solution environment appeared to favor As(V) removal, and the absence of oxygen led to decreases in As(V) removal (see Figure 2). Based on these results, Scenarios 3-5 were attempted; these scenarios utilized air bubbling and/or CO_2 -bubbled acidification.

Scenario 3 results in an improved As(V) removal at a neutral pH level in the presence of oxygen supply when compared with Scenario 2, as shown in Figure 3(a). Then Figure 3(b) shows that the DO for Scenario 3 remained at a relatively higher level due to air bubbling, while the DO for Scenario 2 was almost completely consumed by the end of the reaction. As mentioned earlier, the DO level is strongly correlated with the rate of As(V) removal. As shown in Figure 3(c), for every case in the five scenarios, the pH was found to increase with reaction time.

Scenario 4 was designed to create an acidic environment by using CO_2 bubbling, which is commonly called carbonation in water purification systems. As shown in Figure 3(c), the profile for this scenario demonstrates that acidic environment at the initial point in time was achieved as a consequence of the formation of hydrogen ions according to Reactions (1)-(4). Nevertheless, the solution pH increased as the reaction proceeded. This was a result of Fe^0 corrosion [31], as depicted in Table 2 (see Reactions (6) and (7)). Figure 3(a) shows that Scenario 4 resulted in less removal of As(V) than the scenario with pH adjustment by H_2SO_4 (Scenario 1). The key reason was the stripping of oxygen

through CO₂ bubbling. As illustrated in Figure 3(b), the initial DO was low for Scenario 4 (~1 mg/L) after CO₂ bubbling, whereas it remained relatively high for Scenario 1 (~7 mg/L) after air bubbling.

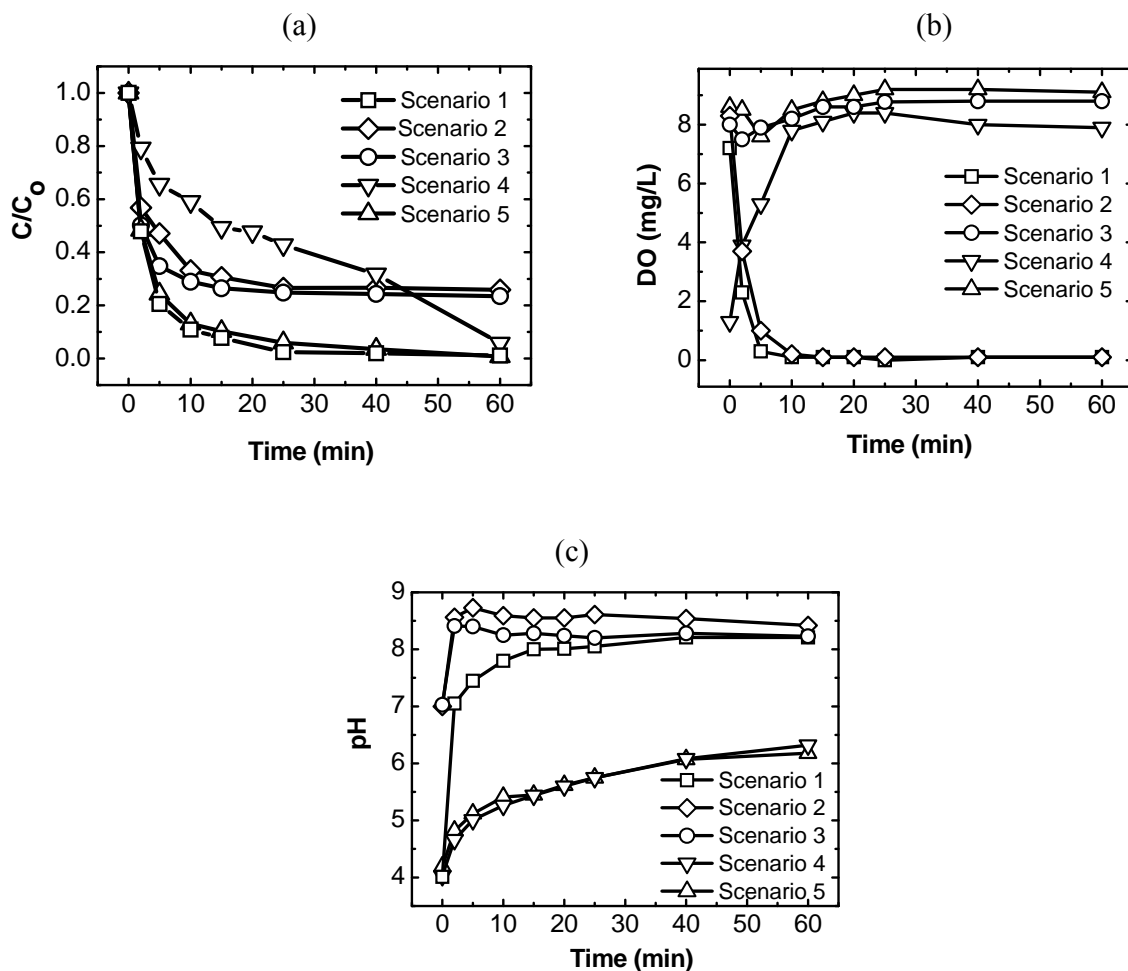


Fig. 3. Profiles of (a) normalized As(V) concentration, (b) DO, and (c) pH for various gas-bubbling scenarios. Initial As(V) concentration = 3000 ppb, NZVI dosage = 0.023 g/L.

Scenario 5 was proposed as a means to achieve the most favorable conditions for As(V) removal, since the outcomes of Scenarios 1-4 established that both low pH and high DO were desired. The solution was pretreated first by CO₂ bubbling for 5 min to bring down the pH level and then by air bubbling for 10 min to elevate the DO level. As shown in Figures 3(b) and 3(c), the DO and pH profiles for Scenario 5 demonstrate that both an acidic environment and high initial DO were obtained. Figure 3(a) shows that the profile of As(V) removal in Scenario 5 is comparable to that in Scenario 1, and even outperforms those in Scenarios 2-4. This indicates that the proposed Scenario 5 can lead to relatively high performance of As(V) removal, without addition of acidic chemical species. Figure 4 illustrates the

conceptual mechanism of As(V) removal in Scenario 5. The CO₂ bubbling enhances the performance of As(V) removal due to adjustments of both pH condition (acidification) and surface charge of adsorbent (positive charge). The acidified solution favors the As(V)-containing form of H₂AsO₄⁻. The opposite charges of As(V) and iron (hydr)oxides accelerate the rate of mass transfer from liquid film to surface of adsorbent through electrostatic attraction force, as has been discussed earlier. As for air bubbling, the supplied DO enhances As(V) removal by promoting the formation of NZVI corrosion products, iron (hydr)oxides, which help adsorb As(V) in a significant way.

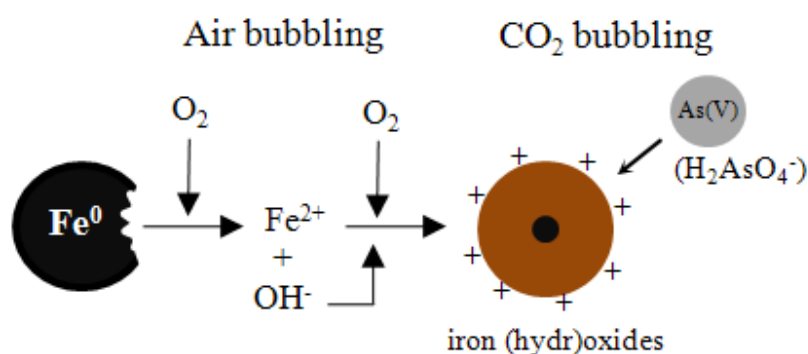


Fig. 4. Conceptual mechanism of As(V) removal for Scenario 5.

3.4. Field groundwater treatment

Figure 5 compares the solution pH, DO, and As(V) removal profiles between Scenarios 1 and 5 by using As(V)-spiked field groundwater. As shown in Figure 5(a), the total arsenic removal in Scenario 5 was much higher than that in Scenario 1. Note that in the DI water system, the As(V) removal in Scenario 5 was comparable with that in Scenario 1, as illustrated in Figure 3(a). The reason for this is the smaller initial DO level in the field groundwater (see Figure 5(c)). As described earlier, the NZVI requires oxygen to generate iron (hydr)oxides, which help remove As(V). Thus, the lower the initial DO, the less As(V) will be removed. However, with Scenario 5, this problem can be resolved by bubbling air into the treatment system prior to NZVI addition. As shown in Figure 5(c), the initial DO was maintained at a relatively high level. Another reason is possibly the competition for adsorptive sites between arsenic species and dissolved background species in the field groundwater. As has been reported, sulfates, bicarbonates and phosphates play significant roles in inhibiting arsenic removal by iron (hydr)oxides [29, 32, 33]. Additionally, high levels of carbonate alkalinity may impact arsenic removal because of carbonate's buffering capacity for acid. As shown in Figure 5(b), when CO₂ bubbling was applied to a treatment system with field groundwater, the initial pH (~5.6) could not be brought down to a level as low as the level with a DI water system (pH ~4; see Figure 3(c)).

With regard to kinetic analysis, a pseudo first-order reaction was assumed since the As(V) concentration profiles for both scenarios were observed to decrease exponentially [32]. As expressed by Equation (16), the sorption performance was evaluated quantitatively in terms of arsenic uptake [34].

$$m (q_e - q_0) = V (C_0 - C_e) \quad (16)$$

Where m is the mass of the NZVI (g); q_e and q_0 are the arsenic uptakes by the sorbent (mg/g) at initial and equilibrium conditions, respectively; C_0 , and C_e are the initial and equilibrium concentrations of arsenic in solution (mg/L); and V is the solution volume (L). The observed rate constant (k_{obs}), half-lives ($t_{1/2}$) and removal performance of reaction were calculated and are presented in Table 3.

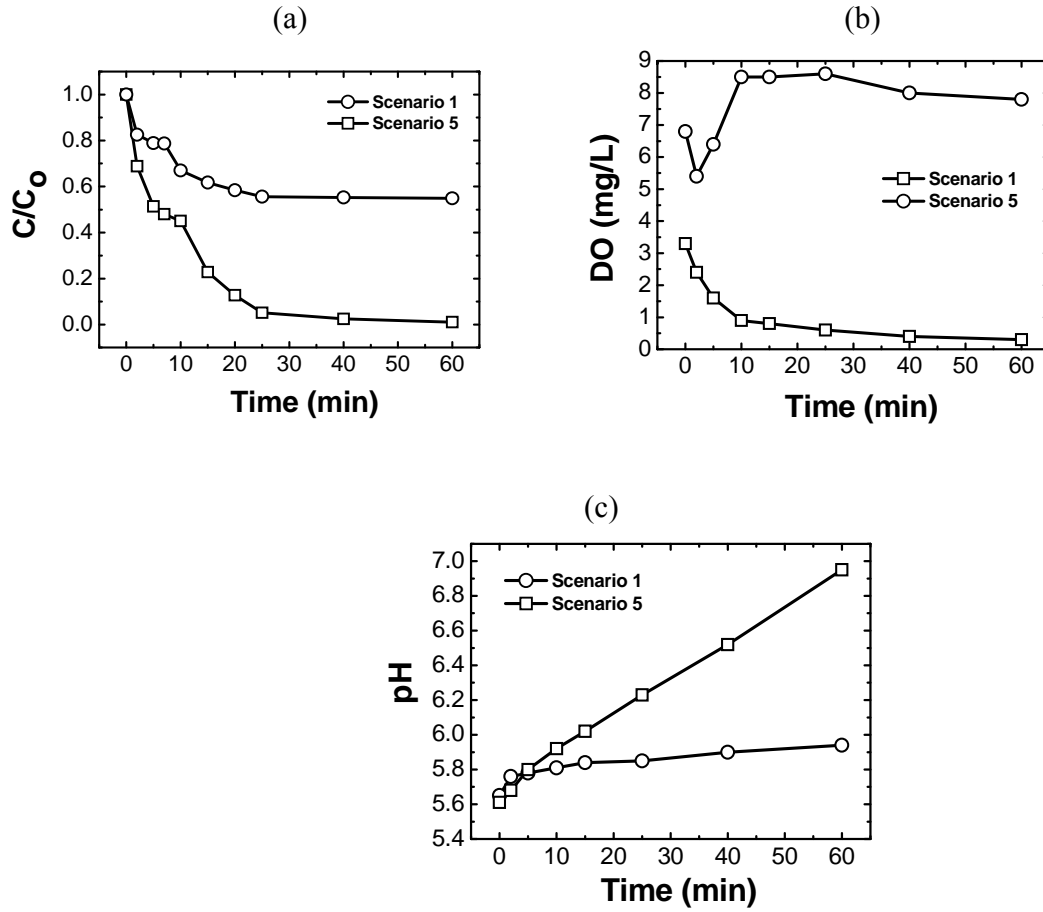


Fig. 5. Profiles of (a) normalized As(V) concentration, (b) DO and (c) pH for Scenarios 1 and 5. Groundwater taken from the field was spiked with initial As(V) concentration of 3000 ppb. NZVI dosage = 0.023 g/L.

Table 3 shows that in Scenario 5 the rate constant and the removal capacity for As(V) removal are much higher than those in Scenario 1. In contrast, the As(V) removal in DI water system remained comparable in both scenarios.

Table 3 Pseudo first-order reaction rate constant (k_{obs}), half-lives ($t_{1/2}$) and removal capacity with regard to As(V) removal

Items	Scenario 1 (acid addition)	Scenario 5 (gas bubbling)
equilibrium time (min)	25	25
equilibrium arsenic conc. ($\mu\text{g/L}$)	1652	153
kinetic parameters		
k_{obs} (min^{-1})	0.022	0.109
$t_{1/2}$ (min)	32.09	6.36
R^2	0.91	0.97
removal capacity (mg/g)	59.31	125.3

4. Conclusions

This research concludes that As(V) was removed most favorably under conditions of acidic environment and higher DO levels. Adjusting solution pH to acidic condition by CO_2 bubbling alone could not improve performance of As(V) removal because of stripping of DO. Pretreatment by CO_2 and air bubbling in sequence is recommended for higher performance of As(V) removal. The advantage of CO_2 bubbling is that it creates a favorable acidic environment for As(V) removal without sacrificing treated water quality. The advantage of air bubbling is that it will help generate iron corrosion products, such as iron (hydr)oxides, which provide reactive sites for arsenic adsorption. When the NZVI process studied here was applied to field groundwater, pretreatment of CO_2 and air bubbling in sequence were proven to be the most favorable operation for high concentration As(V) removal.

Acknowledgements

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program. It is also acknowledged that Mr. Robert Schlatter has polished and proofread this article.

References

- [1] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents - A critical

review, *J. Hazard. Mater.* 142 (2007) 1-53.

- [2] X. Meng, G.P. Korfiatis, S. Bang, K.W. Bang, Combined effects of anions on arsenic removal by iron hydroxides, *Toxicology Letters* 133, 103–111. *Toxicology Letters* 133 (2002) 103–111.
- [3] K. Banerjee, G.L. Amy, M. Prevost, S. Nour, M. Jekel, P.M. Gallagher, C.D. Blumenschein, Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH), *Water Res.* 42 (2008) 3371-3378.
- [4] J. Farrell, J. Wang, P. O'Day, M. Conklin, Electrochemical and spectroscopic study of arsenate removal from water using zero-valent iron media, *Environ. Sci. Technol.* 35 (2001) 2026-2032.
- [5] P.E. Mariner, F.J. Holzmer, R.E. Jackson, H.W. Meinardus, Effects of high pH on arsenic mobility in a shallow sandy aquifer and on aquifer permeability along the adjacent shoreline, commencement bay superfund site, Tacoma, Washington, *Environ. Sci. Technol.* 30 (1996) 1645-1651.
- [6] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [7] S.L. Chen, S.R. Dzenge, M.H. Yang, K.H. Chiu, G.M. Shieh, C.M. Wai, Arsenic species in groundwaters of the blackfoot disease area, Taiwan, *Environ. Sci. Technol.* 28 (1994) 877-881.
- [8] N. Melitas, J. Wang, M. Conklin, P. O'Day, J. Farrell, Understanding soluble arsenate removal kinetics by zero-valent iron media, *Environ. Sci. Technol.* 36 (2002) 2074-2081.
- [9] A.D. Redman, D.L. Macalady, D. Ahmann, Natural organic matter affects arsenic speciation and sorption onto hematite, *Environ. Sci. Technol.* 36 (2002) 2889-2896.
- [10] S. Dixit, J.G. Hering, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility, *Environ. Sci. Technol.* 37 (2003) 4182-4189.
- [11] D. Mishra, J. Farrell, Evaluation of mixed valent iron oxides as reactive adsorbents for arsenic removal, *Environ. Sci. Technol.* 39 (2005) 9689-9694.
- [12] J.A. Lackovic, N.P. Nikolaidis, G.M. Dobbs, Inorganic arsenic removal by zero-valent iron, *Environ. Eng. Sci.* 17 (2000) 29-40.
- [13] S. Bang, M.D. Johnson, G.P. Korfiatis, X. Meng, Chemical reactions between arsenic and zero-valent iron in water, *Water Res.* 39 (2005) 763-770.
- [14] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.* B129 (2006) 297-303.
- [15] G. Jegadeesan, K. Mondal, S.B. Lalvani, Arsenate remediation using nanosized modified zerovalent iron particles, *Environ. Progress.* 24 (2005) 289-296.
- [16] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders, *Inorg. Chem.* 34 (1995) 28-35.
- [17] S.R. Kanel, J.M. Greneche, H. Choi, Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material, *Environ. Sci. Technol.* 40 (2006) 2045-2050.
- [18] S.R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic(III) from groundwater by nanoscale zero-valent iron, *Environ. Sci. Technol.* 39 (2005) 1291-1298.
- [19] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, Effects of water characteristics on nitrate reduction by the Fe⁰/CO₂ process, *Chemosphere* 63 (2006) 335-343.

- [20] C.Y. Hsu, C.H. Liao, M.C. Lu, Treatment of aqueous nitrate by zero valent iron powder in the presence of CO₂ bubbling, *Ground Water Monitoring and Remediation* 24(4) (2004) 82-87.
- [21] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, Innovative process using Fe⁰/CO₂ for the removal of nitrate from groundwater, *Water Sci. Technol.: Water Supply* 5 (2005) 49–56.
- [22] C.W. Li, Y.M. Chen, W.S. Yen, Pressurized CO₂/zero valent iron system for nitrate removal, *Chemosphere* 68 (2007) 310–316.
- [23] J. Anotai, C.H. Liao, C. Ruangchanikom, Nitrate removal by Fe⁰/CO₂ process using an innovative continuous flow reactor, *J. Environ. Eng. Manage.* 20(2) (2010) 77-84.
- [24] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344-349.
- [25] X. Li, D.W. Elliott, W. Zhang, Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects, *Solid State and Mater. Sci.* 31 (2006) 111-122.
- [26] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 (2001) 1487-1492.
- [27] J.T. Mayo, C. Yavuz, S. Yean, L. Cong, H. Shipley, W. Yu, J. Falkner, A. Kan, M. Tomson, V.L. Colvin, The effect of nanocrystalline magnetite size on arsenic removal, *Sci. Technol. Adv. Mater.* 8 (2007) 71-75.
- [28] T. Hiemstra, W.H. Van Riemsdijk, Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxides, *J. Colloid Interface Sci.* 210 (1999) 182–193.
- [29] W. Zhang, P. Singh, E. Paling, S. Delides, Arsenic removal from contaminated water by natural iron ores, *Miner. Eng.* 17 (2004) 517–524.
- [30] S. Fendorf, M.J. Eick, P. Grossl, D.L. Sparks, Arsenate and chromate retention mechanisms on goethite. 1. Surface structure, *Environ. Sci. Technol.* 31 (1997) 315- 320.
- [31] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and of CO₂- bubbled system, *Water Res.* 40 (2006) 195-204.
- [32] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: effect of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride, *Environ. Sci. Technol.* 35 (2001) 4562-4568.
- [33] M. Biterna, A. Arditoglou, E. Tsikouras, D. Voutsas, Arsenate removal by zero valent iron: batch and column tests, *J. Hazard. Mater.* 149 (2007) 548–552.
- [34] D. Borah, S. Satokawa, S. Kato, T. Kojima, Sorption of As(V) from aqueous solution using acid modified carbon black, *J. Hazard. Mater.* 162 (2009) 1269-1277.
- [35] Y. Furukawa, J.W. Kim, J. Watkins, R.T. Wilkin, Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron, *Environ. Sci. Technol.* 36 (2002) 5469-5475.
- [36] J.M. Triszczy, A. Porta, F.S.G. Einschlag, Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal, *Chem. Eng. J.* 150 (2009) 431-439.

- [37] Y.H. Huang, T.C. Zhang, Effects of dissolved oxygen on formation of corrosion products and concomitant oxygen and nitrate reduction in zero-valent iron systems with or without aqueous Fe^{2+} , *Water Res.* 39 (2005) 1751–1760.
- [38] A.B.M. Giasuddin, S.R. Kanel, H. Choi, Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal, *Environ. Sci. Technol.* 41 (2007) 2022–2027.

Background species effect on aqueous arsenic removal by nano zero-valent iron using fractional factorial design

Visanu Tanboonchuy¹, Nurak Grisdanurak^{1,2}, Chih-Hsiang Liao^{3*}

¹Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND.

²National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Pathumthani, THAILAND.

³Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

*Corresponding author: chliao@mail.chna.edu.tw

Abstract

This study describes the removal of arsenic species in groundwater by nano zero-valent iron process, including As(III) and As(V). Since the background species may inhibit or promote arsenic removal. The influence of several common ions such as phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), chloride (Cl^-), and humic acid (HA) were selected to evaluate their effects on arsenic removal. In particular, a 2^{6-2} fractional factorial design (FFD) was employed to identify major or interacting factors, which affect arsenic removal in a significant way. As a result of FFD evaluation, PO_4^{3-} and HA play the role of inhibiting arsenic removal, while Ca^{2+} was observed to play the promoting one. As for HCO_3^- and Cl^- , the former one inhibits As(III) removal, whereas the later one enhances its removal; On the other hand, As(V) removal was affected only slightly in the presence of HCO_3^- or Cl^- . Hence, it was suggested that the arsenic removal by the nanoiron process can be improved through pretreatment of PO_4^{3-} and HA. In addition, for the groundwater with high hardness, the nanoiron process can be an advantageous option because of enhancing characteristics of Ca^{2+} .

Keywords: Arsenic; adsorption; FFD; zero-valent iron.

1. Introduction

High arsenic-contaminated groundwater has become a worldwide issue of concern because of its toxicity and carcinogenicity [1]. The USEPA changed the maximum contaminant level (MCL) for arsenic from 50 $\mu\text{g/L}$ in 1974 to 10 $\mu\text{g/L}$ in 2001 due to its long-term health effect [2]. Arsenic is stable in several oxidation states, of which the arsenite, As(III), and arsenate, As(V), are the most common forms in natural waters. The dominant species of arsenic depend greatly on its surrounding environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [3]. Arsenic is typically associated with iron oxide under oxic environment, and pyrite minerals under anoxic

one [4]. Furthermore, the arsenic may be released into water environments from both natural sources and anthropogenic activities [5, 6].

According to the literature, the adsorption processes coupled with redox processes of zero-valent iron (ZVI) was a promising alternative for arsenic removal. The ZVI was firstly used for arsenic removal by Lackovic et al. (2000) [7]; they reported that ZVI has high capacity for arsenic remediation of both As(III) and As(V) simultaneously. Based on the method of nano-scale ZVI (NZVI) synthesis developed by Glavee et al. (1995) [8], the NZVI possesses much higher capacity for arsenic removal than micro-scale ZVI [9, 10]. However, there still remains great need to focus on background species effect on arsenic removal by this ZVI process, prior to field application. The phosphate (PO_4^{3-}) and bicarbonate (HCO_3^-) were reported that both can reduce performance of arsenic removal due to their competition for active sites on the adsorbent surface [11-13]. Whereas, sulfate (SO_4^{2-}) can play both inhibiting and enhancing roles for arsenic removal, depending on its concentration level and experimental conditions [14, 15]. It was reported that hardness (Ca^{2+}) plays an enhancing role for arsenic removal because it increases the positive surface charges of adsorbent, which favor adsorption for anionic arsenic species [16]. In addition, the HA was reported to result in significant reduction in arsenic removal, due to its high tendency of being adsorbed onto the surface of iron (hydr)oxides [10, 17, 18].

Currently, there still remains lack of information regarding the influence of mixture of background species on the arsenic removal by NZVI. In order to evaluate the performance of arsenic removal in the presence of background species of multi-components, experiments were designed by using two-level fractional factorial design (FFD). Note that the FFD, widely and commonly adopted in industry, is an efficient tool for evaluating a large number of variables with a reasonable number of experimental runs [19]. Additional advantage of the FFD is that no complicated calculations are needed to analyze the produced result [20]. The FFD is generally represented in the form of 2^{k-p} , where k is the number of factors and $1/2^p$ represents the fraction of the full factorial 2^k [21]. In this study, six species were selected and investigated for their effects on arsenic removal, including SO_4^{2-} , PO_4^{3-} , HCO_3^- , Ca^{2+} , Cl^- , and HA. Based on the FFD methodology, both individual and combined influences of background species on arsenic removal were observed when the proposed NZVI process was employed.

2. Materials and method

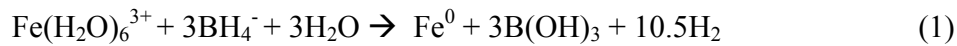
2.1 Chemicals

The chemicals of reagent grade used for NZVI synthesis in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), and NaBH_4 (> 96%), (Merck). The As(III) and As(V) stock solution were prepared from NaAsO_2 (Fluka) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (J.T. Baker), respectively. The selected species for test were prepared from Na_2SO_4 (Merck), $\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$ (Merck), NaHCO_3 (Merck), $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (Merck), NaCl (Merck), and HA (Acros organics). All chemical solutions were prepared with deionized water (18.2 M Ω Mill-Q).

2.2 NZVI synthesis

The NZVI was synthesized according to Glavee et al. (1995) [8]. 0.25 M of NaBH_4 was added into 0.045 M of aqueous FeCl_3 solution, and the mixture was agitated by a revolving propeller. The

ferric iron was reduced by the borohydride, according to Reaction (1):



At the end of reaction, the NZVI particles were separated from liquid solution by a magnet. The dried NZVI was characterized first by TEM (JEL-2010, Japan) for its particle size. The solution pH with zero point charge, denoted as pH_{pzc} , was determined by using zeta-meter system 3.0+ (Meditop Co., Thailand). Table 1 shows the physicochemical properties of the NZVI, including its particle size and solution pH_{pzc} .

Table 1. Characterization of NZVI synthesized in this study

Parameter	Value
Particle size	
95% of the particles	< 90 nm
average of particle size	56 nm
pH_{pzc}	7.8

2.3 Batch test

2.3.1. Single species system

The NZVI (0.023 g/L) synthesized was added into a batch reactor with a volume of 4.4 L for the treatment of arsenic. The initial arsenic concentration was prepared at a level as high as 1000 $\mu\text{g/L}$. Two levels of low and high concentrations for each selected species were listed as follows: SO_4^{2-} : 10, 100 mg/L; HCO_3^- : 50, 500 mg/L; PO_4^{3-} : 1, 5 mg/L; HA: 0.5, 5 mg/L; Ca^{2+} : 50, 500 mg/L; Cl^- : 50, 500 mg/L. The solution pH was adjusted at the beginning of the experiment to 7.90 ± 0.1 . The solution pH was measured by pH meter (Suntex TS1), while the residual arsenic was determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series.

2.3.2. Multiple species system

In this part, the experiments were performed via a 2^{6-2} FFD with resolution IV to identify factors which impose significant effects on arsenic removal. Using a resolution IV design guarantees that no main effects are confounded with two-factor interactions or other main effects, and two-factor interactions are confounded with other two-factor interactions [19]. The basic assumption of the experimental design employed was that the interactions higher than two factors could be considered as insignificant [22]. The design matrix of FFD of each stated species were given in Table 2. The low (-) and high (+) levels of each factor in this FFD were determined by following the same concentration ranges of single species system. It is noticed here that the confounding factor was found by considering the variables E and F as the generators: $E = A \times B \times C$ and $F = B \times C \times D$. In Table 2, the generator

employment for each run was shown in the third row. For instance, for Run #1, the variables A, B, and C have minus sign (-), the variable E ($A \times B \times C$) will then have minus sign (-) as well, resulting from a simple product of three minus signs. The same procedure is applied to determine the sign of variable F ($B \times C \times D$) [23].

Table 2. Design matrix of the 2^{6-2} FFD with resolution IV

Run no.	Factors and codes					
	HA	PO ₄ ³⁻	HCO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Cl ⁻
	A	B	C	D	E=ABC	F=BCD
1	-	-	-	+	-	+
2	+	+	-	-	-	+
3	+	+	+	-	+	-
4	-	+	-	+	+	-
5	-	-	+	-	+	+
6	+	-	+	-	-	+
7	+	+	+	+	+	+
8	+	-	-	+	+	+
9	-	+	+	+	-	+
10	+	+	-	+	-	-
11	-	+	+	-	-	-
12	+	-	-	-	+	-
13	-	+	-	-	+	+
14	+	-	+	+	-	-
15	-	-	+	+	+	-
16	-	-	-	-	-	-

Note: (1) The plus (+) and minus (-) signs indicate the high and low levels of the factors, respectively. (2) The test levels (low, high) in mg/L of codes A through F are as follows: A(0.5, 5), B(1, 5), C(50, 500), D(10, 100), E(50, 500), and F(50, 500).

3. Results and discussion

3.1. Preliminary study

As a preliminary study, the NZVI was tested for the removal of arsenic in both deionized water and groundwater. The groundwater was taken from the monitoring well at Chia Nan University of Pharmacy and Science, Taiwan. The arsenic was spiked into this field groundwater sample to obtain its initial arsenic concentration of 1000 ppb. As shown in Figure 1(a), the performance of both As(III) and As(V) removal in deionized water system was higher than that in groundwater system. The reason appears to be that competition for adsorptive sites exists between arsenic species and background species in field groundwater. Another reason might be due to a lesser content of initial DO in the field

groundwater (Figure 1(b)), which can oxidize the NZVI to generate iron (hydr)oxides for favorably adsorptive removal of arsenic (Sun et al., 2006). As shown in Figure 1(c), all solution pH profiles were observed to rise continuously throughout all reaction period, due to the build-up of OH^- , according to Reactions (2) and (3). Such phenomenon was similar to earlier study with ZVI in micron scale [24]. (Ruangchainikom et al., 2006). However, the pH in the case of groundwater system increased quite slowly, possibly because of buffering capacity of carbonate alkalinity (680 ppm as CaCO_3) contained in the filed groundwater.



In brief, the preliminary study shows that the presence of background species in groundwater can affect greatly the performance of arsenic removal by the studied NZVI process.

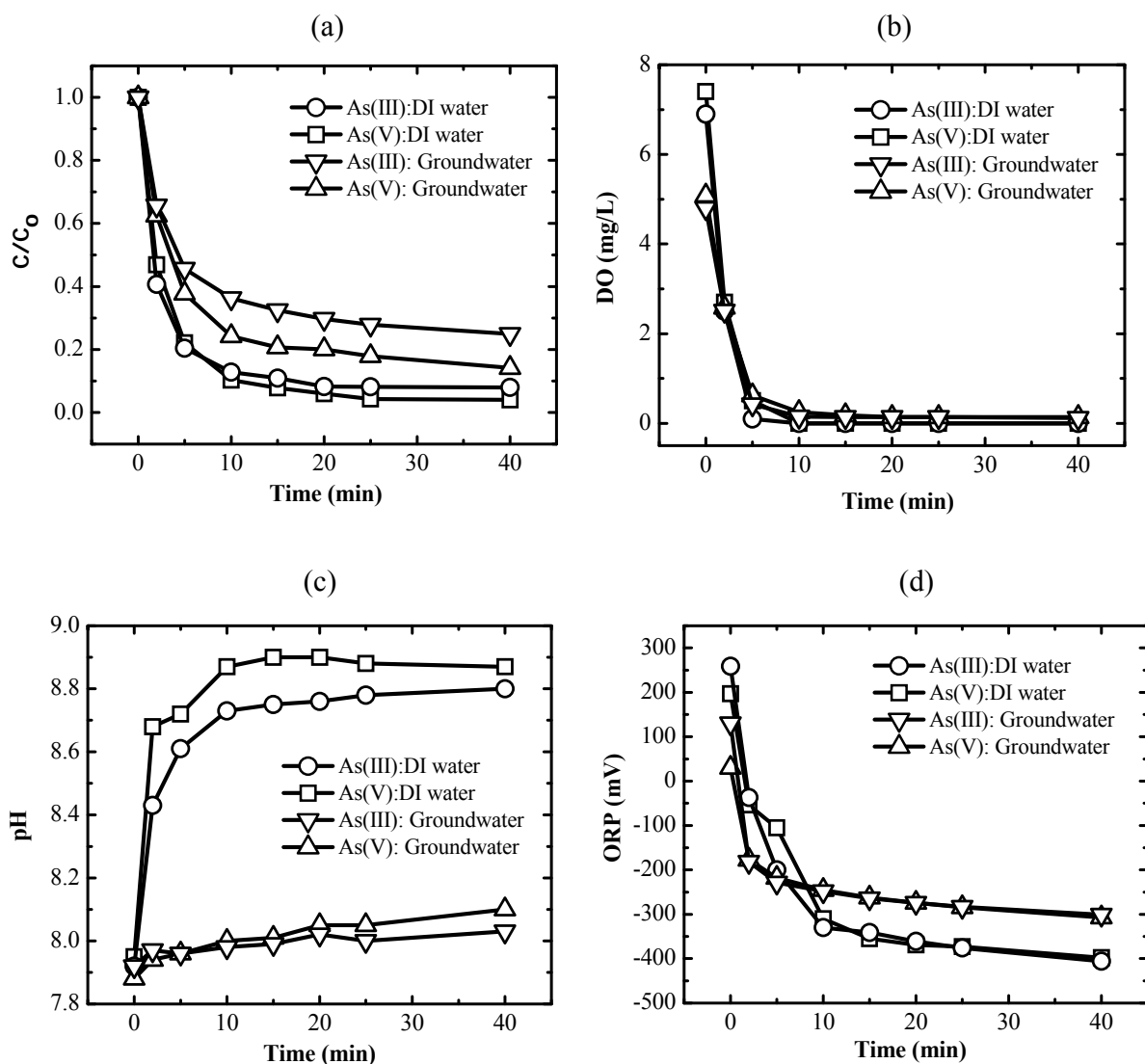


Fig. 1. Behavior of arsenic removal by NZVI in the deionized water and groundwater systems: (a) normalized residual arsenic concentration, (b) DO, (c) pH, and (d) ORP. [As] = 1000 ppb, NZVI dosage = 0.023 g/L, initial pH (DI water system) = 7.9 ± 0.1 .

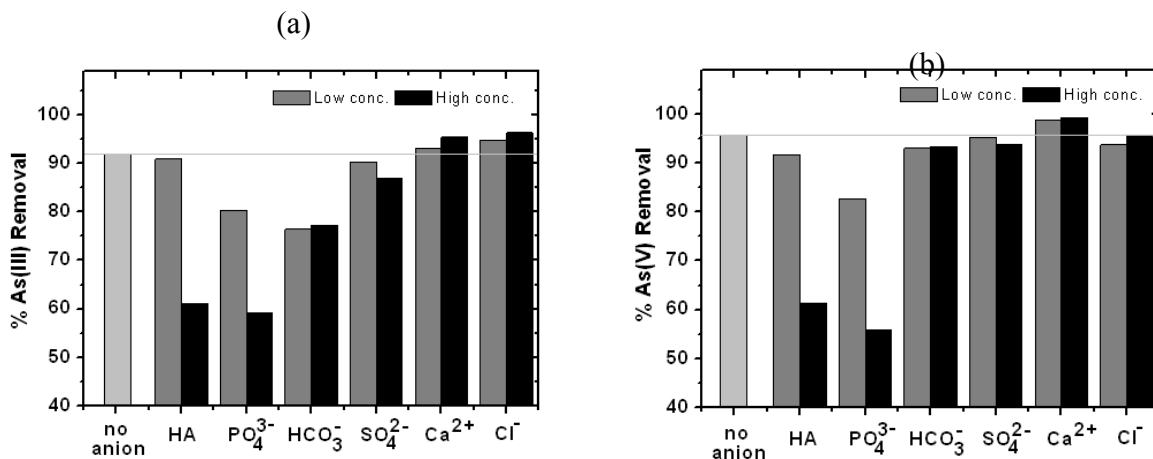


Fig. 2. Percentage of removal of (a) As(III) and (b) As(V) in the presence of low and high concentrations of selected species: [As] = 1000 μ g/L, NZVI = 0.023 g/L, initial pH = 7.9 ± 0.1 .

3.2. Single species system

3.2.1. Humic acid (HA)

As shown in Figure 2, the presence of HA in low concentration slightly decreased the removal performance of both As(III) and As(V). However, when the concentration of HA increases from 0.5 to 5 mg/L, the removal efficiencies of arsenic dramatically decrease from 91% to 61%, and 92% to 61% for As(III) and As(V), respectively. The reduction in arsenic performance is due to that the HA, one kind of natural organic matter (NOM), can be adsorbed onto the surface of iron (hydr)oxides, resulting in less adsorptive surface of iron (hydr)oxides [18].

Table 3. pK_a values of arsenate species and phosphate

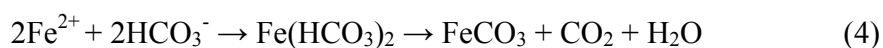
Species	pK _a values			Predominant form at various pH's			Reference
	pK ₁	pK ₂	pK ₃	< pK ₁	pK ₁ – pK ₂	pK ₂ – pK ₃	
As(III)	9.22	12.13	12.7	H ₃ AsO ₃	H ₂ AsO ₃ ⁻	HAsO ₃ ²⁻	[31]
As(V)	2.2	6.97	11.53	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	[31]
PO ₄ ³⁻	2.15	7.1	12.4	H ₃ PO ₄	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	[37]

3.2.2. Phosphate (PO_4^{3-})

The effect of PO_4^{3-} (1 and 5 mg/L) on arsenic removal was presented in Figure 2. The presence of PO_4^{3-} inhibited the removal performance of arsenic, both As(III) and As(V), significantly. Table 3 depicts the pK_a values and predominant forms of arsenic and phosphate species, respectively. Such information indicates that the dominant dissociation species of phosphate and arsenic have similar chemistry, especially those of the phosphate and As(V). In other words, competition between arsenic species and phosphate for the same adsorption sites exists on the surface of iron (hydr)oxides [12]. Phosphate may be adsorbed onto iron (hydr)oxides through the formation of inner-sphere complexes with the hydroxyl groups [25]. In addition, the affinity of phosphate for iron (hydr)oxides was much stronger than arsenic species [4]. Therefore, the phosphate can retard the removal of arsenic significantly.

3.2.3. Bicarbonate (HCO_3^-)

The effect of HCO_3^- on arsenic removal was shown in Figure 2. The As(III) removal was inhibited dramatically in the presence of HCO_3^- , whereas the As(V) removal was affected only slightly. The possible reasons may be due to competition for adsorptive sites between HCO_3^- and arsenic species since the HCO_3^- can form inner-sphere surface complexes with iron (hydr)oxides [15]. In addition, The NZVI can be rapidly oxidized into Fe^{2+} , the primary product, as shown in Equations (2) and (3), and this Fe^{2+} can result in several forms of iron (hydr)oxides, which serve as good sites for arsenic adsorption. Furthermore, in the presence of HCO_3^- , the generated Fe^{2+} may react with HCO_3^- to form iron carbonate (FeCO_3) [26] according to Equation (4). Consequently, lower performance for arsenic adsorption was observed.



As reported in the literature, the release of arsenic from sandstone aquifer was found to be strongly and positively related to the HCO_3^- concentration in the leaching solution [27]. Also another report shows that HCO_3^- can promote iron dissolution from hematite ($\alpha\text{-Fe}_2\text{O}_3$) surface [28], leading to the increase of the dissolved arsenic in solution. In this study, both low and high HCO_3^- concentrations show comparable arsenic removal, indicating significant impact by alkalinity even less than 50 mg/L.

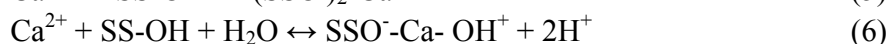
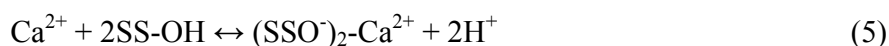
3.2.4. Sulfate (SO_4^{2-})

The removal of both As(III) and As(V) was retarded slightly in the presence of low and high concentrations of SO_4^{2-} , as presented in Figure 2. Such phenomenon was reported due to the electrical repulsion between SO_4^{2-} and arsenic species [29]. Another reason is that the SO_4^{2-} can replace iron (hydr)oxides, which were adsorbed on the iron surface, leading to the decrease of adsorption sites available to arsenic [30].

3.2.5. Calcium (Ca^{2+})

As shown in Figure 2, the efficiency of both As(III) and As(V) removal was enhanced slightly in the presence of Ca^{2+} . The solution pH of this study was set at 7.9, higher than the pH_{pzc} of pristine NZVI.

So the surface of NZVI was with positive charge. However, when the reaction was carried on, the solution pH increased and became even higher than the pH_{pzc} of iron (hydr)oxides, due to the OH^- being produced, according to Equations (2) and (3). This then resulted in negative charge on the surface of iron (hydr)oxides, with charge property identical to arsenic species [31]. Thus, the electrostatic repulsion force led to decreasing adsorption of arsenic. In the presence of Ca^{2+} , it serves to neutralize the negative surface charge of iron (hydr)oxides, and thus reduces the electrostatic repulsion for negatively charged arsenic, allowing the arsenic to remain on the adsorption sites [32]. For the other explanation, the Ca^{2+} forms a complex with surface sites (SS) of iron (hydr)oxides, as depicted in Equations (5) and (6).



Both reactions provide a bridge between surface of adsorbent and the negatively charged arsenic by increasing the positive surface charge of the adsorbent, which favors more negatively charged arsenic species adsorption [16].

3.2.6. Chloride (Cl^-)

Figure 2 indicates that the efficiency of As(V) removal decreased slightly in the presence of low Cl^- concentration, even when Cl^- concentration was high, no significant As(V) removal was observed. However, Cl^- was capable of enhancing the performance of As(III) removal. According to Choe et al. (2004) [33], they reported that Cl^- in solution induces pitting corrosion of the iron surface, which may increase the reactive area of iron for arsenic adsorption

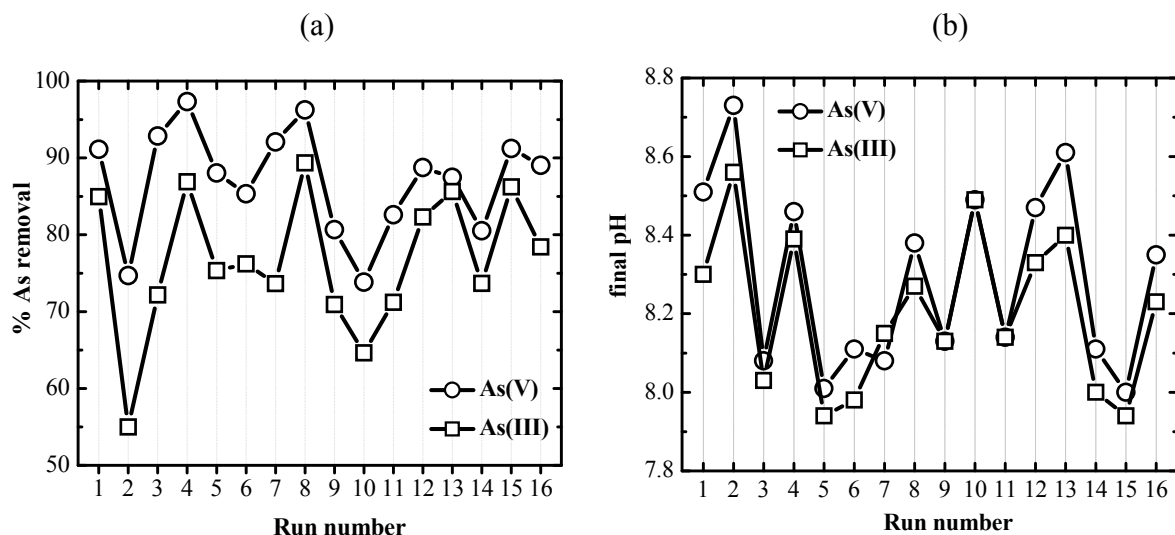


Fig. 3. Effect of six selected species with concentrations of different levels on (a) arsenic removal by NZVI, and (b) the final pH: $[As] = 1000 \mu g/L$, $NZVI = 0.023 g/L$, initial $pH = 7.9 \pm 0.1$.

3.3. Multiple species system

3.3.1. Arsenic removal with species concentrations of different levels

The profiles of arsenic removal by NZVI in the presence of six selected species with concentrations of different levels were shown in Figure 3. It appears that higher arsenic removal was found in Runs # 4 and 8 for both As(III) and As(V). Both runs have the same concentration level of HCO_3^- (-), SO_4^{2-} (+), and Ca^{2+} (+). Thus, it is possible that HCO_3^- will play an inhibiting role for arsenic removal, whereas both the SO_4^{2-} and Ca^{2+} play an enhancing role. In contrast, Runs # 2 and 10, which involve HA and PO_4^{3-} with high concentration, gave lower efficiency of arsenic removal. Such results indicate that arsenic removal was retarded possibly by HA and PO_4^{3-} . The analysis of effect of each species will be further discussed in detail by the FFD method. According to Figure 3(b), all the final solution pH's were higher than the initial pH's, due to ZVI oxidation (Equations (2) and (3)). Additionally, Runs # 3, 5, 6, 7, 9, 11, 14, and 15 gave lower final pH's (< 8.2) because of higher concentration of HCO_3^- , which will provide higher buffering capacity for solution pH.

3.3.2. Effect of main species

The 2^{6-2} FFD with resolution IV was chosen for the experimental design. Thus, average main effects were confounded with three-factor interaction, for instance, $A = A + BCE + DEF$, where the interactions higher than two factors could be assumed to be negligible. In this manner, all estimates of main effects were obtained [21]. The estimate of effect for each of the factors shown in Figure 4 is the difference between the average response of high level (+) and the average response of low level (-) of that particular factor in design matrix of Table 2 [20]. Given the calculation for the estimate of effect of factor A on As(III) removal as an example, the average responses of high level (+) and low level (-) are 73.37 ($= (54.99+72.16+76.23+73.63+89.36+64.62+82.30+73.76)/8$) and 79.94 ($= (84.94+86.88+75.33+70.90+71.19+85.64+86.21+78.42)/8$), respectively. The difference between both levels is -6.57 ($= 73.37 - 79.94$), which is the value plotted in Figure 4(a). Note that the data for average response calculation were taken from those plotted in Figure 3.

As shown in Figure 4, the negative estimates of main effect of A (HA), B (PO_4^{3-}), C (HCO_3^-) were -6.57, -8.31, and -3.48 for As(III) and -2.9, -3.58, and -0.64 for As(V), implying that these main factors play an inhibiting role for arsenic removal. For example, increasing HA concentration from 0.5 to 5 mg/L results in the decrease of As(III) removal by 6.57% (the average response decreases from 79.94 % to 73.37%, when HA concentration changes from low (-) to high (+) level), and increasing PO_4^{3-} concentration from 1 to 5 mg/L leads to the decrease of As(III) removal by 8.31 %. In other words, to improve the removal of arsenic by the proposed NZVI, pretreatment of HA, PO_4^{3-} , and HCO_3^- is strongly recommended.

(a)

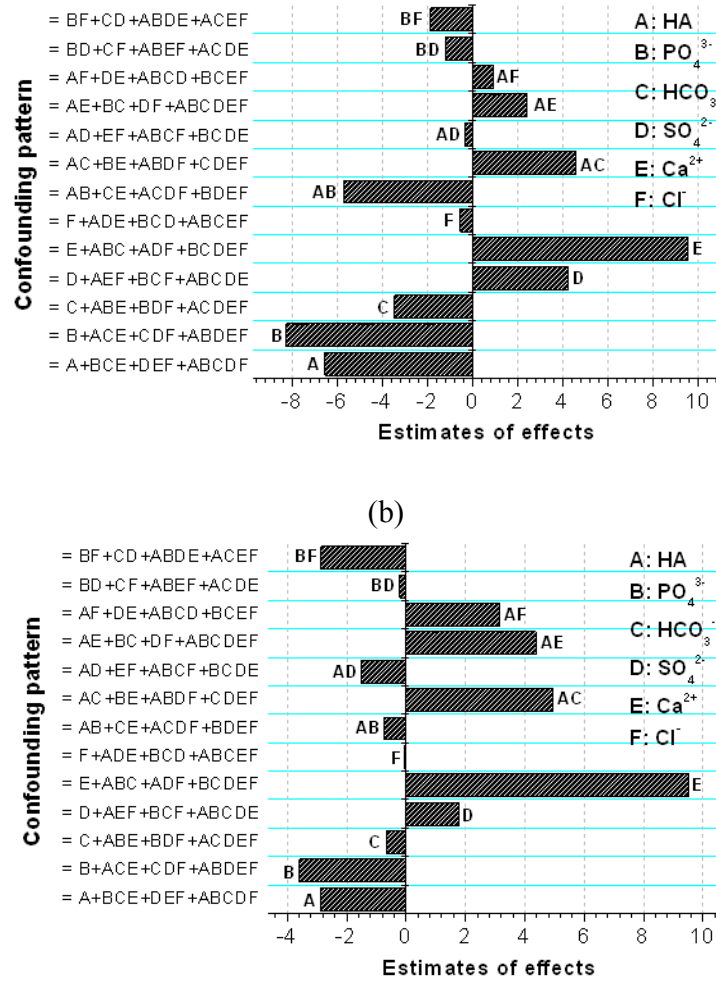


Fig. 4. Identification of main-effect and interacting factors on (a) As(III) and (b) As(V) removal by NZVI: [As] = 1000 $\mu\text{g/L}$, NZVI = 0.023 g/L, initial pH = 7.9 ± 0.1 .

On the other hand, the main factors D (SO_4^{2-}) and E (Ca^{2+}) were observed to enhance arsenic removal, the positive estimates of main effect of D (SO_4^{2-}) and E (Ca^{2+}) were 4.24, and 9.57 for As(III) and 1.79, and 9.51 for As(V). Interestingly, the role of HCO_3^- appears to be quite different from that of other factors, depending on the presence of the species of As(III) or As(V). This is to say that HCO_3^- inhibits As(III) removal, on the contrary, its impact becomes insignificant in the case of As(V). Such result agrees with that in the case of the single species system, which shows that As(III) removal decreased dramatically in the presence of HCO_3^- , whereas only slight decrease was observed in the removal of As(V). In regard to SO_4^{2-} , it plays an inhibiting role for the removal of both As(III) and As(V) in single species system, but its enhancing role was observed in the multiple species system. This might be due to the acceleration of precipitation of arsenopyrite, FeAsS , through the reaction of SO_4^{2-} with the Fe^{2+} , AsO_3^- and H^+ , according to Equation (7) [34].



Another report pointed out that SO_4^{2-} can corrode the surface of iron (hydr)oxides, thereby increasing the reactive sites on the surface [30].

In summary, among the selected species, the estimates of the inhibiting effects on the removal of both As(III) and As(V) are in the order as follows: $\text{PO}_4^{3-} > \text{HA} > \text{HCO}_3^-$, while the estimates of enhancing effects are in the following order: $\text{Ca}^{2+} > \text{SO}_4^{2-}$. As for the Cl^- , it plays no significant role.

3.3.3. Effect of interaction factor

The effect of interaction factor was considered because of its large estimate of effect, as illustrated in Figure 4. A significant two-factor interaction indicates antagonism or synergism between two factors: their combined effect is not the sum of their separate contributions [19]. Interactions are presented in the model matrix by cross-products, as depicted in Table 2. The interaction AB are products of A and B, for example, Run #1: $(-)(-) = (+)$, Run #2: $(+)(+) = (+)$, Run #4: $(-)(+) = (-)$, etc. [25]. According to Figure 4(a), for instance, the estimate of effect of interaction AB, or $\text{HA} \times \text{PO}_4^{3-}$, was -5.73, but this value did not only result from the interaction of A and B, but rather from the estimate of effect of interaction of C and E as well (see Figure 4 for the confounding patterns, where the item higher than two factors could be considered as insignificant). This means that the interaction of $(\text{HA} \times \text{PO}_4^{3-})$ was confounded with $(\text{HCO}_3^- \times \text{SO}_4^{2-})$ and the relationship could be described as $(\text{HA} \times \text{PO}_4^{3-}) = (\text{HA} \times \text{PO}_4^{3-}) + (\text{HCO}_3^- \times \text{SO}_4^{2-})$.

Figure 5 shows two-factor interaction plots for each two-factor interaction, in terms of the percentage of arsenic removal. The interactions between factors are strong for arsenic removal due to factors in x-axis when significant slope of each line within each cell is observed; on the other hand, when the distance between the two data points (black and red) in y-axis remains sufficiently long, the interactions due to factors in y-axis are significant [35]. For instance, for the cell AB in Figure 5(a), Factor B shows strong interaction effect on As(III) removal, when Factor A remains at high concentration level (see the red line). On the other hand, when keeping Factor A at low level, interaction effect of Factor B still exists, yet to a lesser degree (see the black line with lower slope). If Factor B remains at low level, Factor A will impose no impact regardless of its being at high or low level; yet, at high level of Factor B, increasing Factor A from low to high level will lead to significant drop of As(III) removal.

Specifically, as described in single species system, Factor B (PO_4^{3-}) and E (Ca^{2+}) were factors affecting removal; the previous one inhibits arsenic removal, whereas the latter one enhances its removal. Concerning the interaction of BE ($\text{PO}_4^{3-} \times \text{Ca}^{2+}$), the percentage of arsenic removal drops dramatically (78% to 65% for As(III), and 87% to 78% for As(V)), when PO_4^{3-} changes its concentration from low to high level and Ca^{2+} remains at low concentration level. However, the PO_4^{3-} poses insignificant interaction effect on arsenic removal, when concentration of Ca^{2+} is high. In the other way around, at low PO_4^{3-} , the interaction effect of Ca^{2+} resulted in only slight increase of arsenic removal

(78% to 83% for As(III), and 87% to 91% for As(V)); at high PO_4^{3-} , the increase in arsenic removal is relatively more significant (65% to 80% for As(III), and 78% to 92% for As(V)). According to this study, when background species were co-existing, the effect of which on arsenic removal was quite different from that when they exist alone [36].

In general, according to Figure 5(a), among all cells of paired interaction factors, the red lines (high level) in Columns C and F show near zero slopes. In Column F, the black line (low level) is also observed to be horizontal. In addition, the overlapping data points (black and red) exist in the cells of AB (low B), AC (high C), CD (low D), CE (low E), CF (low F) and DF (low F). According to Figure 5(b), the horizontal lines include those cells in Column D (the red lines), and Cell CF (black and red); and the overlapping data points are those in Cells AB (low B), AC (high C), AD (low D), AE (high E), AF (high F), BC (high C), BE (high E), BF (low F), CD (low D), CE (low and high E), CF (low and high F), DE (low E), and DF (low F). Based on the observation of both horizontal lines and overlapping data points, one may single out important factors for interaction within each cell.

4. Conclusions

In this study, the influence of six selected species on arsenic removal by NZVI, both single and multiple species systems, was investigated. The experiments for multiple species system were designed according to the 2^{6-2} FFD with resolution IV. As a result, in both systems, the important species which play a significant role in removing arsenic were HA, PO_4^{3-} , and Ca^{2+} , with the first two species imposing inhibiting effect and the last one enhancing effect. In particular, SO_4^{2-} plays an inhibiting role in single species system, but a promoting role in multiple species system. In the presence of HCO_3^- , in both systems it inhibited As(V) removal only slightly, but the inhibition became significant in As(III) removal. Based on the FFD, the performance of arsenic removal was determined not only by main factors but also by interaction factors. The results of this study suggest that increasing Ca^{2+} concentration but decreasing PO_4^{3-} and HA concentrations create the condition for the best removal of both As(III) and As(V).

(a)

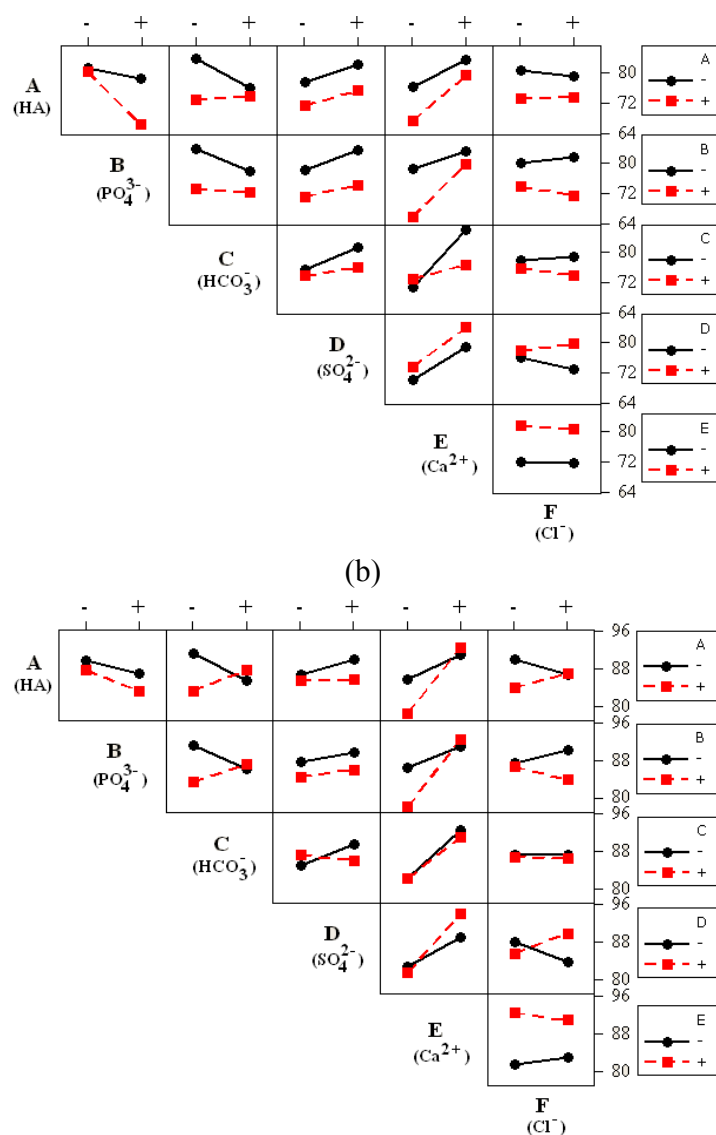


Fig. 5. Interacting effect plots in terms of (a) As(III) and (b) As(V) removal percentage.

Acknowledgements

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

5. References

- [1] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents - A critical review, J. Hazard. Mater. 142 (2007) 1-53.

- [2] N. Melitas, J. Wang, M. Conklin, P. O'Day, J. Farrell, Understanding soluble arsenate removal kinetics by zero-valent iron media, *Environ. Sci. Technol.* 36 (2002) 2074-2081.
- [3] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [4] X. Meng, G.P. Korfiatis, S. Bang, K.W. Bang, Combined effects of anions on arsenic removal by iron hydroxides, *Toxicology Letters* 133, 103–111. *Toxicology Letters* 133 (2002) 103–111.
- [5] K. Banerjee, G.L. Amy, M. Prevost, S. Nour, M. Jekel, P.M. Gallagher, C.D. Blumenschein, Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH), *Water Res* 42 (2008) 3371-3378.
- [6] Y. Li, F.S. Zhang, F.R. Xiu, Arsenic (V) removal from aqueous system using adsorbent developed from a high iron-containing fly ash. *Sci. Total. Environ.* 407 (2009) 5780-5786.
- [7] J.A. Lackovic, N.P. Nikolaidis, G.M. Dobbs, Inorganic arsenic removal by zero-valent iron, *Environ. Eng. Sci.* 17 (2000) 29-40.
- [8] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders, *Inorg. Chem.* 34 (1995) 28-35.
- [9] S.R. Kanel, J.M. Greneche, H. Choi, Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material, *Environ. Sci. Technol.* 40 (2006) 2045-2050.
- [10] A.B.M. Giasuddin, S.R. Kanel, H. Choi, Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal, *Environ. Sci. Technol.* 41 (2007) 2022-2027.
- [11] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 (2001) 1487-1492.
- [12] G. Jegadeesan, K. Mondal, S.B. Lalvani, Arsenate remediation using nanosized modified zerovalent iron particles, *Environ. Progress.* 24 (2005) 289-296.
- [13] W. Zhang, P. Singh, E. Paling, S. Delides, Arsenic removal from contaminated water by natural iron ores, *Miner. Eng.* 17 (2004) 517–524.
- [14] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.* B129 (2006) 297-303.
- [15] M. Biterna, A. Arditoglou, E. Tsikouras, D. Voutsas, Arsenate removal by zero valent iron: batch and column tests, *J. Hazard. Mater.* 149 (2007) 548–552.
- [16] R.C. Vaishya, S.K. Gupta, Modeling arsenic(V) removal from water by sulfate modified iron-oxide coated sand (SMIOCS), *Separation Sci. and Technol.* 39(3) (2004) 645-666.
- [17] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models, *Environ. Sci. Technol.* 28(1) (1994) 38–46.
- [18] P. Rao, M.S.H. Mak, T. Liu, K.C.K. Lai, I.M.C. Lo, Effects of humic acid on arsenic(V) removal by zero-valent iron from groundwater with special references to corrosion products analyses, *Chemosphere* 75 (2009) 156–162.
- [19] P.M. Berthouex, L.C. Brown, *Statistics for environmental engineers*, 2nd ed., Lewis Publishers, FL, 2002.
- [20] D.C. Montgomery, *Design and analysis of experiments*, 5th ed., John Wiley, New York 2001.

- [21] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for experimenters: An introduction to design. Data analysis and model building, John Wiley, New York, 1978.
- [22] J.C. Echeverria, M.T. Morera, C. Mazkiarin, J.J. Garrido, Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments, *Environ. Pollution* 101 (1998) 275-284.
- [23] A.J. Terezo, E.C. Pereira, Fractional factorial design applied to investigate properties of Ti/IrO₂-Nb₂O₅ electrodes, *Electrochimica. Acta.* 45 (2000) 4351-4358.
- [24] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and of CO₂ - bubbled system, *Water Res* 40 (2006) 195-204.
- [25] J.C. Hsu, C.J. Lin, C.H. Liao, S.T. Chen, Evaluation of the multiple-ion competition in the adsorption of As(V) onto reclaimed iron-oxide coated sands by fractional factorial design, *Chemosphere* 72 (2008) 1049-1055.
- [26] J.K. Heuer, J.F. Stubbins, An XPS characterization of FeCO₃ films from CO₂ corrosion, *Corros. Sci.* 41 (1999) 1231-1233.
- [27] M. Kim, J. Nriagu, S. Haack, Carbonate ions and arsenic dissolution by groundwater, *Environ. Sci. Technol.* 34 (2000) 3094-3100.
- [28] Y. Arai, D.L. Sparks, J.A. Davis, Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface, *Environ. Sci. Technol.* 38 (2004) 817-824.
- [29] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: effect of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride, *Environ. Sci. Technol.* 35 (2001) 4562-4568.
- [30] E. Bi, I. Bowen, J.F. Devlin, Effect of mixed anions (HCO₃⁻-SO₄²⁻-ClO₄⁻) on granular iron (Fe⁰) reactivity, *Environ. Sci. Technol.* 43(15) (2009) 5975-5981.
- [31] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344-349.
- [32] J.L. Parks, J. Novak, M. Macphee, C. Itle, M. Edwards, Effect of Ca on As releases from ferric and alum residuals, *J AWWA* 95(6) (2003) 108-118.
- [33] S. Choe, H.M. Liljestrand, J. Khim, Nitrate reduction by zero-valent iron under different pH regimes, *Appl. Geochem.* 19 (2004) 335-342.
- [34] A. Ramaswami, S. Tawachsupa, M. Isleyen, Batch-mixed iron treatment of high arsenic waters, *Water Res.* 35 (2001) 4474-4479.
- [35] J.H. Lim, J.S. Lee, A statistical design and analysis illustrating the interactions between key experimental factors for the synthesis of silver nanoparticles, *Colloids and Surfaces A: Physicochem. Eng. Aspects.* 322 (2008) 155-163.
- [36] X. Meng, G.P. Korfiatis, C. Christodoulatos, S. Bang, Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system, *Water Res* 35 (2001) 2805-2810.
- [37] B.P. Jackson, W.P. Miller, Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides, *Soil. Sci. Soc. Am. J.* 64 (2000) 1616-1622.

Nitrate probe for quantifying reducing power of nanoscale zero-valent iron

Visanu Tanboonchuy¹, Nurak Grisdanurak^{1,2}, Chih-Hsiang Liao^{3*}

¹Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND.

²National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Pathumthani, THAILAND.

³Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

* Corresponding author's email: chliao@mail.chna.edu.tw

Telephone no.: +886-6-266-3230

Fax no.: +886-6-366-3756

Abstract

Nano zero-valent iron (NZVI) has been extensively researched for treatment of hazardous and toxic wastes. In particular, it can be applied to remediate contaminated sites directly. In this study, the NZVI was synthesized by using chemicals of NaBH₄ and FeCl₃. The conditions for NZVI synthesis were varied by such parameters as air exposure, pumping rate of NaBH₄ (4-8 mL/min), and agitation power (100-300 rpm). Right after synthesis of NZVI particles of different varieties, nitrate of 50 ppm was used to probe its reducing power quantitatively. As a result of factorial design (FD) analysis, it appears that the agitation of reaction solution plays a major role in determining its reducing power of NZVI particles. Besides, air exposure of reaction also posed noticeable decrease of the final residual nitrate, whereas the reducing capacity of NZVI synthesized was elevated with lower NaBH₄ pumping rate.

Keywords: Nanotechnology; nanoparticles; nitrate; zero-valent iron

1. Introduction

Zero-valent iron (ZVI) was common and often used as a remediation agent in contaminated groundwater. In early 1990's, it was applied first in permeable reactive barrier (PBR) system [1-3]. ZVI has gained increasing attention for remediation process because of its being inexpensive and nontoxic [4]. ZVI can react to transform the mobile contaminants into immobile and less harmful species, which will be treated more easily [5]. There are two major mechanisms for aqueous contaminant removal by elemental iron, including (1) physicochemical adsorption and (2) oxidation and reduction reaction [6]. Contaminants removed by ZVI include halogenated hydrocarbons such as TCE, PCE, anions (e.g. NO₃⁻,

$\text{Cr}_2\text{O}_7^{3-}$), heavy metal, arsenic, and organic compound [7-11]. However, the problems associated with the use of micro-scale ZVI (MZVI) are that the reaction time required is in days, and a considerable amount of iron is needed for complete removal of target compounds [10, 12]. This serves to address the need of more efficient nano-scale ZVI (NZVI) synthesis development.

Currently, the NZVI has received widespread attention from field researchers for groundwater treatment because of its extremely small particle size, large surface area, high *in situ* reactivity, and high mobility in groundwater [13]. There were many techniques and methods for NZVI synthesis such as chemical method [7, 14], sono-chemical method [15], and thermal decomposition [16]. The sono-chemical method will generate toxic by-product, CO, because this method uses $\text{Fe}(\text{CO})_5$ as a raw material [17]. As for the thermal decomposition method, the produced NZVI particles tend to aggregate, due to the loss of the stabilization ability caused by the disappearance of the initial reactant chemicals during the heating process [16].

Since the NZVI has high reactivity with oxygen and water, inappropriate conditions for synthesis may result in the decrease of reducing capacity of NZVI synthesized. Thus, the goal of this study was to investigate the effect of parameters such as air exposure, pumping rate of reagents, and agitation speed of mixing on the reducing power of NZVI particles. The NZVI was synthesized by using the chemical method because of its ease and simplicity. In addition, there's no need for complicated equipment or instrument for synthesis. In view of the best conditions for NZVI synthesis, one may characterize NZVI synthesized by specific surface area, particle size, and solution pH of zero point charge. However, all these are time and cost consuming. In this study, the produced NZVI particles were tested for their reducing potential by using nitrate (NO_3^-) as the chemical probe. Several studies reported that the final products of NO_3^- reduction by ZVI were nitrite (NO_2^-), ammonium (NH_4^+), or nitrogen (N_2), depending on the reaction conditions [18-21]. Possible reactions of NO_3^- reduction by ZVI were listed in Reactions (1)-(4).



In order to evaluate the impact of parameters for synthesis, experiments were designed by using two-level factorial design (FD). Note that the FD, widely and commonly adopted in industry, is an efficient tool for serving the purpose of this study [22]. Results from this study will illustrate the conditions for synthesizing the NZVI with the best performance. Additionally, based on the FD methodology, both individual and combined influences of parameters for synthesis on reducing capacity of NZVI were observed as well. Consequently, by using nitrate as the electron probe, this study provides an easy and simple way to characterize the reducing potential of NZVI.

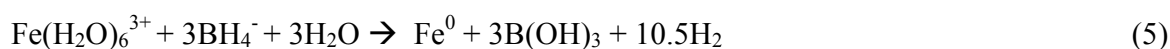
2. Materials and method

2.1. Chemicals

The chemicals of reagent grade used for NZVI synthesis in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), NaBH_4 (> 96%), and KNO_3 (99%), (Merck). All chemical solutions were prepared by using deionized water (18.2 M Ω Mill-Q).

2.2. Batch test

The NZVI was synthesized according to Glavee et al. (1995) [23]. 0.25 M of NaBH_4 solution was pumped into 0.045 M of FeCl_3 aqueous solution. The mixture was agitated by a revolving propeller (see Figure 1). Ferric iron is reduced by the borohydride, according to Reaction (5):



After solution was well mixed, the NZVI was separated from liquid solution by a magnet. The NZVI synthesized was applied immediately for its reducing power test using NO_3^- as a chemical probe. The test was carried out with probe concentration of 50 mg/L and NZVI dosage of 0.2 g/L. Among the reaction products of nitrate, the NH_4^+ was analyzed using the Phenate method through the spectrophotometric reading (SHIMADZU, UV-1201, Japan) with light absorption at 640 nm; the residual NO_3^- and NO_2^- were analyzed by using Ion Chromatography (DINNEX-120, USA).

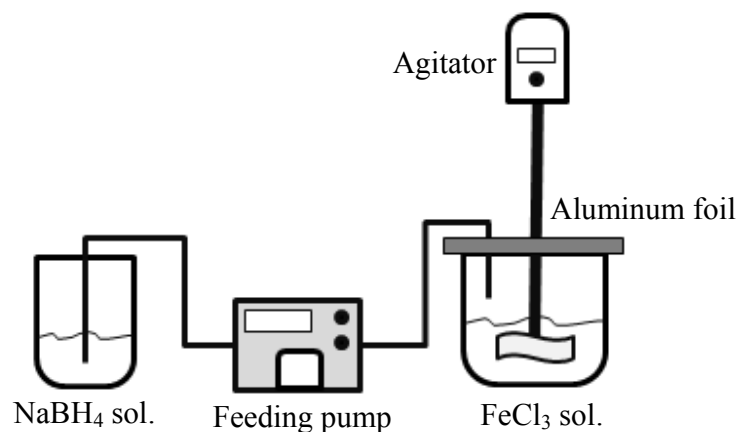


Figure 1. Schematic diagram for NZVI synthesis.

2.3. Experimental design

Two-level FD was employed to evaluate the impact of parameters on the reducing capacity of NZVI synthesized in this study. A full factorial design involves runs of 2^k different experimental conditions, which represent all combinations of the k factors at high and low levels [22]. Note that the “ k ” is independent variables investigated. In this study, three factors were investigated for their effects

on NZVI synthesis, including pumping rate of NaBH₄, agitation speed, and air exposure. Thus, the total experiments to be performed will be 8 runs (=2³). The design matrix for experiment is depicted in Table 1.

Table 1. Design matrix of the 2³ FD

Run no.	Factors and codes		
	Pumping rate of NaBH ₄	Agitation speed	Air exposure
	A	B	C
1	+	+	-
2	-	-	+
3	+	-	+
4	-	-	-
5	-	+	+
6	-	+	-
7	+	-	-
8	+	+	+

Note: (1) The plus (+) and minus (-) signs indicate the high and low level of the factors, respectively. (2) The test levels (low, high) of codes A through C are as follows: A(4, 8) in mL/min, B(100, 300) in rpm, and C(Yes, No).

3. Results and discussion

3.1. Mass balance profile

In the system of Fe⁰/NO₃⁻, the reduction reaction involves electron release from surface of NZVI, dissolved Fe²⁺ or H₂. Note that the latter two are the derived products from iron oxidation (see Reactions (6)-(7)), the reduction potential of which is generally very slow [24]. At any rate, the NO₃⁻ was reductively degraded by the electrons originated from the NZVI.



According to Figure 2, the mass balance profiles seem to indicate that the NZVI synthesized under condition of Run #5 was capable of reducing nitrate into end products NH₄⁺ only, no other species formed in the reaction. Thus, Reaction (3) mentioned earlier was used to address reduction capacity of NZVI synthesized in this study.

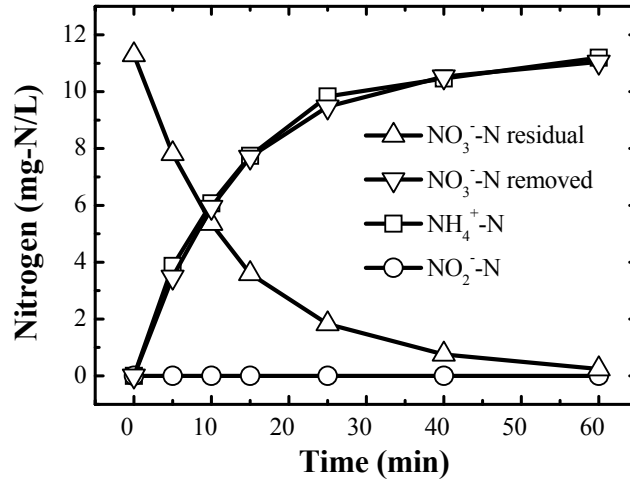


Figure 2. Mass balance profile for the NO₃⁻ reduction by NZVI synthesized under condition of Run #5.

3.2. Electron donating capacity (EDC) of NZVI

The profiles of NO₃⁻ reduction by NZVI under various conditions were shown in Figure 3(a). It appears that higher nitrate removal was found in Run #5, with the level of (-), (+), and (+) for A, B, and C, respectively. In contrast, Run #7, which involves A(+), B(-) and C(-), give lower efficiency of NO₃⁻ reduction. Thus, it is possible that the condition of low pumping rate of NaBH₄, high agitation speed and no air exposure is favorable for increasing reducing capacity of the NZVI synthesized.

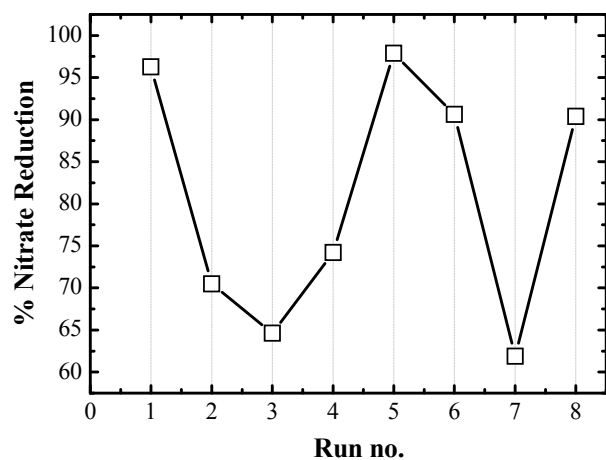
Based on Reaction (3), the electron donating capacity (EDC, mole electrons per unit mass of NZVI) is proposed for the quantitative evaluation of NZVI's reducing power of different types. The EDC can be expressed by Equations (8)-(9).

$$EDC = \frac{2 \times \text{moles of } Fe^0 \text{ reacted}}{\text{initial dosage of } Fe^0} \quad (8)$$

$$= \frac{2 \times 4 \times \text{moles of } NO_3^- \text{ removed}}{\text{initial dosage of } Fe^0} \quad (9)$$

The EDC's for NZVI synthesized under different conditions (see Table 1) were thus calculated by following Equation (9) and presented in Figure 3(b). In summary, the reducing power for different types of NZVI is in the following order: Run #5 >= 1 > 6 >= 8 > 4 > 2 > 3 > 7.

(a)



(b)

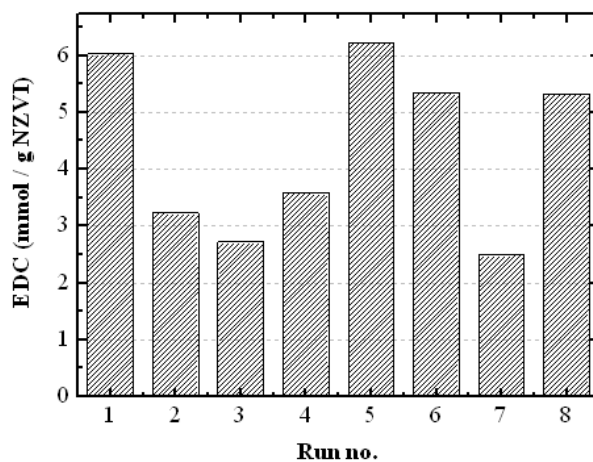


Figure 3. (a) NO_3^- reduction profile and (b) reducing capacity of NZVI synthesized under various conditions: $[\text{NO}_3^-] = 50 \text{ mg/L}$, $\text{NZVI} = 0.2 \text{ g/L}$.

3.3. Estimates of effects of interaction factors

The estimate of effect for each of the factors shown in Figure 4 is the difference between the average response of high level (+) and the average response of low level (-) of that factor in design matrix of Table 1 [25]. Note that the data for average response calculation were taken from those plotted in Figure 2(b). As shown in Figure 4(a), the negative estimate of main effect of A (pumping rate of NaBH_4) was -0.77, implying that this main factor play a negative role in regard to the reducing capacity of NZVI. For example, increasing pumping rate of NaBH_4 from 4 to 8 mL/min results in the decrease of EDC by 0.77 mmol e^-/gNZVI . On the other hand, the positive estimates of effects of main factors B (agitation speed) and C (air exposure) were 2.84 and 0.07, respectively; this indicates that these two main factors play a positive role, with the former one to a much greater degree. The effect of interaction factor was considered because of its large estimate of effect, especially in the cases of AB and AC, as

illustrated in Figure 4(a). Hence, the two-factor interaction plots is further illustrated in Figure 4(b), in terms of the EDC.

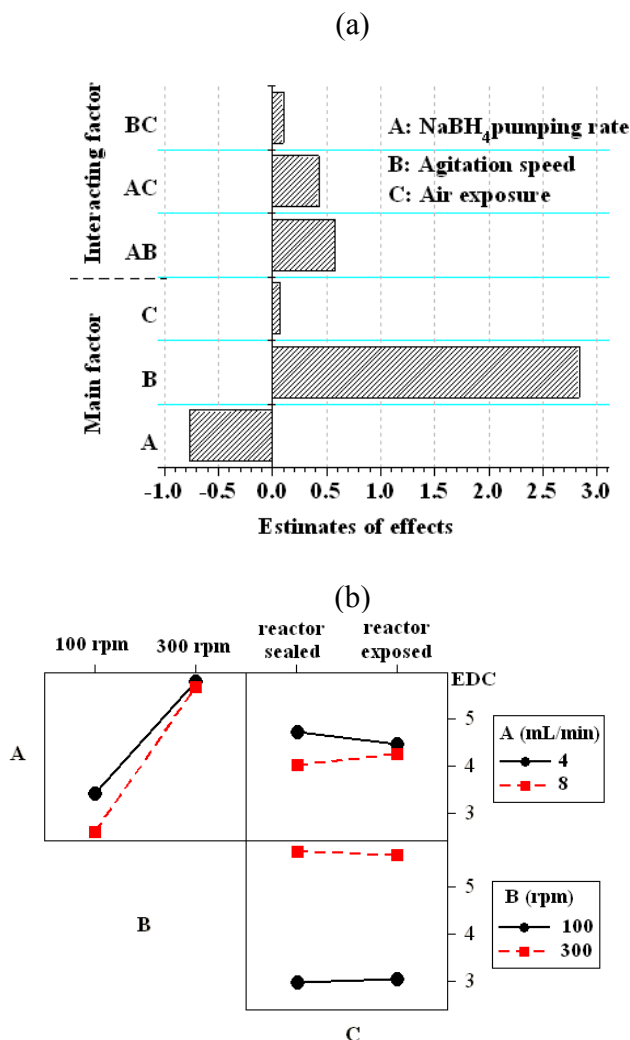


Figure 4. Identification of main effect factors and interaction factors on EDC: $[\text{NO}_3^-] = 50 \text{ mg/L}$, NZVI = 0.2 g/L .

The interaction factor AB (pumping rate of $\text{NaBH}_4 \times$ agitation speed), the EDC drops from 3.4 to 2.6 mmol e⁻/gNZVI, when the pumping rate of NaBH_4 changes from 4 to 8 mL/min and the agitation speed remains at 100 rpm. However, the pumping rate of NaBH_4 poses insignificant interaction effect on EDC, when the agitation speed is kept at 300 rpm. In the same way, when the pumping rate was fixed at either low or high level, the EDC values increased remarkably (3.4 to 5.8 mmol e⁻/gNZVI for the low one, and 2.6 to 5.7 mmol e⁻/gNZVI for the high one, with the agitation speed changing from 100 rpm to 300 rpm. Such results indicate that Factor B (agitation speed) is significant in the interaction factor AB. As for interaction factor AC (pumping rate of $\text{NaBH}_4 \times$ air exposure), for the reaction without air

exposure, the EDC values drop from 4.7 to 4.0 mmol e^- /gNZVI when the pumping rate of NaBH_4 changes from 4 to 8 mL/min. With air exposure, change of the pumping rate of NaBH_4 poses insignificant interaction effect on EDC. On the other hand, keeping the pumping rate of NaBH_4 either at high or low level, the EDC value changes slightly when the reaction condition varies from the one without air exposure to another with air exposure (4.7 to 4.5 mmol e^- /gNZVI for the low pumping rate, and 4.0 to 4.2 mmol e^- /gNZVI for the high pumping rate). In the case of interaction factor BC, the EDC remains rather unchanged whether the reaction is exposed to air or not, when keeping the agitation speed either at high or low level. But, the change of the agitation speed from high to low level results in significant drop of EDC for both conditions of without and with air exposure. Based on the above interaction analysis, among the parameters studied, the reducing power of NZVI is influenced by the following order: the agitation speed > the pumping rate of NaBH_4 > air exposure. Such results can also be observed from Figure 4(a).

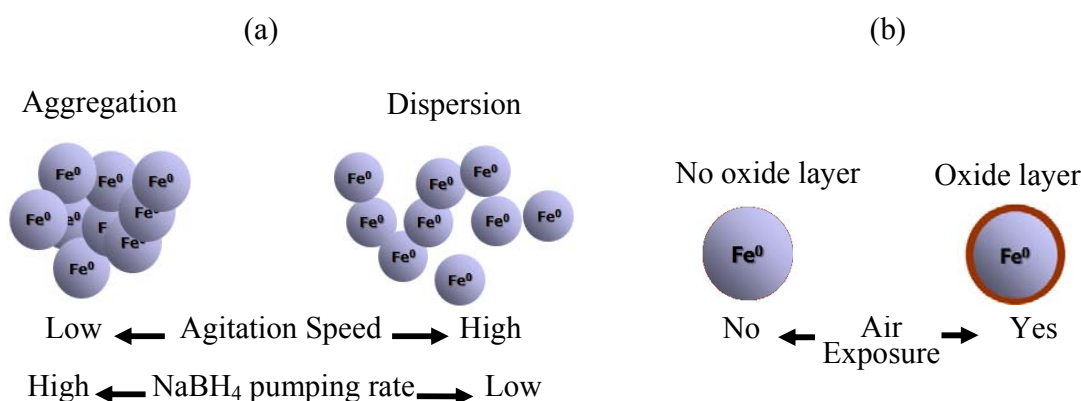


Figure 5. Conceptual behavior of NZVI synthesized under various conditions

3.3. Conceptual interpretation

Agitation speed. Two different agitating speeds, 100 and 300 rpm, were investigated in this study. The purpose was to compare the degree of NZVI particle aggregation. According to Figure 4(a), the higher the agitating speed, the higher the reducing power of NZVI particles. As may be explained in Figure 5(a), higher agitating speed results in more dispersion of NZVI particles, which in turn provides higher area contact between NZVI and nitrate.

Pumping rate of NaBH_4 . To avoid surface oxidation potential of NZVI being produced, it is preferred that the reaction can be completed as soon as possible. On top of this, it's always beneficial to save the reaction time for NZVI synthesis. Of the two feeding rates studied, 4 and 8 mL/min, lower reducing power was observed when higher feeding rate was applied. Choi et al. (2008) reported that rapid feeding of NaBH_4 causes aggregation of NZVI precipitates (Figure 5(a)), whereas slow feeding results in oxidation of NZVI produced [17].

Air Exposure. As shown in Figure 4(a), the reducing capacity of NZVI synthesized decreased when the reaction was exposed to air. This was due to that NZVI became oxidized by oxygen, which came from atmospheric air and dissolved oxygen originally contained in the solution. In the case of solution-contained vessel sealed with aluminum foil (without air exposure), this can effectively prevent atmospheric oxygen from being absorbed into the reaction solution (see Figure 5(b)). Therefore, the reducing capacity of NZVI can remain at a relatively higher level. In the presence of air, the oxygen may render the surface oxidation of produced NZVI during the synthesizing process [14]. In other words, the reducing power for the NZVI synthesized can be weakened because of the iron oxide layer blocking the electron transfer from the active sites of NZVI. As reported, non-conductive solid phases such as products of iron oxidation, Fe_2O_3 and FeOOH , can inhibit electron transfer [26]. As the oxide layer is formed on the NZVI surface, contaminant needs to transfer across the film to reach the Fe^0 surface and further undergoes its reduction reaction [27].

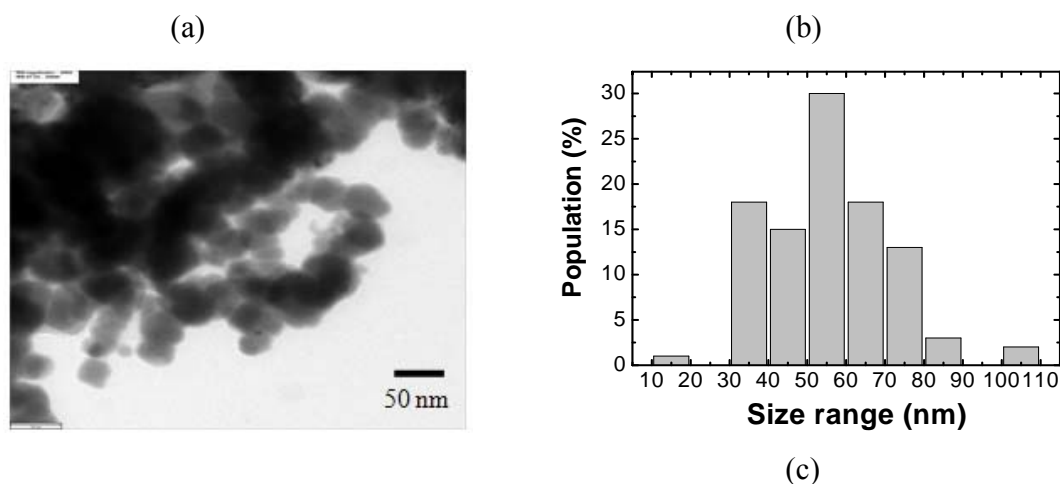


Figure 6. Characterization of NZVI synthesized under condition of Run #5: (a) TEM image, (b) particle size distribution histogram, and (c) point of zero charge.

3.4. Characterization

The NZVI synthesized under condition of Run #5, which led to the highest reducing capacity, was characterized regarding the morphology and histogram of particle size distribution (Transmission Electron Microscopy), specific surface area (Brunauer-Emmett-teller method), and the solution pH of zero point charge (denoted as pH_{pzc}). Figure 6(a) shows that morphology of NZVI has two distinct layers. The inside core represents the Fe^0 itself, while the outer layer covering the Fe^0 is iron oxide(s). In Figure 6(b), the histogram illustrates that more than 95% of the particles are smaller than 90 nm and the average of particle size was 56 nm. The NZVI was further characterized for its specific surface area and a number of $7.67 \text{ m}^2/\text{g}$ was obtained. Additionally, Figure 6(c) shows that the measured solution pH_{pzc} for the lab-synthesized NZVI fell at around 7.8.

4. Conclusions

In this study, the reducing performance of NZVI synthesized under different conditions was tested by using nitrate as a chemical probe. The results from factorial design revealed that the reducing capacity of NZVI will increase when the NZVI was synthesized under the condition of higher agitation of reaction solution (300 rpm). In addition, when the reaction solution-contained vessel was capped with aluminum foil (without air exposure), the reducing capacity for the NZVI synthesized was improved. The pumping rate of NaBH_4 shows that low pumping rate, 4 mL/min, enhance the reducing power of NZVI. Furthermore, a quantitative index, *electron donating capacity*, for evaluating NZVI's reducing power was proposed. With this index available, the chemical probe of nitrate can be adopted as a screening method for NZVI performance evaluation.

Acknowledgements

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

References

- [1] Li, X.Q., D.W. Elliott and W.X. Zhang, Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences*, 31, 111-122 (2006).
- [2] Reynolds, G.W., J.T. Hoff and R.W. Gillham, Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.*, 24, 135-142 (1990).
- [3] Mak, M.S.H., P. Rao and I.M.C. Lo, Effects of hardness and alkalinity on the removal of arsenic(V) from humic acid-deficient and humic acid-rich groundwater by zero-valent iron. *Water Research*, 43, 4296-4304 (2009).

- [4] Tyrovola, K., N.P. Nikolaidis, N. Veranis, N. Kallithrakas-Kontos and P.E. Koulouridakis, Arsenic removal from geothermal waters with zero-valent iron-Effect of temperature, phosphate and nitrate. *Water Research*, 40, 2375-2386 (2006).
- [5] Qiu, S.R., H.F. Lai, M.J. Roberson, M.L. Hunt, C. Amrhein, L.C. Giancarlo, G.W. Flynn and J.A. Yarmoff, Removal of contaminants from aqueous solution by reaction with iron surfaces. *Langmuir*, 16, 2230-2236 (2000).
- [6] Noubactep, C., Processes of contaminant removal in “Fe⁰-H₂O” systems revisited: The importance of co-precipitation. *The Open Environ. J.*, 1, 9-13 (2007).
- [7] Wang, C.B. and W. Zhang, Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environ Sci. Technol.*, 31, 2154-2156 (1997).
- [8] Lien, H.L. and W. Zhang, Transformation of chlorinated methanes by nanoscale iron particles. *J. Environ. Eng.*, 125, 1042-1047 (1999).
- [9] Kanel, S.R., B. Manning, L. Charlet and H. Choi, Removal of arsenic(III) from groundwater by nano scale zero-valent iron. *Environ. Sci. Technol.*, 39, 1291-1298 (2005).
- [10] Kanel, S.R., 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.*, 40, 2045-2050 (2006).
- [11] Joo, S.H., A.J. Feitz, D.L. Sedlak and T.D. Waite, Quantification of the oxidizing capacity of nanoparticulate zerovalent iron. *Environ. Sci. Tech.*, 39, 1263-1268 (2005).
- [12] Jegadeesan, G., K. Mondal and S.B. Lalvani, Arsenate remediation using nanosized modified zerovalent iron particles. *Environ. Progress.*, 24, 289-296 (2005).
- [13] Zhang, W.X., Nano scale iron particles for environmental remediation: an overview. *J. Nanopart. Res.*, 5, 323-332 (2003).
- [14] Ponder, S.M., J.G. Darab and T.E. Mallouk, Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environ. Sci. Technol.*, 34, 2564-2569 (2000).
- [15] Khalil, H. D. Mahajan, M. Rafailovich, M. Gelfer and K. Pandya, Synthesis of zerovalent nanophase metal particles stabilized with poly (ethylene glycol). *Langmuir*, 20, 6896-6903 (2004).
- [16] Amaraa, D., I. Felnerb, I. Nowikb and S. Margel, Synthesis and characterization of Fe and Fe₃O₄ nanoparticles by thermal decomposition of triiron dodecacarbonyl. *Colloids and Surfaces A: Phys. Eng.*, 339, 106-110 (2009).
- [17] Choi, H.C., A.B.M. Giasuddin and R. Kanel, Method of synthesizing air-stable zero-valent iron nanoparticles at room temperature and applications. US Patent 2008/0091054, A1 (2008).
- [18] Ruangchainikom, C., C.H. Liao, J. Anothai and M.T. Lee, Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and CO₂-bubbled system. *Water Research*, 40, 195-204 (2006).
- [19] Yang, G.C.C. and H.L. Lee, Chemical reduction of nitrate by nanosized iron: kinetics and Pathways. *Water Research*, 39, 884–894 (2005).
- [20] Huang, C.P., H.W. Wang and P.C. Chiu, Nitrate reduction by metallic iron. *Water Research*, 32, 2257-2264 (1998).

- [21] Choe, S., Y.Y. Chang, K.Y. Hwang and J. Khim, Kinetics of reductive denitrification by nanoscale zero-valent iron. *Chemosphere*, 41, 1307-1311 (2000).
- [22] Berthouex, P.M. and L.C. Brown, *Statistics for Environmental Engineers*, 2nd Ed., Lewis Publishers, Boca Ration, FL. (2002).
- [23] Glavee, G.N., K.J. Klabunde, C.M. Sorensen and G.C. Hadjipanayis, Chemistry of borohydride reduction of iron(II) and iron(III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders. *Inorg. Chem.*, 34, 28-35 (1995).
- [24] Weber, E.J., Iron-mediated reductive transformations: investigation of reaction mechanism. *Environ. Sci. Technol.*, 30, 716-719 (1996).
- [25] Montgomery, D.C., *Design and analysis of experiments*, 5th Ed, John Wiley, New York, (2001).
- [26] Noubactep, C., A critical review on the process of contaminant removal in Fe⁰-H₂O systems. *Environ. Tech.*, 29, 909-920 (2008).
- [27] Noubactep, C., An analysis of the evolution of reactive species in Fe⁰/H₂O systems. *J. Haz. Mat.*, 168, 1626-1631 (2009).

A NOVEL METHOD FOR QUANTIFYING REDUCING CAPACITY OF NANOIRON PARTICLES

Visanu Tanboonchuy¹, Nurak Grisdanurak^{1,2}, Chih-Hsiang Liao^{3*}

¹Department of Chemical Engineering, Faculty of Engineering,
Thammasat University, Pathumthani, THAILAND.

²National Center of Excellence for Environmental and Hazardous Waste Management,
Thammasat University, Pathumthani, THAILAND.

³Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science,
Tainan, TAIWAN.

* Corresponding author's email: chliao@mail.chna.edu.tw

Telephone no.: +886-6-266-3230

Fax no.: +886-6-366-3756

ABSTRACT

Nano zero-valent iron (NZVI) has been extensively researched for treatment of hazardous and toxic wastes. In particular, it can be applied to remediate contaminated sites directly. In this study, the NZVI was synthesized by using chemicals of NaBH₄ and FeCl₃. The conditions for NZVI synthesis were varied by such parameters as air exposure, pumping rate of NaBH₄ (4-8 mL/min), and agitation power (100-300 rpm). Right after synthesis of NZVI particles of different varieties, nitrate of 50 ppm was used to probe its reducing power quantitatively. As a result of factorial design (FD) analysis, it appears that the agitation of reaction solution plays a major role in determining its reducing power of NZVI particles. Besides, air exposure of reaction also posed noticeable decrease of the final residual nitrate, whereas the reducing capacity of NZVI synthesized was elevated with lower NaBH₄ pumping rate.

Keywords: Nanotechnology; nanoparticles; nitrate; zero-valent iron

INTRODUCTION

Zero-valent iron (ZVI) was common and often used as a remediation agent in contaminated groundwater. In early 1990's, it was applied first in permeable reactive barrier (PBR) system [1-3]. ZVI has gained increasing attention for remediation process because of its being inexpensive and nontoxic [4]. ZVI can react to transform the mobile contaminants into immobile and less harmful species, which will be treated more easily [5]. There are two major mechanisms for aqueous contaminant removal by elemental iron, including (1) physicochemical adsorption and (2) oxidation and reduction reaction [6].

Contaminants removed by ZVI include halogenated hydrocarbons such as TCE, PCE, anions (e.g. NO_3^- , $\text{Cr}_2\text{O}_7^{3-}$), heavy metal, arsenic, and organic compound [7-11]. However, the problems associated with the use of micro-scale ZVI (MZVI) are that the reaction time required is in days, and a considerable amount of iron is needed for complete removal of target compounds [10, 12]. This serves to address the need of more efficient nano-scale ZVI (NZVI) synthesis development.

Currently, the NZVI has received widespread attention from field researchers for groundwater treatment because of its extremely small particle size, large surface area, high *in situ* reactivity, and high mobility in groundwater [13]. There were many techniques and methods for NZVI synthesis such as chemical method [7, 14], sono-chemical method [15], and thermal decomposition [16]. The sono-chemical method will generate toxic by-product, CO, because this method uses $\text{Fe}(\text{CO})_5$ as a raw material [17]. As for the thermal decomposition method, the produced NZVI particles tend to aggregate, due to the loss of the stabilization ability caused by the disappearance of the initial reactant chemicals during the heating process [16].

Since the NZVI has high reactivity with oxygen and water, inappropriate conditions for synthesis may result in the decrease of reducing capacity of NZVI synthesized. Thus, the goal of this study was to investigate the effect of parameters such as air exposure, pumping rate of reagents, and agitation speed of mixing on the reducing power of NZVI particles. The NZVI was synthesized by using the chemical method because of its ease and simplicity. In addition, there's no need for complicated equipment or instrument for synthesis. In view of the best conditions for NZVI synthesis, one may characterize NZVI synthesized by specific surface area, particle size, and solution pH of zero point charge. However, all these are time and cost consuming. In this study, the produced NZVI particles were tested for their reducing potential by using nitrate (NO_3^-) as the chemical probe. Several studies reported that the final products of NO_3^- reduction by ZVI were nitrite (NO_2^-), ammonium (NH_4^+), or nitrogen (N_2), depending on the reaction conditions [18-21]. Possible reactions of NO_3^- reduction by ZVI were listed in Reactions (1)-(4).



In order to evaluate the impact of parameters for synthesis, experiments were designed by using two-level factorial design (FD). Note that the FD, widely and commonly adopted in industry, is an efficient tool for serving the purpose of this study [22]. Results from this study will illustrate the conditions for synthesizing the NZVI with the best performance. Additionally, based on the FD methodology, both individual and combined influences of parameters for synthesis on reducing capacity of NZVI were observed as well. Consequently, by using nitrate as the electron probe, this study provides an easy and simple way to characterize the reducing potential of NZVI.

MATERIALS AND METHOD

The chemicals of reagent grade used for NZVI synthesis in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), NaBH_4 (> 96%), and KNO_3 (99%), (Merck). All chemical solutions were prepared by using deionized water (18.2 M Ω Mill-Q).

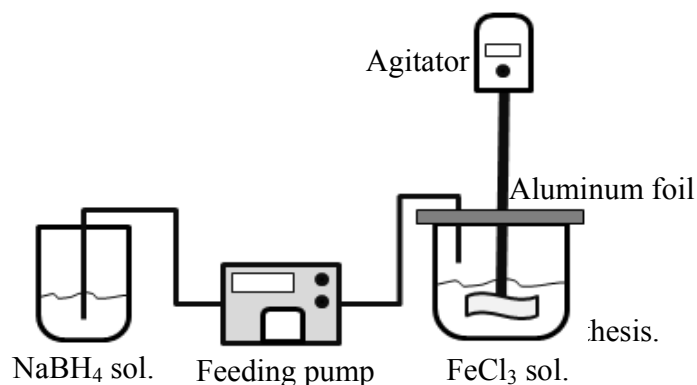
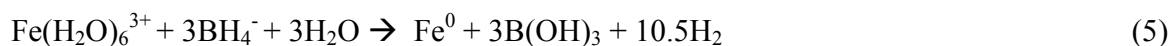


Figure 1. Schematic diagram for NZVI synthesis.

The NZVI was synthesized according to Glavee et al. (1995) [23]. 0.25 M of NaBH_4 solution was pumped into 0.045 M of FeCl_3 aqueous solution. The mixture was agitated by a revolving propeller (see Figure 1). Ferric iron is reduced by the borohydride, according to Reaction (5):



After solution was well mixed, the NZVI was separated from liquid solution by a magnet. The NZVI synthesized was applied immediately for its reducing power test using NO_3^- as a chemical probe. The test was carried out with probe concentration of 50 mg/L and NZVI dosage of 0.2 g/L. Among the reaction products of nitrate, the NH_4^+ was analyzed using the Phenate method through the spectrophotometric reading (SHIMADZU, UV-1201, Japan) with light absorption at 640 nm; the residual NO_3^- and NO_2^- were analyzed by using Ion Chromatography (DINNEX-120, USA).

Two-level FD was employed to evaluate the impact of parameters on the reducing capacity of NZVI synthesized in this study. A full factorial design involves runs of 2^k different experimental conditions, which represent all combinations of the k factors at high and low levels [22]. Note that the “ k ” is independent variables investigated. In this study, three factors were investigated for their effects on NZVI synthesis, including pumping rate of NaBH_4 , agitation speed, and air exposure. Thus, the total experiments to be performed will be 8 runs ($=2^3$). The design matrix for experiment is depicted in Table 1.

Table 1. Design matrix of the 2^3 FD

Run no.	Factors and codes		
	Pumping rate of NaBH ₄	Agitation speed	Air exposure
	A	B	C
1	+	+	-
2	-	-	+
3	+	-	+
4	-	-	-
5	-	+	+
6	-	+	-
7	+	-	-
8	+	+	+

Note: (1) The plus (+) and minus (-) signs indicate the high and low level of the factors, respectively. (2) The test levels (low, high) of codes A through C are as follows: A(4, 8) in mL/min, B(100, 300) in rpm, and C(Yes, No).

RESULTS AND DISCUSSION

Mass balance profile

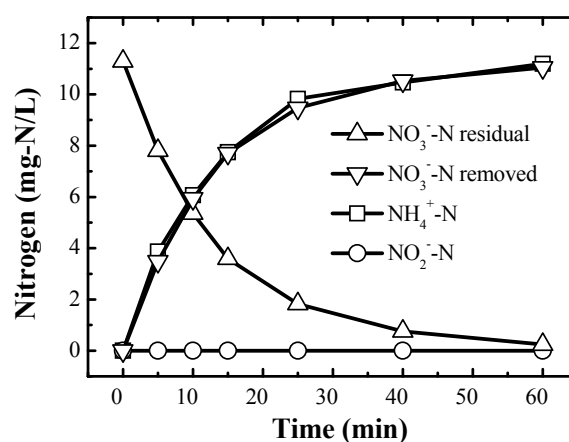


Figure 2. Mass balance profile for the NO₃⁻ reduction by NZVI synthesized under condition of Run #5.

In the system of Fe⁰/NO₃⁻, the reduction reaction involves electron release from surface of NZVI, dissolved Fe²⁺ or H₂. Note that the latter two are the derived products from iron oxidation (see Reactions (6)-(7)), the reduction potential of which is generally very slow [24]. At any rate, the NO₃⁻ was reductively degraded by the electrons originated from the NZVI.



According to Figure 2, the mass balance profiles seem to indicate that the NZVI synthesized under condition of Run #5 was capable of reducing nitrate into end products NH_4^+ only, no other species formed in the reaction. Thus, Reaction (3) mentioned earlier was used to address reduction capacity of NZVI synthesized in this study.

Electron donating capacity (EDC) of NZVI

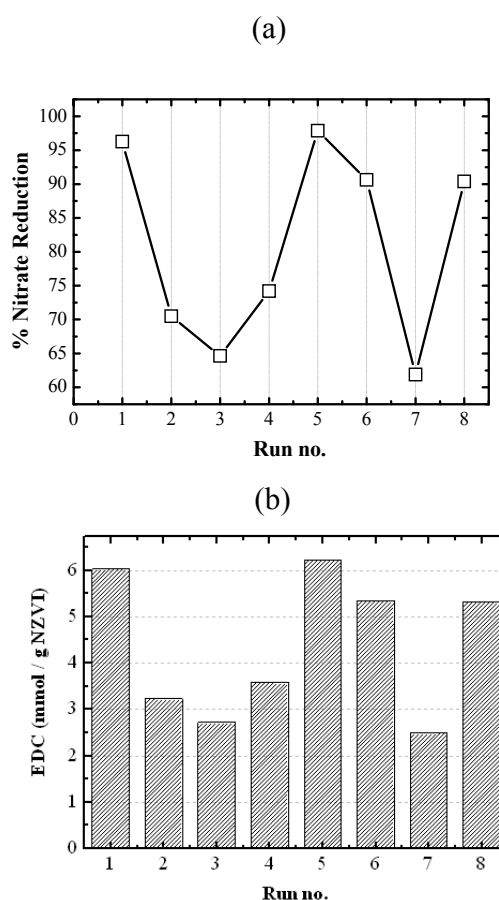


Figure 3. (a) NO_3^- reduction profile and (b) reducing capacity of NZVI synthesized under various conditions: $[\text{NO}_3^-] = 50 \text{ mg/L}$, $\text{NZVI} = 0.2 \text{ g/L}$.

The profiles of NO_3^- reduction by NZVI under various conditions were shown in Figure 3(a). It appears that higher nitrate removal was found in Run #5, with the level of (-), (+), and (+) for A, B, and C, respectively. In contrast, Run #7, which involves A(+), B(-) and C(-), give lower efficiency of NO_3^-

reduction. Thus, it is possible that the condition of low pumping rate of NaBH₄, high agitation speed and no air exposure is favorable for increasing reducing capacity of the NZVI synthesized.

Based on Reaction (3), the electron donating capacity (EDC, mole electrons per unit mass of NZVI) is proposed for the quantitative evaluation of NZVI's reducing power of different types. The EDC can be expressed by Equations (8)-(9).

$$EDC = \frac{2 \times \text{moles of } Fe^0 \text{ reacted}}{\text{initial dosage of } Fe^0} \quad (8)$$

$$= \frac{2 \times 4 \times \text{moles of } NO_3^- \text{ removed}}{\text{initial dosage of } Fe^0} \quad (9)$$

The EDC's for NZVI synthesized under different conditions (see Table 1) were thus calculated by following Equation (9) and presented in Figure 3(b). In summary, the reducing power for different types of NZVI is in the following order: Run #5 >= 1 > 6 >= 8 > 4 > 2 > 3 > 7.

Estimates of effects of interaction factors

The estimate of effect for each of the factors shown in Figure 4 is the difference between the average response of high level (+) and the average response of low level (-) of that factor in design matrix of Table 1 [25]. Note that the data for average response calculation were taken from those plotted in Figure 2(b). As shown in Figure 4(a), the negative estimate of main effect of A (pumping rate of NaBH₄) was -0.77, implying that this main factor play a negative role in regard to the reducing capacity of NZVI. For example, increasing pumping rate of NaBH₄ from 4 to 8 mL/min results in the decrease of EDC by 0.77 mmol e⁻/gNZVI. On the other hand, the positive estimates of effects of main factors B (agitation speed) and C (air exposure) were 2.84 and 0.07, respectively; this indicates that these two main factors play a positive role, with the former one to a much greater degree. The effect of interaction factor was considered because of its large estimate of effect, especially in the cases of AB and AC, as illustrated in Figure 4(a). Hence, the two-factor interaction plots is further illustrated in Figure 4(b), in terms of the EDC.

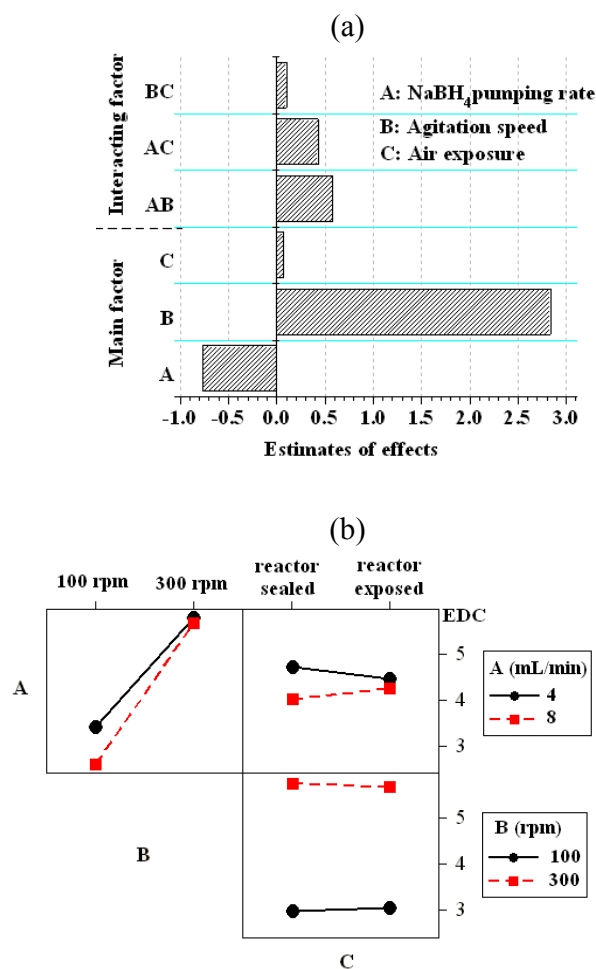


Figure 4. Identification of main effect factors and interaction factors on EDC: $[\text{NO}_3^-] = 50 \text{ mg/L}$, $\text{NZVI} = 0.2 \text{ g/L}$.

The interaction factor AB (pumping rate of $\text{NaBH}_4 \times$ agitation speed), the EDC drops from 3.4 to 2.6 mmol e⁻/gNZVI, when the pumping rate of NaBH_4 changes from 4 to 8 mL/min and the agitation speed remains at 100 rpm. However, the pumping rate of NaBH_4 poses insignificant interaction effect on EDC, when the agitation speed is kept at 300 rpm. In the same way, when the pumping rate was fixed at either low or high level, the EDC values increased remarkably (3.4 to 5.8 mmol e⁻/gNZVI for the low one, and 2.6 to 5.7 mmol e⁻/gNZVI for the high one, with the agitation speed changing from 100 rpm to 300 rpm). Such results indicate that Factor B (agitation speed) is significant in the interaction factor AB. As for interaction factor AC (pumping rate of $\text{NaBH}_4 \times$ air exposure), for the reaction without air exposure, the EDC values drop from 4.7 to 4.0 mmol e⁻/gNZVI when the pumping rate of NaBH_4 changes from 4 to 8 mL/min. With air exposure, change of the pumping rate of NaBH_4 poses insignificant interaction effect on EDC. On the other hand, keeping the pumping rate of NaBH_4 either at high or low level, the EDC value changes slightly when the reaction condition varies from the one without air exposure to another with air exposure (4.7 to 4.5 mmol e⁻/gNZVI for the low pumping rate,

and 4.0 to 4.2 mmol e^- /gNZVI for the high pumping rate). In the case of interaction factor BC, the EDC remains rather unchanged whether the reaction is exposed to air or not, when keeping the agitation speed either at high or low level. But, the change of the agitation speed from high to low level results in significant drop of EDC for both conditions of without and with air exposure. Based on the above interaction analysis, among the parameters studied, the reducing power of NZVI is influenced by the following order: the agitation speed > the pumping rate of NaBH_4 > air exposure. Such results can also be observed from Figure 4(a).

Conceptual interpretation

Agitation speed. Two different agitating speeds, 100 and 300 rpm, were investigated in this study. The purpose was to compare the degree of NZVI particle aggregation. According to Figure 4(a), the higher the agitating speed, the higher the reducing power of NZVI particles. As may be explained in Figure 5(a), higher agitating speed results in more dispersion of NZVI particles, which in turn provides higher area contact between NZVI and nitrate.

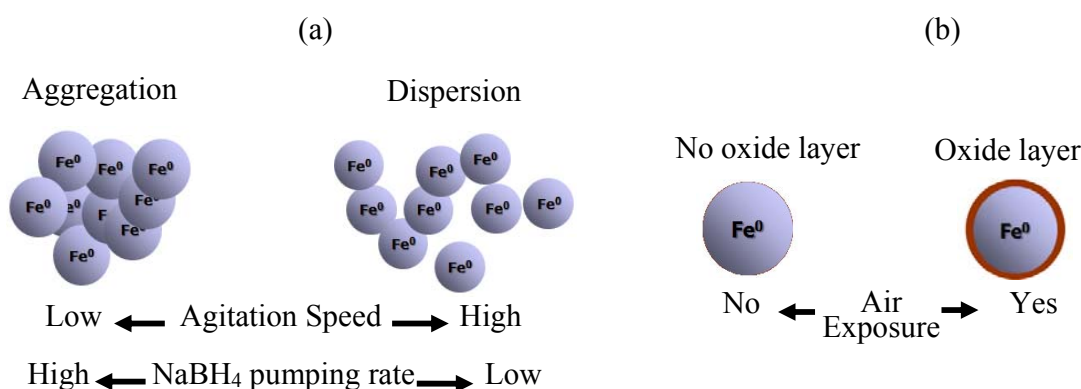


Figure 5. Conceptual behavior of NZVI synthesized under various conditions

Pumping rate of NaBH_4 . To avoid surface oxidation potential of NZVI being produced, it is preferred that the reaction can be completed as soon as possible. On top of this, it's always beneficial to save the reaction time for NZVI synthesis. Of the two feeding rates studied, 4 and 8 mL/min, lower reducing power was observed when higher feeding rate was applied. Choi et al. (2008) reported that rapid feeding of NaBH_4 causes aggregation of NZVI precipitates (Figure 5(a)), whereas slow feeding results in oxidation of NZVI produced [17].

Air Exposure. As shown in Figure 4(a), the reducing capacity of NZVI synthesized decreased when the reaction was exposed to air. This was due to that NZVI became oxidized by oxygen, which came from atmospheric air and dissolved oxygen originally contained in the solution. In the case of solution-contained vessel sealed with aluminum foil (without air exposure), this can effectively prevent atmospheric oxygen from being absorbed into the reaction solution (see Figure 5(b)). Therefore, the

reducing capacity of NZVI can remain at a relatively higher level. In the presence of air, the oxygen may render the surface oxidation of produced NZVI during the synthesizing process [14]. In other words, the reducing power for the NZVI synthesized can be weakened because of the iron oxide layer blocking the electron transfer from the active sites of NZVI. As reported, non-conductive solid phases such as products of iron oxidation, Fe_2O_3 and FeOOH , can inhibit electron transfer [26]. As the oxide layer is formed on the NZVI surface, contaminant needs to transfer across the film to reach the Fe^0 surface and further undergoes its reduction reaction [27].

CONCLUSIONS

In this study, the reducing performance of NZVI synthesized under different conditions was tested by using nitrate as a chemical probe. The results from factorial design revealed that the reducing capacity of NZVI will increase when the NZVI was synthesized under the condition of higher agitation of reaction solution (300 rpm). In addition, when the reaction solution-contained vessel was capped with aluminum foil (without air exposure), the reducing capacity for the NZVI synthesized was improved. The pumping rate of NaBH_4 shows that low pumping rate, 4 mL/min, enhance the reducing power of NZVI. Furthermore, a quantitative index, *electron donating capacity*, for evaluating NZVI's reducing power was proposed. With this index available, the chemical probe of nitrate can be adopted as a screening method for NZVI performance evaluation.

ACKNOWLEDGEMENTS

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

REFERENCES

- [1] Li, X.Q., Elliott, D.W., and Zhang, W.X. (2006). Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. *Critical Reviews in Solid State and Mat. Sci.* 31: pp 111-122.
- [2] Reynolds, G.W., Hoff, J.T., and Gillham, R.W. (1990). Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.* 24: pp 135-142.
- [3] Mak, M.S.H., Rao, P., and Lo, I.M.C. (2009). Effects of hardness and alkalinity on the removal of arsenic(V) from humic acid-deficient and humic acid-rich groundwater by zero-valent iron. *Water Res.* 43: pp 4296-4304.
- [4] Tyrovola, K., Nikolaidis, N.P., Veranis, Kallithrakas-Kontos, N., and Koulouridakis, (2006). P.E. Arsenic removal from geothermal waters with zero-valent iron-Effect of temperature, phosphate and nitrate. *Water Res.* 40: pp 2375-2386.
- [5] Qiu, S.R., Lai, H.F., Roberson, M.J., Hunt, M.L., Amrhein, C., Giancarlo, L.C., Flynn, G.W., Yarmoff, J.A. (2000). Removal of contaminants from aqueous solution by reaction with iron surfaces. *Langmuir* 16: pp 2230-2236.

- [6] Noubactep, C. (2007). Processes of contaminant removal in “Fe⁰-H₂O” systems revisited: The importance of co-precipitation. *The Open Environ. J.* 1: pp9-13.
- [7] Wang, C.B., and Zhang, W. (1997). Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environ Sci. Technol.* 31: pp 2154-2156.
- [8] Lien, H.L. and Zhang, W. (1999). Transformation of chlorinated methanes by nanoscale iron particles. *J. Environ. Eng.* 125: pp 1042-1047.
- [9] Kanel, S.R., Manning, B., Charlet, L., and Choi, H. (2005). Removal of arsenic(III) from groundwater by nano scale zero-valent iron. *Environ. Sci. Technol.* 39: pp1291-1298.
- [10] Kanel, S.R., Greneche, J.M., and Choi, H. (2006). Arsenic(V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. *Environ. Sci. Technol.* 40: pp 2045-2050.
- [11] Joo, S.H., Feitz, A.J., Sedlak, D.L., and Waite, T.D. (2005). Quantification of the oxidizing capacity of nanoparticulate zerovalent iron. *Environ. Sci. Tech.* 39: pp 1263-1268.
- [12] Jegadeesan, G., Mondal, K., and Lalvani, S.B. (2005). Arsenate remediation using nanosized modified zerovalent iron particles. *Environ. Progress.* 24: pp 289-296.
- [13] Zhang, W.X. (2003). Nano scale iron particles for environmental remediation: an overview. *J. Nanopart. Res.* 5: pp 323-332.
- [14] Ponder, S.M., Darab, J.G., and Mallouk, T.E. (2000). Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environ. Sci. Technol.* 34: pp 2564-2569.
- [15] Khalil, H., Mahajan, D., Rafailovich, M., Gelfer, M., and Pandya, K. (2004). Synthesis of zerovalent nanophase metal particles stabilized with poly (ethylene glycol). *Langmuir* 20: pp 6896-6903.
- [16] Amaraa, D., Felnerb, I., Nowikb, I., and Margel, S. (2009). Synthesis and characterization of Fe and Fe₃O₄ nanoparticles by thermal decomposition of triiron dodecacarbonyl. *Colloids and Surfaces A: Phys. Eng.* 339: pp 106-110.
- [17] Choi, H.C., Giasuddin, A.B.M., and Kanel, R. (2008). Method of synthesizing air-stable zero-valent iron nanoparticles at room temperature and applications. US Patent 2008/0091054, A1.
- [18] Ruangchainikom, C., Liao, C.H., Anothai, J., and Lee, M.T. (2006). Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and CO₂-bubbled system. *Water Res.* 40: pp 195-204.
- [19] Yang, G.C.C., and Lee, H.L. (2005). Chemical reduction of nitrate by nanosized iron: kinetics and Pathways. *Water Res.* 39: pp 884–894.
- [20] Huang, C.P., Wang, H.W., and Chiu, P.C. (1998). Nitrate reduction by metallic iron. *Water Res.* 32: pp 2257-2264.
- [21] Choe, S., Chang, Y.Y., Hwang, K.Y. and Khim, J. (2000). Kinetics of reductive denitrification by nanoscale zero-valent iron. *Chemosphere* 41: pp 1307-1311.
- [22] Berthouex, P.M., and Brown, L.C. (2002). Statistics for Environmental Engineers, Second ed., Lewis Publishers, Boca Ration, FL.

- [23] Glavee, G.N., Klabunde, K.J., Sorensen, C.M., and Hadjipanayis, G.C. (1995). Chemistry of borohydride reduction of iron(II) and iron(III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders. *Inorg. Chem.* 34: pp 28-35.
- [24] Weber, E.J. (1996). Iron-mediated reductive transformations: investigation of reaction mechanism. *Environ. Sci. Technol.* 30: pp716-719.
- [25] Montgomery, D.C. (2001). Design and analysis of experiments, fifth ed, John Wiley, New York.
- [26] Noubactep, C. (2008). A critical review on the process of contaminant removal in Fe⁰-H₂O systems. *Environ. Tech.* 29: pp 909-920.
- [27] Noubactep, C. (2009). An analysis of the evolution of reactive species in Fe⁰/H₂O systems. *J. Haz. Mat.* 168: pp 1626-1631.

Arsenic Removal by Nanoiron in the Gas-bubbled Aqueous Solution

Visanu Tanboonchuy
Department of Chemical Engineering
Thammasat University
Pathumthani, THAILAND

Chih-Hsiang Liao*
Department of Environmental Resources Management
Chia Nan University of Pharmacy and Science
Tainan, TAIWAN.
chliao@mail.chna.edu.tw

Nurak Grisdanurak
Department of Chemical Engineering
National Center of Excellence for Environmental and Hazardous Waste Management
Thammasat University
Pathumthani, THAILAND

Abstract - Nano-scale zero-valent iron (NZVI) was used for the removal of both As(III) and As(V) in aqueous solution. Firstly, batch experiments were conducted to investigate the effects of initial pH and dissolved oxygen (DO). Arsenic removal rates were found higher in the system with lower initial pH and higher DO. Secondly, the gas bubbling of solution was the focus to improve arsenic removal by NZVI. The CO₂ bubbling resulted in not only acidification of solution but also stripping of DO; consequently, the arsenic removal was observed to decrease significantly. Thus, with the gas bubbling scenario of pretreatment of CO₂ and the subsequent air bubbling, it was demonstrated that the As(V) was removed remarkably, and the As(III) to a lesser degree.

Keywords: *Arsenic; arsenate; nanoscale iron; gas bubbling*

I. INTRODUCTION

The contamination of arsenic in groundwater has become an issue of worldwide concern because of its toxicity and health hazards. Arsenic exists in natural waters mostly in the forms of arsenite (As(III)) and arsenate (As(V)) in reducing and oxidizing environments, respectively [1]. Arsenic is typically associated with iron oxide under oxic condition, and pyrite minerals under anoxic one [2]. Arsenic may be released to the environment from natural sources (e.g., the oxidative weathering and geochemical reaction) as well as from anthropogenic activities (e.g., industrial waste discharge containing arsenic, mining, and arsenical pesticides) [3-5]. Consuming water with high level of arsenic will cause skin, lung, bladder, kidney cancer and black foot diseases [1]. As was reported, the countries affected by high arsenic concentration in groundwater include Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [6, 7]. To mitigate health impact by arsenic, the standard of maximum contamination level of arsenic in drinking water was set at 10 $\mu\text{g/L}$, according to USEPA [8].

There are many technologies for removing arsenic from groundwater such as precipitation, coagulation and filtration, reverse osmosis, electrodialysis, and ion exchange [9], but these are only effective for As(V), and require a preoxidation step for As(III) removal [10]. Thus, the adsorption process of zero-valent iron (ZVI) is a promising alternative for arsenic removal because this adsorptive media can remove both As(V) and As(III) simultaneously, without the need of pre-oxidation [11], and such a process does not require the use of additional chemical reagent. The ZVI was first used for arsenic removal by Lackovic et al. (2000) [10]; they reported that the ZVI has a high capacity for arsenic remediation, both As(III) and As(V). Afterwards, there were many other researchers reporting arsenic removal by the ZVI. Bang et al. (2005) [12] used iron filings for arsenic removal in a batch system, with iron filings pretreated by acid to remove the oxide layer on the iron surface. They revealed that the removal rate of As(V) under oxic condition was faster than under anoxic condition and the removal rate was higher at pH 4 than at pH 7. Sun et al. (2006) [11] performed experiments by using packed column of iron chippings. Their results show that As(III) was removed more rapidly than As(V) under deoxygenated condition, but the reverse phenomenon was observed under oxic condition. Melitas et al. (2002) [8] reported the effectiveness of packed column of iron fillings for As(V) removal. They concluded that the performance of As(V) removal was dependent on the adsorptive sites of iron oxide generated from reaction, and on the ability of As(V) reaching to those adsorptive sites. However, the problem associated with the use of ZVI is that the reaction time required for the complete removal of arsenic is in days [13]. However, based on the method of nano-scale ZVI (NZVI) synthesis developed by Lehigh university research group in 1995 [14], Kanel et al. (2005) investigated the As(III) and As(V) removal by NZVI [15, 16] and they found that the arsenic was rapidly removed in minutes, and a pseudo-first order reaction was observed.

Based on the above, it appears that the arsenic can be better removed under acidic condition than under base condition. However, to adjust solution pH by using acidic species results in undesirable species, which will affect the treated water quality. According to the study earlier [17], the above issue

of concern can be resolved by CO₂ bubbling, which can adjust the solution pH to acidic condition due to the hydrogen ions generated from carbonated water, as described in Reactions (1)-(4):



In addition, it was reported that high amount of NZVI was required for arsenic removal in field groundwater [16], due to the competition between arsenic species and the background species of groundwater, or due to the inadequate amount of dissolved oxygen (DO) required for iron oxidation to enhance the process performance. With such understanding in mind, the air bubbling was employed and tested in the studied process. Thus, this paper focuses on the effect of gases bubbling on the arsenic removal rate by the NZVI, including CO₂ and air. In addition, characterization of the NZVI behavior in solution was also performed for the treatment system design purpose.

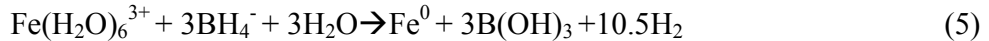
II. MATERIALS AND METHOD

A. Materials

The chemicals of reagent grade used in this study include FeCl₃·6H₂O (99%, Merck), and NaBH₄ (> 96%; Merck). Both the As(III) and As(V) stock solution were prepared from NaAsO₂ (Fluka) and Na₂HAsO₄·7H₂O (J.T. Baker), respectively. The H₂SO₄ and NaOH were used for adjusting the initial solution pH. All chemical solutions were prepared with deionized water (18.2 MΩ Mill-Q). Gases of CO₂ (99.5%), Air (O₂ 21%, N₂ 79%), and N₂ (99.99%) used in this study were purchased from a local supplier (Tainan, Taiwan).

B. NZVI synthesis

The NZVI was synthesized according to Glavee et al. (1995) [14]. A liquid volume of 40 mL of 0.25 M NaBH₄ were added into 40 mL of 0.045 M FeCl₃ aqueous solution to form nanoiron particles. The mixture was agitated by a revolving propeller. The reaction for NZVI formation is shown in Reaction (5).



The NZVI particles formed were separated from the liquid solution using a magnet. Immediately, it was then used in the treatment system.

C. Reaction system

The NZVI was used in the arsenic treatment system right after it was synthesized. A dosage of 0.023 g/L of NZVI was applied throughout all experiments. As described in earlier study [18], the reactor with liquid volume of 4.4 L was designed to combine the two chambers for both reactants reaction and particles settling in one unit. The external-circulating pump was installed at outlet of the reactor to form a recirculation mode for arsenic removal (see Figure 1). The solution pH was measured by pH meter (Suntex TS1), while the DO was measured by DO meter (Oxi 330i). The total arsenic, (As(V) and As(III)), was determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series (Thermo Scientific, USA).

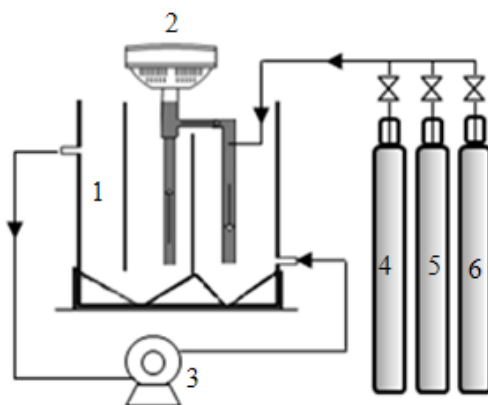


Figure 1. Experimental setup for arsenate treatment: 1. Reactor; 2. Internal recirculated pump; 3. External recirculated pump; 4. CO₂ tank; 5. Air tank; 6. N₂ tank

D. Batch experiments

The initial arsenic concentration applied was 1000 µg/L for all experiments studied, while the initial solution pH's were 4.0, 7.0 and 9.0. To reveal the role of DO in the reaction solution, experiments were designed to explore arsenic removal under deoxygenated and oxygenated conditions. Prior to reaction, the solution was bubbled with N₂ gas for 30 min to strip out dissolved oxygen from the solution until the DO level was less than 0.5 mg/L, a deoxygenated condition.

In the part of gas bubbling, several sets of experiments were designed to optimize the process performance for arsenic removal. Three various gas-bubbled scenarios were proposed and tested. The details were further explained in Table 1. In Scenario 1, the initial solution pH was controlled within neutral range, and the system was then treated by continuous CO₂ bubbling to create a favorable acidic condition. In Scenario 2, the solution was initially acidified by CO₂ bubbling, and then followed by its treatment without any gas bubbling. In Scenario 3, the solution was bubbled in sequence by CO₂ gas and by air to create a low pH and high DO condition, and it was then treated by continuous air aeration.

TABLE I. GAS BUBBLING SCENARIOS IN THE ARSENIC TREATMENT SYSTEM

Scenario	Pre-treatment	Treatment
1	pH adjusted to 7 by H ₂ SO ₄ or NaOH	CO ₂ gas bubbling at 300 mL/min
2	pH adjusted to around 4 by CO ₂ bubbling of 300 mL/min for 30 min	No gas bubbling
3	pH adjusted to around 4 by CO ₂ bubbling of 300 mL/min for 5 min; oxygen supply by air bubbling of 300 mL/min for 10 min	Air bubbling of 300 mL/min

III. RESULTS AND DISCUSSION

A. Effect of initial pH and DO

As shown in Figure 2, the removal performance of arsenic was highly influenced by the initial pH: the arsenic was removed more under acidic condition than under base condition. Such phenomenon can be elucidated from speciation of arsenic in solution. Arsenic exists in solution by different forms, depending on the pH condition. According to the available literature data, the pH of zero point charge (pH_{pzc}) for iron oxides was 8.0 [19]. Also, the pK_a values reported for As(III) are listed as follows: pK₁ = 9.22, pK₂ = 12.13, and pK₃ = 12.7; as for the As(V), they are: pK₁ = 2.2, pK₂ = 6.97, and pK₃ = 11.53 [20]. In the range of pH 2-7, the dominant form of As(V) is H₂AsO₄⁻, whereas the adsorbent surface shows a positive charge. The opposite charges of the ion and the adsorbent surface led to the enhancement of the arsenic removal through electrostatic attraction force. For the basic pH condition (7-12), the dominant form of As(V) is HAsO₄²⁻, whereas the adsorbent surface became negatively charged. Thus the electrostatic repulsion force resulted in the decrease of As(V) adsorption. Similarly, under conditions of pH 4-7, the dominant form for As(III) is H₃AsO₃ which is with the form of neutral charge. Still this can result in attraction with the positively charged adsorbent, however, with a lesser degree of attraction tendency. However, for the basic pH condition, the dominant forms of As(III) are with the negative charges, H₂AsO₃⁻ and HAsO₃²⁻, while the adsorbent surface is also negatively charged. Therefore, the As(III) removal decreased.

Concerning the effect of DO on arsenic removal, Figure 2 shows that arsenic removal was enhanced in the presence of oxygen because arsenic can form inner- and/or outer-sphere complexes with the oxygen-induced iron corrosion products such as iron (hydr)oxides, according to several recent

spectroscopic studies [21-24]. In other words, the presence of DO promotes the rate of iron corrosion, and indirectly improves the arsenic adsorption as well.

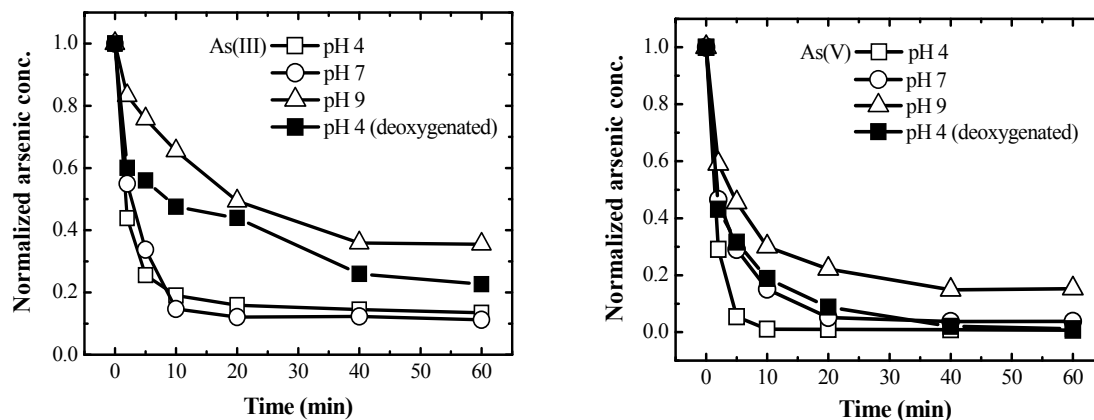


Figure 2. Effect of initial solution pH and DO on As(III) and As(V) removal: NZVI dosage = 0.023 g/L, initial As concentration = 1000 µg/L.

B. Effect of gas bubbling

For Scenario 1, as shown in Figure 3, the arsenic concentrations of both As(III) and As(V) decreased for the first 5 min and then increased gradually. As can be seen from the two DO profiles, because of the DO consumed by NZVI and stripped out by CO₂ gas bubbling, the DO level decreased rapidly in the initial period of reaction, and after 5 min, the system became anoxic condition. In addition, the supply of CO₂ gas can result in the increase of bicarbonate (HCO₃⁻) species. As reported in the literature, the release of arsenic from sandstone aquifer was found to be strongly and positively related to the HCO₃⁻ concentration in the leaching solution [25]. Another report describes that the HCO₃⁻ can promote iron dissolution from hematite (α-Fe₂O₃) surface [26], leading to the increase of the dissolved arsenic in solution. The evidence of this study exists in the DO profiles of the later reaction period, which show a gradual increase with the increasing arsenic concentration due to the oxygen release from dissolution reaction of arsenic-adsorbed iron oxides.

As was concluded from the previous results of this study, the initial pH is an important parameter to affect the performance of arsenic removal. Thus, Scenario 2 was designed to create acidic environment through bubbling of CO₂ gas. According to Figure 3, the percentage of equilibrium concentration was around 50% of the initial arsenic concentration for As(III), and it was around 40% for As(V). If compared to the two arsenic profiles of solution pH 4 in Figure 2, where the pH was adjusted by H₂SO₄, Scenario 2 shows a lower performance of arsenic removal. The key reason behind such difference was its lack of dissolved oxygen, due to the stripping by CO₂ gas bubbling. As can be seen from Figure 3, the initial DO (1-2 mg/L) was low for Scenario 2, after CO₂ bubbling. A low DO level will slow the rate of iron oxidation, resulting in the decrease of arsenic removal.

Based on the above results, Scenario 3 was further proposed to verify the most favorable condition for arsenic removal, i.e., lower pH and higher DO condition. As shown in Figure 3, the pH and DO

profiles for Scenario 3 demonstrate that both acidic environment and high initial DO has been obtained. In addition, the removal efficiency of As(V) was higher than that of As(III). The As(III) concentration decreased gradually over the later reaction period, with the final concentration around 20% of the initial arsenic concentration, whereas the As(V) was rapidly removed and reached to its equilibrium concentration at 10 min. Such results indicate that Scenario 3 is recommended to achieve a satisfactory removal of As(V), without addition of any acidic species. On the other hand, it will take much more reaction time to remove As(III) to achieve the same degree of removal as As(V). Preoxidation of As(III) can be considered when Scenario 3 is applied.

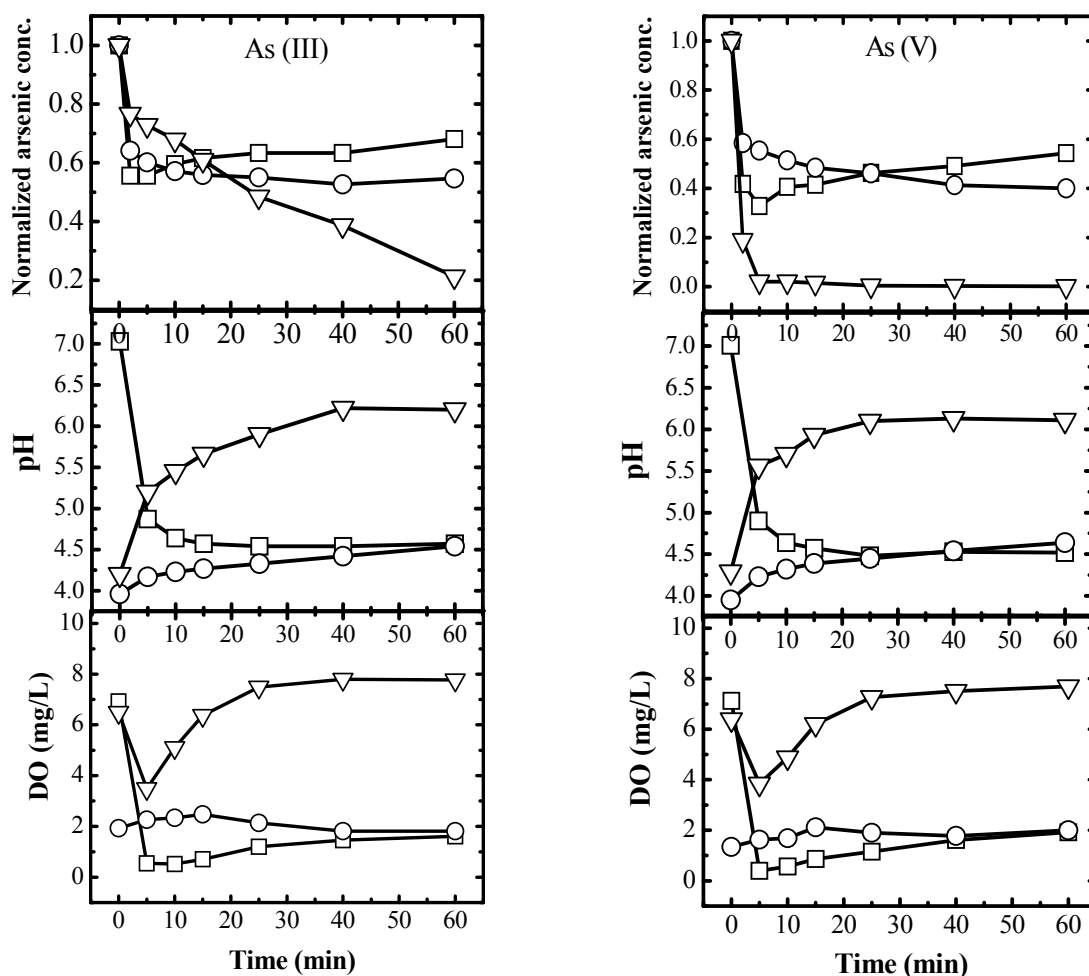


Figure 3. Behavior of As(III) and As(V) removal by NZVI under various gas-bubbling conditions: Scenario 1(-□-), Scenario 2(-○-), Scenario 3 (- △ -); arsenic concentration = 1000 ppb; NZVI dosage = 0.023 g/L.

IV. CONCLUSIONS

This study was conducted to investigate performance of NZVI in removing arsenic from aqueous solutions. Different parameters such as initial solution pH and DO were studied for their effects on arsenic removal. It was observed that arsenic can be removed favorably under acid condition and high DO level. To avoid the use of acidic species, which may deteriorate the water quality, different gas bubbling scenarios were investigated. Consequently, pretreatment by CO₂ and air bubbling in sequence is recommended for satisfactory performance of As(V) removal. The advantage of CO₂ bubbling is to create favorable acidic environment for arsenate removal, without sacrificing the treated water quality. As for air bubbling, it will help generate iron corrosion products such as iron (hydr)oxides, providing reactive sites for arsenic adsorption. To remove As(III) by following the gas bubbling scenario proposed in this study, a preoxidation process needs to be considered to achieve a desired performance of its removal.

ACKNOWLEDGEMENTS

This research was sponsored by Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

REFERENCES

- [1] D. Mohan, and C.U. Pittman Jr., "Arsenic removal from water/wastewater using adsorbents - A critical review," *J. Hazard. Mater.*, vol. 142, pp. 1-53, 2007.
- [2] X. Meng, G.P. Korfiatis, S. Bang, and K.W. Bang, "Combined effects of anions on arsenic removal by iron hydroxides," *Toxicology Letters*, vol. 133, pp. 103-111, 2002.
- [3] K. Banerjee, G.L. Amy, M. Prevost, S. Nour, M. Jekel, P.M. Gallagher, and C.D. Blumenschein, "Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH)," *Water Res.*, vol. 42, pp. 3371-3378, 2008.
- [4] J. Farrell, J. Wang, P. O'Day, and M. Conklin, "Electrochemical and spectroscopic study of arsenate removal from water using zero-valent iron media," *Environ. Sci. Technol.*, vol. 35, pp. 2026-2032, 2001.
- [5] P.E. Mariner, F.J. Holzmer, R.E. Jackson, and H.W. Meinardus, "Effects of high pH on arsenic mobility in a shallow sandy aquifer and on aquifer permeability along the adjacent shoreline, commencement bay superfund site, Tacoma, Washington," *Environ. Sci. Technol.*, vol. 30, pp. 1645-1651, 1996.
- [6] B.K. Mandal, and K.T. Suzuki, "Arsenic round the world: a review," *Talanta*, vol. 58, pp. 201-235, 2002.
- [7] S.L. Chen, S.R. Dzung, M.H. Yang, K.H. Chiu, G.M. Shieh, and C.M. Wai, "Arsenic species in groundwaters of the blackfoot disease area, Taiwan," *Environ. Sci. Technol.*, vol. 28, pp. 877-881, 1994.

- [8] N. Melitas, J. Wang, M. Conklin, P. O'Day, and J. Farrell, "Understanding soluble arsenate removal kinetics by zero-valent iron media," *Environ. Sci. Technol.*, vol. 36, pp. 2074-2081, 2002.
- [9] J.M. Triszcz, A. Porta, and F.S. Garca Einschlag, "Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal," *Chem. Eng. J.*, vol. 150, pp. 431 – 439, 2009.
- [10] J.A. Lackovic, N.P. Nikolaidis, and G.M. Dobbs, "Inorganic arsenic removal by zero-valent iron," *Environ. Eng. Sci.*, vol. 17, pp. 29-40, 2000.
- [11] H. Sun, L. Wang, R. Zhang, J. Sui, and G. Xu, "Treatment of groundwater polluted by arsenic compounds by zero valent iron," *J. Hazard. Mater.*, vol. B129, 297-303, 2006.
- [12] S. Bang, M.D. Johnson, G.P. Korfiatis, and X. Meng, "Chemical reactions between arsenic and zero-valent iron in water," *Water Res.*, vol. 39, pp. 763-770, 2006.
- [13] G. Jegadeesan, K. Mondal, and S.B. Lalvani, "Arsenate remediation using nanosized modified zerovalent iron particles," *Environ. Progress*, vol. 24 , pp. 289-296, 2005.
- [14] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, and G.C. Hadjipanayis, "Chemistry of borohydride reduction of iron(II) and iron(III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders," *Inorg. Chem.*, vol. 34, pp. 28-35, 1995.
- [15] S.R. Kanel, B. Manning, L. Charlet, and H. Choi, "Removal of arsenic(III) from groundwater by nanoscale zero-valent iron," *Environ. Sci. Technol.*, vol. 39, pp. 1291-1298, 2005.
- [16] 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.*, vol. 40, pp. 2045-2050, 2006.
- [17] C. Ruangchainikom, C.H. Liao, J. Anotai, and M.T. Lee, "Effects of water characteristics on nitrate reduction by the Fe⁰/CO₂ process," *Chemosphere*, vol. 63, pp. 335-343, 2006.
- [18] J. Anotai, C.H. Liao, and C. Ruangchanikom, "Nitrate removal by Fe⁰/CO₂ process using an innovative continuous flow reactor," *J. Environ. Eng. Manage.*, vol. 20, pp. 77-84, 2010.
- [19] X. Li, D.W. Elliott, and W. Zhang, "Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects," *Solid State and Mater. Sci.*, vol. 31, pp. 111-122, 2006.
- [20] K.P. Raven, A. Jain, and R.H. Loeppert, "Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes," *Environ. Sci. Technol.*, vol. 32, pp. 344-349, 1998.
- [21] B. Sunbaek, D.J. Mark, P.K. George, and X. Meng, "Chemical reactions between arsenic and zero-valent iron in water, *Water Res.*, vol. 39, pp. 763-770, 2005.
- [22] J.T. Mayo, C. Yavuz, S. Yean, L. Cong, H. Shipley, W. Yu, J. Falkner, A. Kan, M. Tomson, and V.L. Colvin, "The effect of nanocrystalline magnetite size on arsenic removal," *Sci. Technol. Adv. Mater.*, vol. 8, pp. 71-75, 2007.

- [23] D. Mishra, and J. Farrell, "Evaluation of mixed valent iron oxides as reactive adsorbents for arsenic removal," *Environ. Sci. Technol.*, vol. 39, pp. 9689-9694, 2005.
- [24] W. Zhang, P. Singh, E. Paling, and S. Delides, "Arsenic removal from contaminated water by natural iron ores," *Miner. Eng.*, vol. 17, pp. 517-524, 2004.
- [25] Y. Arai, D.L. Sparks, and J.A. Davis, "Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface," *Environ. Sci. Technol.*, vol. 38, pp. 817-824, 2004.
- [26] M. Kim, J. Nriagu, and S. Haack, "Carbonate ions and arsenic dissolution by groundwater," *Environ. Sci. Technol.*, vol. 34, pp. 3094-3100, 2000.

Arsenate removal by nano zero-valent iron in the gas bubbling system

V. Tanboonchuy, J.C. Hsu, N. Grisdanurak, and C.H. Liao

Abstract— This study focused on arsenate removal by nano zero-valent iron (NZVI) in the gas-bubbled aqueous solution. It appears that solution acidified by H_2SO_4 is far more favorable than by CO_2 -bubbled acidification. In addition, as dissolved oxygen was stripped out of solution by N_2 gas bubbling, the arsenate removal dropped significantly. To take advantages of common practice of carbonation and oxic condition, pretreatment of CO_2 and air bubbling in sequence are recommended for a better removal of arsenate.

Keywords— Arsenic, arsenate, zero-valent iron.

INTRODUCTION

Arsenic is hazardous material. Consuming water with high level of arsenic will cause skin, lung, bladder, and kidney cancers [1]. The standard of maximum contamination level (MCL) of arsenic in drinking water is 10 $\mu\text{g/L}$ according to U.S. Environmental Protection Agency [2]. Arsenic is stable in several oxidation states, of which the arsenite (As(III)) and arsenate (As(V)) are the most common forms in natural waters. The dominant arsenic species depend greatly on condition of water environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [1]. The adsorption process by using ZVI is a promising alternative for arsenic removal because of its capability of removing both As(V) and As(III) simultaneously [3]. Lackovic et al. (2000) first reported arsenic removal by using ZVI in 2000 for remediation purpose [4]; On the other hand, based on the method of nano-scale zero valent (NZVI) synthesis developed by Lehigh university research group in 1995 [5]; it was found that

V. Tanboonchuy is with Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND

J.C. Hsu is with Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

N. Grisdanurak is with National Center of Excellence for Environmental and Hazardous Waste Management and with Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, THAILAND.

C.H. Liao is with *Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.* (corresponding author's e-mail: chliao@mail.chna.edu.tw).

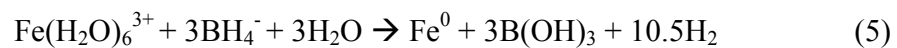
NZVI possesses higher capacity for arsenic removal than micro-scale zero valent (MZVI) [6, 7]. According to the literature [6], the As(V) can be better removed in acidic condition than in base condition. But, to adjust solution pH by using acidic species H₂SO₄, HCl, or acetic acid may produce undesirable alien species such as sulfate, chloride, and acetate, which will affect the treated water quality. Based on the earlier report [8], the above issue of concern can be resolved by CO₂ bubbling, which can adjust the solution pH to acidic condition due to the increased hydrogen ions from carbonated water, as described below:



Thus, attempt was made to investigate the effects of gases bubbling, including CO₂, air, and N₂ on the rates of arsenate removal by NZVI. In addition, characterization of NZVI behavior in solution was also performed for the treatment system design purpose

Materials and methods

The chemicals of reagent grade used in this study include FeCl₃·6H₂O (99%) and NaBH₄ (> 96%) (Merck). The As (V) stock solution was prepared from Na₂HAsO₄·7H₂O (J.T. Baker). The CO₂ gas with high purity (99.5%), Air, and N₂ were purchased from a local supplier. All chemical solutions were prepared with deionized water (18.2 MΩ Mill-Q). The NZVI was synthesized according to Glavee et al.(1995) [5]. 0.25 M of NaBH₄ was added into 0.045 M of FeCl₃ aqueous solution. The mixture was agitated by a revolving propeller. The ferric iron is reduced by the borohydride, as shown in Reaction (5):



Right after the synthesis of NZVI, it was applied immediately in the arsenic treatment system (Figure 1), in which the arsenate concentration (C₀) and NZVI dosage were 1000 µg/L and 0.023 g/L, respectively. As for the gas bubbling system, four scenarios were designed to evaluate each individual performance of arsenate removal. As depicted in Table 1, the solution pH was adjusted either by H₂SO₄ or CO₂ bubbling. To obtain the oxic and anoxic environment, with and without N₂ gas bubbling were applied to control the level of dissolved oxygen in the solution.

TABLE I
GAS BUBBLING SCENARIOS IN
THE ARSENATE TREATMENT SYSTEM

Scenario	pH adjustment and gas bubbling
1	The pH was adjusted to 4 by H ₂ SO ₄ .
2	The pH was adjusted to 4 by CO ₂ gas bubbling at 300 mL/min for 30 min.
3	The pH was adjusted to 4 by H ₂ SO ₄ , and immediately this was then followed by N ₂ gas bubbling to strip out dissolved oxygen from solution.
4	The pH was adjusted to 4 by CO ₂ gas bubbling at 300 mL/min for 5 min, and immediately this was then followed by air bubbling until the end of reaction at

As shown in Figure 1, the total bed volume of reactor used in this study was 4.4 L. In addition, the treated liquid samples were filtrated by using a 0.45 μ m membrane filter and the solution pH and ORP were measured by pH and ORP meter (Suntex TS1), while the dissolved oxygen was measured by DO meter (Oxi 330i). The residual arsenic (C) was determined by Inductively Coupled argon Plasma (ICP) using Thermo Scientific Model iCAP 6000 series.

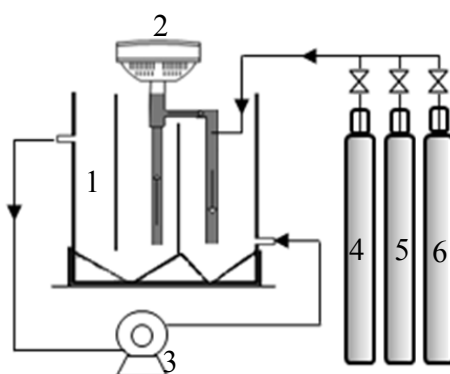


Fig. 1 Experimental setup for arsenate treatment: 1. Reactor; 2. Internal recirculated pump; 3. External recirculated pump; 4. CO₂ tank; 5. Air tank; 6. N₂ tank

Results and discussion

A. Effect of gas bubbling scenario

Effect of DO on arsenate removal performance comparison can be made between Scenario 1: oxic condition and Scenario 3: anoxic condition. As shown in Figure 2, the arsenate was removed under oxic condition more than anoxic condition. The reason is due to enhanced adsorption through oxygen-induced corrosion iron (hydr)oxide products [4, 9, 10].

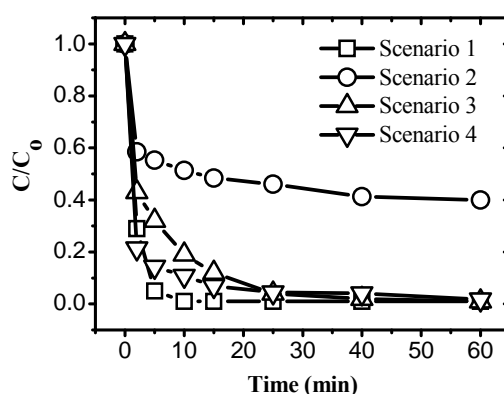


Fig. 2 Comparison of arsenate removal under various gas bubbling conditions

Effect of pH adjusted either by acid or by CO₂ gas bubbling was investigated through Scenario 1 (H₂SO₄ addition) and Scenario 2 (CO₂ bubbling). As shown in Figure 2, the one with H₂SO₄ adjustment has higher removal of arsenate than the one with CO₂ bubbling. The key reason is the stripping of oxygen because of CO₂ bubbling. In Scenario 2, the resulted DO was near to zero (anoxic), while the DO remained relatively high in Scenario 1. As mentioned earlier, dissolved oxygen can promote the adsorption of arsenate. Without DO, Scenario 2 exhibits lower removal of arsenate though it's in favorable acidic condition.

In summary, the following conditions are desired to remove arsenate effectively: lower pH and higher DO. Based on this principle, Scenario 4 was designed to achieve the best removal of arsenate: CO₂ bubbling plus air bubbling. The first bubbling is to ensure a favorable acidic environment, while the second bubbling is for increasing DO content in the solution to be treated. In so doing, the adverse water quality effect by acidic species H₂SO₄ can be prevented. As a result, Figure 2 shows a profile for the Scenario 4 comparable to that for Scenario 1. The removal efficiency for Scenario 4 is more than 95% at time of 25 min.

B. Treated water characterization

Based on the four mentioned scenarios, Figure 3 shows the three important profiles of pH, DO, and ORP. From Figure 3(a), the initial pH of all scenarios were around 4; the pH's with

Scenarios 1 and 3 were adjusted by H_2SO_4 and Scenarios 2 and 4 by CO_2 gas bubbling. All solution pH profiles were observed rise continuously throughout reaction period, due to the build-up of OH^- as presented in Reactions (6) and (7) [11].

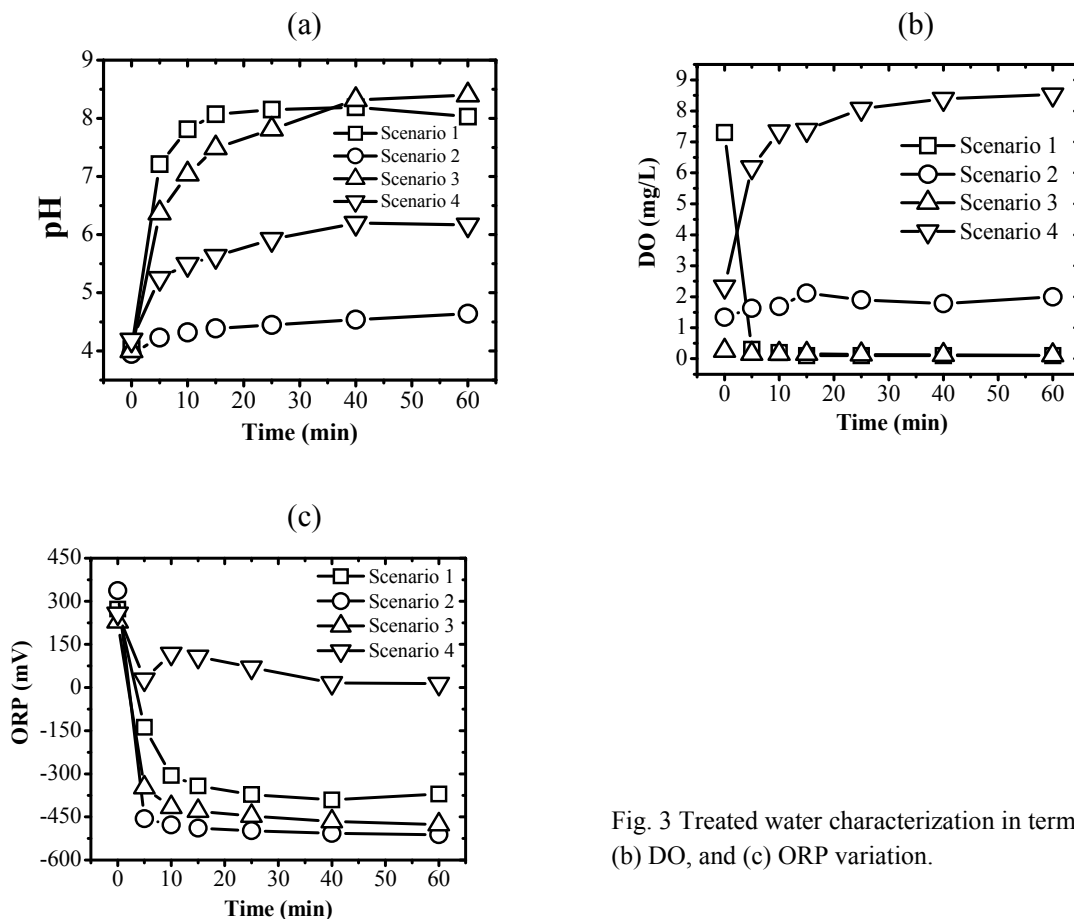


Fig. 3 Treated water characterization in terms of (a) pH, (b) DO, and (c) ORP variation.

In Figure 3(b), the DO profile for Scenario 1 was seen to decrease rapidly according to Equation (7). Whereas the profiles for Scenarios 2 and 3 remain rather unchanged since the solution has been pretreated by bubbling of CO_2 and N_2 , respectively, resulting in low DO value. On the other hand, for Scenario 4, the air bubbling was supplied continuously throughout all reaction period, and this resulted in increasing DO value. In Figure 3(c), as the NZVI was added into arsenic-contaminated solution, the ORP value decreased rapidly from the positive values to the negative ones. Such situation occurs due to the electrons being released from the NZVI. At time of around 5 min, the ORP for all scenarios, except Scenario 4, were negative values,

indicating that the reducing environment of solution has been created [11]. Furthermore, the ORP profiles for Scenarios 2 and 3 were lower than the one for Scenario 1. This suggests that the ORP strongly relates with the DO in solution; the higher the DO, the higher the ORP. Thus, the ORP for Scenario 4 was observed to maintain in positive value because of air bubbling and thus higher DO in the solution

Conclusions

This study was conducted to investigate performance of arsenic removal by using NZVI under different gas bubbling conditions. It was found that As(V) can be removed favorably in acid condition and high DO. Adjusting solution pH to acidic condition by CO₂ bubbling alone could not improve performance of arsenate removal because DO had been stripped out of solution. To avoid the use of acidic species H₂SO₄, which may deteriorate the water quality because of sulfate, a scenario was recommended by bubbling CO₂ and air in sequence, and this thus resulted in satisfactory removal of arsenate.

ACKNOWLEDGMENTS

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

REFERENCES

- [1] D. Mohan, C.U. Pittman, Jr., "Arsenic removal from water/wastewater using adsorbents - A critical review," *J. Hazard. Mater.*, vol 142, 2007, pp. 1-53.
- [2] N. Melitas, J. Wang, M. Conklin, P. O'Day, J. Farrell, "Understanding soluble arsenate removal kinetics by zerovalent iron media," *Environ. Sci. Technol.*, vol 36, 2002, pp. 2074-2081.
- [3] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, "Treatment of groundwater polluted by arsenic compounds by zero valent iron," *J. Hazard. Mater.*, vol B129, 2006, pp. 297-303.
- [4] J.A. Lackovic, N.P. Nikolaidis, G.M. Dobbs, "Inorganic arsenic removal by zero-valent iron," *Environ. Eng. Sci.*, vol 17, 2000, pp. 29-40.
- [5] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, "Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders," *Inorg. Chem.*, vol 34, 1995, pp. 28-35.
- [6] S.R. Kanel, J.M. Greneche, C. Choi, "Arsenic(V) Removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material," *Environ. Sci. Technol.*, vol. 40, 2006, pp. 2045-2050.

- [7] A.M. Giasuddin, S.R. Kanel, H. Choi, Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environ. Sci. Technol.*, vol 41, 2007, pp. 2022-2027.
- [8] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, "Effects of water characteristics on nitrate reduction by the Fe⁰/CO₂ process," *Chemosphere*, vol 63, 2006, pp. 335-343.
- [9] G. Jegadeesan, K. Mondal, S.B. Lalvani, "Arsenate Remediation Using Nanosized Modified Zerovalent Iron Particles," *Environ. Progress.*, vol 24 (3), 2005, pp. 289-296.
- [10] S. Banga, M.D. Johnsonb, G.P. Korfiatisa, X. Meng, "Chemical reactions between arsenic and zero-valent iron in water," *Water Research*, vol 39, 2005, pp. 763–770.
- [11] C. Ruangchainikom, C.H. Liao, J. Anotai, M.T. Lee, "Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and of CO₂ – bubbled system,' *Water Research*, vol 40, 2006, pp. 195-204.

**Influence of selected anions on arsenic removal
by nano-zero valent iron**

Visanu Tanboonchuy¹, Jia-Chin Hsu², Nurak Grisdanurak^{1,3}, Chih-Hsiang Liao^{4*}

¹*Department of Chemical Engineering, Faculty of Engineering,
Thammasat University, Pathumthani, THAILAND.*

²*Department of Environmental Engineering and Science,
Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.*

³*National Center of Excellence for Environmental and Hazardous Waste Management,
Thammasat University, Pathumthani, THAILAND.*

⁴*Department of Environmental Resources Management, Chia Nan University of
Pharmacy and Science, Tainan, TAIWAN.*

**Corresponding author: chliao@mail.chna.edu.tw*

ABSTRACT

Batch experiments were conducted to investigate the influence of several anions such as phosphate, sulfate, and bicarbonate on the removal of arsenic by lab-synthesized nano-zero valent-iron (NZVI). The experiments were carried out to treat 1000 µg/L of arsenic concentration in the presence of low and high concentrations of anions. The results revealed that the anions studied plays an inhibiting role in arsenic removal, with the following order, (1) As(III): phosphate > bicarbonate > sulfate, and (2) As(V): phosphate > bicarbonate ≅ sulfate.

KEYWORDS: Arsenic; Iron; Adsorption; Zero valent

1. INTRODUCTION

Arsenic, with its toxicity to human health, is typically associated with iron oxide under oxic environment and with pyrite minerals under anoxic environment [1]. It can be released to the environment from both natural sources such as the oxidative weathering and geochemical reaction, and anthropogenic activities such as industrial waste discharge containing arsenic [2], mining, and arsenical pesticides [3, 4]. The presence of arsenic compound in groundwater is a serious environmental problem because consuming water with high level of arsenic will cause

skin, lung, bladder, kidney cancer and black foot diseases [5]. The standard of maximum contamination level (MCL) of arsenic in drinking water is 10 µg/L, according to USEPA [6]. Several countries have been reported that there was serious problem about arsenic in groundwater, including Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [7, 8]. Arsenic is stable in several oxidation states, of which the arsenite, As(III), and arsenate, As(V), are the most common form in natural waters. The dominant species of arsenic depend greatly on its surrounding environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [7]. Adsorption process by using low cost adsorbents has been a promising alternative for arsenic removal. Zero-valent iron (ZVI) was firstly used for arsenic removal by Lackovic et al. [9]; they reported that ZVI has a high capacity for arsenic remediation of both As(III) and As(V) simultaneously, without the need of pre-oxidation step [10], and such process does not require the use of additional chemical reagent. However, the problem associated with the use of ZVI is that the reaction time required for the complete removal of arsenic is in days [11]. As developed by Lehigh university research group in 1995 [12], the nano-scale zero-valent iron (NZVI) possesses much faster reaction and higher capacity for arsenic removal than the micro-scale zero-valent iron (MZVI) [13, 14]. However, the ion species contained in field groundwater such as sulfate, phosphate, bicarbonate, chloride, silicate, calcium, and humid acid may affect the performance of arsenic removal by NZVI. Thus, the objective of this study was to investigate the performance of arsenic removal in the presence of low and high concentrations of selected anions such as phosphate, sulfate, and bicarbonate by the lab-synthesized nano-zero valent-iron (NZVI).

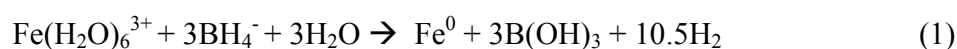
2. MATERIALS AND METHOD

2.1 Chemicals

The chemicals of reagent grade used in this study include FeCl₃·6H₂O (99%), and NaBH₄ (> 96%), (Merck). The As (V) stock solution was prepared from **Na₂HAsO₄·7H₂O** (J.T. Baker). The anions studied were prepared from Na₂SO₄ (Merck), NaHCO₃ (Merck), and Na₂PO₄·12H₂O (Merck). All chemical solutions were prepared with deionized water (18.2 MΩ Mill-Q).

2.2 NZVI synthesis

The NZVI was synthesized according to Glavee et al.(1995) [12]. 0.25 M of NaBH₄ was added into 0.045 M of FeCl₃ aqueous solution. The mixture was agitated by a revolving propeller. The ferric iron is reduced by the borohydride, as shown in Reaction (1):



At the end of reaction, the NZVI particles were separated from liquid solution by a magnet. Then the NZVI synthesized was characterized the morphology with Transmission Electron Microscopy (TEM) (JEL-2010, Japan). Brunauer-Emmett-teller (BET) N₂ method was used for its specific surface area. The pH with zero point charge denoted as pH_{pzc} was determined by using zeta-meter system 3.0+ (Meditop Co., Thailand).

2.3 Batch test

The NZVI (0.023 g/L) synthesized was applied in the arsenic treatment system (see Figure 1). Note that the volume for the reactor in Figure 1 is 4.4 L. The initial arsenic concentrations used was 1000 µg/L. Experiments were carried out at low and high concentrations of anions: SO₄²⁻ = 10 and 100 mg/L, HCO₃⁻ = 50 and 500 mg/L, and PO₄³⁻ = 1 and 5 mg/L. The solution pH was adjusted at the beginning of the experiment to 7.90 ± 0.1 by using H₂SO₄ and NaOH. The solution pH was measured by pH meter (Suntex TS1). The residual arsenic (C) was determined by inductively coupled argon plasma (ICP) using **Thermo Scientific Model iCAP 6000 series**.

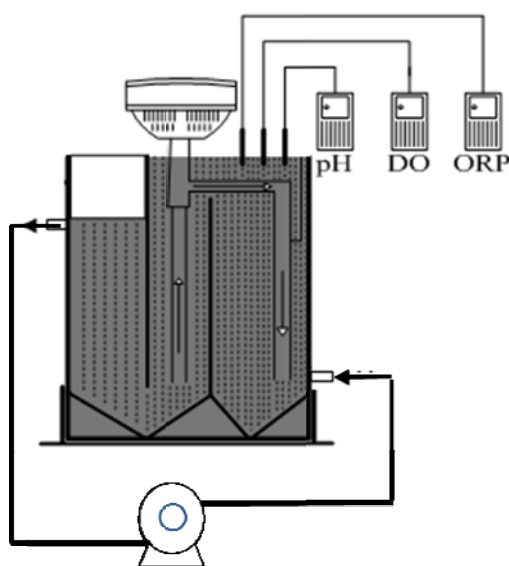


Figure 1. Experimental setup for arsenic removal by NZVI

3. RESULTS AND DISCUSSION

3.1. Characterization of NZVI

TEM was used to characterize the morphology and histogram of particle size distribution of untreated NZVI. Figure 2(a) shows that morphology of NZVI has two distinct layers. The inside core represents the Fe⁰ while the outer layer covering the Fe⁰ was iron oxide(s). As shown in

Figure 2(b), the histogram reveals that more than 95% of the particles are smaller than 90 nm and the average of particle size was 56 nm. The NZVI was further characterized by BET method and its specific surface area was 7.67 m²/g. Additionally, Figure 2(c) shows the measured pH_{pzc} for the lab-synthesized NZVI, the pH with zero charge, was 7.8.

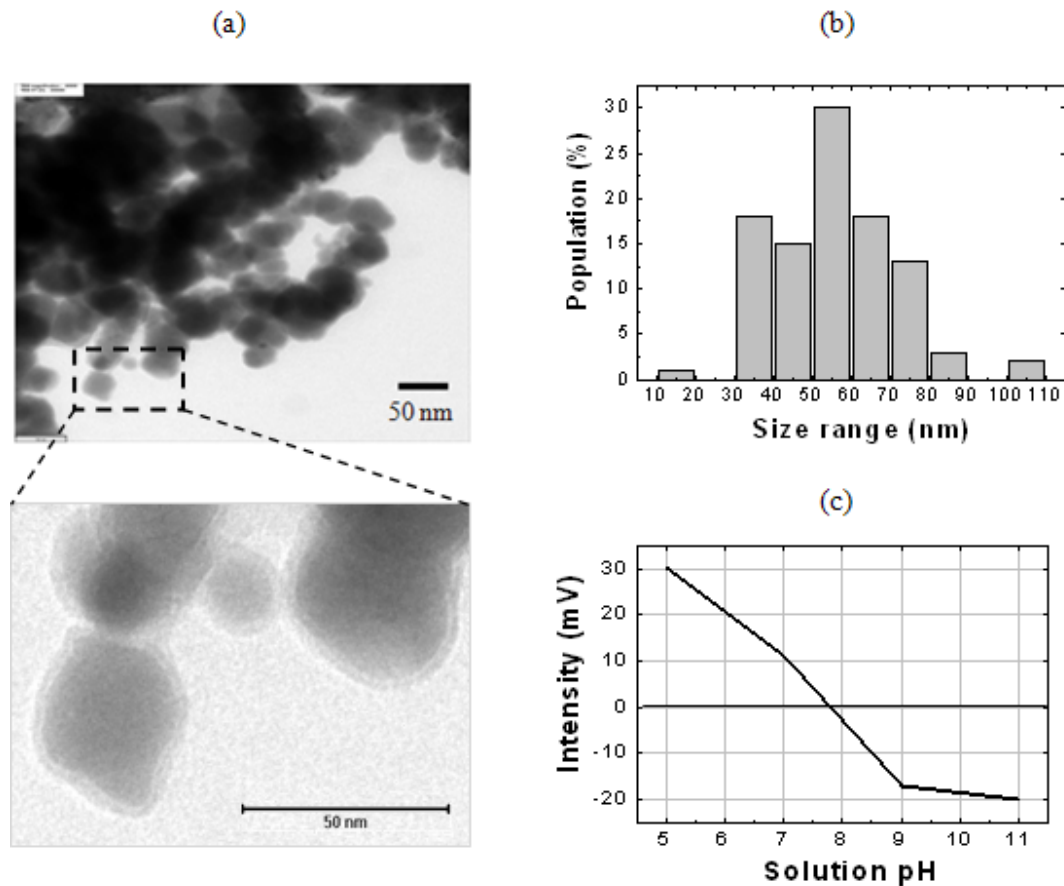


Figure 2. Characterization of untreated NZVI (a) TEM image, (b) its histogram, and (c) the point of zero charge

3.2. Effect of anions

3.2.1. Sulfate (SO₄²⁻)

The removal of both As(III) and As(V) was retarded slightly in the presence of low and high concentrations of SO₄²⁻ as present in Figure 3(a). Such phenomenon was reported due to the electrical repulsion between SO₄²⁻ and arsenic species [15]. Another reason, as reported, is that the SO₄²⁻ can replace iron oxide and hydroxides, which were adsorbed on the iron surface, and result in the decrease of sorption sites available to arsenic [16]. It appears that such results differ

from some other report possibly because of different experimental conditions. According to the report [10], the As(V) removal efficiency increased when the sulfate concentration increased to a higher level, due to the acceleration of precipitation of arsenopyrite, FeAsS, through the reaction of SO_4^{2-} with the Fe^{2+} , AsO_3^{2-} and H^+ , as shown in Equation (2) [17]

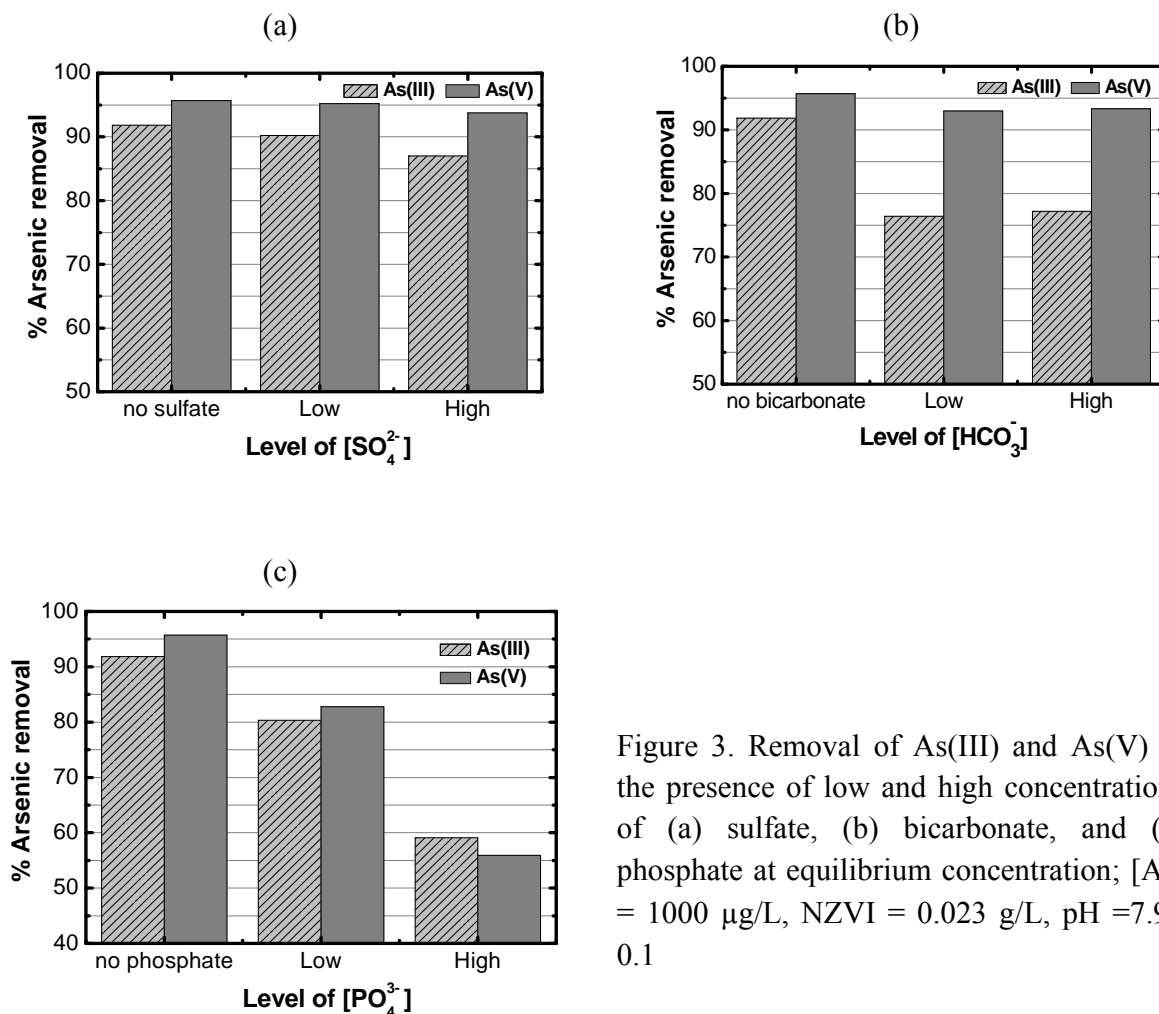
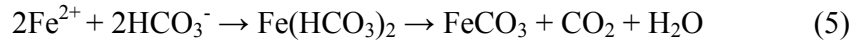
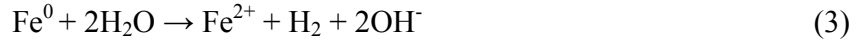


Figure 3. Removal of As(III) and As(V) in the presence of low and high concentrations of (a) sulfate, (b) bicarbonate, and (c) phosphate at equilibrium concentration; $[\text{As}] = 1000 \mu\text{g/L}$, $\text{NZVI} = 0.023 \text{ g/L}$, $\text{pH} = 7.9 \pm 0.1$

3.2.2. Bicarbonate (HCO_3^-)

The effect of HCO_3^- (50 and 500 mg/L) on arsenic removal was shown in Figure 3(b). The As(III) removal decreased dramatically in the presence of bicarbonate, whereas the As(V) removal was only affected slightly. The possible reasons may be due to competition between HCO_3^- and arsenic species since the HCO_3^- can form inner-sphere surface complexes with amorphous iron oxide [18]. In addition, The NZVI can be rapidly oxidized into Fe^{2+} , the primary

product, as shown in Equations (3) and (4). This Fe^{2+} can result in several forms of iron (hydr)oxides, which serve as good sites for arsenic adsorption. However, in the presence of HCO_3^- , the Fe^{2+} can form with HCO_3^- to generate iron carbonate (FeCO_3) [19], as shown in Equation (5), which appears to have lower performance for arsenic adsorption than iron (hydr)oxides.



Some other article reported that the release of arsenic from sandstone aquifer was found to be strongly and positively related to the HCO_3^- concentration in the leaching solution [20]. Also there's another article showing that HCO_3^- can promote iron dissolution from hematite ($\alpha\text{-Fe}_2\text{O}_3$) surface [21], leading to the increase of the dissolved arsenic in solution. In this study with HCO_3^- concentration as high as 500 mg/L, the arsenic removal was comparable to the one with 50 mg/L.

3.2.3. Phosphate (PO_4^{3-})

The effect of PO_4^{3-} (1 and 5 mg/L) on arsenic removal was shown in Figure 3(c). The presence of phosphate inhibited the removal performance of arsenic, both As(III) and As(V), significantly. Table 1 shows the pK_a values and predominance forms of arsenic and phosphate species. Such information indicates that the dominant dissociation species of phosphate and arsenic had similar chemistry, especially the phosphate and As(V). In other words, there was competition between arsenic species and phosphate for the same sorption sites on the surface of iron (hydr)oxides [11]. Phosphate can be adsorbed onto iron (hydr)oxides through the formation of inner-sphere complexes with the hydroxyl groups [22], and the affinity of phosphate for iron (hydr)oxides was much stronger than arsenic species [1]. With this, the phosphate can retard the removal of arsenic significantly.

Table 1: pK_a of arsenate species and phosphate

Species	pK _a values			Predominance form in various pH			Reference
	pK ₁	pK ₂	pK ₃	< pK ₁	pK ₁ – pK ₂	pK ₂ – pK ₃	
Arsenite, As(III)	9.22	12.1	12.7	H ₃ AsO ₃	H ₂ AsO ₃ ⁻	HAsO ₃ ²⁻	[23]
Arsenate, As(V)	2.2	6.97	11.5	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	[23]
Phosphate	2.15	7.1	12.4	H ₃ PO ₄	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	[24]

4. CONCLUSIONS

The experiments were conducted to investigate the effect of several selected anions on the removal of arsenic by NZVI. The results revealed that in presence of anions such as sulfate, bicarbonate, and phosphate lead to the decrease of performance of arsenic removal by NZVI. The phosphate anion had the greatest adverse effect on the removal of both As(III) and As(V). In the presence of sulfate and bicarbonate, both inhibit As(V) removal slightly, but the inhibition even more significantly in removing As(III).

Acknowledgements

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

5. REFERENCES

- [1] Meng X., Korfiatis G.P., Bang S., Bang K.W. (2002) Combined effects of anions on arsenic removal by iron hydroxides. *Toxicology Letters*. **133**, 103–111.
- [2] Banerjee K., Amy G.L., Prevost M., Nour S., Jekel M., Gallagher P.M., Blumenschein C.D. (2008) Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH). *Water Research*. **42**, 3371-3378.
- [3] Farrell J., Wang J., O'Day P., Conklin M. (2001) Electrochemical and spectroscopic study of arsenate removal from water using zero-valent iron media. *Environ. Sci. Technol.* **35**, 2026-2032.
- [4] Mariner P.E., Holzmer F.J., Jackson R.E., Meinardus H.W. (1996) Effects of high pH on arsenic mobility in a shallow sandy aquifer and on aquifer permeability along the adjacent

- shoreline, commencement bay superfund site, Tacoma, Washington. *Environ. Sci. Technol.* **30**, 1645-1651.
- [5] Mohan D., Pittman Jr. C.U. (2007) Arsenic removal from water/wastewater using adsorbents - a critical review. *J. Hazard. Mater.* **142**, 1-53.
- [6] Melitas N., Wang J., Conklin M., O'Day P., Farrell J. (2002) Understanding soluble arsenate removal kinetics by zero-valent iron media. *Environ. Sci. Technol.* **36**, 2074-2081.
- [7] Mandal B.K., Suzuki K.T. (2002) Arsenic round the world: a review. *Talanta*. **58**, 201-235.
- [8] Chen S.L., Dzeng S.R., Yang M.H., Chiu K.H., Shieh G.M., Wai C.M. (1994) Arsenic species in groundwaters of the blackfoot disease area, Taiwan. *Environ. Sci. Technol.* **28**, 877-881.
- [9] Lackovic J.A., Nikolaidis N.P., Dobbs G.M. (2000) Inorganic arsenic removal by zero-valent iron. *Environ. Eng. Sci.* **17**, 29-40.
- [10] Sun H., Wang L., Zhang R., Sui J., Xu G. (2006) Treatment of groundwater polluted by arsenic compounds by zero valent iron. *J. Hazard. Mater.* **B129**, 297-303.
- [11] Jegadeesan G., Mondal K., Lalvani S.B. (2005) Arsenate remediation using nanosized modified zero valent iron particles. *Environ. Progress*. **24**, 289-296.
- [12] Glavee G.N., Klabunde K.J., Sorensen C.M., Hadjipanayis G.C. (1995) Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders. *Inorg. Chem.* **34**, 28-35.
- [13] Kanel S.R., Greneche J.M., Choi C. (2006) Arsenic(V) removal from groundwater using nano-scale zero-valent iron as a colloidal reactive barrier material. *Environ. Sci. Technol.* **40**, 2045-2050.
- [14] Giasuddin A.M., Kanel S.R., Choi C. (2007) Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environ. Sci. Technol.* **41**, 2022-2027.
- [15] Su C.M., Puls R.W. (2001) Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. *Environ. Sci. Technol.* **35**, 4562-4568.
- [16] Bi E., Bowen I., Devlin J.F. (2009) Effect of mixed anions (HCO_3^- - SO_4^{2-} - ClO_4^-) on granular iron (Fe^0) reactivity. *Environ. Sci. Technol.* **43 (15)**, 5975-5981.
- [17] Ramaswami A., Tawachsupha S., Isleyen M. (2001) Batch-mixed iron treatment of high arsenic waters. *Water Res.* **35**, 4474-4479.
- [18] Biterna M., Arditoglou A., Tsikouras E., Voutsas D. (2007) Arsenate removal by zero valent iron: batch and column tests. *J. Hazard. Mater.* **149**, 548-552.
- [19] Heuer J.K., Stubbins J.F. (1999) An XPS characterization of FeCO₃ films from CO₂ corrosion. *Corros. Sci.* **41**, 1231-1243.
- [20] Kim M., Nriagu J., Haack S. (2000) Carbonate ions and arsenic dissolution by groundwater. *Environ. Sci. Technol.* **34**, 3094-3100.

- [21] Arai Y., Sparks D.L., Davis J.A. (2004) Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface. *Environ. Sci. Technol.* **38**, 817-824.
- [22] Hsu J.C., Lin C.J., Liao C.H., Chen S.T. (2008) Evaluation of the multiple-ion competition in the adsorption of As(V) onto reclaimed iron-oxide coated sands by fractional factorial design. *Chemosphere.* **72**, 1049–1055.
- [23] Raven K.P., Jain A., Loepper R.H. (1998) Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **32**, 344-349.
- [24] Jackson B.P., Miller W.P. (2000) Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides. *Soil Sci. Soc. Am. J.* **64**, 1616–1622.

ARSENIC REMOVAL BY NANO ZERO-VALENT IRON: EFFECT OF INITIAL CONCENTRATION AND DISSOLVED OXYGEN

Visanu Tanboonchuy¹, Jia-Chin Hsu², Nurak Grisdanurak^{1,3}, Chih-Hsiang Liao^{4*}

¹*Department of Chemical Engineering, Faculty of Engineering,
Thammasat University, Pathumthani, THAILAND.*

²*Department of Environmental Engineering and Science,
Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.*

³*National Center of Excellence for Environmental and Hazardous Waste Management,
Thammasat University, Pathumthani, THAILAND.*

^{4*}*Department of Environmental Resources Management, Chia Nan University of
Pharmacy and Science, Tainan, TAIWAN.*

* Corresponding author's email: chliao@mail.chna.edu.tw

INTRODUCTION

As was reported, the countries affected by high arsenic concentration in groundwater include Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [1]. The standard of maximum contamination level (MCL) of arsenic in drinking water is 10 µg/L according to U.S. Environmental Protection Agency [2]. Consuming water with high level of arsenic will cause skin, lung, bladder, and kidney cancers [3] which are difficult to treat by medicine. Arsenic is stable in several oxidation states, of which the arsenite (As(III)) and arsenate (As(V)) are the most common form in natural waters. The dominant species of arsenic depend greatly on condition of environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [1].

There are many technologies for removing arsenic from groundwater such as precipitation, coagulation and filtration, reverse osmosis, electrodialysis, and ion exchange [4], but these are only effective for As(V), and require a preoxidation step for As(III) removal [5]. As reported, adsorption process using zero-valent iron (ZVI) is a promising alternative for arsenic removal because this sorption media can remove both As(V) and As(III) simultaneously without the need of pre-oxidation [6]. Lackovic et al. (2000) first reported

arsenic removal by using ZVI in 2000 [5]; they reported that ZVI has a high capacity for arsenic remediation. On the other hand, based on the method of nano-scale zero valent (NZVI) synthesis developed by Lehigh university research group in 1995 [7], it was found that NZVI possesses higher capacity for arsenic removal than micro-scale zero valent (MZVI) [8, 9]. Thus, this study attempted to investigate the effect of initial arsenic concentration and dissolved oxygen (DO) on the rate of arsenic removal by NZVI. Throughout this study, the NZVI was synthesized in the laboratory and further characterized for data interpretation.

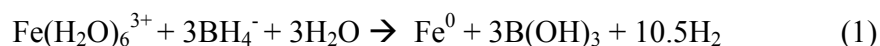
MATERIALS AND METHODS

Chemicals and reagents

The chemicals of reagent grade used in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), and NaBH_4 (> 96%), (Merck). The As(III) and As(V) stock solution were prepared from AsNaO_2 (Fluka) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (J.T. Baker), respectively. All chemical solutions were prepared with deionized water (18.2 M Ω Mill-Q).

Method of NZVI synthesis

The NZVI was synthesized according to Glavee et al. (1995) [7]. 0.25 M of NaBH_4 was added into 0.045 M of FeCl_3 aqueous solution. The mixture was agitated by a revolving propeller. Ferric iron is reduced by the borohydride, as shown in Reaction (1):



After solution was well mixed, the NZVI was separated from liquid solution by magnet. The NZVI was then produced and readily available for use. The NZVI synthesized was characterized first by the Brunauer-Emmett-teller (BET) N_2 method for its specific surface area, which was 7.67 m^2/g in this study. Then, the point of zero charge, pH_{pzc} , for the prepared NZVI was further measured, and its measured pH_{pzc} was 7.8.

Batch test

The synthesized NZVI (0.023 g/L) was applied in the system of arsenic treatment; reactor volume is 4.4 L. The initial arsenic concentrations used range from 1000 to 2500 $\mu\text{g/L}$. The solution pH was adjusted at 4. The effect of DO was investigated by purging reaction solution with nitrogen gas for 30 min to strip out dissolved oxygen. Then the reaction was carried on with continuous nitrogen purging throughout all reaction period. The total arsenic was determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series. To determine individual arsenic species, the anion-exchange

cartridge, DSC-SAX 500 mg (Supelco) was employed [10]. As the arsenic-contained water samples pass through the cartridge, the As(V) will be retained inside, while the As(III) will be carried out, rendering the separation of As(V) and As(III). The eluent is then analyzed for the As(III) concentration by ICP. Finally, the As(V) concentration is obtained by subtracting measured As(III) concentration from the total arsenic concentration.

RESULTS AND DISCUSSION

Effect of initial arsenic concentration

As presented in Figure 1, the equilibrium As(III) concentrations remained at higher levels as its initial concentration increased from 1000 to 2500 ppb. Interestingly, as As(V) was applied, all the equilibrium concentrations approach to zero value, with its initial concentrations varying from 1000 to 2500 ppb. The arsenic can exist in different forms, depending on the pH condition. According to this study, the pH_{pzc} for NZVI synthesized was 7.8, while the available pH_{pzc} data for iron oxides was 8.0 [11]. Also, the pK_a values reported for As(III) are $\text{pK}_1 = 9.22$, $\text{pK}_2 = 12.13$, and $\text{pK}_3 = 12.7$, and they are $\text{pK}_1 = 2.2$, $\text{pK}_2 = 6.97$, and $\text{pK}_3 = 11.53$ for As(V) [12]. As understood, the NZVI particles are with positive charge on the surface. In the range of pH 2-7, the dominant form for As(V) species is H_2AsO_4^- , the negative charge; for As(III) species, it is H_3AsO_3 , zero charge, as the solution pH ranges from 4 to 7. Such charge difference results in more favorable sorption of As(V) than As(III).

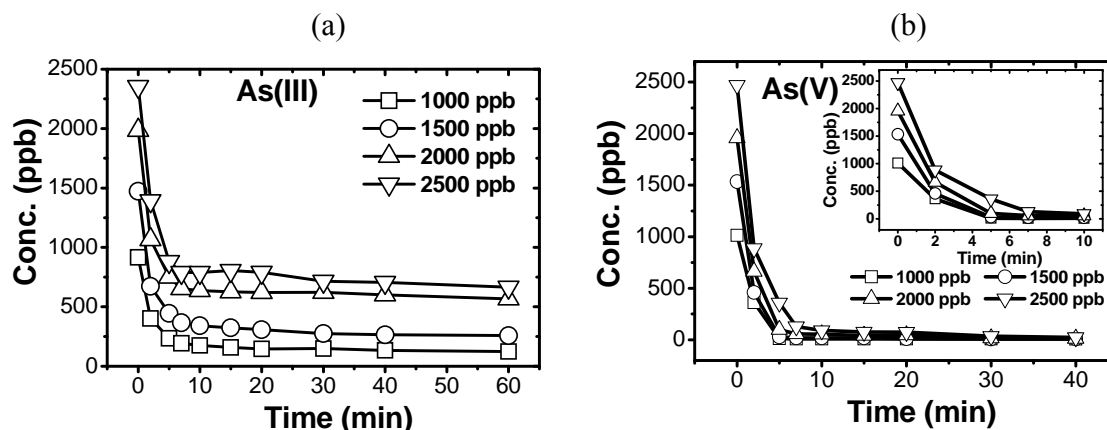


Figure 1 Effect of initial concentration of (a) As(III) and (b) As(V) on arsenic removal: NZVI dosage = 0.023 g/L, initial solution pH = 4.

Effect of DO

As shown in Figure 2, the As(III) removed was more than 80% after 10 min of reaction

when the solution was oxic condition, without purging of nitrogen gas, while 52% was removed under anoxic condition. For As(V), 99% and 76% was removed after 7 min of reaction under oxic condition and anoxic condition, respectively.

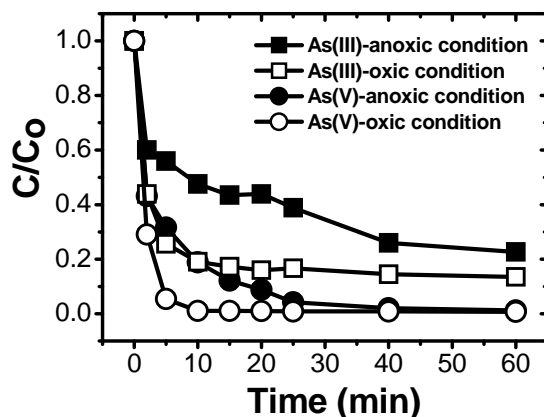


Figure 2 Comparison of As(III) and As(V) removal under oxic and anoxic conditions: NZVI dosage = 0.023 g/L, initial arsenic concentration = 1000 µg/L.

The NZVI reacting with water and the dissolved oxygen, which result in the formation of hydroxide and the decrease of DO in solution, as can be explained by Reactions (2) and (3) [13].



Then the Fe^{2+} present in the aqueous form can be oxidized by oxygen in the solution into Fe^{3+} which leads to production of corrosion products of different iron (hydr)oxide such as Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$, depending on solution pH conditions. Arsenic can form inner sphere complex with these iron oxides [14]. Thus, the presence of DO will enhance the rate of iron corrosion and subsequently improve the arsenic adsorption as well.

CONCLUSIONS

This study was conducted to investigate arsenic removal performance using NZVI as a media of sorption. Specifically, it was aimed to understand how the factors of initial arsenic concentration and DO may impose on the treatment system. As a result, As(V) is far more easily removed than As(III) at pH 4, with the initial concentration range of 1000-2500 ppb. It was found that dissolved oxygen can enhance the removal of both As(III) and As(V) significantly.

ACKNOWLEDGMENTS

This research was sponsored by (1) Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and (2) Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program.

REFERENCES

- [1] Ahuja S.: Arsenic contamination of groundwater: Mechanism, Analysis, and Remediation, John Wiley & Sons, Inc. (2008) Chapter 1.
- [2] Melitas N., Wang J., Conklin M., O'Day P., Farrell J.: *Environ. Sci. Technol.* 36 (2002) 2074-2081.
- [3] Mohan D., Pittman Jr. C.U.: *J. Hazard. Mater.* 142 (2007) 1–53.
- [4] Triszcz J.M., Porta A., Garca Einschlag F. S.: *Chem. Eng. J.* 150 (2009) 43 - 439.
- [5] Lackovic J.A., Nikolaidis N.P., Dobbs G. M.: *Environ. Eng. Sci.* 17 (2000) 29-40.
- [6] Sun H., Wang L., Zhang R., Sui J., Xu G.: *J. Hazard. Mater.* B129 (2006) 297-303.
- [7] Glavee G.N. Klabunde K.J. Sorensen C.M., Hadjipanayis G.C.: *Inorg. Chem.* 34 (1995) 28-35.
- [8] Kanel S.R., Greneche J.M ., Choi C.: *Environ. Sci. Technol.* 40 (2006) 2045-2050.
- [9] Giasuddin A.M., Kanel S.R., Choi C.: *Environ. Sci. Technol.* 41 (2007) 2022-2027.
- [10] Kom I., Kim J., Kim K.W.: *Colloids Surf. A.* 234 (2004) 43-50.
- [11] Li X., Elliott D.W., Zhang W.: *Solid State and Mater. Sci.* 31 (2006) 111-122.
- [12] Raven K.P., Jain A., Loeppert R.H.: *Environ. Sci. Technol.* 32 (1998) 344-349.
- [13] Ruangchainikom C., Liao C.H., Anotai J.: *Water Research.* 40 (2006) 195-204.
- [14] Mayo J.T., Yavuz C., Yean S., Cong L., Shipley H., Yu W., Falkner J., Kan A., Tomson M., Colvin V.L.: *Sci. Technol. Adv. Mater.* 8 (2007) 71-75.

Nanoiron technology for arsenic-contaminated groundwater treatment

Visanu Tanboonchuy¹, Jia-Chin Hsu², Nurak Grisdanurak^{1,3}, Chih-Hsiang Liao^{4*}

¹*Department of Chemical Engineering, Faculty of Engineering,
Thammasat University, Pathumthani, THAILAND.*

²*Department of Environmental Engineering and Science,
Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.*

³*National Center of Excellence for Environmental and Hazardous Waste Management,
Thammasat University, Pathumthani, THAILAND.*

⁴*Department of Environmental Resources Management, Chia Nan University of
Pharmacy and Science, Tainan, TAIWAN.*

* Corresponding author's email: chliao@mail.chna.edu.tw

ABSTRACT

This study focused on arsenate removal in aqueous solution under various pH conditions. The results reveal that higher arsenate removal can be obtained in acidic environment rather than in base condition. Kinetic analysis suggests that arsenate removal can be described as a first-order reaction for all pH values studied; the reaction rate constants were 0.76 (pH=4), 0.16 (pH=7), and 0.04 min⁻¹ (pH=9). In addition, as a result of sorption investigation, the sorption performance was 43.62 (pH=4), 42.73 (pH=7), and 37.48 mg As/g iron (pH=9).

KEYWORDS: Arsenic; Iron; Adsorption; Zero valent

1. INTRODUCTION

The contamination of arsenic in groundwater has become an issue of worldwide concern because of its toxicity and health hazards. Consuming water with high level of arsenic will cause skin, lung, bladder, kidney cancer and black foot diseases [1]. The standard of maximum contamination level (MCL) of arsenic in drinking water is 10 $\mu\text{g/L}$ according to U.S. Environmental Protection Agency [2]. As was reported, the countries affected by high arsenic concentration in groundwater include Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [3]. Arsenic is stable in several oxidation states, of which the arsenite (As(III)) and arsenate (As(V)) are the most common form in natural waters. The dominant species of arsenic depend greatly on condition of environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [1]. There are many technologies for removing arsenic from groundwater such as precipitation, coagulation and filtration, reverse osmosis, electrodialysis, and ion exchange [4], but these are only effective for As(V) , and require a preoxidation step for As(III) removal [5]. Thus, adsorption process by using ZVI is a promising alternative for arsenic removal because this sorption media can remove both As(V) and As(III) simultaneously, without pre-oxidation [6], and such process does not require the use of additional chemical reagent. Lackovic et al. (2000) first reported arsenic removal by using ZVI in 2000 [5]; they revealed that ZVI has a high capacity for arsenic remediation. Then the synthesis of nano-scale zero valent (NZVI) was developed by Lehigh university research group in 1995 [7]; it was found that NZVI possesses higher capacity for arsenic removal than micro-scale zero valent (MZVI) [8, 9]. Specifically, the objective of this study was to investigate the effect of solution pH on the rate of As(V) removal by NZVI, and the removal kinetics was explored as well. In addition, characterization of NZVI behavior in “pure” water was performed for the treatment system design purpose.

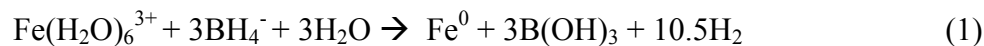
2. MATERIALS AND METHOD

2.1 Chemicals

The chemicals of reagent grade used in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), and NaBH_4 (> 96%), (Merck). The As (V) stock solution was prepared from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (J.T. Baker). The solution pH was adjusted by NaOH and H_2SO_4 . All chemical solutions were prepared with deionized water (18.2 M Ω Mill-Q).

2.2 NZVI synthesis

The NZVI was synthesized according to Glavee et al.(1995) [7]. 0.25 M of NaBH₄ was added into 0.045 M of FeCl₃ aqueous solution. The mixture was agitated by a revolving propeller. The ferric iron is reduced by the borohydride, as shown in Reaction (1):



At the end of reaction, the NZVI particles were separated from liquid solution by a magnet. The NZVI was then produced and readily available for use.

2.3 Batch test

Right after the synthesis of NZVI, it was applied immediately in the system of arsenic treatment, in which the As(V) concentration (C₀) and NZVI dosage were 1000 µg/L and 0.023 g/L, respectively. The initial pH's of the solution studied were 4.0, 7.0 and 9.0. As shown in Figure 1, the total bed volume of reactor used in this study was 4.4 L. In addition, the treated liquid samples were filtrated by using a 0.45µm membrane filter to remove the solids from solution before analysis of residual arsenic concentration.

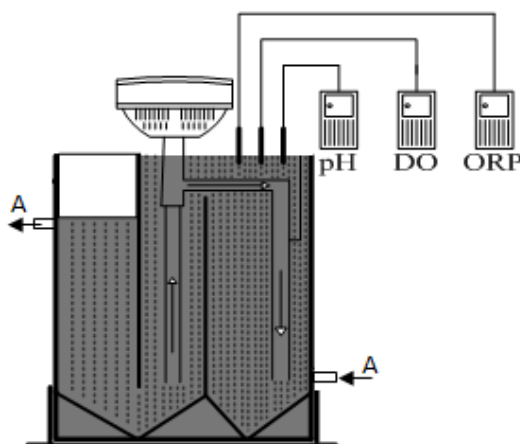


Figure 1. Experimental setup for batch study

2.4 Analytical methods

The solution pH and ORP were measured by pH and ORP meter (Suntex TS1), while the dissolved oxygen was measured by DO meter (Oxi 330i). The residual arsenic (C) was determined by Hydride Generation Inductively Coupled argon Plasma Optical Emission Spectroscopic (HG-ICP-OES) using Perkin Elmer Model Optima 2000 DV.

3. THEORIES OF SORPTION

3.1 Sorption performance

The sorption performance is evaluated quantitatively in terms of arsenic uptake, as expressed by Equation (2) [10].

$$m (q_e - q_o) = V (C_o - C_e) \quad (2)$$

Where m is the mass of the sorbent (g); q_o and q_e are the arsenic uptakes by the sorbent (mg/g) at initial and equilibrium conditions, respectively; C_o , and C_e are the initial and equilibrium concentrations of arsenic in solution (mg/L); V is the solution volume (L).

3.2 Sorption kinetics parameters

The results of this study were analyzed by using the pseudo-first-order kinetic model in order to express the kinetics of the sorption process, according to Equations (3) and (4).

$$\frac{dC}{dt} = -k_{obs} C \quad (3)$$

$$\ln C = -k_{obs} t + \ln C_o \quad (4)$$

Where C_o and C are the concentrations of arsenic at initial condition and time of reaction, t (min); k_{obs} is the specific sorption rate constant (min^{-1}). The half-lives ($t_{1/2}$) of reaction can be calculated according to Equation (5).

$$t_{1/2} = \frac{\ln(0.5C_o / C_o)}{-k_{obs}} \quad (5)$$

4. RESULTS AND DISCUSSION

4.1 Effect of pH

Figure 2 presents the adsorption data under various pH conditions, which are 4, 7, and 9.

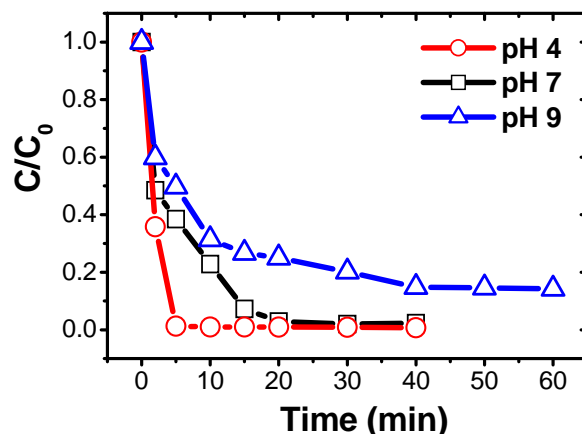


Figure 2. Effect of pH on arsenate removal

As shown in Figure 2, more than 50% of As(V) was rapidly removed within the first 5 min for the three pH values. The sorption reaction reaches equilibrium at time of 7, 20, and 40 min for pH 4, 7, and 9, respectively. The percentages of equilibrium concentration correspond to 99% (pH 4), 97% (pH 7) and 82% (pH 9) of the initial As concentration. The rate of As adsorption decreases when the pH increases from pH 4 to pH 9, due to electrostatic interaction mechanism between adsorbate and adsorbent. According to the literature [11], the zero point charge of NZVI is at pH 7.7. As depicted in Figure 3, within the range of pH 2-7.7, the dominant form of As(V) is H_2AsO_4^- , the negative charge, whereas the NZVI surface shows positive charge. As understood, the opposite charge of adsorbate and adsorbent will enhance the arsenic removal through electrostatic attractions. For the base pH condition (7.7-12), the dominant form of As(V) is HAsO_4^{2-} (see Figure 3.), whereas the NZVI surface becomes negatively charged. Thus, the electrostatic repulsion results in decreased adsorption of As.

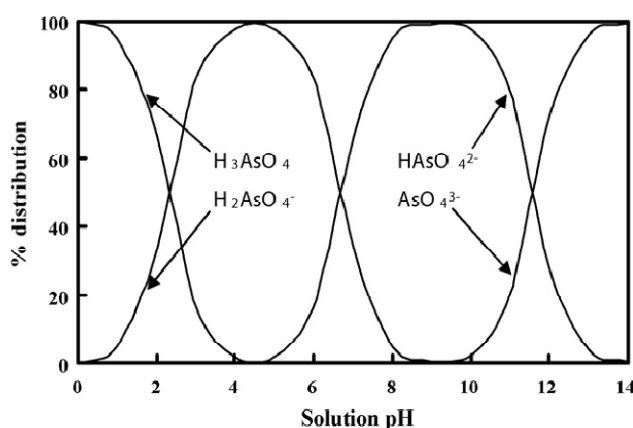


Figure 3. Distribution (%) of various As(V) species as a function of solution pH [10].

4.2 Sorption performance and kinetic parameters

The results presented in Figure 2 indicate that the kinetics of sorption follow a pseudo first-order reaction with a correlation coefficient value of $R^2 > 0.85$. The slopes of the data-fitted line provide the rate constants, k_{obs} , which are 0.76 min^{-1} (pH 4), 0.16 min^{-1} (pH 7) and 0.04 min^{-1} (pH 9). The As(V) removal tends to follow a pseudo first-order reaction because there are abundant active sites of NZVI in the beginning of reaction, and thus the As(V) species in solution can be adsorbed without sorptive competition. However, with increasing reaction time, the deviation from first-order kinetics was observed, obviously due to the loss of active surface sites. Based on Equation (2), the pseudo first-order reaction rate constant (k) and half-lives ($t_{1/2}$), were calculated and presented in Table 1.

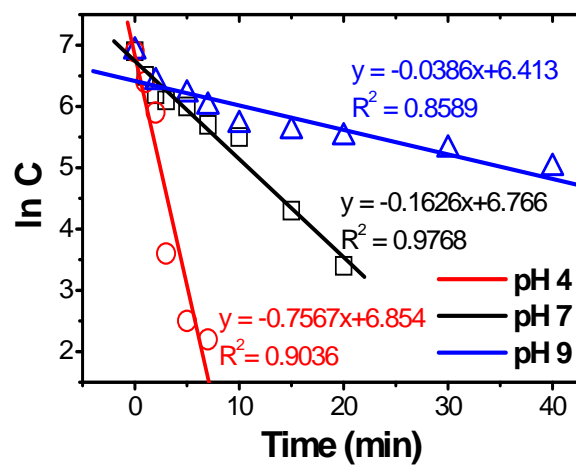


Figure 4. Linear regression for the pseudo first-order reaction

Table 1: Pseudo first-order reaction rate constant (k), half-lives ($t_{1/2}$) and sorption performance (q_e) in regard to As adsorption

pH	k_{obs} (min^{-1})	$t_{1/2}(\text{min})$	$q_e(\text{mg/g})$	R^2
4.0	0.76	0.92	43.62	0.9036
7.0	0.16	4.33	42.73	0.9768
9.0	0.04	17.33	37.48	0.8589

4.3 System characterization

Based on the earlier study [12], it is understood that the As(V) removal is affected not only by pH but also by some other factors such as DO, surface area of NZVI, chemical composition of solution,

and solution mixing intensity. Figure 5 shows the profiles of pH, DO and ORP under various initial solution pH values as the As(V) was treated in the system. As shown in Figure 5, the pH starts to increase rapidly in the beginning stage for the two cases of pH 4 and 7. This is due to hydroxyl ion produced from the corrosion of iron, according to the following two reactions [13].

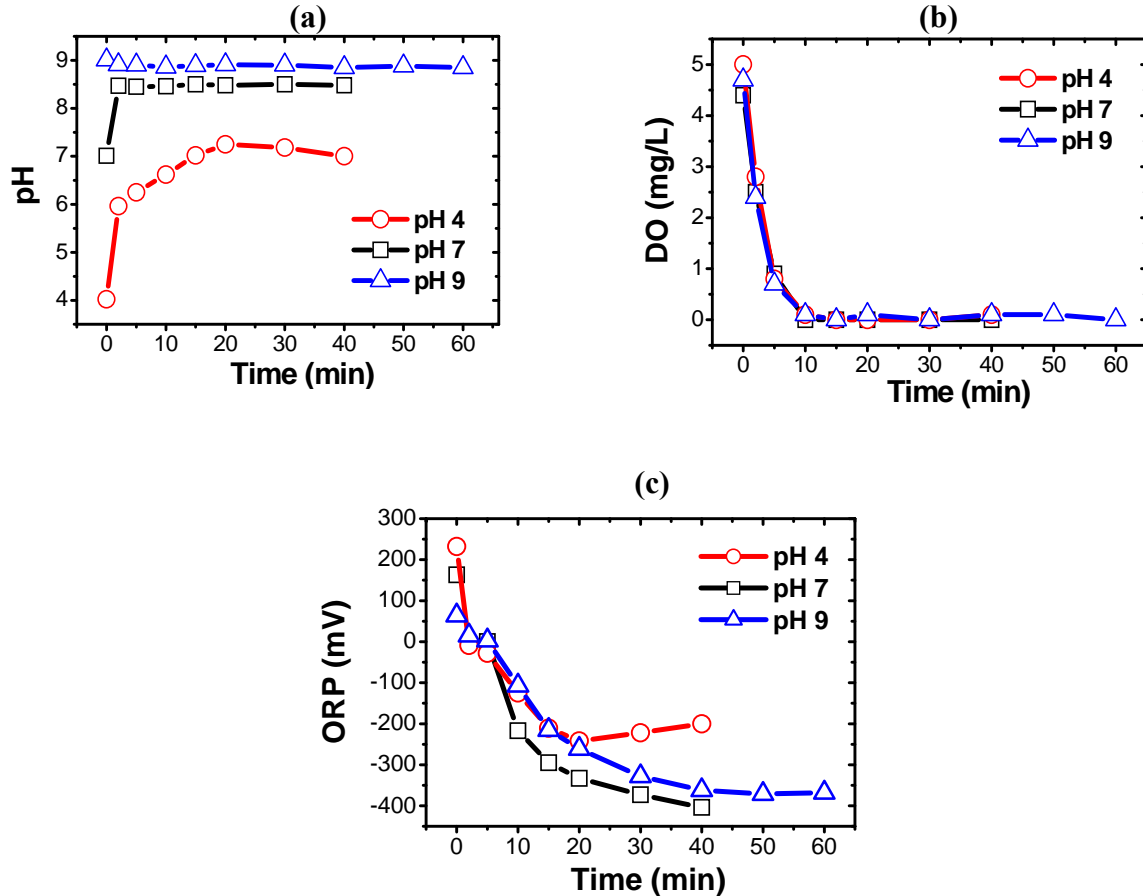


Figure 5. Effect of initial pH on (a) pH, (b) DO and (c) ORP profiles

The final pH equilibrium was around 8.5 when the initial pH was 7, and it was 8.9 for the initial pH 9. As for the initial pH 4, the final pH dropped after 20 min, due to that NZVI was consumed almost completely, resulting in less hydroxyl ion formation. In view of DO profiles, the results show that dissolved oxygen was rapidly consumed by NZVI, as can be explained by Equation (7). The DO profiles reach to zero within 10 min for all pH conditions. As for the ORP profiles, the values decreased from positive to negative ones when the NZVI was applied into the solution because of electrons being released from the iron. The negative values of ORP indicate that the solution conditions became a reducing environment [14].

5. CONCLUSIONS

This study was conducted to investigate the effect of initial solution pH on As(V) removal by using NZVI as a media of sorption. The results reveal that acidic condition favors more in As removal than in base condition, due to electrostatic force between adsorbate and the adsorbent. The As sorption kinetics for all pH values studied follows closely a pseudo first-order reaction because of excess of sorption sites of NZVI in the initial time of reaction. The kinetic rate constant (k) for the pH 4 was around 4.7 and 18.8 times higher than those for the pH 7 and 9, respectively.

Acknowledgements

This research was sponsored by the Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Thailand.

REFERENCES

- [1] Mohan, D., Pittman Jr., C.U. (2007) Arsenic removal from water/wastewater using adsorbents - A critical review. *J. Hazard. Mater.* 142, 1–53.
- [2] Melitas, N., Wang, J., Conklin, M., O'Day, P., Farrell, J. (2002) Understanding soluble arsenate removal kinetics by zerovalent iron media. *Environ. Sci. Technol.* 36, 2074-2081.
- [3] Ahuja, S. (2008) Arsenic contamination of groundwater: Mechanism, Analysis, and Remediation. John Wiley & Sons, Inc. Chapter 1.
- [4] Triszcz., J. M., Porta, A., Garça Einschlag, F. S. (2009) Effect of operating conditions on iron corrosion rates in zero-valent iron systems for arsenic removal. *Chem. Eng. J.* 150, 43 - 439.
- [5] Lackovic, J. A., Nikolaidis, N.P., Dobbs, G. M. (2000) Inorganic arsenic removal by zero-valent iron. *Environ. Eng. Sci.* 17, 29-40.
- [6] Sun, H., Wang, L., Zhang, R., Sui J., Xu, G. (2006) Treatment of groundwater polluted by arsenic compounds by zero valent iron. *J. Hazard. Mater.* B129, 297-303.
- [7] Glavee, G.N. Klabunde, K.J. Sorensen, C.M. Hadjipanayis, G.C. (1995) Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe₂B powders. *Inorg. Chem.* 34, 28-35.
- [8] Kanel, S . R., Greneche, J.M . Choi, C. (2006) Arsenic(V) Removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. *Environ. Sci. Technol.* 40, 2045-2050.
- [9] Giasuddin, A. M ., Kanel, S . R., Choi, C. (2007) Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal. *Environ. Sci. Technol.* 41, 2022-2027.
- [10] Borah, D., Satokawa, S., Kato, S., Kojima T. (2009) Sorption of As (V) from aqueous solution using acid modified carbon black. *J. Hazard. Mater.* 162, 1269–1277.

- [11] Manning, B.A., Hunt, M. L., Amrhein, C., Yarmoff, J. A. (2002) Arsenic(III) and arsenic(V) reactions with zerovalent iron corrosion products. *Environ. Sci. Technol.* 36 (24), 5455-546.
- [12] Su, C., Puls, R.W. (2001) Arsenate and arsenite removal by zerovalent iron: Kinetics, redox transformation, and implications for in situ groundwater remediation. *Environ. Sci. Technol.* 35, 1487-1492.
- [13] Noubactep, C. (2009) An analysis of the evolution of reactive species in $\text{Fe}^0/\text{H}_2\text{O}$ systems. *J. Hazard. Mater. (in press)*.
- [14] Ruangchainikom, C, Liao, C.H., Anotai, J., Lee, M.T. (2006) Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and of CO_2 - bubbled system. *Water Research.* 40, 195-204.

**Test of reducing power of nano zero-valent iron particles
using nitrate as a chemical probe**

Visanu Tanboonchuy¹, Jia-Chin Hsu², Nurak Grisdanurak^{1,3}, Chih-Hsiang Liao^{4*}, Yu-Lun Wei⁴

¹Department of Chemical Engineering, Faculty of Engineering,
Thammasat University, Pathumthani, THAILAND.

²Department of Environmental Engineering and Science,
Chia Nan University of Pharmacy and Science, Tainan, TAIWAN.

³National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat
University, Pathumthani, THAILAND.

⁴Department of Environmental Resources Management, Chia Nan University of
Pharmacy and Science, Tainan, TAIWAN.

* Corresponding author's email: chliao@mail.chna.edu.tw

NSC 97-2221-E-041 -010 -MY3

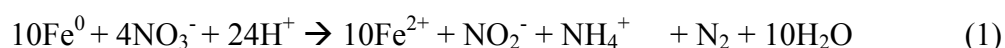
Abstract

Nano zero-valent iron (NZVI) has been extensively researched for treatment of hazardous and toxic wastes. In particular, it can be applied to remediate contaminated sites directly. In this study, the NZVI was synthesized by using chemicals of NaBH₄ and FeCl₃. The conditions for NZVI synthesis were varied by these parameters such as air exposure, feeding rate of NaBH₄ (3.3-10 mL/min), and agitation power (200-300 rpm). Right after completion of NZVI particles of different varieties, nitrate of 100 ppm was used to probe its reducing power. Of these three parameters investigated, it appears that the agitation of reaction solution plays a major role in determining its reducing power of NZVI particles. Besides, air exposure of reaction also posed noticeable change on the final residue of nitrate, whereas the synthesis with the studied range of NaBH₄ feeding rate exhibited no significant effect on nitrate reduction.

Keywords: environmental nanotechnology, nanoparticles, nitrate, zero-valent iron

1. Introduction

Currently, the nano zero-valent iron (NZVI) has received much attention from field researchers for its *in situ* groundwater treatment. There were many techniques and synthetic methods for NZVI synthesis such as chemical method [1, 2, 3], sono-chemical method [4], and thermal decomposition [5]. The sono-chemical method will generate toxic by-product, CO, because this method uses $\text{Fe}(\text{CO})_5$ as a raw material [6]. As for the thermal decomposition method, the produced NZVI particles tend to aggregate, due to the loss of the stabilization ability caused by the disappearance of the initial reactant chemicals during the heating process [5]. Thus, this study focuses on the NZVI synthesis by the chemical method because of its ease and simplicity, using only two common reagents, ferric salts and sodium borohydride. In addition, there's no need for complicated equipment or instrument for synthesis. In this study, the produced NZVI particles were tested for their reducing potential by the chemical probe, nitrate. As depicted in Reaction (1), the end products of the reaction might be nitrite, ammonia, and nitrogen, depending on the reaction condition [7].



The goal of this study was to investigate the effect of parameters such as air exposure of synthesis, feeding rate of NaBH_4 , and agitation speed of mixing on its reducing power of NZVI synthesized under various operating conditions. Results from this study will reveal the conditions for synthesizing the NZVI with the best performance.

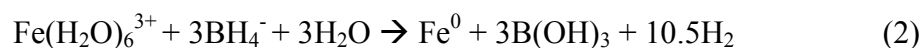
2. Materials and method

2.1. Chemicals

The chemicals of reagent grade used in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), NaBH_4 (> 96%), KNO_3 (99%)(Merck). All chemical solutions were prepared by using deionized water (18.2 M Ω Mill-Q).

2.2. Method of synthesis

The NZVI was synthesized according to Glavee et al.(1995) [1]. 0.25 M of NaBH_4 was added into 0.045 M of FeCl_3 aqueous solution. The mixture was agitated by a revolving propeller. Ferric iron is reduced by the borohydride, as shown in Reaction (2):



After solution was well mixed, the NZVI was separated from liquid solution by magnet. The NZVI was then produced and readily available for use. Table 1 depicts the various conditions for NZVI synthesis, in view of changing the three parameters such as air exposure, feeding rate of NaBH_4 , and agitation power.

Table 1 Conditions for NZVI synthesis

Condition	Air exposure	Feeding rate (mL/min)	Agitation speed (rpm)
A	Yes	3.3	200
B	Yes	6.6	200
C	Yes	3.3	300
D	No	6.6	300
E	No	3.3	300
F	No	10.0	300

2.3. Batch test

The synthesized NZVI was applied immediately for its reducing power test using nitrate as a chemical probe. The test was carried out with probe concentration (C_0) of 100 mg/L and NZVI dosage of 0.5 g/L. After the test, the reacted liquid samples were filtrated using a 0.45 μ m membrane filter to remove the iron from solution. Then, the residual nitrate (C) was analyzed by using Ion Chromatography (DINNEX-120, USA).

3. Results and discussion

3.1. Effect of synthesizing parameters

Air Exposure. In the presence of air, the oxygen may render the surface oxidation of produced NZVI during the synthesizing process (Reaction 3) [3]. In other words, the reducing power for the NZVI synthesized can be weakened because of the iron oxide layer blocking the electron transfer from the active sites of NZVI.



As shown in Figure 1, the nitrate was reduced by around 65% at time of 60 min under Condition C (air exposure), while the efficiency of nitrate reduction was 72% under Condition E (without air exposure). As understood, the sources of oxygen reacting with NZVI may come from atmospheric air and dissolved oxygen originally contained in the solution. In the case of solution-contained vessel sealed with aluminum foil, this can effectively prevent atmospheric oxygen from being absorbed into the reaction solution. Therefore, the nitrate-reduced capacity of NZVI can remain at a relatively higher level.

Feeding rate of NaBH₄. To avoid surface oxidation potential of NZVI being produced, it is preferred that the reaction can be completed as soon as possible. On top of this, it's always beneficial to save the reaction time for NZVI synthesis. Figure 1 shows that the three feeding rates studied, 3.3, 6.6, and 10.0 mL/min, have no significant effect on the nitrate-reduced power when the agitation speeds were at 200 (Conditions A and B) and 300 rpm (Conditions D and E), respectively. Choi et al. (2008) reported that rapid feeding of NaBH₄ may cause aggregation of NZVI precipitates, whereas slow feeding may result in oxidation of NZVI formed [6]. Comparatively speaking, it appears that the studied range of feeding rates, 3.3-10.0 mL/min, imposes neither aggregation nor oxidation of NZVI particles in a significant way.

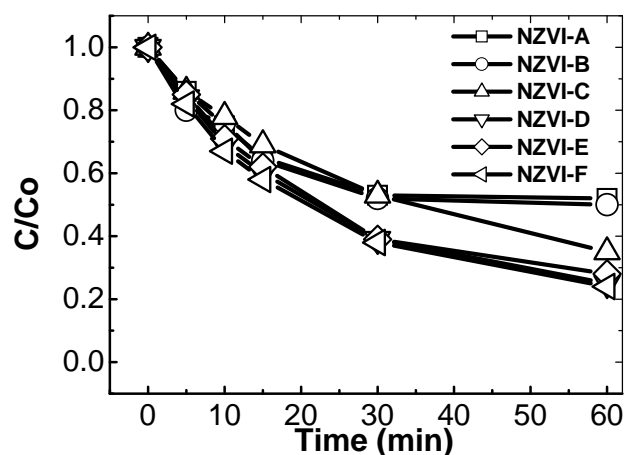


Figure 1. Capacity of nitrate reduction under various conditions of NZVI synthesis

Agitation speed. Two different agitating speeds, 200 and 300 rpm, were investigated in this study. The purpose was to compare the degree of NZVI particle aggregation. The results show that the NZVI synthesized with higher agitating speed (Condition C) has higher reducing power than that with lower one (Condition A). As is evidenced, higher agitating speed results in smaller NZVI particles, which in turn provides higher contact area between NZVI and nitrate.

3.2. Electron donating capacities (EDC's) of NZVI

The nitrate was reductively degraded by the electrons donated from the NZVI. Thus, the best type of NZVI is intended to be evaluated through an index which can describe its reducing power. According to Figure 2, the NZVI synthesized under Condition A was capable of reducing nitrate into end products such as ammonium (NH_4^+) and nitrite (NO_2^-). The mass balance profiles seem to indicate that there's other species formed in the reaction. As mentioned earlier in Reaction (1), most probably the nitrogen gas is responsible for the difference between the two profiles, the line with nitrate removed and the line with addition of ammonium and nitrite. Based on Reaction (1), the electron donating capacity (EDC, mole electron per unit mass of NZVI) is proposed for the quantitative evaluation of NZVI reducing power of different types. The equations for EDC calculation are listed in Equations (4)-(5).

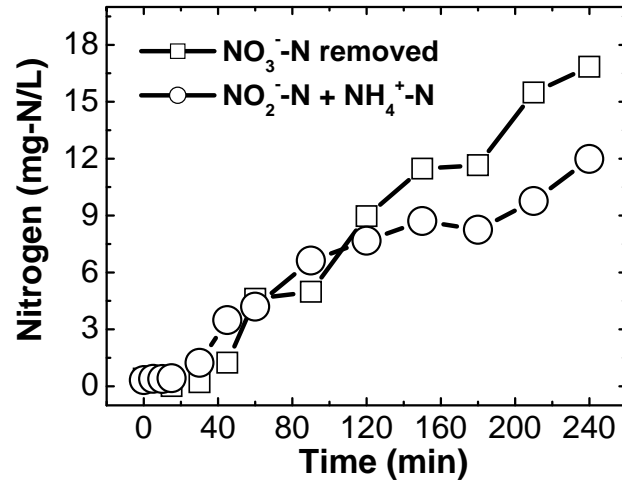


Figure 2. Mass balance profile for the nitrate reduction by NZVI synthesized under Condition A.

$$EDC = \frac{2 \times \text{moles of } Fe^0 \text{ reacted}}{\text{initial dosage of } Fe^0} \quad (4)$$

$$= \frac{2 \times \text{moles of } NO_3^- \text{ removed} \times \frac{5}{2}}{\text{initial dosage of } Fe^0} \quad (5)$$

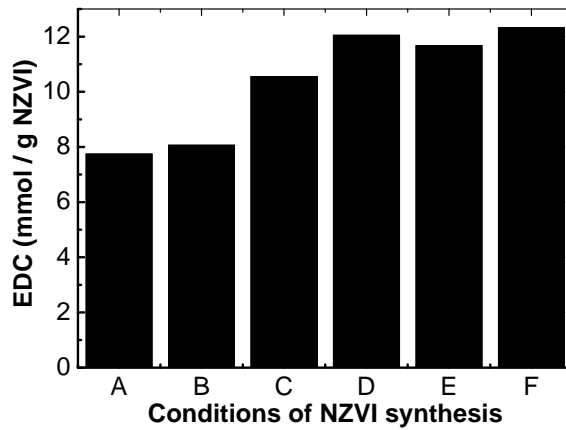


Figure 3. Comparison of electron donating capacities for NZVI synthesized under various conditions

The EDC's for NZVI synthesized under different conditions (See Table 1) were thus calculated and presented in Figure 3. The reducing power for different types of NZVI is in the order: $F \geq D > E > C > B > A$, where the importance for the parameter, agitating speed, dominates over the other two, air exposure and feeding rate.

4. Conclusions

In this study, the reducing performance of NZVI synthesized under different conditions was tested by using nitrate as a chemical probe. The results revealed that the reducing capacity of NZVI will increase when NZVI was synthesized under the condition of higher agitation of reaction solution, 300 rpm. In addition, when the reaction solution-contained vessel was capped with aluminum foil, the reducing capacity for the NZVI synthesized was improved. The feeding rates of NaBH₄, which fall within the range of 3.3-10.0 mL/min, show no significant effect on the reducing power of NZVI. This can be beneficial in view of saving the time required for NZVI synthesis when higher feeding rate is applied. Furthermore, a quantitative index, electron donating capacity, for evaluating NZVI's reducing power was proposed. With this index available, the chemical probe of nitrate can be adopted as a screening method for NZVI performance evaluation.

Acknowledgements

The research was sponsored by the Taiwan National Science Council (NSC) under project No.: NSC 97-2221-E-041-010-MY3 and National Center of Excellence for Environmental and Hazardous Waste Management, Thammasat University, Thailand.

References

1. Glavee, G.N. Klabunde, K.J. Sorensen, C.M. Hadjipanayis, G.C. "Chemistry of Borohydride Reduction of Iron (II) and Iron (III) Ions in Aqueous and Nonaqueous Media. Formation of Nanoscale Fe, FeB, and Fe₂B Powders", *Inorg. Chem.*, 34, 28-35 (1995).
2. Wang, C.B. Zhang, W.X. "Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs", *Environ. Sci. Technol.*, 31, 2154-2156(1997).
3. Ponder, S.M. Darab, J.G. Mallouk, T.E. "Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported, Nanoscale Zero-valent Iron", *Environ. Sci. Technol.*, 34, 2564-2569 (2000).
4. Khalil, H. Mahajan, D. Rafailovich, M. Gelfer, M. Pandya, K. "Synthesis of zerovalent nanophase metal particles stabilized with poly (ethylene glycol)", *Langmuir*, 20, 6896-6903 (2004).
5. Amaraa, D. Felnerb, I. Nowikb, I. Margel, S. "Synthesis and characterization of Fe and Fe₃O₄ nanoparticles by thermaldecomposition of triiron dodecacarbonyl", *Colloids and Surfaces A: Phys. Eng. (in press)* (2009).
6. Choi, H.C. Giasuddin, A.B.M. Kanel, R. "Method of synthesizing air-stable zero-valent iron nanoparticles at room temperature and applications", US Patent 2008/0091054, A1 (2008).
7. Ruangchainikom, C. Liao, C.H. Anothai, J. Lee, M.T. "Characteristics of nitrate reduction by zero-valent iron powder in the recirculated and CO₂-bubbled system", *Water Research*, 40, 195-204 (2006).

國科會補助專題研究計畫成果報告自評表

1. 請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☒ 達成目標

☐ 未達成目標（請說明，以 100 字為限）

☐ 實驗失敗

☐ 因故實驗中斷

☐ 其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☒已發表(2 篇) ☒未發表之文稿(2) ☒撰寫中(1) ☐無

專利：☐已獲得 ☐申請中 ☒無

技轉：☐已技轉 ☐洽談中 ☒無

其他：3 件博士生論文著作(預計)、1 件碩士生論文著作、研討會論文 9 篇

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

本研究案主要之技術創新性在於以 CO_2 結合奈米技術處理水中之砷物質，而奈米鐵材料之應用研究，目前已相當普遍。但是，處理系統引入氣相二氧化碳，構成異相程序(heterogeneous process)以提升砷去除效率，就筆者所知，到目前為止，並未有任何代表性之文章發表。而從本研究案之成果展現， Fe^0/CO_2 程序證明是一種可行、有效之淨水程序，對於地下水深受高濃度砷污染的國家（例如：台灣西南沿海、越南河內、孟加拉），提供了另類解決方案。換言之，這種因砷引致烏腳病變之社會大眾公共衛生議題，我們的成果可以納入政府決策之重要參考資訊。從技術應用層面來看，奈米鐵製備程序已相當純熟，而 CO_2 應用於淨水程序(Carbonation and recarbonation processes)中也已相當普遍。所以，結合本研究之發現與結論，將 Fe^0/CO_2 應用於淨水廠之淨水單元中，乃是簡單易行。唯一需要進一步評估的是其成本效益，例如，納入國家醫療成本及水處理成本等因素，以確認本技術之應用價值。

國科會補助計畫衍生研發成果推廣資料表

日期：__年__月__日

國科會補助計畫	計畫名稱： Fe⁰/CO₂程序串聯流體化床反應槽新穎技術處理含砷地下水 計畫主持人： 廖志祥 計畫編號： NSC 97-2221-E-041 -010 -MY3 領域： 淨水技術		
研發成果名稱	(中文) 結合奈米鐵與二氧化碳之淨水技術		
	(英文) Combination of nanoiron and CO₂ for water purification technology		
成果歸屬機構	嘉南藥理科技大學	發明人 (創作人)	廖志祥
技術說明	(中文) (尚未申請專利) (200-500 字)		
	(英文)		
產業別	用水及回收相關事業		
技術/產品應用範圍	自來水或廢水處理		
技術移轉可行性及預期效益	詳“研究計畫成果報告自評表”中第3項之說明。		

註：本項研發成果若尚未申請專利，請勿揭露可申請專利之主要內容。