

Arsenate removal by zero valent iron: Batch and column tests

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Abstract

This study investigates the efficiency of zero valent iron (ZVI) to remove arsenate from water. Batch experiments were carried out to study the removal kinetics of arsenate under different pH values and in the presence of low and high concentrations of various anions (chloride, carbonate, nitrate, phosphate, sulphate and borate), manganese and dissolved organic matter. Borate and organic matter, particularly at higher concentrations, inhibited the removal of arsenic. Column tests were carried out to investigate the removal of arsenate from tap water under dynamic conditions. The concentrations of arsenic and iron as well as the pH and Eh were measured in treated water. Efficient removal of arsenate was observed resulting at concentrations below the limit of 10 $\mu\text{g/L}$ in treated waters.

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1. Introduction

The presence of arsenic compounds in groundwater, and eventually in drinking water, is a serious environmental problem. Arsenic is released to the environment mostly through natural processes, due to the presence of arsenical minerals, volcanic emissions and inputs from geothermal sources, as well as a consequence of anthropogenic activities, such as mining activities, combustion of fossil fuels and use of arsenical pesticides [1,2]. Arsenic is present in the aquatic environments mostly in inorganic species, arsenate and arsenite. Arsenate, As(V), is the predominant arsenic form in oxidizing conditions while arsenite, As(III), occurs mainly in reducing environment. Arsenite is considered more toxic than arsenate and tends to be more mobile in the environment [2]. Long-term exposure in high levels of arsenic may cause skin changes, damage to major body organs and some types of cancer.

Increased concentrations of arsenic in natural water have been reported in many areas all over the world such as, in South East Asia (Bangladesh, Vietnam, West Bengal-India, Nepal, Cambodia, Mongolia, China, Thailand, Pakistan and Taiwan), in Central and South America (Mexico, Chile and Argentina) and in North America (USA and Canada) and in Australia [2,3]. Elevated concentrations of arsenic have been also found in various

European countries, i.e., Finland, Hungary, Germany, Croatia, Romania, Italy, Spain and Greece [2–7].

In order to minimize the possible risk from arsenic, a parametric value of 10 $\mu\text{g As/L}$ has been set for water intended for human consumption according to Directive 98/83/EC. Thus, many municipalities that have problems with elevated arsenic concentrations should apply a method for the efficient removal of arsenic. Several techniques have been proposed for the removal of arsenic from waters or wastes. The most common are coagulation—precipitation using iron and aluminum substances, ion exchange, reverse osmosis, nanofiltration, bioremediation and adsorption [8–12]. Various adsorption materials have been used such as activated alumina, activated carbon, fly ash, ferric hydroxide and zero valent iron [13–18]. Zero valent iron (ZVI) has been used for the removal of organic and inorganic contaminants from aqueous solutions [15]. Several studies report that ZVI has also high arsenic removal capacity and could be used as a permeable reactive barrier for remediation of polluted groundwater. The removal of arsenic by employing ZVI depends on the type of material, the composition of treated water, the initial arsenic concentrations and the arsenic speciation.

The aim of this study was to investigate the efficiency of ZVI under various conditions to remove arsenate. Batch tests were conducted under different pH and different concentrations of anions (chloride, phosphate, carbonate, sulfate, nitrate and borate), manganese and dissolved organic matter to study the kinetics of arsenic removal. Moreover, column tests were carried

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out in tap water spiked with arsenate to investigate the removal efficiency of two ZVI materials.

2. Materials and methods

2.1. Materials

Iron powder (–325 mesh, 97%, Aldrich) and iron filings (produced from commercial steel) were used without pretreatment. Stock solution of 1000 mg As(V)/L (H_3AsO_4) purchased from Merck. Stock solutions of chloride, sulphate, nitrate, phosphate, carbonate, borate, manganese and iron were prepared from NaCl, K_2SO_4 , KNO_3 , KH_2PO_4 , NaCO_3 , H_3BO_3 , $\text{Mn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$, respectively, according to standard methods [19]. Stock solution of organic matter was prepared from humic acid purchased from Fluka. Fine (1500 mesh) and coarse (500–1000 mesh) grained silica sand was used.

2.2. Batch tests

Batch experiments were designed to investigate the kinetics and efficiency of arsenate removal in different initial pH values (4 and 7) and in the presence of various anions, manganese and organic matter. Conical flasks containing 0.1 g of Fe powder and 50 ml of arsenic solution (200 $\mu\text{g/L}$) were placed on an orbital shaker at room temperature for different time periods. Experiments were carried out at low and high concentrations of ions: $\text{Cl}^- = 200$ and 2000 mg/L, $\text{SO}_4^{2-} = 200$ and 2000 mg/L, $\text{NO}_3^- = 50$ and 500 mg/L, $\text{PO}_4^{3-} = 200$ and 2000 $\mu\text{g/L}$, $\text{B-BO}_3^{3-} = 400$ and 4000 $\mu\text{g/L}$, $\text{CO}_3^{2-} = 200$ and 1600 mg/L, $\text{Mn} = 200$ and 2000 $\mu\text{g/L}$ and humic acid = 5 and 50 mg/L. The initial pH of the solution was adjusted at the beginning of the experiment using hydrochloric acid or sodium hydroxide. The suspensions were open to the atmospheric air and at the end of the experiment were filtrated. Arsenic, iron and pH were measured in filtrates.

2.3. Column tests

Column experiments were carried out to investigate the removal efficiency of arsenate by ZVI powder and iron filings. Glass columns with 1.2 cm inner diameter were loaded with 5 g fine sand, 2 g coarse sand 1 g iron powder or iron filings. The porosity of the columns was 0.62 and 0.67, respectively. Tap water spiked with As(V) (100 $\mu\text{g As/L}$) was passed through column downward at various flows rates using a peristaltic pump. The pH of the influent water was 7.5. The effluents were filtrated and analyzed for arsenic and iron. The pH and Eh values of treated water were also measured.

2.4. Analytical methods

Arsenic was measured by hydride generation with Flame AAS (HG-FAAS) and iron by Flame AAS (FAAS) according to standard methods [19]. Eh and pH were measured by a pH/mV meter (Dr Lange, ECM). A combined Pt–Ag/AgCl redox electrode (4M KCl) was used for the measurement of Eh. The

instrument was calibrated using Zobell's solution (3×10^{-3} M potassium ferrocyanide and 3×10^{-3} M potassium ferricyanide in 0.1 M KCl) with a standard potential of +228 mV at 25 °C.

3. Results and discussion

3.1. Batch tests

The removal of arsenate by ZVI powder in different pH values is shown in Fig. 1. The results indicate a fast initial removal (60%) of arsenate at first 15 min of mixing followed by a gradual decrease. Over 99.9% of As(V) was removed in 6 h when initial pH was controlled at 7 ± 0.2 and nearly 90% at $\text{pH } 4 \pm 0.2$ (Fig. 1a). Similar results have been reported from other investigators; Bang et al. [17] reported 99.8% removal of arsenate under oxic conditions at pH 6 after 9 h of reaction and Sun et al. [18] found over 95% removal at pH 8.28. The pH dependence of arsenic removal is due to differences in arsenic adsorption in terms of ionization of both adsorbates and adsorbents [15]. Dissolved iron in treated waters exhibited high concentrations at short mixing periods, whereas a decrease trend was observed at higher reaction periods. Lien and Wilking [20] also found high dissolved concentrations of iron at the beginning of the experiment, gradually removed with time. Elevated concentrations of dissolved iron in batch experiments have been also reported by other investigators, though the levels of the iron concentrations vary due to different experimental conditions [17,20].

The removal kinetics of arsenate in the presence of low and high concentrations of various ions are illustrated in Fig. 2. The presence of sulfate accelerates the removal of arsenate, resulting at arsenic concentrations $< 1 \mu\text{g/L}$ within 30 min. Similar behavior exhibited the ions chloride, nitrate, phosphate, carbonate and the manganese that also enhance the removal rate of arsenate. Comparative data of the effects of individual ions on the removal of arsenate after 30 min of reaction are shown in Fig. 3. Within the first 30 min of the experiment a significant increase ($\sim 40\%$) of arsenic removal was observed in the presence of sulfate, chloride, nitrate, phosphate, carbonate and manganese. A decrease of arsenic removal in the presence of CO_3 was observed when there was not any pH adjustment at the beginning of the experiment (Table 1). The removal of arsenate was 98%, 86% and

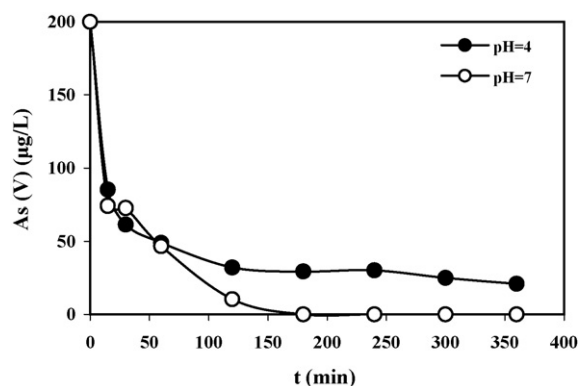


Fig. 1. Removal kinetics of arsenate in different initial pH values. Experimental conditions: $[\text{As}] = 200 \mu\text{g/L}$, $\text{ZVI} = 2 \text{g/L}$.

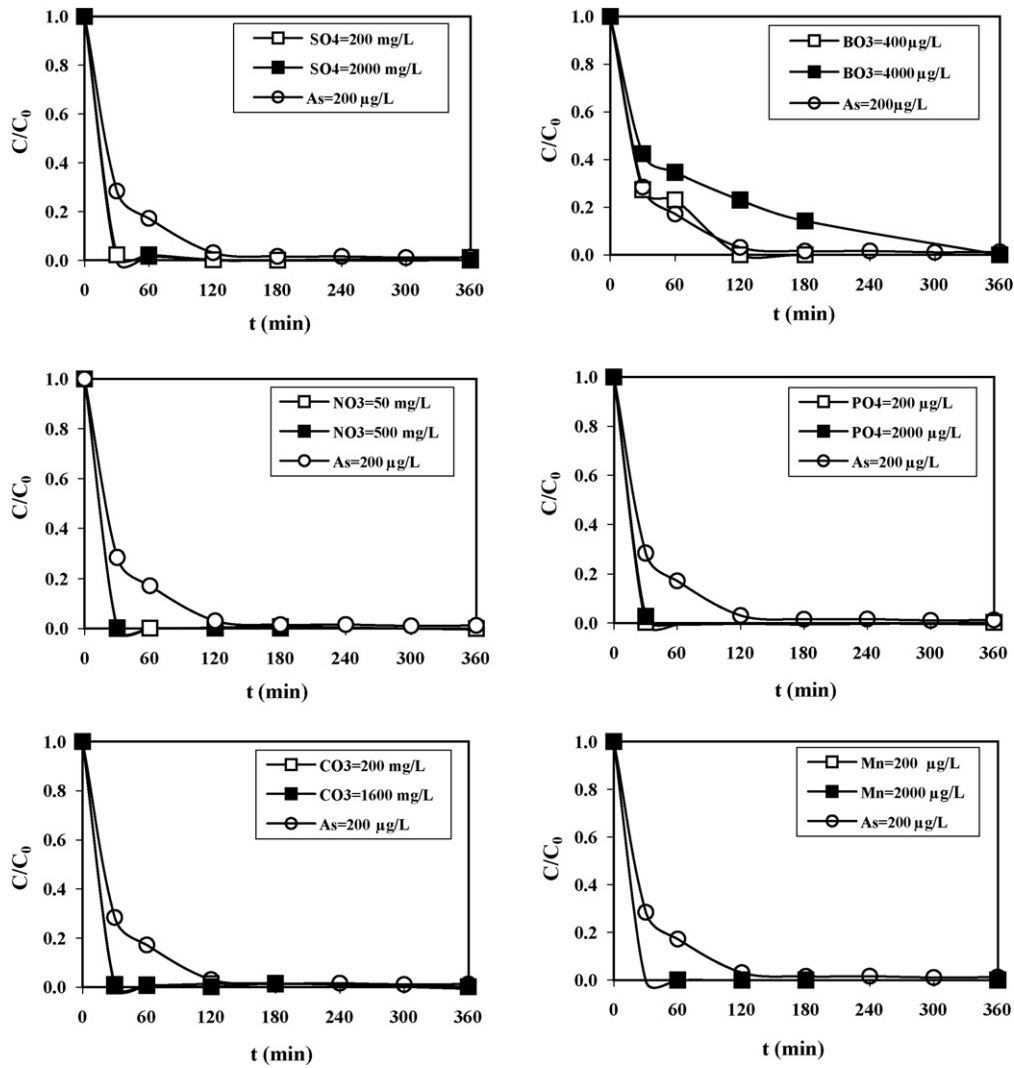


Fig. 2. Removal kinetics of arsenate in the presence of low and high concentrations of anions and manganese. Experimental conditions: $[As] = 200 \mu\text{g/L}$, $ZVI = 2 \text{ g/L}$, $\text{pH} = 7 \pm 0.2$.

Table 1
Removal (%) of arsenate by ZVI in the presence of various anions

| Anions | Concentration | Removal | Anions | Concentration | Removal |
|---------------------|---------------|---------|---------------------|---------------|---------|
| No addition of ions | – | 100 | No addition of ions | – | 100 |
| Cl | 100 mg/L | 100 | PO ₄ | 100 µg/L | 100 |
| | 200 | 100 | | 200 | 100 |
| | 400 | 100 | | 400 | 100 |
| | 800 | 100 | | 800 | 100 |
| SO ₄ | 50 mg/L | 100 | CO ₃ | 200 mg/L | 98 |
| | 100 | 100 | | 400 | 86 |
| | 200 | 100 | | 800 | 81 |
| | 400 | 100 | | 1600 | 81 |
| NO ₃ | 25 mg/L | 100 | B–BO ₃ | 400 µg/L | 100 |
| | 50 | 100 | | 800 | 100 |
| | 100 | 100 | | 1600 | 100 |
| | 200 | 100 | | 3200 | 100 |

Experimental conditions: $[As] = 200 \mu\text{g/L}$, $ZVI = 2 \text{ g/L}$, pH not adjusted, $t = 9 \text{ h}$.

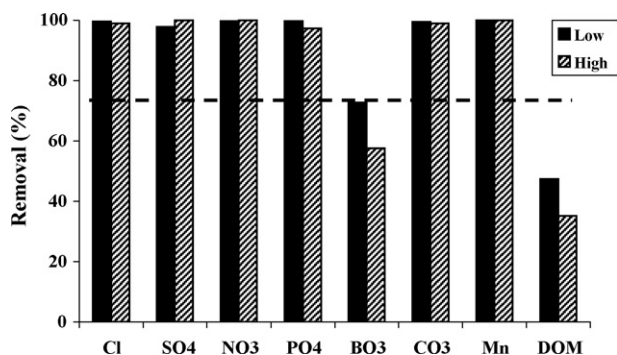


Fig. 3. Removal of As(V) in the presence of low and high concentrations of anions, manganese and dissolved organic matter after 30 min reaction. Dotted line represents the removal of arsenate in the absence of the studied parameters. Experimental conditions: [As] = 200 $\mu\text{g/L}$, ZVI = 2 g/L, pH = 7 \pm 0.2.

81% in the presence of 200, 400 and 1600 mg/L of carbonate, respectively with pH values ranged from 8.5 to 9.5. In the literature, there are various observations, contradictory in some cases, about the effect of ions on arsenic removal, highly dependent on the experimental conditions (pH values, initial concentrations, the ratio between ions and arsenic, etc.). An increase of arsenate removal in the presence of relatively high concentrations of sulfate has been reported by other investigators and was attributed to acceleration of precipitation of arsenic in the form of FeAsS [18], however, Su and Puls [21] reported a slight decrease of As(V) removal. The presence of nitrate results to the increase of arsenate removal according to Sun et al. [18] due to acceleration of ZVI corrosion, however, other investigators reported a significant decrease of the arsenic removal [21,22]. The presence of phosphate decreases the removal of arsenate through competition for sorption sites at the surface of iron oxides. This inhibiting effect depends on the initial concentration of phosphate and the ratio P:As [20]. In our study, relatively low, although environmental relevant, concentrations of phosphate were used with low P:As ratio (0.3–3) whereas significant higher ratios have been used in other studies (150–1500) [9]. A decrease of arsenate removal in the presence of bicarbonate has been reported by other investigators, probably due to the formation of protonated and nonprotonated inner-sphere monodentate surface complexes with amorphous iron oxides [21].

Borate showed different behavior on arsenate removal. Low concentrations of borate did not affect the removal. However, high concentrations (4000 $\mu\text{g B-BO}_3/\text{L}$) exhibited a significant inhibiting effect resulting at arsenic concentrations <1 $\mu\text{g/L}$ after 6 h (Fig. 2). High concentrations of borate resulted in 20% decrease of arsenic removal after 30 min of reaction (Fig. 3). The same behavior was reported by Su and Puls [21] that also found an inhibition on arsenic removal in the presence of borate depending on the pH values and arsenic speciation. The removal kinetics of arsenate in the presence of dissolved organic matter (DOM) is shown in Fig. 4. The presence of DOM decreased the rates of arsenic removal. At the first 30 min of the reaction the removal was reduced to 67% and 50% in the presence of 5 and 50 mg/L of humic acid, respectively. Sun et al. [18] reported similar behavior at the removal kinetics of arsenic in the presence of natural organic matter. Recently, Giasuddin et al.

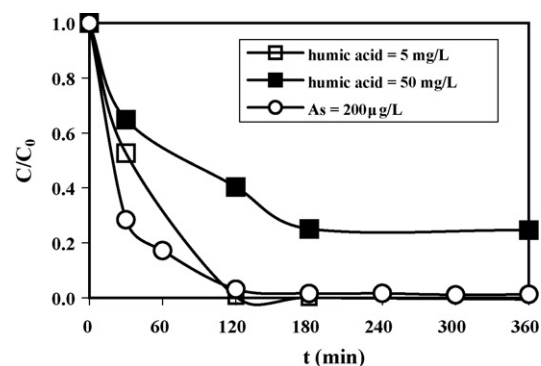


Fig. 4. Removal kinetics of arsenate in the presence of low and high concentrations of dissolved organic matter. Experimental conditions: [As] = 200 $\mu\text{g/L}$, ZVI = 2 g/L, pH = 7 \pm 0.2.

[23] also reported that humic acid has competitive effects with arsenic during water treatment with nanoscale ZVI. The surface normalized rate constant of adsorption of As(V) onto nanoscale ZVI was reduced to 68%, in the presence of 20 mg/L humic acid.

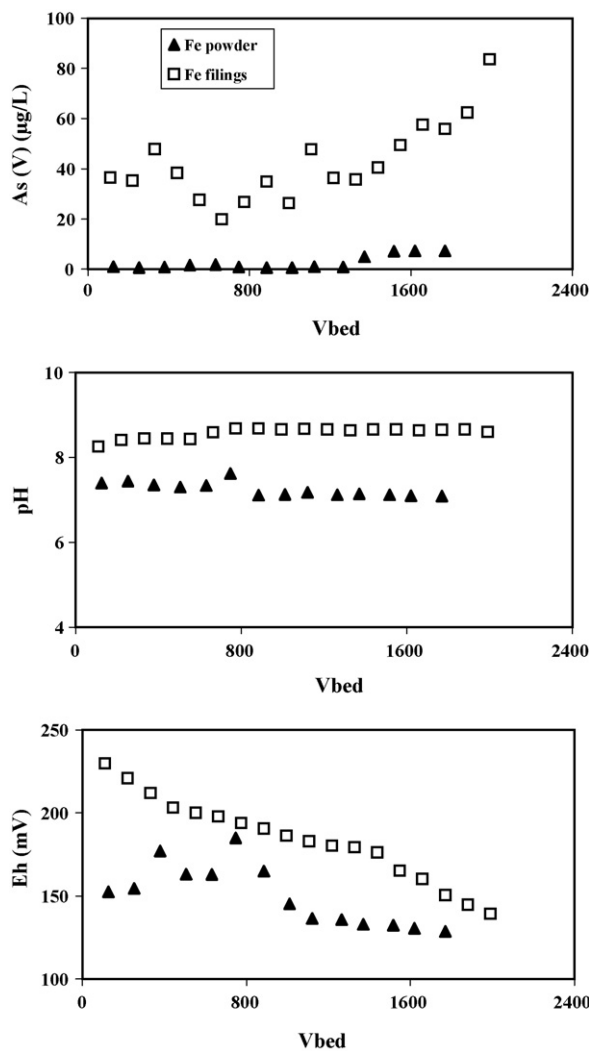


Fig. 5. Column experiments for the removal of arsenate by different ZVI materials. Arsenic concentration, pH and Eh values in treated water vs. bed volumes. Experimental conditions: tap water spiked with 100 $\mu\text{g As(V)/L}$, flow rate 1 L/h.

Fig. 4 shows that at high levels of DOM (50 mg/L) the concentration of arsenic in the solution remains stable ($\sim 50 \mu\text{g/L}$) even after 6 h of reaction; this effect could be attributed to the mobilization of arsenic from iron oxides in the presence of dissolved organic matter [24].

3.2. Column tests

Column experiments were conducted to investigate the removal of arsenate by two different iron materials, ZVI powder (325 mesh) and iron filings. The concentration of arsenic, the pH and Eh values measured in treated water are shown in Fig. 5. ZVI powder efficiently eliminated arsenate from water. The arsenic concentration remained below $1 \mu\text{g/L}$ up to 1300 bed volumes and the arsenic drinking water standard of $10 \mu\text{g/L}$ was not exceeded up to 1900 bed volumes. Iron filings exhibited lower removal efficiency, with arsenate concentrations in effluents above the limit of $10 \mu\text{g/L}$. This difference in removal efficiency could be attributed to the different surface area of these materials. Treated water by iron filings showed higher pH values (8–9) than that of iron powder (7–8). The increase of pH values has been attributed to water decomposition by Fe^0 and adsorption reaction of arsenic which release OH^- groups from adsorbents as a result of ligand exchange. The Eh values in treated water showed a decreased trend with time up to $\sim 100 \text{mV}$. Similar observations for pH and Eh have been reported by other investigators [15,21]. The concentration of dissolved iron in effluents was relatively low ($<250 \mu\text{g/L}$).

4. Conclusions

The efficiency of ZVI for removal of arsenate from water was studied. Batch experiments were conducted to investigate the effect of the pH and of the presence of various anions (chloride, carbonate, nitrate, phosphate, sulphate and borate), manganese and organic matter on removal of arsenate. Borate and organic matter, particularly at higher concentrations, decrease the removal of arsenate. The other anions enhance the removal rate of arsenate. Column tests were employed to study the arsenic removal efficiency of two ZVI materials (iron powder and iron filings). Efficient removal of As(V) ($<10 \mu\text{g/L}$ in treated waters) by employing iron powder was observed.

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References

- [1] C.K. Jain, I. Ali, Arsenic: occurrence, toxicity and speciation techniques, *Water Res.* 8 (2000) 4304–4312.

- [2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behavior and distribution of arsenic in natural water, *Appl. Geochem.* 17 (2002) 517–568.
- [3] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, Arsenic contamination of groundwater and drinking water in Vietnam: a human health treat, *Environ. Sci. Technol.* 35 (2004) 2621–2626.
- [4] S. Cavar, T. Klapeč, R.J. Grubesić, M. Valek, High exposure to arsenic from drinking water at several localities in eastern Croatia, *Sci. Total Environ.* 339 (2005) 277–282.
- [5] D. Voutsas, C. Samara, Th. Kouimtzi, Ground water quality in the major industrial area of Thessaloniki, Greece. Part 2: Heavy metal distribution, source, identification, *Toxicol. Environ. Chem.* 45 (1994) 105–119.
- [6] A. Kouras, I. Katsoyiannis, D. Voutsas, Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece, *J. Hazard. Mater.* 147 (2007) 890–899.
- [7] I. Meladiotis, N. Veranis, N.P. Nikolaidis, Arsenic contamination in Central Macedonia, Northern Greece: extent of the problem and potential solutions, in: *Proceedings of Conference on the Protection and Restoration of the Environment, Skiathos, Greece, 2002*.
- [8] Y. Sato, M. Kang, T. Kamei, Y. Magara, Performance of nanofiltration for arsenic removal, *Water Res.* 36 (2002) 3371–3377.
- [9] K. Jaeshin, M.M. Benjamin, Modeling a novel ion exchange process for arsenic and nitrate removal, *Water Res.* 38 (2004) 2053–2062.
- [10] E.O. Kartinen Jr., C.J. Martin, An overview of arsenic removal processes, *Desalination* 103 (1995) 79–88.
- [11] A.I. Zouboulis, I.A. Katsoyiannis, Recent advances in the bioremediation of arsenic-contaminated groundwaters, *Environ. Int.* 31 (2005) 213–219.
- [12] B. Van der Bruggen, C. Vandecasteele, Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry, *Environ. Pollut.* 122 (2003) 435–445.
- [13] T.F. Lin, J.K. Wu, Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics, *Water Res.* 35 (2001) 2049–2057.
- [14] B. Daus, R. Wennrich, H. Weiss, Sorption materials for arsenic removal from water: a comparative study, *Water Res.* 38 (2004) 2948–2954.
- [15] 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.
- [16] N.P. Nikolaidis, G.M. Dopps, J.A. Lackovich, Arsenic removal by zerovalent iron: field, laboratory and modeling studies, *Water Res.* 37 (2003) 1417–1425.
- [17] S. Bang, G.P. Korfiatis, X. Meng, Removal of arsenic from water by zerovalent iron, *J. Hazard. Mater.* 121 (2005) 61–67.
- [18] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.* 129 (2006) 297–303.
- [19] APHA, AWWA, WPCF, Standard methods for the examination of water and wastewater, 16th ed., 1985.
- [20] H.L. Lien, R.T. Wilking, High-level arsenite removal from groundwater by zero-valent iron, *Chemosphere* 59 (2005) 377–386.
- [21] C. Su, R.W. Puls, 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 (2001) 4562–4568.
- [22] K. Tyrovolas, N.P. Nikolaidis, N. Veranis, N. Kallithrakas-Kontos, P.E. Koulouridakis, Arsenic removal from geothermal waters with zero-valent iron—effect of temperature, phosphate and nitrate, *Water Res.* 40 (2006) 2375–2386.
- [23] 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.
- [24] M. Bauer, C. Blodau, Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments, *Sci. Total Environ.* 354 (2006) 179–190.