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A COMPARATIVE STUDY ON ARSENIC (III) REMOVAL FROM AQUEOUS SOLUTION USING NANO AND MICRO SIZED ZERO-VALENT IRON

***[1]A. R. Rahmani, [2]H.R. Ghaffari, [1]M.T. Samadi,**

[1] Department of Environmental Health Engineering, Faculty of Health and Research Center for Health Sciences, Hamedan University of Medical Sciences, Hamedan, Iran
[2] Department of Environmental Health Engineering, Faculty of Health, Hormozgan University of Medical Sciences, Bandarabbas, Iran

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ABSTRACT

The present study was conducted for Arsenic (III) removal, one of the most poisonous groundwater pollutants, by synthetic nano and micro size zerovalent iron (n-mZVI). Batch experiments were performed to investigate the influence of As (III), nZVI and mZVI concentration, pH of solution and reaction time on the efficiency of As (III) removal by Fe^0 particles. Nano ZVI was synthesized by reduction of ferric chloride by sodium borohydrid. Scanning Electron microscope and X-Ray diffraction were used to determine particle size and characterization of produced nanoparticles. Results showed up to 99.9% removal efficiency for arsenic (III) that was obtained by nZVI dosage of 1 g/L at equal time of 10 min and pH=7. The maximum removal efficiency by mZVI obtained in initial arsenic concentration of 1 mg/L and mZVI dosage of 10 g/L after 120 min. and pH=7. It could be concluded that the removal efficiency was enhanced with increasing n-mZVI dosage and reaction time, but decreased with increasing of arsenic concentration and pH for both nano and micro sized ZVI. Nano ZVI presented an outstanding ability to remove As (III) due to not only a high surface area and low particle size but also to high inherent activity.

Key words: Aqueous solution; Arsenic; Removal; Zero-valent iron; Nano particles

INTRODUCTION

Arsenic (As), one of the common constituent of earth crust, is a contaminant of groundwater and surface water resources. Arsenic may be introduced into environment through both natural and anthropogenic activity. This element is carcinogenic and very toxic for human and other organisms (Kanel *et al*., 2005, 2006; Tyrovolas *et al*., 2006, 2007). Most important arsenic health effects are gastrointestinal symptom, disturbance of cardiovascular and nervous system function, pigmentation, depigmentation, keratosis, skin cancer, teratogenicity, reproduction disorder and death (Kanel *et al*., 2005). Also the general features of chronic arsenic poisoning include malaise, weakness, general debility, decreased appetite and peripheral neuropathy (Mosaferi *et al*., 2005).

The major pathway to human exposure by arsenic is drinking of polluted groundwater (Tyrovola *et al*., 2006). The Maximum Contaminant Level (MCL) of Arsenic in drinking water is 10 µg/L, confirmed by USEPA, World Health Organization (WHO) and the European Commission (EC) (Kanel *et al*., 2005, 2006; Tyrovola *et al*., 2006).

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*Corresponding author: E-mail: rahmani@umsha.ac.ir
Tel/Fax: +98 811 8255301

In natural water resourses, the inorganic forms of arsenic such as arsenite species (arsenious acid, H_3AsO_3) and negatively charged arsenate (H_2AsO_4 and $HAsO_4$) are prevailing (Kanel *et al*., 2005; Tyrovola *et al*., 2006 and 2007). Many different technologies have been used for removal of arsenic from drinking water. The common method for removal of arsenic from water is physiochemical treatment including precipitation, adsorption, ion exchange, membrane filtration and also microbial transformation (Kanel *et al*., 2005; Tyrovola *et al*., 2006). Also iron oxides, iron oxides-coated sand, treated activated carbon by various cationic metal salts and pretreated waste tea fungal biomass were used (Mamisahebei *et al.,* 2007). Recently zero-valent iron (ZVI)is used as most effective agent for rapid removal of Arsenic (III) and Arsenic(V) from subsurface environment (Bang *et al*., 2005; Kanel *et al*., 2005; Tyrovola *et al*., 2007).

ZVI as a remediation agent in groundwater treatment was first used early 1990s in permeable reactive barrier (PRBs) systems (Li *et al*., 2006). Reactivity of ZVI can be improved by decreasing the particle size in nanoscale zero-valent iron (nZVI) form (Kanel *et al*., 2005). Nanoscale iron particle have been used for transforming and detoxification of wide variety of contaminants, such as perchlorate, brominated methane, Cr (VI), Pb (II), three chloro etan (TCE), humic acids, nitrate, biosolids, copper and zinc (Chen *et al*., 2005; Yang and Lee, 2005; Rangsivek and Jekel, 2005; Niu *et al*., 2005; Plagentz *et al*., 2006; Chen *et al*., 2007; Giasuddin *et al*., 2007; Li *et al*., 2007; Xu and Brown, 2007).

For this reason and in view of highly efficiency of nZVI, the aim of this study was the synthesis of nanoparticles zero valent iron by a cheap method and comparison of its efficiency with microparticles zero valent iron (mZVI) in As (III) removal from aqueous solutions. Also the effects of initial As (III), nZVI and mZVI concentrations, pH and reaction time on the As (III) removal efficiency were investigated.

MATERIALS AND METHODS

Chemicals

All chemical reagents used in this study were obtained from Merck Company (Germany). The extra pure zero valent iron powder with particle size of 150 micron was also obtained from the same company. The solutions were prepared by dissolving the adequate quantities of the compounds in distilled water. Arsenic solutions were prepared by dissolving the $NaAsO_2$ in distilled water and determined in 520 nm by UV/Vis spectrophotometer (Shimadzo-1700, Japan). 1 M HCl or NaOH was used for adjustment of pH and controlled by pH meter (Suntex model sp-701). Water was purified with a water distiller (Fater Electronic model 2104).

Preparation of particles nZVI

Nano sized particles were produced by reduction of ferric iron in the presence of sodium borohydrid. These particles were prepared freshly each day by adding 0.16 M $NaBH_4$ aqueous solution drop wise to a 0.1 M $FeCl_3$-$6H_2O$ aqueous solution laboratory temperature and under atmospheric conditions (Sung and Francis, 2006). The preparation of solutions involved the following steps: sodium borohydride ($NaBH_4$, 0.6053 g) solids were dissolved in 100 mL of 0.1 M NaOH solution (0.16 M $NaBH_4$ in 0.1 M NaOH solution), and then 2.703 g of $FeCl_3.6H_2O$ was dissolved into 100-mL pure water (0.1 M $FeCl_3.6H_2O$). $NaBH_4$ solution can be made either in water or NaOH solution; $NaBH_4$ is unstable in water and can quickly result in a loss of reduction power. Addition of the $NaBH_4$ to the $FeCl_3$ solution in the presence of vigorous magnetic stirring results in the rapid formation of fine black precipitates as the ferric iron reduced to Fe and precipitated according to the reaction (1):

$$2\,FeCl_3 + 6\,NaBH_4 + 18\,H2O \rightarrow 2Fe^{o}_{(s)} + 6\,B\,(OH)_3 + 6\,NaCl \qquad (1)$$

The particles were washed 3 to 4 times with a 10-4 M HCl (pH=4) solution, stored as a 5-mg Fe/mL concentrate at pH=4 and kept in a refrigerator at <4ºC. The characterizations of solid-phase nZVI were carried out using XRD (Philips X-Rert) and SEM (Philips XL30).

Batch experiments by nano sized ZVI

Batch experiments were performed in 100 ml beaker covered with aluminum foil. The beaker was mixed by magnetic stirrer (150 rpm) at laboratory. temperature. After given period of time, the sample was centrifuged at 3000 rpm for 15 min. Then the solution was filtered through 0.45 µm membrane filter and analyzed for arsenic by Silver Diethyldithiocarbamate method (SDDC) (APHA, 2005). The effect of various parameters such as reaction time (2, 5, 10 and 15 min), pH (4, 7 and 11), initial nZVI weight (0.1, 0.25, 0.5 and 1 g/L) and initial arsenic concentration (1, 3, 5, 10, 15, 20, 25 and 30 mg/L) were studied in term of their effect on removal process.

Batch experiment using micron particle zero valent iron (mZVI)

Batch experiments were conducted at atmospheric condition in 100 mL beaker capped by aluminum foil to prevent water loss through evaporation. The iron filling were pretreated with concentrated HCl. After preparation, the iron filling quickly transferred into the arsenic solution to start the batch test. The samples were rotated by orbital shaker (1000 rpm). After mixing time period, the sample was filtered and analyzed for arsenic by SDDC methods. Similar to nZVI system, various parameters such as pH (4, 7 and 11), reaction time (30, 60 and 120 min), initial iron powder weight (1, 3, 5 and 10 g/L) and initial arsenic concentration (0.5, 1, 3, 5 and 10 mg/L) were investigated.

RESULTS

Characterization of ZVI nanoparticles

The pristine samples collected from different crops synthesis of nZVI were tested for characterization. Our result was similar to those reported in the literatures (Kanel *et al*., 2005, 2006). The SEM micrograph of the iron nanoparticles is shown in Fig. 1 (a-b). Synthetic nZVI particle was in the size range of 10-100 nm as measured by SEM. This micrograph showed that the *ZVI* nanoparticles do not appear as discrete particles but form much larger dendritic flocs whose size could reach micron scale. The aggregation is attributed to the magnetic forces among the iron particles. Similar phenomenon was observed by other researchers (Niu *et al*., 2005). X-Ray diffraction of nZVI surface composition indicated that surface species of prepared nZVI is Fe^0 and FeOOH.

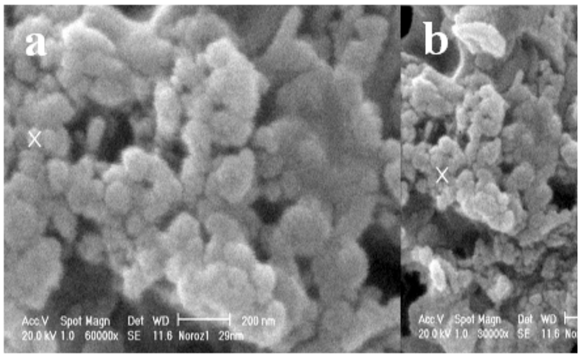

Fig. 1: SEM image of synthesized nZVI

Effect of pH

The effect of pH on As (III) removal using nano and micro particle zero-valent iron was examined at various pH ranges (4, 7 and 11), 10 mg/L As (III) and 1 g/L of nZVI and mZVI, respectively. Adsorption efficiency of As (III) on nZVI and mZVI as a function of pH and time are shown in Figs. 2-3.

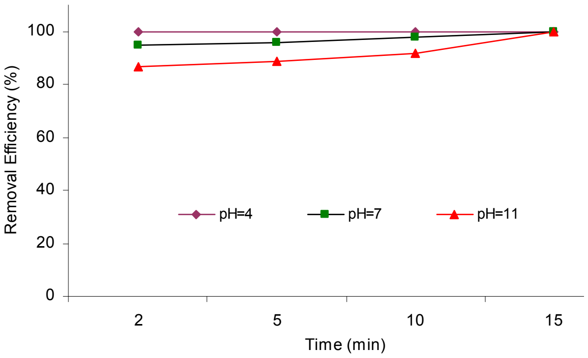

Fig. 2: Adsorption efficiency of As (III) on nZVI as a function of pH and time. Reaction conditions: 10 mg/L As (III) adsorbed on 1.0 g/L nZVI

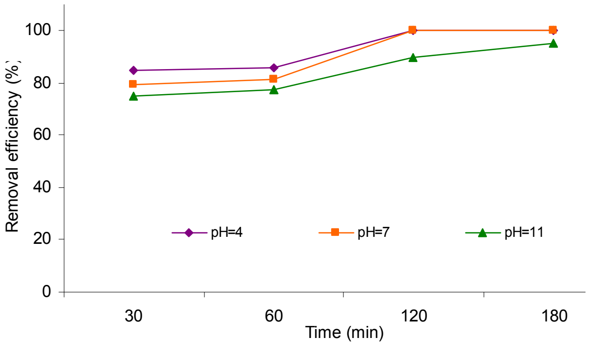

Fig. 3: Adsorption efficiency of As (III) on mZVI as a function of pH and time. Reaction conditions: 10 mg/L As (III) adsorbed on 1.0 g/L mZVI

Effect of nZVI and mZVI dosage

Adsorption studies of As (III) onto nZVI and mZVI were performed using 10 mg/L As (III) treated with varying nZVI and mZVI solid concentrations. Adsorption efficiency of As (III) on nZVI and mZVI as a function of pH and nZVI dosage are shown in Figs. 4-5.

Effect of reaction time

Adsorption of As(III) on nZVI and mZVI as a function of time and adsorbents dosage at pH=7 are shown in Figs. 6-7. As shown in these figures. the removal efficiency increased with elapse of contact time.

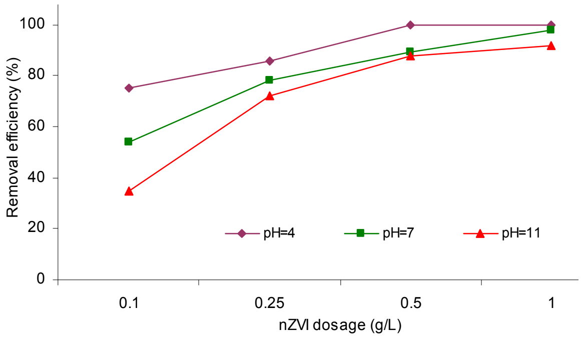

Fig. 4: Adsorption efficiency of As (III) on nZVI as a function of pH and nZVI dosage. Reaction conditions: 10 mg/L As (III), reaction time 10 min

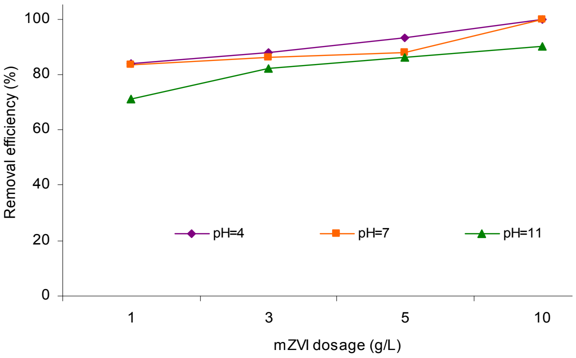

Fig. 5: Adsorption efficiency of As (III) on mZVI as a function of pH and mZVI dosage. Reaction conditions: 10 mg/L As (III), reaction time 120 min

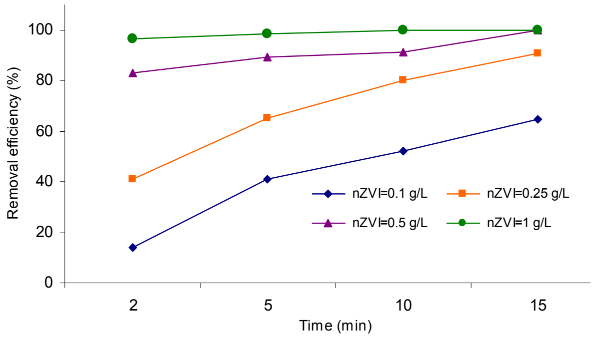

Fig. 6: Adsorption efficiency of As (III) on nZVI as a function of reaction time and nZVI dosage. Reaction conditions: 10 mg/L As (III), pH=7

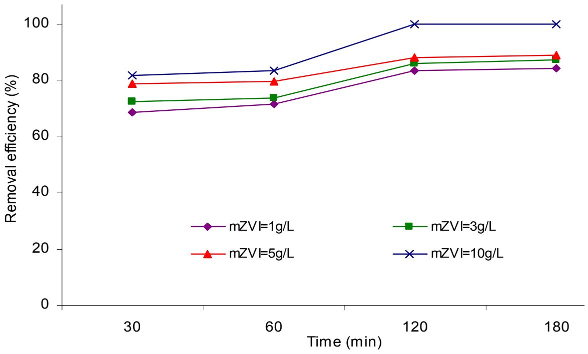

Fig. 7: Adsorption efficiency of As (III) on mZVI as a function of reaction time and mZVI dosage. Reaction conditions: 10 mg/L As (III), pH=7

Effect of initial As (III) concentration

The effect of initial As (III) concentration on adsorption efficiency using nZVI and mZVI are shown in Figs. 8-9.

DISCUSSION

The results of this experiment described that the polluted water containing arsenic can be remediated by nano and micro size ZVI. Nano ZVI could remove arsenic from aqueous solution at a short time (minute scale), whereas it took a long time (hours scale) for mZVI (Kanel *et al.* 2006). pH is one of the most important parameters affecting As removal by ZVI. The results of pH effect on the removal efficiency of As (III) using nZVI and mZVI are shown in Figs. 2-3. It was determined that As (III) can be removed at different pH values. The As (III) removal efficiency using nZVI increased significantly with decreasing pH. The removal efficiency in detention time of 10 min and pH range of 4-11 was 92%-99.9%. Also the pH effect on As (III) adsorption into mZVI, similar to adsorption on nZVI, indicates that removal efficiency decreased by increasing of pH.

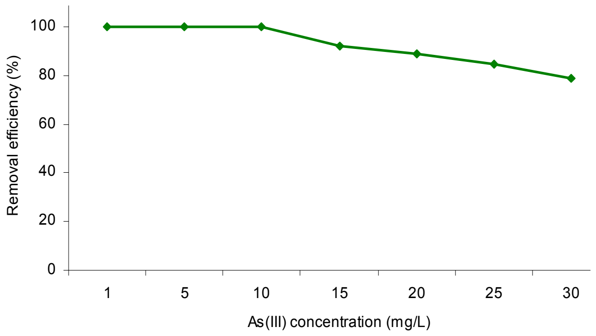

Fig. 8: Adsorption efficiency of As(III) on nZVI as a function of initial As (III) concentration. Reaction conditions: pH=7, initial nZVI weight 1.0 g/L and reaction time 10 min

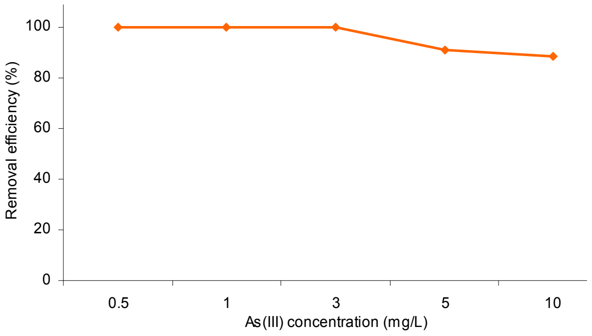

Fig. 9: Adsorption efficiency of As (III) on mZVI as a function of initial As (III) concentration. Reaction conditions: pH=7, initial mZVI weight 10 g/L and reaction time 120 min

The removal efficiency in reaction time of 2 h achieved 100 % adsorption of As (III) at pH=4 and decreased to 90 % at pH=11. Also in the use of pretreated waste tea fungal biomass for the arsenic removal from aqueous solution, the sharpest increase in arsenic uptake was obtained between pH=3 and 5 (Mamisahebei *et al.* 2007). The pH dependent behavior can be explained by ionization of both the adsorbate and the adsorbent causing repulsion at the surface and decreasing the net As (III) adsorption (Kanel *et al.* 2005, 2006). Below pH=9.2, H_3AsO_3 is the predominant species and presumably the major species being adsorbed. When pH is above 9.2, $H_2AsO_3^-$ is the predominant As species while the nZVI corrosion product surfaces are also negative (Fe (III)-O-) causing electrostatic repulsion.

A similar pH dependence trend in As adsorption amorphous iron oxide, synthetic goethite, and magnetite has been observed (Kanel *et al.* 2005). Other reason for this phenomena is accelerated corrosion of Fe^0 in acid condition (Kanel *et al.* 2005, 2006; Shu *et al.,* 2007). Also when the ferrous ions dissolve though the iron surface collided with hydroxyl ions in alkaline solution, produce ferrous hydroxide precipitation on the iron surface, occupying the reactive sites to hinder the reaction. This means that acidic condition is better for this process (Shu *et al*., 2007).

The results of different nZVI and mZVI dosage and pH (4, 7, and 11) on adsorption of As (III) (10 mg/L) are shown in Figs. 4-5: Increases of zero valent iron concentration greatly enhanced the removal efficiency. In reaction time of 10 min and pH=7, all As (III) was removed when the nZVI concentration was 1 g/L, but only 52.1% was removed when the nZVI concentration was 0.1 g/L.

Adding more mZVI particles reduced the smaller residual As (III) concentrations in solution with time for an initial As (III) of 10 mg/L with mZVI dosages from 1 to 10 g/L. In reaction time of 120 min and pH=7, all As (III) was removed when the mZVI mass concentration was 10 g/L, but only 83.3% was removed when the mZVI mass concentration was 1 g/L. More nZVI or mZVI particles are able to provide more iron surface-active sites for collision with As (III) molecules to accelerate the As (III) removal efficiencies (Niu *et al*., 2005; Yang and Lee, 2005; Shu *et al.*, 2007).

Reaction time is another important parameter on adsorption of As(III) on nZVI and mZVI. As shown in Figs. 6-7, the removal efficiency increased with elapse of contact time. For a 10 mg/L initial As (III) concentration and nZVI dosage of 0.1 g/L, a residual of about 86% was found after the first 2 minutes, promptly increased to about 59% after 5 min, and about 48% and 35% at 10 and 15 min, respectively. For 1 g/L nZVI, removal efficiency was 96.5%-100% at reaction time range of 2-15 minutes. Also results of As (III) removal by mZVI (Fig. 7) showed that by increasing of time, removal efficiency was prompted. With increasing time from 30 to 180 min at mZVI dosage 10 g/L, arsenic removal increased about 17%. At this condition and varying of mZVI dosage to 1 g/L, removal efficiency of 68.7% at 30 min increased to 84% at 180 min reaction time.

The higher As (III) removal with time elapse is due to the superior surface area of nZVI particles demanding a much lower dose than that of micro scale iron (Shu *et al*., 2007). In other study in which iron impregnated activated carbon was used for removal of arsenic from water, it was obtained that adsorption efficiency increased in contact time up to 150 min and a maximum removal efficiency of 75% was achieved and remained relatively constant (Ghanizadeh *et al.,* 2010).

The arsenic removal efficiency as a function of initial As (III) concentration with nZVI, showed that the As (III) adsorption efficiency steadily decreased linearly from 100% to 88.3% when the initial concentration increased from 1 to 30 mg/L (Fig. 8). Fig. 9 shows that results of batch experiments with mZVI conducted at As concentrations of 1 to 10 mg/L. The As (III) removal efficiency decreased with increasing initial As(III) concentration from 3 to 10 mg/L.

In despite of slow reaction between arsenic and mZVI, because of low cost and its availability, mZVI can be used as remediation agent for removal of arsenit. In addition, the removal efficiency has direct relation with contact time and dosage of nZVI and mZVI. Due to the low amount of nZVI or mZVI used, the mass of produced sludge in the process was significantly low; so, the flocs may be removed by magnetic techniques, often more efficient and faster than centrifugation or filtration.

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