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Remediation of Natural Arsenic Contamination in Groundwater using Zero Valent Iron

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Synopsis

Naturally occurring arsenic in groundwater used for drinking, cooking and irrigation is a catastrophe of global proportions. Therefore, greatly increased mitigation efforts are needed to reduce, and eventually eliminate, exposure to arsenic. Zero valent iron (ZVI) is more practical and promising to mitigate arsenic from the contaminated water resources especially groundwater. Hence, batch tests were conducted to assess the performance of ZVI with reference to pH, Eh and Dissolve oxygen (DO). Test results showed that arsenic removal by ZVI depends on three basic factors viz. contact time, amount of iron and pH of the solution. Arsenic concentration decreases with the passing of time. Among the zero valent iron KB-90 showed the best performance. Ninety nine percent (99%) arsenic was removed after 15 hrs elapsed time. Drinking water standard for Bangladesh (MPL 0.05 mg/L) was achieved after 10 hrs contact time with ZVI. Neutral pH (pH 7.0) showed the best performance over control and pH 5.0.

Keywords: Arsenic, Naturally contaminated groundwater, zero valent iron

1. Introduction

Contamination of groundwater resources by arsenic (As) is recognized as a great environmental crisis in the world especially in Bangladesh and it has severe human health implications. The world health organization (WHO) described the situation in Bangladesh as "the largest poisoning of a population in history" (Smith et al 2000). At the end of the 20th century, the arsenic contamination in groundwater has been documented as a serious environmental health disaster with severe socioeconomic consequences; a great challenge for the Government of Bangladesh is to provide safe drinking water for the urban and rural population. Traditionally surface water was used for drinking purposes in Bangladesh, which led to widespread gastrointestinal problems. Consequently people started using groundwater resources. Groundwater exploitation has increased dramatically in Bangladesh and nearly 4-5 million tube-wells have been installed to provide safe drinking water to nearly 97% of the population. Unfortunately, high As levels in groundwater has raised a serious threat to public health. In addition, the use of As rich groundwater in agriculture has resulted in bioaccumulation of As and elevated levels of As have been reported in rice and vegetables (Mukherjee and Bhattacharya 2001). Therefore, it is urgently needed to treat the arsenic contaminated water and water sources or to avoid the arsenic contaminated water. The removal of arsenic by using zero valent iron (ZVI) has received much attention because this has a high arsenic removal capacity. Thus, in the present research a series of batch tests are designed to assess performances of different types of zero valent irons in terms of arsenic removal efficiency, to study the effect of

DO and redox potential condition on arsenic removal using ZVI and to find out a suitable pH on arsenic removal by ZVI. The knowledge which will be gained from this study will aid in the understanding and development of sustainable, efficient point of use water treatment system for arsenic contaminated groundwater in Bangladesh, India, Nepal and other developing countries.

2. Materials

All the chemicals used in this study were analytical grade and all the stock solutions were prepared with deionized water (DI). The arsenic stock solution was prepared by $Na_2HAsO_4 \cdot 7H_2O$ in DI water. Three zero valent iron materials viz. KB-90, TK-H and K-100T were obtained from JFE Steel Corporation, Japan. The characteristics of zero valent iron from JFE Steel Corporation are shown in Table 1.

3. Experimental Section

A series of batch tests utilized ZVI were conducted on 500 mL conical flasks. In all cases, 500 ml of arsenic contaminated water was loaded with different levels of iron. Then the conical flask containing different levels of arsenic contaminated water and different levels of iron were placed on an orbital shaker at room temperature (24 ºC) for different time periods (Fig. 1 shown bellow). In case I, 50 mg/L arsenic contaminated water was loaded with two levels of iron viz. 0.5, 1.0 g/L with three different types of iron without any adjustment of pH. The sampling periods were 1, 7, 14 and 21. In case II, 1 mg/L arsenic contaminated water was mixed with 1.0 g/L of three types of previous iron. The sampling period were 1, 5, 10 and 24 hrs later. In case III, 1 mg/L arsenic contaminated water was mixed with 1.0 g/L iron (KB-90). In this experiment, pH 5.0 and pH 7.0 were adjusted using 0.1M NaOH and HCl. The sampling periods were 1, 2, 3, 4, 5, 10, 15 and 24 hrs later. In case IV and V, 0.2 mg/L arsenic contaminated waster was loaded with 1.0 and 2.0 g/L iron (KB-90) respectively with three levels of pH viz. control, 5.0 and 7.0. The sampling periods were similar to case III.

4. Measurements and Chemical Analysis

The DO content, pH and Eh were measured immediately after collection of samples by DO meter and combined pH and Eh meter respectively. The pH meter was calibrated with three buffers (pH 4.0, 7.0 and 10) before measurement. Then the suspension was filtered through syringe filter with 0.20µm pore size. Arsenic concentrations were measured by Graphite furnace atomic absorption spectrophotometer and Hydride generation atomic absorption spectrophotometer.

Fig.1: Three types of zero valent iron

Table 1:The Characteristics of Zero Valent Iron

Types of ZVI	Chemical composition %		Particle size distribution %							
	Metal Fe	Total Carbon	>250 µm	>180 µm	>150 µm	>106 µm	>75 µm	>63 µm	>45 µm	<45 µm
KB-90	93.5	0.482	0	0.2	0.9	25.5	32.9	8.6	13.9	18.0
TK-H	98.1		0	16.0	40.1	23.2	7.3	1.3	2.5	9.6
K-100T	94.8		0	0	2.7	36.3	20.9	6.7	10.9	22.5

5. Results and Discussion

5.1. Performance of Different ZVI

Arsenic removal on a mass basis followed the order, KB-90 > K-100T > Tk-H when the initial As concentration was 50 mg/L (Table 2). The performance variation was evident at 14 day after sampling time. Among the three ZVI types, KB-90 shows best performance to remove arsenic from the water source.

In figure 2, the results followed the same order when the initial As concentration was 1 mg/L. The performances of the three zero valent iron was more prominent in this test, although KB-90 and K-100T ZVI have more or less similar performance.

5.2 Arsenic Removal Ability

Arsenic removal from water was largely affected by contact time, types of zero valent iron and lesser degree of amount of iron. In all ZVI system, arsenic concentration gradually decreased over time. The result showed that after 15 hrs elapsed time, arsenic concentration is 0.003 mg/L (below the WHO's drinking water standard 0.01 mg/L) i.e. 99% of arsenic is removed, where the initial arsenic concentration was 0.2 mg/L and ZVI 2 g/L, respectively and in the same time 97.5% of arsenic is removed using 1.0 g/L zero valent iron (Fig. 3). The results also meet the Bangladesh drinking water standards (Maximum Permissible Limit 0.05 mg/L) after 10 hrs elapsed time.

5.3 Effects of pH and Eh on Arsenic Removal by ZVI

The pH/Eh relationship is key in understanding arsenic mobility in groundwater and the effectiveness of arsenic water treatment systems. The consequence of pH on arsenic removal from arsenic contaminated water using zero valent iron is illustrated in Fig. 4 and 5. The maximum arsenic removal occurred at pH 7 over other two cases. More than 99% of the arsenic was removed after 15 hours of reaction at pH 7. Similar, results have been reported from other investigators; Biterna et al. (2007) reported over 99% of As(V) was removed in 6 hrs when initial pH was controlled at 7.0 and nearly 90% at pH 4.0 and Sun et al. (2006) observed

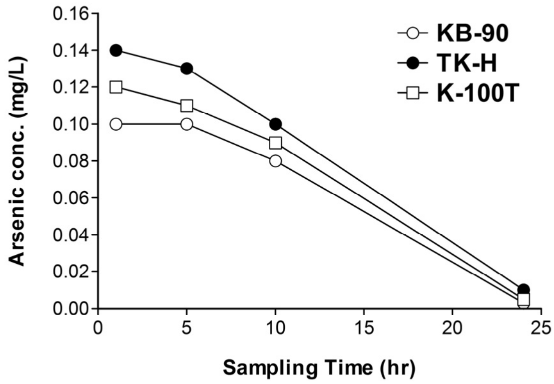

Fig. 2: Arsenic removal by ZVI (As conc. 1 mg/L and ZVI 1 g/L)

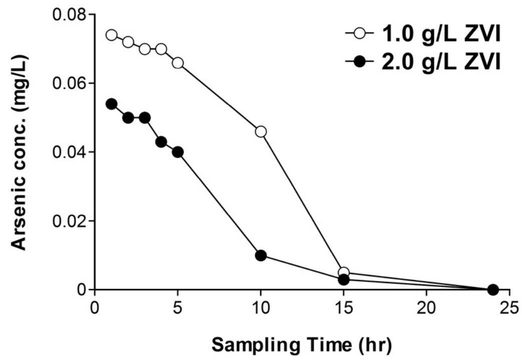

Fig. 3: Arsenic removal by ZVI (As conc. 0.2 mg/L, without pH adjustment and ZVI type KB-90)

Table 2: Arsenic Removal (mg/L) by ZVI

Arsenic conc. using 0.5 g/L ZVI				Arsenic conc. using 1.0 g/L ZVI			
Day	KB-90	TK-H	K-100T	Day	KB-90	TK-H	K-100T
1	1.60	1.66	1.61	1	1.54	1.63	1.61
7	1.58	1.61	1.25	7	1.42	1.60	1.60
14	1.57	1.60	1.11	14	1.38	1.60	1.55
21	1.57	1.60	1.58	21	1.37	1.44	1.40

Conditions: Initial arsenic conc.: 50 mg/L over 95% removal at pH 8.28. Furthermore, the pH 7.0 also showed the highest performance when initial arsenic concentration was 1.0 mg/L.

Redox reaction (Eh) is directly related to the pH of the solution and is instrumental in controlling As concentrations by their effects on As speciation and reduction of metal oxides which adsorb or precipitate arsenic. The result showed that the redox potential (Eh) in the KB-90 ZVI system decreased with time from positive values of 284 to 76 mV (Fig. 6 & 7).

5.4 Effects of DO on Arsenic Removal by ZVI

The effect of DO content on the removal of arsenic was evaluated by comparing the experimental results obtained under a series of batch tests (Fig. 8 & 9). High DO content will increase the rate of iron oxidation and subsequently improve the removal of arsenic by zero valent iron. Actually DO content in groundwater ranges from zero to several

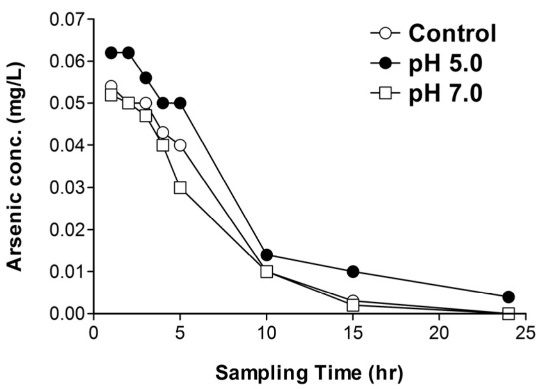

Fig. 4: Arsenic removal by ZVI (As 0.2 mg/L & ZVI (KB-90) 2.0 g/L)

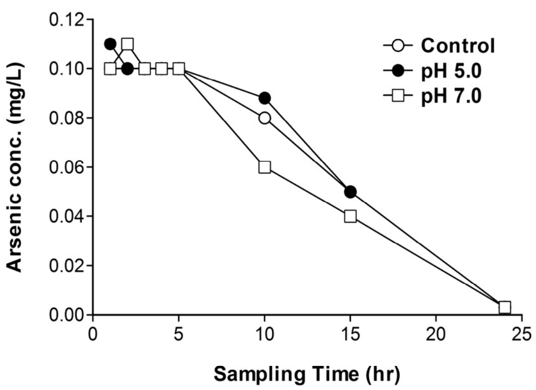

Fig. 5: Arsenic removal by ZVI (As 1.0 mg/L & ZVI (KB-90) 1.0 g/L)

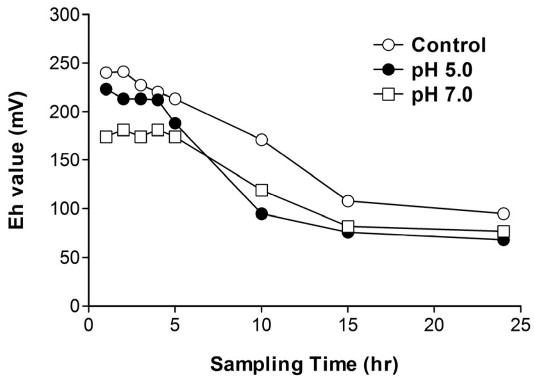

Fig. 6: Eh variation with time (As 0.2 mg/L & ZVI (KB-90) 2.0 g/L)

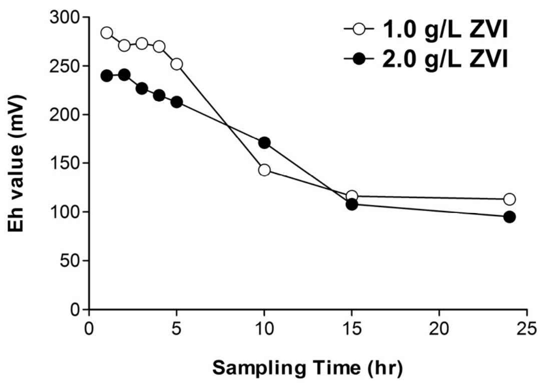

Fig. 7: Eh variation with time (As 0.2 mg/L, control pH & ZVI type KB-90)

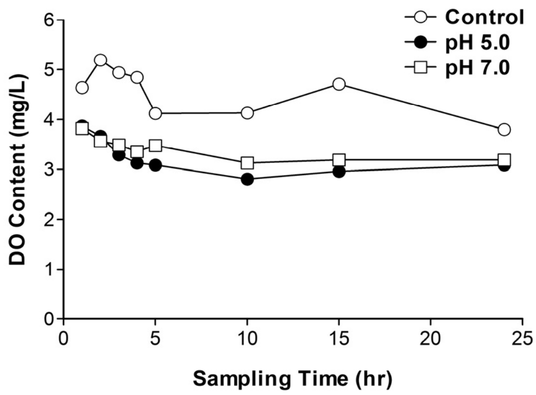

Fig. 8: DO variation with time (As 0.2 mg/L & ZVI (KB-90) 2.0 g/L)

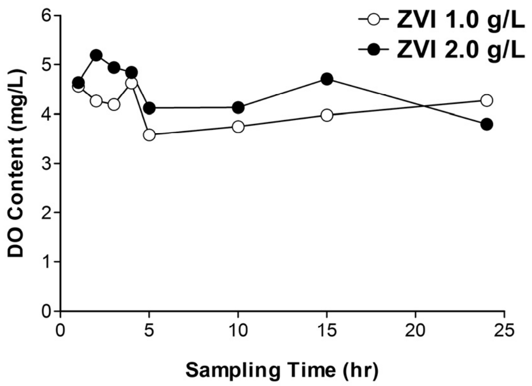

Fig. 9: DO variation with time (As 0.2 mg/L, control pH & ZVI type KB-90)

mg/L. During the experiment the DO content varies between 5.19 ~ 3.58 and 5.19 ~ 2.96 mg/L. In this connection Bang et al. (2005) reported that the ineffective removal of arsenic under low DO content conditions was due to lack of ferric hydroxide formation and slow kinetics of electrochemical reduction of As(V) and As(III) to As(0) by ZVI.

6. Conclusion

Arsenic pollution is a very burning issue all over the world especially in South and South East Asia (Bangladesh, Vietnam, West Bengal India, Nepal, and Cambodia). However, the situation in Bangladesh is alarming in environment and public health view point. Thus, the present investigation on the mitigation of arsenic with ZVI suggests that zero valent iron can be used as an effective remedial means for ex-situ mitigation of groundwater contamination with arsenic. The pH, redox potential (Eh) and DO are the influential factor for the mitigation of arsenic from the groundwater. Efficient arsenic removal by employing ZVI was observed at concentrations below 10 μg/L in the treated waters. Neutral pH of the contaminated groundwater is suitable for treatment process. The information achieved from these experiments will assist to prepare remedial action plan with participation of experts in the relevant fields and community representatives to supply arsenic free groundwater for the people of arsenic affected developing countries.

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自然由来のヒ素による地下水汚染のゼロ価鉄粉を用いた浄化技術の開発

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要　旨

自然由来のヒ素を含む地下水の飲用利用・灌漑利用することによる人の健康への影響や作物の生育障害はバングラデシュ等において大きな問題となっている。このことから，ヒ素への曝露を低減、防止するための対策技術の確立が望まれており，その研究開発が進められている。特に，ゼロ価の鉄粉を用いたヒ素を含有する地下水の浄化は実用的で適用性の高い技術として期待されている。本研究ではバッチ試験によって複数のゼロ価の鉄粉によるヒ素の浄化性能とpH，酸化還元電位，溶存酸素濃度の影響を調査した。その結果，ヒ素の浄化性能は，反応時間，鉄粉量，pHに依存することが明らかになった。地下水中のヒ素濃度は時間の経過とともに低下し，15時間経過後には99%のヒ素を除去することができた。pHの影響については，7.0の中性付近で最も優れた浄化性能を示した。

キーワード：自然由来ヒ素，地下水汚染，ゼロ価鉄粉