Subsurface iron and arsenic removal: low-cost technology for community-based water supply in Bangladesh

ABSTRACT

The principle of subsurface or in situ iron and arsenic removal is that aerated water is periodically injected into an anoxic aquifer through a tube well, displacing groundwater containing Fe(II). An oxidation zone is created around the tube well where Fe(II) is oxidised. The freshly formed iron hydroxide surfaces provide new sorption sites for soluble Fe(II) and arsenic. The system’s efficiency is determined based on the ratio between abstracted volume with reduced iron/arsenic concentrations (V) and the injected volume (Vi). In the field study presented in this paper, the small-scale application of this technology was investigated in rural Bangladesh. It was found that at small injection volumes (<1 m³) iron removal was successful and became more effective with every successive cycle. For arsenic, however, the system did not prove to be very effective yet. Arsenic retardation was only limited and breakthrough of 10 μg/L (WHO guideline) was observed before V/Vi = 1, which corresponds to arrival of groundwater at the well. Possible explanations for insufficient arsenic adsorption are the short contact times within the oxidation zone, and the presence of competing anions, like phosphate.

Key words | arsenic, Bangladesh, community-based, drinking water, iron, subsurface

INTRODUCTION

The most well known and severe case of arsenic poisoning through drinking water is currently ongoing in Bangladesh. Two-thirds of the tube wells installed over the last three decades, roughly three million in total, have been reported to contain arsenic in concentrations above the permissible level of 10 μg/L set by the World Health Organization (BGS/DPHE 2001). It is estimated that 35 to 57 million people are at risk of drinking arsenic-contaminated water in Bangladesh above the WHO guideline (BGS/DPHE 2001; WHO 2001). In a bulletin (Smith et al. 2000), the World Health Organization reports that long-term exposure to arsenic in groundwater, at concentrations over 500 μg/L, causes death in 1 in 10 adults (including lung, bladder and skin cancers). The tube wells were installed with the firm conviction that they would contribute to a secure and reliable drinking water supply, in order to put an end to various contagious diseases caused by the use of (microbially unsafe) surface water. It is a bitter observation that it is this very approach that has led to widespread arsenic poisoning through drinking water. The large well-to-well variability in arsenic concentrations bears the consequence that in the villages all wells need to be tested. Currently an estimated...
5 million wells have been tested and in 1.4 million wells the arsenic concentration was measured above the national standard of 50 μg/L. In Bangladesh, the source of arsenic in groundwater is deposited sediments from the Himalayas and strongly reducing conditions cause reductive dissolution of the arsenic-rich iron hydroxides (Smedley & Kinniburgh 2002). In the reducing environment arsenic predominantly occurs as arsenite or As(III), when oxidising conditions prevail the dominant species is generally arsenate or As(V).

In industrialized countries arsenic contamination is also a recognised problem (van Halem et al. 2009). The removal of arsenic is achieved through commercial adsorption media, e.g. GFH (granular ferric hydroxide), or by means of coagulation/filtration, ion exchange or membrane filtration. These methods are expensive and therefore unavailable to the poor living in rural areas. Household water treatment systems with non-commercially available adsorption media, such as Sono and Alcan, show potential (Sutherland et al. 2002). However, further research and documentation is needed on the long-term efficacy and potential risk of microbial contamination of the treated water. All filters will at one stage either clog and/or show breakthrough of arsenic. Some filters can be regenerated; however, many leave an arsenic-rich waste stream. The treatment option presented in this paper can be operated without a waste stream, because the iron and arsenic are retained in the subsurface. The adsorption sites for arsenic are generated in the aquifer, providing a low-cost and robust subsurface filter.

The principle of subsurface iron removal is that aerated water is periodically injected into an anoxic aquifer through a tube well (Figure 1, left), partially displacing the groundwater. The injected water oxidises adsorbed Fe(II) on the soil grains, resulting in adsorptive surface area of iron hydroxides. When the flow is reversed, soluble Fe(II) in the abstracted groundwater is adsorbed onto the Fe(III) coated soil grains and water with reduced iron concentrations is abstracted (Figure 1, right). Injection is started again once elevated iron levels arrive at the well. The affected area in the subsurface around the tube well is referred to in this article as the oxidation zone. Subsurface or in-situ iron removal has been used in central Europe for many decades (Hallberg & Martinell 1976; van Beek 1985), but the application of subsurface treatment for the removal of arsenic from groundwater is a relatively new approach (Rott et al. 2002; van Halem et al. 2008). This technology has the potential to be a cost-effective way to provide safe drinking water in rural areas in decentralized applications. Existing shallow tube wells can be modified to be operated under infiltration and abstraction conditions. The objective of this paper is to study the small-scale application of subsurface iron and arsenic removal in rural Bangladesh.

In literature, the dominant mechanism in subsurface iron removal is proposed to be adsorption-oxidation (Rott & Friedle 1985; van Beek 1985; Appelo et al. 1999). The adsorption-oxidation mechanism is based on the premise that, in the presence of oxygen, the adsorbed Fe(II) is oxidised forming a new surface for adsorption (Sharma et al. 2001). Heterogeneous oxygenation is therefore expected to be

![Figure 1](https://iwaponline.com/wst/article-pdf/62/11/2702/445739/2702.pdf)
dominant during subsurface treatment; however, insufficient data are available to exclude the contribution of homogeneous oxygenation. Sharma (2001) studied the adsorption-oxidation mechanism and characterized iron (oxy)hydroxide coatings in iron filters. The coatings were found to be X-ray amorphous or poorly crystalline. Around subsurface treatment wells the iron precipitates have been identified to consist mainly of goethite, with only small traces of ferrihydrite (Mettler et al. 2001). It is likely that soluble Fe(II) initially oxidises to form amorphous ferrihydrite and subsequently slowly transforms to crystalline goethite (Houben 2003). Some researchers have observed a catalytic reaction after a coating of iron oxide had developed; also, Fe(III) precipitates usually have high (adsorptive) surface areas and enhance the removal of Fe(II) by the adsorption-oxidation mechanism. Therefore it may require a number of injection-abstraction cycles before the processes develop to their full extent. Once the oxidation zone is developed, more water can be abstracted than injected, i.e., this volumetric ratio determines the efficiency of this system.

The injection of aerated water for subsurface removal of arsenic has also been reported. Arsenic is known to adsorb to iron hydroxides (Dzombak & Morel 1990), and since these are formed during subsurface treatment, arsenic can be retained in the subsurface. Welch et al. (2000) investigated subsurface or in-situ arsenic removal with a combination of aerated water and the injection of ferric chloride. Preliminary results showed reduction of 100 μg/L As(V) to below the WHO guideline of 10 μg/L (WHO 2006). Miller (2006) combined the pulsed injection of aerated water and ferrous iron to remove As(V). Other researchers have found reduction of arsenic concentrations from around 40 μg/L to below the WHO guideline with the injection of aerated water only (Rott et al. 2002; Appelo & de Vet 2003). In Bangladesh higher arsenic levels were investigated by Sarkar & Rahman (2001), namely, 500 - 1300 μg/L. In this case concentrations as low as 10 μg/L were not reached, but still, more than 50% removal was observed. Recently a similar study was performed in India with injection volumes of 2 m³ (Sen Gupta et al. 2009), achieving arsenic concentrations below the WHO guideline.

**METHODOLOGY**

Household shallow tube wells with suction hand pumps are widely distributed in Bangladesh and the objective of the subsurface treatment is to use the existing infrastructure optimally. The Manikganj district, just west of Dhaka, was selected for this study, since this area is known to have high iron, arsenic and manganese concentrations in the groundwater. After testing numerous wells, two sites (A and B) were selected with the same arsenic concentrations (145 μg/L). The groundwater pH at the two test locations was 6.85 and the groundwater composition is illustrated in Table 1. The initial iron concentrations varied at location A and B, with (A) 1.0 mg/L and (B) 15 mg/L, respectively. Manganese concentrations also differed at the two locations, namely, (A) 2.5 mg/L and (B) 0.3 mg/L.

The experimental set-up (Figure 2) was connected to an existing hand pump with tube well in the upper aquifer. The 1.5-inch tube-well had a depth of 51 m and a perforated well length of 3 m. As an added precaution, the set-up was placed with a family who already had arsenic treatment since 2001 (SIDKO system). For the purpose of subsurface treatment, the existing situation was modified with a pipe and valve for injection. After subsurface treatment, the groundwater was pumped (electrical suction pump) into the SIDKO system for aeration, sand filtration and Granular Ferric Hydroxide filtration (AdsorpAs, Harbauer GmbH). The treated water, low in arsenic (<10 μg/L) and iron (below detection limit), was collected in a 1 m³ storage tank and used for injection into the aquifer. The maximum

<table>
<thead>
<tr>
<th>Location</th>
<th>As</th>
<th>As(III)</th>
<th>Fe</th>
<th>Mn</th>
<th>PO₄</th>
<th>Ca</th>
<th>Na</th>
<th>pH</th>
<th>Eh</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>145</td>
<td>120</td>
<td>1.0</td>
<td>2.5</td>
<td>3.3</td>
<td>82</td>
<td>8.9</td>
<td>6.8</td>
<td>n.m.*</td>
</tr>
<tr>
<td>B</td>
<td>145</td>
<td>124</td>
<td>15</td>
<td>0.3</td>
<td>5.0</td>
<td>113</td>
<td>24</td>
<td>6.8</td>
<td>−170</td>
</tr>
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</table>

*n.m. = not measured.
injection volume was therefore limited to 1 m³. Analysis of the water samples was done with field test kits (Wagtech International: Palintest and Arsenator) and confirmed in the laboratory (Perkin-Elmer Flame AAS 3110; Perkin-Elmer GF-AAS 5100PC). Duplicates or triplicates were taken to check the method of sampling and accuracy of analysis. Arsenic speciation was done with a field method (Clifford et al. 2004) using anion exchange resin columns (Amberlite IRA400). Multimeters (HACH 340i) were fixed inline to the experimental set-up to monitor pH (WTW SenTix 41), dissolved oxygen (WTW Cellox 325), OR potential (WTW SenTix ORP) and electric conductivity (TetraCon 325). Measurements were registered on a computer with Multilab Pilot v5.06 software. The injection and abstraction volumes were monitored using water meters. Operation started in October 2008, just after the monsoon season, and continued until May 2009. At both locations, the families shared their arsenic treatment facility with the community and the weekly water consumption was 5.7–8.7 m³ and 2.4–2.9 m³ for location A and B, respectively. Operational conditions, such as injection frequency and production discharge, varied due to irregular operation. Normally the set-ups were used for the families’ water production, however, during research periods the operation was intensified and controlled by the researchers. In this paper, all results are presented using the ratio between abstracted volume (V) and injected volume (Vᵢ), V/Vᵢ. This volumetric ratio determines the efficiency of the system. Every period of injection-abstraction starts at V/Vᵢ = 0 and is referred to as a cycle, with the first injection-abstraction period being cycle 1. Injection was done the night before, so abstraction was started at 12–16 hours after injection.

RESULTS AND DISCUSSION

Typical breakthrough curve

The graph in Figure 3 represents a typical breakthrough curve after injection. The electrical conductivity of the injection water was slightly lower than of the groundwater, and thus gives a good indication when the groundwater water arrives in the well and can be considered a conservative tracer. This was, as expected, at the moment when the volume of produced water was equal to the injected volume for this particular cycle, i.e., C/C₀ = 0.5 at around V/Vᵢ = 1. Although the tracer arrived at the well at this point, it is noteworthy that it took multiple V/Vᵢ units before complete breakthrough was observed. The tailing of this curve suggests that injection water remains in the subsurface after V/Vᵢ = 1 and a mixture of groundwater and injection water is withdrawn. It has been suggested before that stagnant zones, or “dead-end pores” in the oxidation zone influence the subsurface removal of iron (Rott et al. 2002). Diffusion between these stagnant zones and the passing groundwater delays the complete breakthrough of a constituent. This would mean that although the majority of the injected water volume arrived at the well before
V/V$_i$ = 1.5, there was still a small percentage in the stagnant zones at that moment and equilibrium was only found after V/V$_i$ = 5. The dissolved oxygen curve did not show similar tailing, since oxygen concentrations reduced immediately after the start of abstraction to $\ll$ 0.1 mg/L which means that most injected oxygen is consumed in the subsurface. This may also be expected, since water was injected 16 hours before abstraction started. The iron breakthrough was retarded compared to the arrival of groundwater at the well, indicating that dissolved Fe(II) adsorbs and/or precipitates on its route to the well. These measurements correspond with existing literature, since the fronts are reported to be in the following order from the well: oxygen front – injection water/groundwater front – iron front (Appelo et al. 1999). Arsenic concentrations rose significantly faster than iron concentrations, as can be seen from Figure 3. Nevertheless in this particular cycle, some retardation compared to the conservative tracer was observed. With a breakthrough curve like this a mass balance can be calculated and, for this cycle, resulting in a mass balance with an approximate removal of 37 mg and 58 mg for iron and arsenic, respectively. One isolated cycle does however not describe the potential of subsurface iron and arsenic removal, since this technology is known for its increasing efficacy with every successive cycle. The removal of arsenic and iron for multiple cycles is presented later in this section.

**Influence of Fe:As ratio in the groundwater**

Subsurface iron and arsenic removal is applied directly at the shallow tube well and therefore depends greatly on the occurring groundwater geochemistry. One of the parameters that may enhance the effective co-removal of arsenic with the iron is the presence of significant iron levels in the groundwater. Figure 4 shows the breakthrough of arsenic and iron for cycle 6 at location A (molar Fe:As = 9.5, V$_i$ = 657 L) and B (molar Fe:As = 141, V$_i$ = 744 L). At V/V$_i$ = 2.5, an arsenic concentration of C/C$_0$ = 0.8 had been reached, which exceeds more than 10 times the WHO guideline of 10 µg/L. It is noteworthy that the original arsenic concentration was not reached within the research period of V/V$_i$ = 6, potentially due to the long lasting effects of diffusion in the stagnant zones. Manganese concentrations were also measured at location A showed a similar breakthrough trend as arsenic, with C/C$_0$ = 0.5 at V/V$_i$ = 1. At location B, the iron concentration was significantly higher at 15 mg/L (molar Fe:As = 141), which could potentially result in better arsenic removal. Figure 5 shows temperature of 25°C, arsenic predominantly occurs as H$_3$AsO$_3$ in the aquatic environment (Ferguson & Gavis 1972). Subsurface iron removal at location B shows for cycle 6 that after V/V$_i$ = 6 the measured concentration was still 65% lower than the initial iron level. Although iron levels are significantly reduced by the subsurface, only small amounts of arsenic were removed from the groundwater.

![Breakthrough of arsenic and iron during cycle 6 at location A (molar Fe:As = 9.5, V$_i$ = 657 L) and B (molar Fe:As = 141, V$_i$ = 744 L).](https://iwaponline.com/wst/article-pdf/62/11/2702/445739/2702.pdf)
that iron breakthrough was faster at this location, which was expected since the same amount of oxygen was injected at both locations. The breakthrough of arsenic is comparable with location A, and although the curve shows some tailing, it is clear that the arsenic concentration rose more or less simultaneously with the groundwater front at \( V/V_i = 1 \). This strongly indicates that the occurrence of high iron concentrations in the groundwater does not promote the effective co-removal of arsenic during subsurface treatment. The formed adsorptive iron hydroxide surface area is apparently either insufficiently present for arsenic adsorption, or other compounds, such as competing anions, are occupying the available adsorption sites.

**Oxygen level of injection water**

In theory, 1 mol of oxygen can oxidise 4 moles of Fe(II). It might seem logical to assume that the more oxygen is injected into the subsurface, the higher the removal of iron will be. During the injection phase, the oxygen front lags behind the injected water front, as illustrated in Figure 4. This results in a limited mixing of iron-rich groundwater and oxygen-rich injection water. Instead, the dissolved oxygen reaches the adsorbed Fe(II) on the soil grains. Heterogeneous oxygenation is reported to be extremely fast after injection (Metaller 2002), so in that case, consumption by other reducing compounds will start once iron oxidation is complete. This would mean that if more oxygen is injected into the subsurface than adsorbed Fe(II) is available for oxidation, this oxygen will be consumed by other (a)biotic reactions. In other words, the injection of high oxygen levels may not contribute to more oxidation of iron and is instead potentially consumed in other reactions. For the design of a community-scale subsurface treatment plant it is useful to know what oxygen concentrations are at least required in the injection water. Simple aeration tanks, as used in this study, have a limited capacity and aeration of anoxic (iron-rich) groundwater to saturation levels is difficult to reach. Figure 5 shows the breakthrough curves for iron after injecting different oxygen concentrations into the subsurface. Increased iron retardation is visible for higher oxygen concentrations. The difference between \(<1/3.7\text{ mg } O_2/L \) and \( 5.3/6.1\text{ mg } O_2/L \) shows either that (i) 3.7 mg O_2/L is insufficient to oxidise all adsorbed Fe(II) and/or (ii) the higher the oxygen concentration the more precipitation due to diffusion in stagnant zones and/or at the interface between injection and groundwater. Arsenic retardation did not vary for different oxygen concentrations (not shown in graph), supporting the finding that better retention of iron does not promote the co-removal of arsenic. It can be concluded that injection of higher oxygen concentrations does enhance the subsurface removal of iron. At small injection volumes (<1 m³) and relatively low oxygen concentrations it is unlikely that the Fe(II) on affected aquifer sediments will be completely oxidised. It is therefore recommendable, especially when starting up a new location, to aerate the groundwater extensively before injection. It would however be interesting to repeat these experiments under laboratory conditions. If the catalytic adsorption-oxidation mechanism is dominant in this process, the operation mode should focus on larger injection volumes. If the mixed or interface between injected water and groundwater, is dominant, then injection of higher oxygen concentrations should immediately result in more iron precipitation.

**Successive cycles**

At larger injection volumes, > 500 m³, it is known that iron is retained in the subsurface (van Beek 1985; Halem et al. 2008). The objective of this study is, however, to apply this technology on a small-scale with injection volumes no more than 1 m³. As mentioned before, subsurface iron removal increases in efficiency with every successive cycle. The \( V/V_i \) ratio where complete breakthrough occurs will thus rise. Figure 6(a) shows the iron breakthrough curves at location B for cycle 1, 3, 6, 12, 16, and 20. It clearly shows that iron removal improved significantly in this period. During cycle 1, \( C/C_0 = 0.5 \) for iron was measured just after \( V/V_i = 2 \), whilst during cycle 20 this was at \( V/V_i > 5 \). When extrapolating these results linearly, \( C/C_0 = 0.5 \) was potentially even as late as \( V/V_i > 15 \), but the duration of the experiment was not long enough to confirm this with measurements. Based on these findings it can therefore be concluded that subsurface iron removal can be applied at decentralized small-scale treatment plants with injection volumes as low as 1 m³.

The breakthrough curves for arsenic were also monitored and did not show the same improvement as for
The curves for all cycles show more or less the same trend, with $C/C_0 = 0.5$ around $V/V_i = 1.5$. The WHO drinking water standard of 10 $\mu$g/L is already exceeded before $V/V_i = 1$, which is clearly insufficient retardation for this system to be called an arsenic removal technique. These findings do not correspond with earlier publications (Rott et al. 2002; Appelo & de Vet 2003; van Halem et al. 2008).

The limited arsenic adsorption to the freshly formed iron hydroxide surfaces could be caused by insufficient contact time in the subsurface during production to reach equilibrium in the oxidation zone. Rough calculations show that the oxidation zone, with an injection volume of 0.9 m$^3$ is approximately 0.5 m around the well. At an average pumping rate of 1.2 m$^3$/h this would result in a contact time in the oxidation zone of approximately 20 minutes. In other words, once the groundwater arrives at the oxidation zone, 0.5 m from the well, it takes the water a travel time of 20 minutes to reach the well. It is noteworthy that in reality the oxidation front lags behind the injected water front, so the actual oxidised zone may be even smaller.

Though arsenic adsorption may not be complete within 20 minutes, it would theoretically suffice to adsorb part of the arsenic. A design consideration to increase the contact time is to reduce the length of the well filter. Adsorption of zero-valent As(III) is known to be less effective to iron hydroxides than the negatively charged As(V). Since arsenic occurs at these sites predominantly as As(III), adsorption may be limited. Another explanation for the absence of arsenic adsorption may be sought in the competition with other anions (Stachowicz 2007). Especially phosphate is present in concentrations high enough to interfere with arsenic adsorption (5 mg/L). Phosphate was measured to be retarded during abstraction, also when arsenic was already breaking through (Figure 7). The competition of phosphate during subsurface arsenic removal has been reported before by Appelo & de Vet (2003).

**CONCLUSIONS**

Subsurface treatment was successfully operated at small-scale (injection volumes less than 1 m$^3$) for the removal of iron. For arsenic, however, the system did not prove to be very effective yet. Arsenic retardation was only limited and breakthrough of 10 $\mu$g/L (WHO guideline) was observed before $V/V_i = 1$, which corresponds to arrival of groundwater at the well. Two explanations are proposed to be responsible for this result, either (i) contact times with the freshly formed iron hydroxides were insufficient,
or (ii) competing anions, such as phosphate, interfered with the adsorption process. It is recommended to continue this research with laboratory experiments to study the competitive arsenic and phosphate adsorption, and to study the contribution of heterogeneous and homogenous Fe(II) oxidation in subsurface iron removal.

REFERENCES


