



A combined treatment approach using Fenton's reagent and zero valent iron for the removal of arsenic from drinking water

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Abstract

Studies on the development of an arsenic remediation approach using Fenton's reagent (H_2O_2 and $Fe(II)$) followed by passage through zero valent iron is reported. The efficiency of the process was investigated under various operating conditions. Potable municipal water and ground water samples spiked with arsenic(III) and (V) were used in the investigations. The arsenic content was determined by ICP-QMS. A HPLC-ICPMS procedure was used for the speciation and determination of both As(III) and (V) in the processed samples, to study the effectiveness of the oxidation step and the subsequent removal of the arsenic.

The optimisation studies indicate that addition of 100 μ l of H_2O_2 and 100 mg of $Fe(II)$ (as ferrous ammonium sulphate) per litre of water for initial treatment followed by passing through zero valent iron, after a reaction time of 10 min, is capable of removing arsenic to lower than the US Environmental Protection Agency (EPA) guideline value of 10 μ g/l, from a starting concentration of 2 mg/l of As(III). Using these suggested amounts, several experiments were carried out at different concentrations of As(III). Residual hydrogen peroxide in the processed samples can be eliminated by subsequent chlorination, making the water, thus, processed, suitable for drinking purposes. This approach is simple and cost effective for use at community levels. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic contamination; Arsenic remediation; Drinking water; Fenton's reagent; Zero valent iron; ICP-QMS

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1. Introduction

Contamination of arsenic in ground waters (used for drinking and cooking) has attracted worldwide attention. From many countries, incidents of arsenic contamination have been reported [1]. Recently, major ground water contamination problems have been reported from Bangladesh, West Bengal, India, inner Mongolia and Taiwan and some South American countries. More than 100 million people are reported to be at risk. In many districts of Bangladesh, water drawn from tube wells are reported to be tainted with much higher levels of arsenic [2].

The US Environmental Protection Agency (EPA) has recently announced the reduction of permissible values of arsenic in drinking water from 50 to 10 $\mu\text{g/l}$ in the light of recent epidemiological evidence to support the carcinogenic nature of the ingested arsenic and its connection with liver, lung and kidney diseases and other dermal effects [3]. Many groups are working on remediation technologies that will effect the reduction of arsenic to less than 10 $\mu\text{g/l}$ levels, in a cost effective manner with ease of operation that can be adopted at community or house-hold levels.

Arsenic contamination of the groundwater is believed to be caused by the dissolution of geological deposits containing iron, which had trapped arsenic. In addition, environmental arsenic contamination from uncontrolled industrial discharges, use of arsenical pesticides/herbicides and power generation from coal or geothermal sources also contribute to the arsenic contamination [4].

The biological effects of arsenic depend mainly on the chemical form in which the element is ingested, the route of entry, the dose and the duration of exposure. Inorganic As(III) and (V) are identified to be more toxic than its organic forms. The arsenic is built up through intake of food or potable water contaminated with arsenic. In water, arsenate is more prevalent in aerobic surface waters and arsenite is more likely to occur in anaerobic ground waters.

A number of meetings, workshops, symposia, both at national and international level have been conducted and the details on the worldwide effort on mitigating the arsenic contamination problem can be obtained in the web-site maintained by Dr. Wilson at Harvard [5].

Variety of treatment technologies have been used for the removal of arsenic from water [6]. The common methods adopted for arsenic treatment include (i) co-precipitation (using $\text{Fe}_2(\text{SO}_4)_3$ or FeCl_3); (ii) coagulation (with ferric or aluminium salts such as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ as coagulants); (iii) passing through activated alumina; (iv) ion-exchange; (v) use of adsorption media like activated carbon, ferric oxide, titanium oxide, bone charcoal, iron oxide/ MnO_2 coated sands, cellulose materials (saw dust and news paper pulp), etc.; (vi) the use of zero valent iron in the presence of sulphate; and (vii) reverse osmosis and electrodialysis.

Despite the fact that a variety of treatment methods are available, the efficiency of these methods is not completely known. Many of them have been reported to be capable of removing arsenic to levels lower than 50 $\mu\text{g/l}$. With the impending revision of the permissible levels to 10 $\mu\text{g/l}$ or lower, it is necessary to investigate remediation approaches that would consistently provide drinking water with arsenic at less than 10 $\mu\text{g/l}$ levels.

This paper describes the development of a remediation approach based on the pre-oxidation of arsenic(III) using hydrogen peroxide and the subsequent removal of total

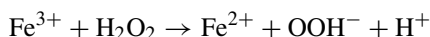
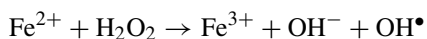
(inorganic) arsenic using ferric (oxy) hydroxide co-precipitation. This approach is simple, cost effective and produces water with total arsenic concentration close to 50 $\mu\text{g/l}$. Further reduction is achieved by passing through iron scrap. We have used potable municipal water and ground water samples spiked with arsenic throughout our investigations. A HPLC–ICPMS procedure was used for the determination of both As(III) and (V) in the processed samples, to study the effectiveness of the oxidation step and the subsequent removal of the arsenic.

2. Methodology

The principal forms of inorganic arsenic in ground water are the arsenite and arsenate. As(III) is likely to be found more in anaerobic ground waters and As(V) in aerobic surface waters. Preliminary experiments based on the co-precipitation using ferric salts or like passing the water containing the arsenic species through iron filings (scrap obtained from a workshop) showed that nearly 90% of arsenate (at 1 $\mu\text{g/ml}$ levels of As(V)) is removed and that the removal efficiency of arsenite is just about 50% or less. This observation is in conformity with the observations of other workers that majority of the remediation approaches work effectively for As(V) only.

Thus, oxidation of all As(III) to (V) is a key factor in developing a remediation method. Various experiments were carried out using different treatment approaches with H_2O_2 and chlorine water.

Fenton's reagent (H_2O_2 in the presence of Fe^{2+} catalyst) is known to be a powerful oxidising agent because of the generation of OH radical during the reaction [7,8].



The hydroxyl radical is one of the most reactive chemical species known, second only to elemental fluorine in its reactivity (relative to chlorine). Fenton's reagent is used to treat a variety of industrial wastes containing toxic organic compounds, such as phenols, formaldehyde and complex wastes, for organic pollutant destruction, toxicity reduction, biodegradability, improvement of odour and colour removal [9].

Treatment of drinking water with hydrogen peroxide is allowed for the removal of specific species like dissolved iron, hydrogen sulphide and for destroying excess ozone. The National Sanitation Foundation (NSF) Standard 60 on drinking water treatment chemicals, has specified the levels of treatment with hydrogen peroxide. The decomposition products, oxygen and water are harmless. Different manufacturers now produce hydrogen peroxide for such treatment purposes (commercial products, such as BIOX A, Oxy Pure etc.) which are certified by the NSF [10].

We have investigated the use of Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe(II)}$ salt as catalyst) as a first level treatment to oxidise As(III) to (V), through the formation of the powerful oxidant OH^\bullet radicals. The Fe(II) is converted to Fe(III) which forms a precipitate that gathers all the As(V). A column loaded with Fe filings as a secondary treatment effectively reduces the

residual arsenic further. All the experiments are performed at the natural pH of the water samples (6.8–7.1).

The residual As in the processed samples was determined using ICP–QMS. Since arsenite is found to be predominant from arsenic in ground waters, it is necessary to determine the amount of As(III) and (V) contents in the treated water samples to assess the efficacy of the oxidation step and the subsequent removal of arsenic as As(V). A considerable amount of has been done on ion-exchange [11,12] and reverse phase ion pairing chromatography [13,14] coupled with ICP–MS or HGAAS/AFS for the determination of As species. As(III) and (V) contents in these samples were determined using a reverse phase ion pair chromatography (RPIPC)–ICPMS technique standardised in our laboratory [15].

3. Experimental

3.1. Instrumentation

ICP–QMS measurements were made with a VG-Plasma Quad 3 (VG Elemental, Winsford, Cheshire, UK) system with a Meinhard concentric nebuliser and a Scott double pass cooled spray chamber. The optimised parameters are given in Table 1. All the measurements were performed using the peak jump mode.

HPLC: A Dionex Model 2000i/SP HPLC/IC system with a pulse dampener (Dionex, Sunnyvale, CA, USA) along with a pneumatically activated Rheodyne 9126 loop injection valve (Rheodyne, Cotati, CA, USA) incorporating a 100 μ l injection loop was used. A Dionex Ion Pac NG1 guard column (50 mm \times 4 mm i.d.) and an Ion Pac NS1 reverse phase column (250 mm \times 4 mm i.d.) were used for the separation of As(III) and (V) species. The analytical column was connected to the nebuliser by a 50 cm long, 1/16" o.d., 0.15 mm i.d. PEEK tubing. A time resolved mode of data acquisition was used. The interference at m/z , 75 due to ArCl^+ was monitored using m/z , 77. The instrument sensitivity was optimised using 10 ppb As standard taken in eluent prior to the HPLC–ICPMS runs.

Table 1
Operating conditions for the ICP–QMS

ICP–MS system	
Instrument	VG plasmaquad PQ3
Torch type	Fassel
Plasma FW power	1380 W
Reflected power	<10 W
Gas flow rates	
Coolant gas	13.4 l/min
Auxiliary gas	0.66 l/min
Nebuliser gas	0.55 l/min
Sampler cone	1.0 mm Ni
Skimmer cone	0.7 mm Ni
Ions monitored	75 and 77

3.2. Sample preparation

Water samples laced with arsenic were prepared by adding known quantities of arsenic(III) and (V) to the tap water (municipal drinking water with total As <5 ppb). Arsenic(III) standard was prepared by dissolving As₂O₃ in 50% HCl under warm conditions. Then the solution was evaporated to near dryness and made to required volume with 10% HCl in the presence of 5% hydroxylamine hydrochloride.

Arsenic(V) standard was prepared by dissolving arsenic powder at a temperature of 80°C in sub-boiled nitric acid in the presence of a small amount of H₂O₂ in order to facilitate faster reaction and evaporated to near dryness then made to required volume in 5% nitric acid.

3.3. Optimisation of the quantity of reagents

In order to optimise the concentrations of H₂O₂ and Fe(II) salt (catalyst) (for treating 1 l of water), we have carried out a factorial (two factors, three level) experimental design approach and determined the residual arsenic at each level of the treatment. The base level was chosen as 200 mg of Fe(II) salt (ferrous ammonium sulphate) and 500 μl of 30% H₂O₂. The upper and lower levels were obtained using a difference of ±100 mg for Fe(II) and ±250 μl for H₂O₂ (30%) from the base level (set I). The spiked concentration of arsenic in all the cases was 2.5 mg/l of As(III). The water was filtered through a sand bed which yielded clear water and the residual arsenic was determined using ICP–MS. The optimum amount for the maximum reduction of total arsenic was estimated to be 200 mg of Fe(II) salt + 750 μl of H₂O₂, using a surface fitting approach.

An additional set of factorial experiments with a base level of 100 μg Fe(II) salt and 100 μl of H₂O₂ with steps of ±50 mg Fe salt and ±50 μl of H₂O₂ was also performed, with a starting concentration of 2 mg/l of As(III) at each level (set II). In both sets of experiments, the reaction was carried out for 10 min after the addition of reagents, with occasional stirring.

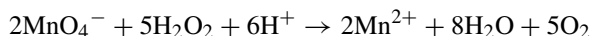
A glass column of the size 25 cm × 5 cm i.d. with a leak proof stopcock was packed with about 150 g of Fe scrap obtained from a workshop. A wad of glass wool was kept at the bottom of the column. Then the processed water was passed through the column of scrap iron at a flow rate of about 150 ml/min and then through a sand bed, which yielded clear water.

3.4. Determination of residual H₂O₂ in the processed samples

The residual peroxide in the processed water samples was determined using the permanganate method [16].

A total of 50 ml of processed water was taken in a beaker and 3 ml of 6 M sulphuric acid and two drops of 5% aqueous manganous sulphate solution were added. This sample was titrated against standardised 0.1N potassium permanganate solution to the first pink colour. Blank titration was also carried out with 50 ml of water containing 3 ml of 6 M sulphuric acid.

This method is based on the following reaction:



$$\text{H}_2\text{O}_2 \text{ wt.}\% = \frac{(A - B) \times N \times 17.007 \times 100}{W \times 1000}$$

where A is the volume of the permanganate solution used for the titration in millilitre, B the volume of the permanganate solution used for the blank titration in millilitre, N the normality of the permanganate solution, and W is the sample weight, in grams.

3.5. Studies using chlorine water

Though the oxidation power of the chlorine (1.0) is lower than that of the hydroxyl radical (2.8), studies were carried out to investigate the efficiency of chlorine to oxidise As(III) to (V) in the presence of Fe(II) salt. Water samples were spiked with As(III), 100 mg of ferrous ammonium sulphate and 250–1500 μl of chlorine water (as sodium hypochlorite solution, 4% available chlorine), to 1 l of water. The filtered water samples were analysed for residual arsenic.

4. Results and discussion

The first set of factorial experiments was carried out to study the efficiency of the treatment with Fenton's reagent. The typical results from these experiments are shown in Fig. 1. It is found that the addition of 300 mg of Fe(II) salt and H_2O_2 in the range of 500–750 $\mu\text{l/l}$ of water is capable of removing arsenic close to 20 $\mu\text{g/l}$ levels. Using suggested optimum amounts of these reagents (200 mg Fe(II) salt + 750 μl H_2O_2) several experiments were carried out at different concentrations of As(III) in the range of 0.5–2.5 mg/l. Even though arsenic removal was found to be very good (2–10 $\mu\text{g/l}$), it is essential to know that the levels of residual peroxide are also acceptable for drinking purposes. The information pertaining to the permitted levels of hydrogen peroxide in drinking water adopted in different countries is not readily available but a legal limit of 0.1 mg/l of residual hydrogen peroxide levels has been adopted in Germany (as per Trinkwasser — Vernordnung BRD; personnel communication from Emons, Forschungszentrum, Juelich). The residual levels of peroxide determined using the potassium permanganate method, were found to be around 15–20 ppm. The excess peroxide could be eliminated by chlorination but the extent of chlorination could be high.

In view of this, we have carried out another set of optimisation experiments using lower amounts of these reagents (100 μg ferrous ammonium sulphate + 100 μl H_2O_2 as base level) and the results are shown in Fig. 2. A response surface fitting approach of the dataset suggested a treatment level of 125 μl of hydrogen peroxide per litre of water with 100 mg of Fe(II) ammonium sulphate. Since the level is close to the initial base level, the same was adopted for further experiments. It was found that the residual peroxide levels were lower but close to 3–4 mg/l levels, which again is much higher than the permitted level. Experiments with starting concentrations of 0.1–2 mg/l of As(III), revealed that the residual arsenic levels were reduced to close to 40–50 $\mu\text{g/l}$ levels in the treated samples, indicating that higher levels of peroxide treatment would be required, if only Fenton's reagent is used for the remediation purposes.

With this view, a two stage treatment approach, viz. addition of Fenton's reagent as a preliminary treatment followed by passing through zero valent iron has been investigated. Treatment with (100 mg Fe(II) ammonium sulphate + 100 μl H_2O_2 per litre) for 10 min followed by passing through the iron scrap and filtering through sand, consistently yielded waters with arsenic less than 10 ppb from a starting level of 2.5 mg/l of As(III).

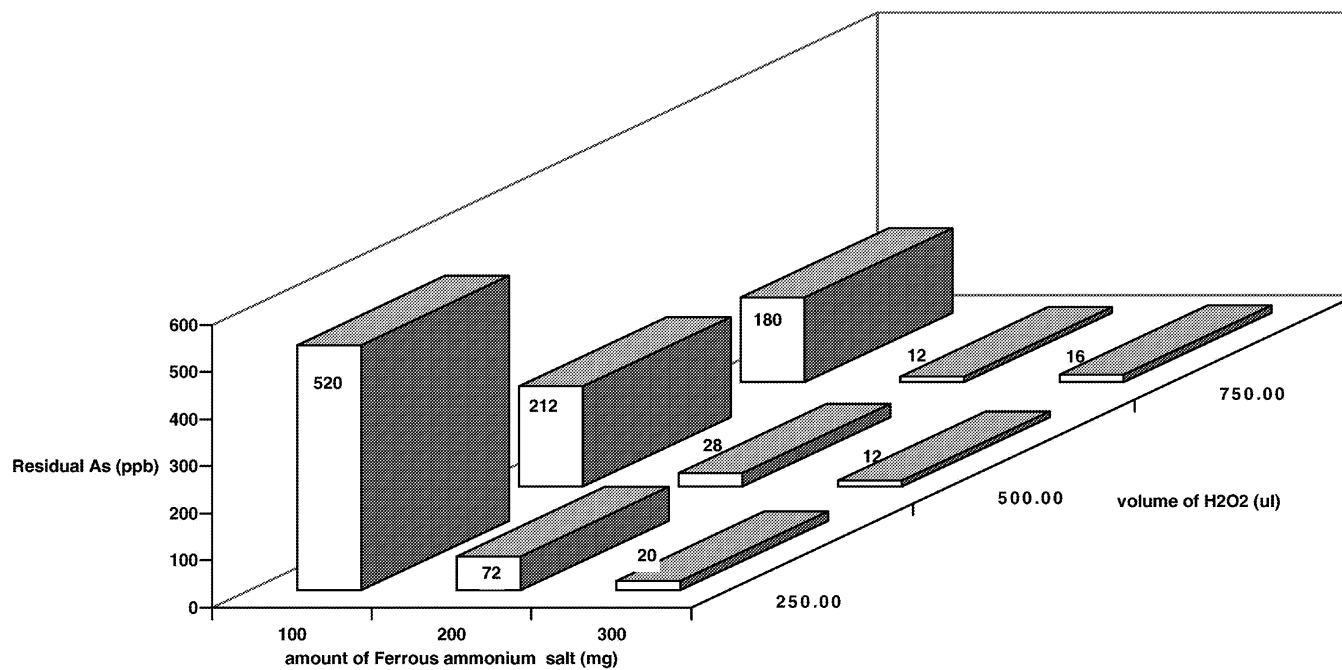


Fig. 1. Residual arsenic after treating with Fenton's reagent (optimisation experiments — set I).

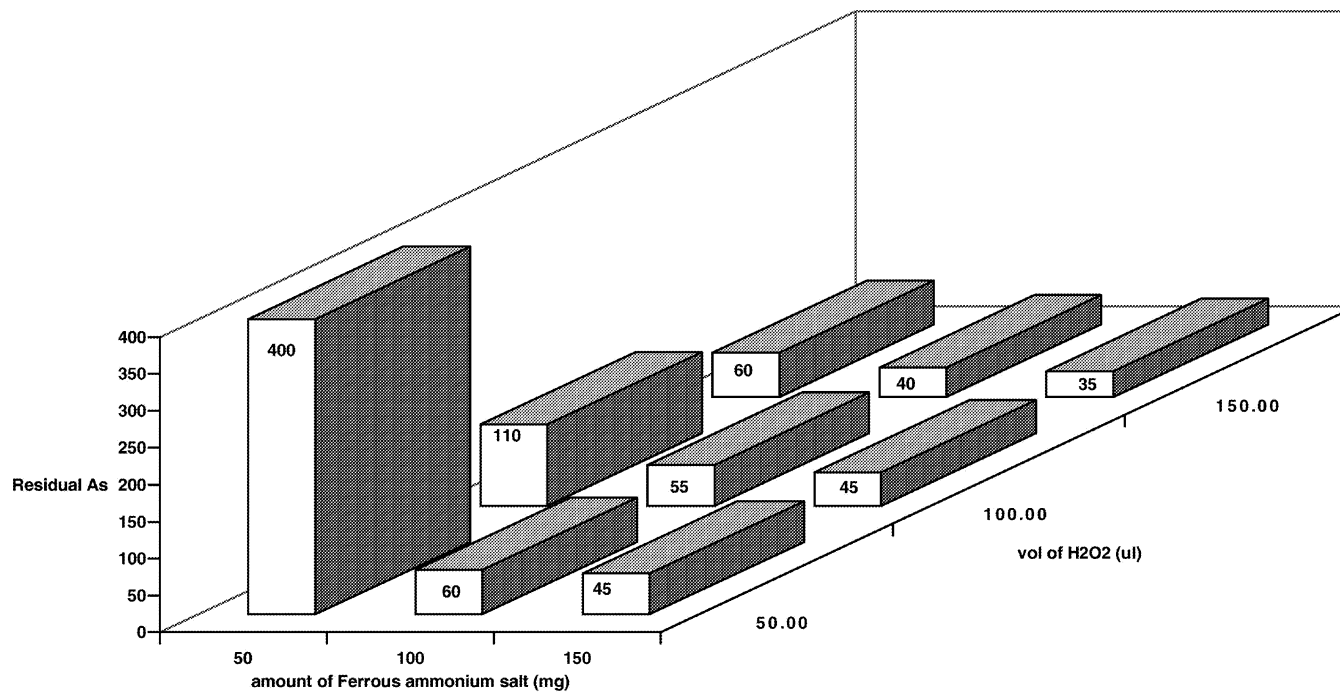


Fig. 2. Residual arsenic after treating with Fenton's reagent (optimisation experiments — set II).

After treatment with iron filings and sand the residual peroxide levels were found to be less than 0.5 mg/l in each case which can be eliminated by much lower levels of chlorination (100 μ l of chlorine water, as sodium hypochlorite solution with 4% available chlorine, was found to be sufficient per litre of the processed water).

4.1. HPLC–ICPMS studies

A method has been developed in our laboratory for the speciation of As(III) and (V) using RPIPC–ICPMS. This hyphenated technique offers the advantage of both, the separation power offered by IC and the high sensitivity, selectivity and large dynamic range offered by

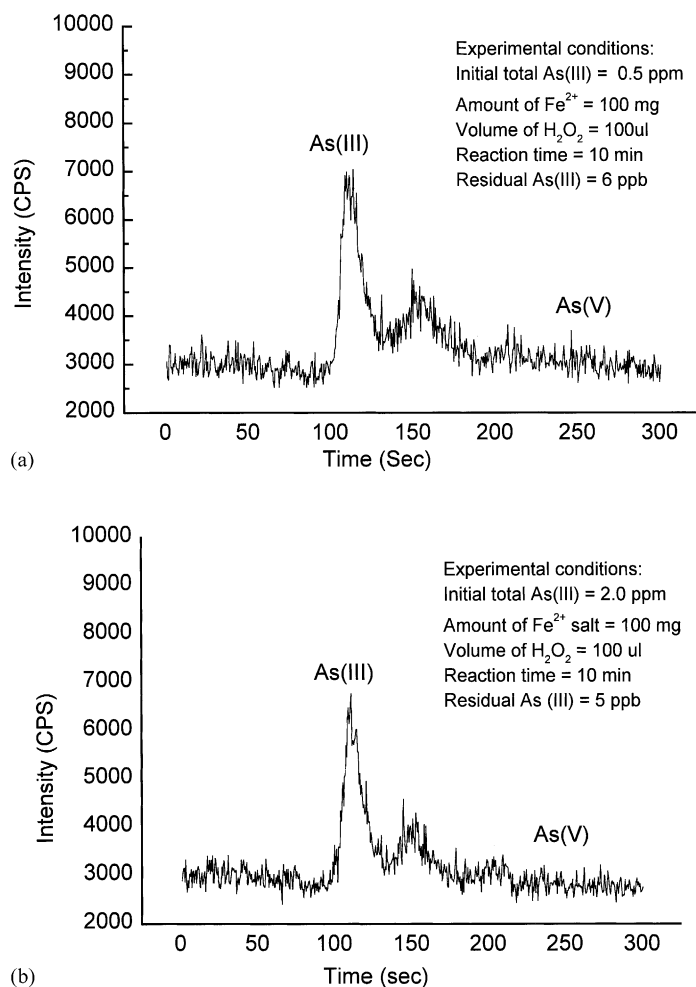


Fig. 3. (a) Residual As after treating with Fenton's reagent and iron filings. (b) Residual As after treating with Fenton's reagent and iron filings.

ICPMS. The mobile phase is a mixture of 1 mM tetrabutyl ammonium hydroxide (TBAOH) and 8% isopropyl alcohol (IPA). Many ground water sample have been analysed by this approach for the detection and determination of As(III) and (V) species at low ppb levels [10].

The processed water samples were analysed by this approach to identify the residual arsenic species and their levels. The typical chromatograms obtained for two starting concentrations of 0.5 and 2.0 mg/l As(III) spiked municipal potable water samples (after treatment with Fenton's reagent and after passing through zero valent iron) are shown in Fig. 3(a) and (b). The further reduction in the arsenic levels by passing through iron is clearly evident. It is seen that the residual arsenic in the processed waters is mainly arsenic(III) and almost all the As(V) formed by oxidation with Fenton's reagent has been effectively removed by the precipitate formed.

Fig. 4 shows the chromatograms, obtained on a ground water sample, treated with only Fenton's reagent (Fig. 4(a)) and after passing through iron scrap (Fig. 4(b)). The count rates for m/z , 77, also shown in the figure indicate that the chloride present in the ground water, has no interference in the arsenic measurements. The much higher levels of base lines of the chromatograms for mass 75 (when compared to Fig. 3) is suspected to have arisen from residual arsenic present in a different batch of TBAH used in these measurements.

Experiments carried out with higher volumes (up to 20 l of water) with proportional increase in the quantity of the reagents showed that the two stage treatment approach is successful in reducing the total arsenic content to less than 10 $\mu\text{g/l}$ levels.

Chlorine water also serves as good oxidant for As(III) at the natural pH of water. A typical set of results obtained on residual arsenic after treatment with different amounts of chlorine water in the presence 100 mg of ferrous ammonium sulphate (per litre of water) is given in Fig. 5. The residual chlorine levels are much higher than the permissible levels for drinking purposes. Additional experiments are being carried out to optimise this treatment procedure.

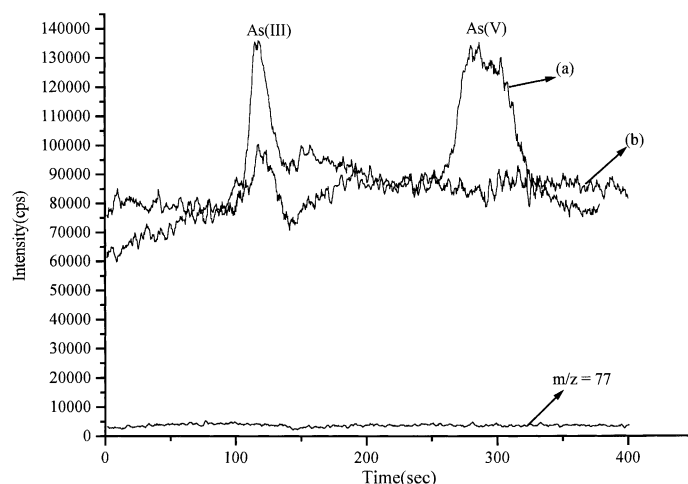


Fig. 4. Residual As after treating with (a) Fenton's reagent, and (b) Fenton's reagent + filings.

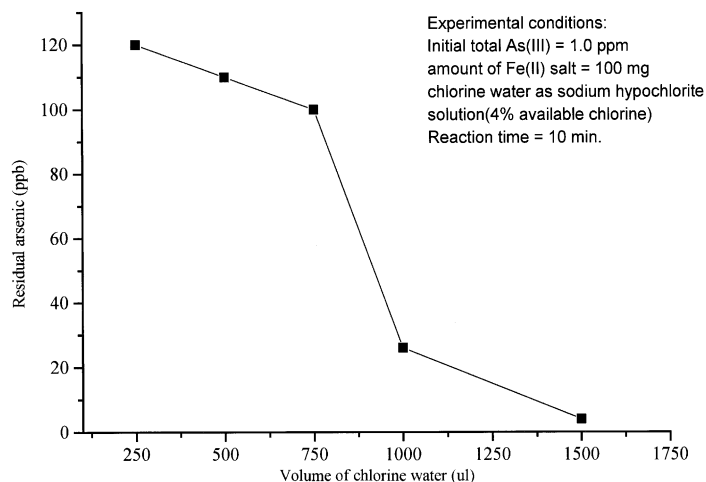


Fig. 5. Removal of As after treating with chlorine water and Fe(II) salt.

5. Conclusions

The two stage treatment approach, viz. treatment with Fenton's reagent (100 mg Fe(II) ammonium sulphate + 100 μ l H_2O_2 per litre) for 10 min followed by passing through iron scrap and filtering through sand, was found to be suitable for consistently producing waters with arsenic content less than 10 ppb, even from starting concentration levels of 2.5 mg/l of As(III). Though the water was passed through the iron scrap at a fairly high flow rate (150 ml/min), the process was found to be effective. The HPLC–ICPMS study indicates that the oxidation using the hydrogen peroxide step is fairly rapid and processing of large volume of water by this approach would not be a time consuming affair as is the case with some of the approaches reported which require long treatment times (sometimes overnight duration). Treatment with chlorine requires consideration of the many reaction products that may be produced while treating ground waters. The waters produced by the two stage approach reported here is free of any harmful reactions products. The residual peroxide can be eliminated by mild levels of chlorination. It can be easily adopted at the community level. Presently, we are investigating the scaling up of this procedure. A comprehensive evaluation of different approaches is also in progress.

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