Enhancing arsenic removal from groundwater at household level with naturally occurring iron

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ABSTRACT

A supply of drinking water low in Arsenic (As) prevents arsenic poisoning. The presence of high concentrations of iron (Fe) in groundwater under the alluvial plains of the large rivers in Southeast Asia is a prerequisite for the simple removal of As. This study investigated the mechanisms and possibilities for enhancing As removal with naturally occurring Fe in a reliable, low cost and sustainable way. The results of the study show that As removal with Fe is greatly enhanced by the addition of an oxidizing agent (preferably $KMnO_4$) immediately after the pumping of groundwater. Further enhancement of As removal in the presence of Fe can be achieved by adding a small volume of a concentrated basic solution of MnO_4^- and AlO_2^-, which has a combined oxidation, coagulation and buffering capacity. Best results were obtained when this solution was mixed with the groundwater immediately after its pumping until a pale pink color appeared. Maximum required reaction time was 10 minutes and subsequent filtration of the water was able to reduce the As concentration to near zero. Concentrations of MnO_4^- and AlO_2^- can be varied in the solution to achieve sufficient As removal to suit different Fe/As ratios and the presence of interfering co-occurring anions.

Keywords: aluminum, metal removal, oxidation.

Melhoria na remoção de arsênio de água subterrânea em nível doméstico com ferro de ocorrência natural

RESUMO

O abastecimento de água potável com baixa concentração de arsênio (As) é uma das soluções contra a Arsenicose. A presença de altas concentrações de ferro (Fe) na água subterrânea das várzeas dos grandes rios no sudeste da Ásia é um pré-requisito para uma remoção simplificada de arsênio. O objetivo deste estudo foi avaliar os mecanismos e as

possibilidades de melhorar a remoção de arsênico de águas subterrâneas com a ocorrência natural de ferro de modo confiável, de baixo custo e sustentável. Os resultados mostraramm que a remoção do arsênio com ferro é mais efetiva com a adição de um agente oxidante (de preferência com $KMnO_4$) imediatamente após o bombeamento de águas subterrâneas. Uma melhoria adicional na remoção do arsênio na presença de ferro pode ser alcançada pela adição de um pequeno volume de uma solução concentrada de MnO_4^- básico e AlO_2^-, que tem um efeito combinado de oxidação, coagulação e capacidade tampão. Os melhores resultados foram obtidos quando a solução era misturada imediatamente depois de bombear água até que se adquira uma cor rosa-pálido. O tempo máximo de reação necessário foi de dez minutos e uma subsequente filtração da água pode reduzir a concentração de arsênio até próximo de zero. As concentrações de MnO_4^- e AlO_2^- podem ser variadas na solução de modo a obter uma remoção de arsênio suficiente para satisfazer diferentes taxas de Fe/AS e a presença de ânions de interferência simultânea.

Palavras-chave: alumínio, oxidação, remoção de metais.

1. INTRODUCTION

Occurrence of inorganic Arsenic (As) in groundwaters under the alluvial plains of the large rivers in Southeast Asia (West Bengal, Bangladesh, Vietnam and other regions) may seriously and adversely affect the health of the population, resulting in skin diseases and various kinds of cancer (WHO, 2011). The prevailing national Maximum Concentration Level (MCL) value for drinking water in most of the countries in Southeast Asia is 50 µg L^{-1}, and it is estimated that more than 40 million people are exposed to As concentrations above that threshold (Smedley and Kinniburgh, 2002; Chakraborti et al., 2004; Berg et al., 2007).

Various measures like the installation of As-free deep-tube wells, the reintroduction of surface water, rainwater harvesting, supplying of bottled water, piped water supply and As removal using various treatment methods have been suggested as mitigating options (Ahmed and Rahman, 2003). One unique solution may not be appropriate for the vast As-contaminated regions, as the best choice depends on many factors, such as affordability (economy, time), availability of alternative water sources, flexibility in adopting a new technology, awareness, etc. Low-cost treatment of groundwater for As removal at the household level can a viable option for safeguarding water supplies, especially when individuals are willing to adopt simple procedures to obtain good drinking water.

The chemistry involved in the efficient yet simple removal of As(III) with iron (Fe) is the oxidation of As(III) to As(V) and concurrent adsorption of As(V) and As(III) onto precipitating iron-hydroxides ($Fe(OH)_3$). Oxidation of As(III) to As(V) takes place only in parallel to the oxidation of Fe added as Fe(II), and most probably due to intermediate oxidants formed during oxidation of Fe(II) to Fe(III) in presence of air (Hug and Leupin, 2003).

Subsequent removal of the formed $Fe(OH)_3$ flocs by filtration significantly improves As removal.

Simple household treatment methods based on oxidation, coagulation (with Al or Fe salts) and filtration are available and implemented in the field for removal of Arsenic (BAMWSP, 2001, Cheng et al., 2004). Oxidation with air/oxygen is a very slow process, as it requires days rather than hours to be completed (Cherry et al., 1979); therefore, a more effective oxidation of As(III) can be obtained by means of chemical ($KMnO_4$, $Ca(ClO)_2$ or NaClO), photochemical (UV+Citrate), and photocatalytic processes. Sharma (2006), Sorlini and Gialdini (2010) showed that a complete oxidation of As(III) into As(V) can be obtained with $KMnO_4$ during the first minute of oxidation in pure water spiked with As(III), while an oxidation of 80% after the first minute and 100% after 15 minutes was obtained for raw groundwater. However, most of the results from the Bengal Delta show that these methods are

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often not able to decrease the concentration of As to below the Indian and Bangladeshi MCL of 50 µg L^{-1} (BAMWSP, 2001), and this is mostly due to insufficient oxidant and/or coagulant amounts. Furthermore, people are reluctant to use some of the methods due to the bad taste and odor from oxidants like (Ca(ClO)$_2$ or NaClO) (BAMWSP, 2001).

The groundwater below the Southeast Asian alluvial plains is mostly in the near-neutral pH range with trivalent arsenite (As(III)) being the predominant As species; moreover, several studies have shown that groundwater with high As concentrations also contain higher iron (Fe) concentrations. For example, in Bangladesh, 74% of the tube wells with As concentrations higher than 50 µg L^{-1} also have Fe^{2+} concentrations higher than 2 mg L^{-1} (BGS, 2003), which is above the MCL for Fe in drinking water (WHO, 2011). The occurrence of As in the Bengal Delta is of natural origin and microbially mediated reductive dissolution of Fe hydroxides with adsorbed As and P is the most accepted theory for the elevated As concentrations up to 4000 µg L^{-1}(Smedley and Kinniburgh, 2002). Hence, taking advantage of the naturally occurring Fe for As removal would be an ideal solution, as indicated by various authors (Hug et al., 2008; Mamtaz and Bache, 2001; Roberts et al., 2004; Meng et al., 2001).

For these reasons, oxidization with potassium permanganate is an interesting option for arsenic removal due to the fast oxidation kinetics. Potassium permanganate is also readily available in developing countries, and it is more stable than bleaching powder and has a long shelf life. Simple options for the application of this process based on As oxidation with potassium permanganate and chemical precipitation by means of the natural occurring Iron have been evaluated by different authors (Ahmed, 2013). Bortoloi et al. (2013) highlighted that the high efficiency, an extremely low cost, safety, non-requirement of power and simplicity of operation make the technique potentially viable for rural application. Removal of As with Fe depends on many factors and around neutral pH the most important one is the oxidation state of As. According to Roberts et al. (2004) approximately 18 times more Fe is required for As(III) compared with arsenate (As(V)) to achieve similar As removals. In addition, co-occurrence of high levels of anions like phosphate (P), and silicate (Si) decreases removal of As(V) (Smedley and Kinniburgh, 2002; Hug et al., 2008; Mamtaz and Bache, 2001; Roberts et al., 2004; Meng et al., 2001). Previous field investigations (Sharma et al., 2005) with varying P and Si concentrations and naturally occurring Fe showed that an Fe/As(III) > 120 (M/M) is required to achieve residual As concentrations below the MCL of 50 µg L^{-1} which will limit the method to only 14% of the tube wells in Bangladesh.

The present study examines the mechanisms and possibilities for enhancing As removal from groundwater with naturally occurring Fe and proposes a reliable, low-cost and sustainable method based on concurrent oxidation of As(III) and Fe^{2+} with subsequent association of As(V) to coagulating/precipitating of Fe(OH)$_3$ flocs. KMnO$_4$ is chosen as the oxidant since it is easy to administer the necessary amount of oxidant based on the color development.

2. MATERIALS AND METHODS

2.1. Chemicals

All chemicals, NaHCO$_3$, NaAsO$_2$, Na$_2$HAsO$_4$·7H$_2$O, NaOH, HCl, NaBH$_4$, FeCl$_3$·6H$_2$O, FeCl$_2$·4H$_2$O, KMnO$_4$ and Al$_2$(SO$_4$)$_3$·18H$_2$O used in this study are of reagent grade and no additional purification was necessary. For this study a method based on HGAAS (MHS-20) in batch system was developed for As analysis in water using HCl and NaBH$_4$. The applicability of alum as coagulant was investigated by means of Al$_2$(SO$_4$)$_3$·18H$_2$O. The oxidizing agent was KMnO$_4$. To simulate the concentration of contaminants in groundwater of the Bengal Delta, stock solutions of arsenic and iron were prepared using NaAsO$_2$,

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$Na_2HAsO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, and $FeCl_2 \cdot 4H_2O$. To adjust the pH, NaOH and HCl were used, while $NaHCO_3$, was used as a buffer.

2.2. Experiments on oxidation of As(III) with $KMnO_4$

The first stage experiments were conducted to study oxidation and removal of As(III) with $KMnO_4$ in the presence of Fe^{2+} and Fe^{3+}. These experiments were conducted in distilled water with 5 mM $NaHCO_3$ as a buffer, with initial As(III) and Fe concentrations of 1 and 10 mg L^{-1}, respectively. pH was adjusted to 7 by adding dilute NaOH or HCl before the addition of Fe and/or $KMnO_4$. The final pH varied $\pm$ 0.2 units compared to the set pH and no attempts were made to adjust the pH after the addition of Fe. In experiments with Fe^{2+}, $KMnO_4$ was added at stoichiometric ratio (SR) of 0, 0.2, 0.7, 1 and 1.3. In experiments with Fe^{3+}, $KMnO_4$ was added at stoichiometric ratios (SR) of 1. The stoichiometric ratio SR denotes the ratio between added equivalents of oxidant (MnO_4^-) and reductants (As(III) and Fe^{2+}) in the experimental solutions.

Equations 1 and 2 show oxidation of As(III) and Fe^{2+} with MnO_4^-:

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + 2MnO_2 + H_2O + H^+ \tag{1}$$

$$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+ \tag{2}$$
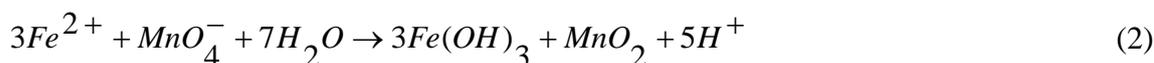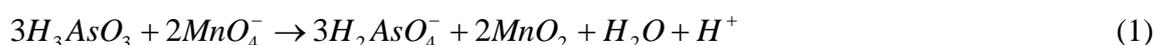
The pH generally dropped within the first 10 minutes upon the oxidation and precipitation of $Fe(OH)_3$, followed by an increase due to CO_2 expulsion. As(III) concentration was measured continuously after passing an on-line anion exchanger removing As(V) (Sharma, 2006). Filtered discrete samples (0.45 μm) were taken at intervals for measuring total dissolved As concentrations (As(III) + As (V)) and As(III).

2.3. Experiments on removal of As(III) with $KMnO_4$ and $Al_2(SO_4)_3$

Based on the results from the first stage, a second stage of experiments was conducted to improve oxidation and removal of As(III) with a basic solution of $KMnO_4 + Al_2(SO_4)_3$. The effects of the initial Fe concentration, pH, and filtration on removal of As(III) were studied. These experiments were done in a 1:1 mixture of distilled water and tap water to simulate the groundwater conditions in the Bengal Delta. Table 1 shows the composition of the diluted tap water and the average concentrations and range of major ions present in the Bengal plains ground (BGS, 2003). An initial As(III) concentration of 0.5 mg L^{-1} was chosen for the second stage of experiments in order to simulate the common contamination of arsenic found in groundwaters of the Bengal Delta.

Table 1. Composition of tap water and Bangladesh water (mM).

Ion	Tap water (1:1diluted) (mM)	Bangladesh water (mM)	
		Average	Concentration range
Ca^{2+}	3	1.3	<0.002-9.1
Mg^{2+}	0.55	0.86	<0.001-12.5
Na^+	1	3.9	<0.03-118
K^+	0.1	0.12	<0.007-3.4
HCO_3^-	5.3	5.4	1.1-11.5
Cl^-	0.17	1.86	0.08-67
SO_4^{2-}	0.06	0.52	<0.002-7.8
P	<0.003	0.025	0.003-0.61
Si	0.25	0.73	0.3-45

The effect of co-occurring iron on As removal was studied in the Fe^{2+} concentration range of 0 to 10 mg L^{-1} using a 2 mg L^{-1} concentration-increasing step. The effect of pH was studied in the pH range of 6.0 – 7.5, where pH between 6.0 and 7.5 was adjusted by adding dilute NaOH or HCl before the addition of Fe and/or oxidant. The effect of time of sedimentation on As removal was studied at 0, 10 and 20 minutes of sedimentation time. The effect of filtration on As removal compared to prolonged sedimentation time was studied, by filtering the samples 2 minutes after the addition of Fe^{2+} and oxidant compared to 1 h and 1.5 h sedimentation time.

All the experiments were conducted at room temperature (~25°C). To simulate the anaerobic conditions in groundwater under the plains, nitrogen gas was bubbled through the water for about 10 minutes to reach an oxygen concentration below 2 mg L^{-1}.

2.4. Lab-scale equipment

A jar test apparatus (Nordic Scientific – six stirrers) was used at low speed to conduct the experiments in beakers of 1L (flash mixing for 1-2 minutes at 90-130 rpm). The test conditions evaluated different stoichiometric ratios of reagents (range of 0 to 1.3), initial oxidation state of Fe, time of oxidant addition (after 15 and 30 minutes), simultaneous or delayed addition of the oxidant and coagulant reagents; finally, the development of pale pink color was considered.

2.5. Analytical methods

As(III) and total As analysis was carried out on a Perkin-Elmer 5000 AAS (Atomic Absorption Spectrometry) using the continuous hydride generation method (Sharma, 2006). To evaluate the oxidation state of arsenic, ion exchange resins were used (mixed-bed ion exchanger composed of OH-form and H-form in ratio 2:1) (SERDOLIT$^®$ MB). The ion exchange resins were prepared with 1g of ion exchanger and cotton wool, put together in a plastic pipette. Total Fe was measured using Flame-AAS (APHA et al., 1995).

3. RESULTS AND DISCUSSION

3.1. As(III) oxidation with KMnO₄

Results for experiments on the effectiveness of KMnO₄ on As(III) oxidation and the effect of presence of Fe^{2+} on As(III) oxidation are shown in Figure 1.
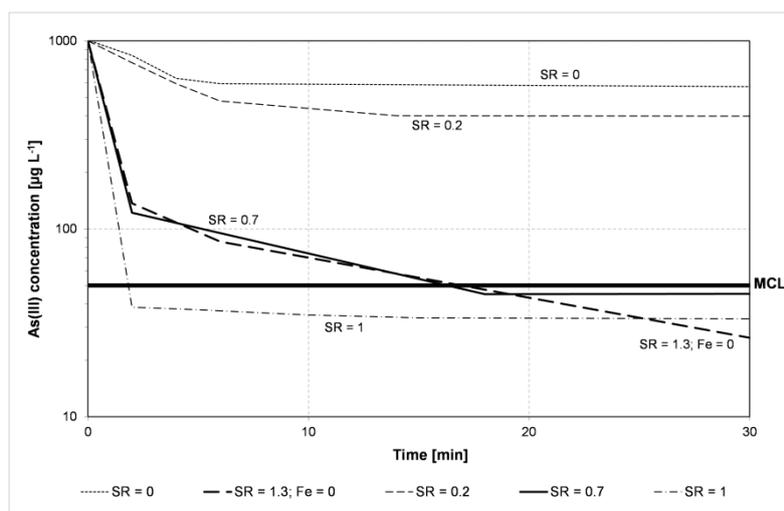

Figure 1. Effect of KMnO₄ on oxidation of As(III) in the presence and absence of Fe^{2+}. Initial Fe^{2+} concentration: 10 mg L^{-1}.

As shown in the literature (Hug and Leupin, 2003; Roberts et al., 2004), As(III) oxidation was concomitant with the oxidation of Fe^{2+} and was very rapid within the first 10 minutes of the experiment, while after this As(III) oxidation was very slow. Furthermore, the results show that a SR of 0.7 ($KMnO_4/(As(III)+Fe^{2+})$) in presence Fe^{2+} results in similar oxidation kinetics as a SR of 1.3 in absence of Fe^{2+}. With a SR=1, complete oxidation of As(III) occurs within 2 minutes after the $KMnO_4$ addition in the presence of Fe^{2+}. Ghurye and Clifford (2004) showed that an oxidation yield higher than 95% was obtained in 15 seconds at similar conditions, but at a SR=3 in the absence of any interfering ions. They also demonstrated that an increase in pH from 7.3 to 8.3 did not have any effect on the oxidation yield, whereas a decrease in pH from 7.3 to 6.3 increased the time required for reaching the same oxidation effect.

3.2. Effect of time of addition of $KMnO_4$ on As(III) oxidation

Since Fe^{2+} is easily oxidized in presence of O_2, and pumping and transporting of groundwater in rural areas may take 10-15 minutes, some experiments were done in order to study the influence of a delayed addition of $KMnO_4$ on the oxidation of As(III). The influence of the initial oxidation state of added Fe (Fe^{2+} or Fe^{3+} (as sulphate)) on As(III) oxidation and removal of As was also investigated. Figure 2 shows the results for the oxidation of As(III). $KMnO_4$ was added 15 and 40 minutes after the addition of Fe and the amount of $KMnO_4$ added was constant at an SR ratio of 1 for oxidation of initial As(III) alone.
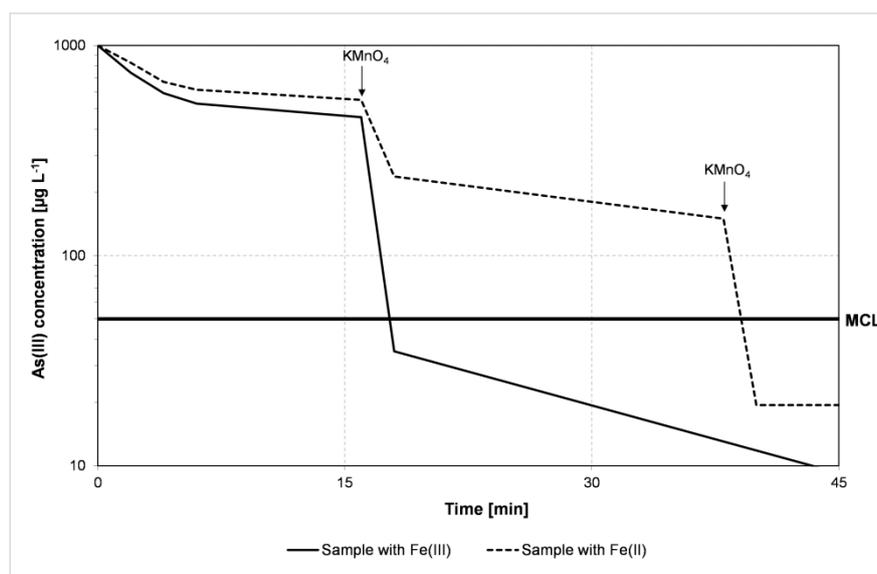

Figure 2. Effect of initial oxidation state of Fe and time of $KMnO_4$ addition on As(III) oxidation. In the case of Fe^{3+}, $KMnO_4$ addition after 15 minutes and in the case of Fe^{2+}, $KMnO_4$ addition after 15 minutes and 30 minutes. (MCL: Maximum Concentration Level).

The results show that a better oxidation of As(III) occurred in the presence of Fe^{3+} in comparison to Fe^{2+} and in the case of Fe^{2+} an extra dosage of $KMnO_4$ was required to achieve a final As(III) concentration below 50 µg L^{-1}. This was obviously due to the fact that Fe^{2+} competes with As(III) in $KMnO_4$ consumption during the oxidation process. The extra amount of $KMnO_4$ required for oxidation of As(III) in presence of Fe^{2+} could be due to incomplete oxidation of Fe^{2+} before the addition of $KMnO_4$. Comparing Figures 1 and 2 further shows that the presence of Fe^{3+} had a positive effect on As(III) oxidation, since complete oxidation of As(III) occurred within 2 minutes upon the delayed addition of $KMnO_4$ with initial Fe^{3+}, compared to 20 minutes in the absence of any Fe.

3.3. Removal of As(III) in the presence of $KMnO_4$

Figure 3 shows removal results of As in filtered samples (0.45 μm) for the same experiments as in Figure 2. Figure 3 further shows the removal of As upon immediate addition of Fe^{2+} and $KMnO_4$ at an SR=1. In the case of delayed $KMnO_4$ addition and Fe initially present as Fe^{3+}, $KMnO_4$ was added 15 minutes after the addition of Fe; and in case of delayed $KMnO_4$ addition and Fe initially present as Fe^{2+}, $KMnO_4$ was added both 15 minutes and 30 minutes after the addition of Fe. $KMnO_4$ and Fe were added concurrently in simultaneous cases. SR = 0.2 is equal to the amount of $KMnO_4$ needed for oxidation of As(III) alone. Comparison of Figures 1, 2 and 3 shows that the simultaneous addition of $KMnO_4$ and Fe^{2+} equal to SR=1 results in both oxidation and removal of As(III) below the MCL within the first couple of minutes of $KMnO_4$ addition. The results also show that the delayed addition of $KMnO_4$ in the presence of Fe^{3+} did result in sufficient oxidation of As(III) but failed to achieve As removals below the MCL. The lower As removal upon the delayed addition of $KMnO_4$ can be explained by the observation that formation and coagulation of $Fe(OH)_3$ upon addition of Fe^{3+} is a rapid process and takes less than 5 seconds in the case of Fe^{3+} (Crosby et al., 1983). Because As(V) is better adsorbed compared to As(III) on $Fe(OH)_3$, the best removal of As would be achieved when As(V) is present during formation of $Fe(OH)_3$. The results further show that the delayed addition of $KMnO_4$ resulted in higher As(III) removals compared to the simultaneous addition of $KMnO_4$ at SR = 0.2 (which is equal to SR 1 of As(III) alone) and initial Fe^{2+}.
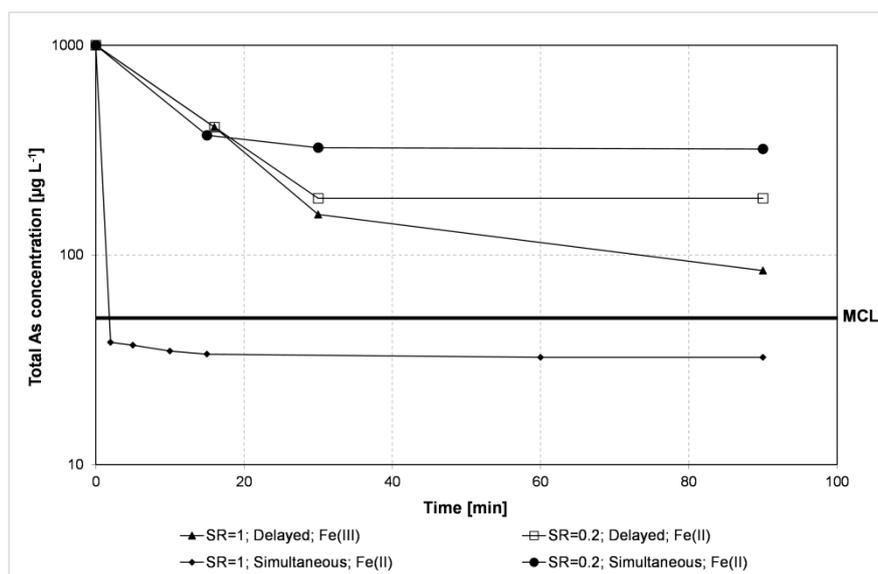
Figure 3. Effects of initial oxidation state of Fe and time of $KMnO_4$ addition on total As removal in filtered samples (0.45 μm).

The observed positive effect of the delayed addition of $KMnO_4$ on As(III) oxidation could be explained in two ways, when Fe^{2+} is used. The first is that As(III) oxidation occurs in parallel to Fe^{2+} oxidation and hence lower As(III) concentrations would be present upon the delayed addition of $KMnO_4$. The second is that the interfering effect of Fe^{2+} reduces with time due to the oxidation of the Fe^{2+}, with oxygen (natural oxidation with air), resulting in lower Fe2+ concentrations. The different effect of the time of $KMnO_4$ addition on As removals can also be explained based upon the oxidation of Fe^{2+} with oxygen. Literature reports that the oxidation of Fe^{2+} with O_2 depends on many factors (Wolthoorn et al., 2004; Tufekci and Sarikaya, 1996; Moses and Herman, 1989). Calculations based on Sung and Morgan (1980) show that complete oxidation of Fe^{2+} was not achieved within 15 minutes after the addition of Fe^{2+} and approximately 1/3 of the initial Fe^{2+} was still present as Fe^{2+}. Addition of $KMnO_4$ at

this time would result in the oxidation of remaining Fe^{2+} and As(III). Oxidation of Fe^{2+} would result in the formation of additional $Fe(OH)_3$, leading to higher As removals. This positive effect of the delayed addition of $KMnO_4$ on As removals would only be observed if Fe^{2+} is present, resulting in freshly formed $Fe(OH)_3$. If $KMnO_4$ is added after the complete oxidation of Fe^{2+} and subsequent coagulation of $Fe(OH)_3$, no further As removals would take place, as it was observed when an additional amount of $KMnO_4$ was added 40 minutes after the addition of Fe^{2+} to achieve the complete oxidation of As(III). These results indicate that if an insufficient amount of $KMnO_4$ is added simultaneously with Fe^{2+}, $KMnO_4$ would be utilized to oxidize Fe^{2+}. Upon delayed addition of $KMnO_4$, most of the Fe^{2+} is oxidized in the presence of oxygen and the added $KMnO_4$ would oxidize the remaining Fe^{2+} and As(III). The outcome is that oxidation with $KMnO_4$ proves to be a promising method. Enough $KMnO_4$ should be added to oxidize both the Fe^{2+} and the As(III) immediately after collecting the water. Incomplete oxidation of As(III) may be one of the reasons for the reported poor performance of some of the removal methods applied in the field based on the coagulation principle. For example, a study by Cheng et al. (2004) reported that the residual As concentrations in the field were in the form of As(III). The As removal was based on $Ca(ClO)_2$ as an oxidizing agent and Fe^{3+} added in the form of $Fe_2(SO_4)_3$. In the two bucket systems developed by DANIDA (Danish development assistance program) only 2mg L^{-1} $KMnO_4$ (13 µM) is used for oxidation of As(III) (BAMWSP, 2001). Our results indicate that the added $KMnO_4$ will not be sufficient if Fe^{2+} is present, as it is in most groundwaters under alluvial plains. Based on these results, it can be concluded that the removal of As with naturally occurring Fe was greatly improved by adding sufficient amounts of $KMnO_4$ to oxidise both As(III) and Fe^{2+}.

3.4. A practical method for oxidation and removal of As(III) using $KMnO_4$ + $Al_2(SO_4)_3$

In devising a practical method for field application, three major obstacles are evident:

- fast oxidation is necessary in order to form As(V) before all Fe^{2+} is precipitated;

- naturally occurring Fe is not always present in adequate concentrations (example Fe/As > 120 in Bangladesh with co-occurrence of competing ions) in all groundwaters;

- filtering/sedimentation of flocs with adsorbed As is probably necessary;

- interfering ions (P and Si) can considerably decrease As removal efficiency.

The three first points can be solved most conveniently by adding an oxidant ($KMnO_4$) together with an auxiliary coagulant (Al) if Fe^{2+} is present at low concentrations. Therefore, efforts were made to prepare a solution, which carried both oxidizing capacity and coagulation ability. The fourth point is illustrated in earlier studies on the effect of ions on As removal (Sharma, 2006), which showed that the presence of high P and Si concentrations increased the colloidal stability and hence decreased the As removal efficiency. Therefore, this study focused on the addition of coagulants like Al and Fe for destabilising the colloids and increasing the floc size for enhanced filterability. A single aqueous solution of $KMnO_4$ and the coagulant Fe^{2+} cannot be made since Fe would be oxidized. Laboratory observation shows that a solution of $KMnO_4$ and $Al_2(SO_4)_3$ (0.06 M of $Al_2(SO_4)_3$ and 0.02 M of MnO_4^-) is stable for years at pH ~11 adjusted with NaOH. At this strength, a volume of 1-3 mL per liter of water is sufficient and it is an optimal volume to handle in practice. The total concentrations and the molar ratios of the reagents can be widely altered to suit the predominant types of groundwater to be treated. Results for the applicability of this solution at varying Fe concentrations at an initial As concentration of 500 µg L^{-1} are shown in Figure 4. The effect of adding this solution in an amount exactly equal to SR=1 and in amounts equal to a slight excess indicated by the appearance of a faint pink color

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(very dilute MnO_4) is shown. Moreover, the effect of the reaction time required for maximum As removals was studied for both SRs.
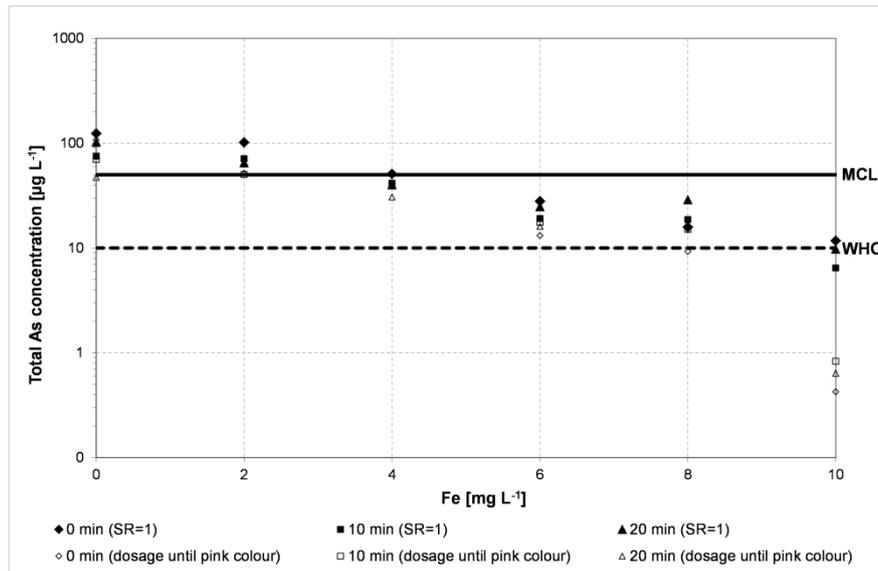
Figure 4. Influence of initial Fe concentration, time of sedimentation and amount of $KMnO_4+Al$ on As removals at an initial As(III) concentration of 500 μg L^{-1} in filtered samples (0.45 μm). Filled symbols represent the addition of $KMnO_4$ and Al equal to SR = 1 and open symbols represent a slight excess of $KMnO_4$ and Al until a pink color appears. 0, 10 and 20 min represent sedimentation times.

As expected, the results show that higher Fe concentrations increase As removal and As concentrations below the MCL of 50 μg L^{-1} were achieved at an initial Fe/As ratio of 11 or above. Moreover, the figure shows that slightly better As removal was achieved when the $KMnO_4+Al$ solution was added in slight surplus to attain the pink color and a slightly better removal was achieved with a reaction time of 10-20 minutes compared to a 0 time of sedimentation. In all cases, the daily generation of As contaminated sludge is very low; however, care should be taken to avoid the disposal of the sludge near children's playing area or edible crops. A suitable way of disposal of this sludge would be to bury it. Instead of waiting for an expensive solution based upon construction of deep-tube wells, taking years and reaching few, removal of As based on naturally occurring Fe along with application of $KMnO_4$ supplemented with Fe/Al could be recommended as a mitigating option for the affected rural areas of the Bengal Delta. The application of chemicals in solution would result in better mixing and the results showed that this mixture would have great potential for the treatment of As. However, field verification is required.

Moreover, currently there is no evidence that potassium levels in municipally treated drinking water, even water treated with potassium permanganate, are likely to pose any risk to the health of consumers. It is not considered necessary to establish a health-based guideline value for potassium in drinking-water (WHO, 2011).

### 3.5. Advantages of adding oxidant and coagulant simultaneously to water

The advantage of using $KMnO_4$ together with $Al_2(SO_4)_3$ is that addition of Al ions increases the filterability of the $Fe(OH)_3$ flocs, which grow larger in the presence of Al. An added advantage of using the strongly basic mixture is the neutralization of the acidity produced due to $Fe(OH)_3$ and $Al(OH)_3$ formation. This could in turn lower residual soluble Al concentrations and hence limit potential adverse health effects. The third advantage is that by

increasing the amount of added Al the method can be applied in waters with low Fe concentrations. The results on the effect of filtration as a useful step for adequate As removal are shown in Figure 5. It clearly demonstrates that filtration after flocculation for 20 minutes removed most As, and As concentrations below 50 μg L^{-1} were achieved at Fe concentrations of 5 mg L^{-1}, i.e., at Fe/As ratio of 13. At higher Fe/As ratios, As concentrations below 10 μg L^{-1} were achieved. Without filtration too much As is tied to dispersed colloids and flocs. The effect of pH on As removal using the KMnO$_4$+ Al$_2$(SO$_4$)$_3$ mixture was also investigated in the pH range of 6.0-7.5, and the results are shown in Figure 6. The results show that As(III) oxidation and removal was slightly higher at higher pH; however, As removal below 50 μg L^{-1} was achieved in the studied pH range. This is probably due to the buffering capacity of the KMnO$_4$+ Al$_2$(SO$_4$)$_3$ solution. A previous study (Sharma, 2006), without addition of any oxidizing agent, showed that As(III) removal was reduced by approximately 40% at pH 6 compared with pH 7.
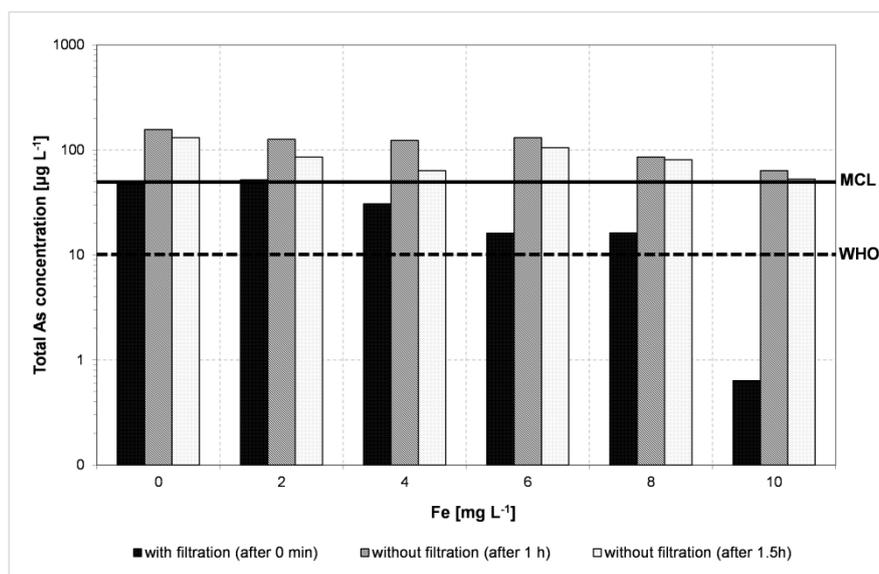
Figure 5. Removal of As in filtered and non-filtered samples with different Fe concentrations after treatment to pink color of the KMnO$_4$+Al$_2$(SO$_4$)$_3$ solution.
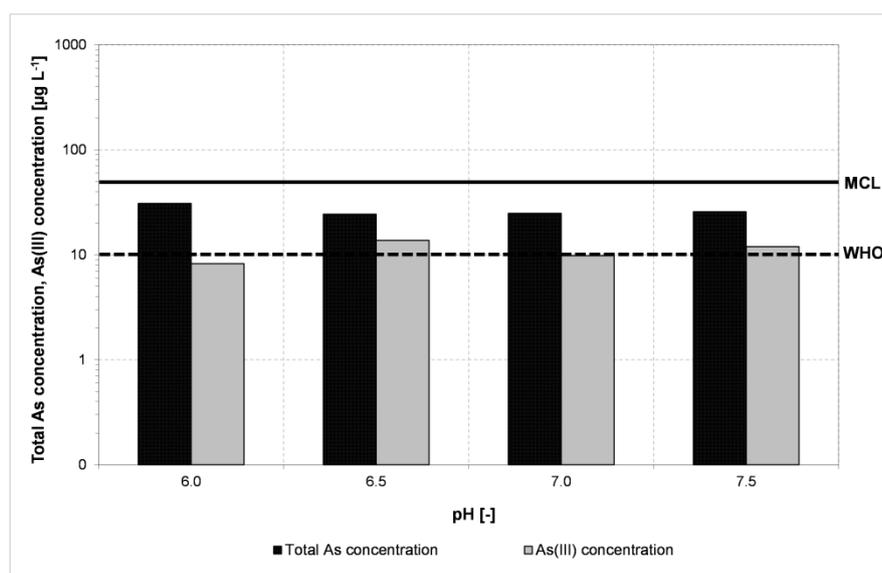
Figure 6. Effect of pH on oxidation and removal of As(III) in filtered samples (0.45 μm) at SR=1 using KMnO$_4$+Al$_2$(SO$_4$)$_3$ solution.

4. CONCLUSIONS

This work shows that oxidation of As(III) can effectively be obtained by adding $KMnO_4$, until a pale pink color occurs, immediately after collecting the groundwater in order to improve the passive sedimentation with initial Fe^{2+} precipitating as $Fe(OH)_3$ flocs after oxidation. Moreover, the results show that presence of Fe^{2+} has a positive effect of As(III) oxidation with $KMnO_4$.

The practical effect of using $KMnO_4$ can be greatly improved if a strongly basic solution of MnO_4^- and AlO_2^- is added. The advantages of using this solution are easy oxidation and floc formation, and it can be applied to waters in the pH range of 6.0-7.5. To achieve sufficient As removals, treated water filtering is necessary.

The treatment of Fe^{2+} and As(III) laden groundwater can easily be achieved by the addition of a basic solution of $KMnO_4$ and AlO_2 to aid the oxidation and floc and total As concentrations below 50 µg L^{-1} can be achieved at Fe/As ratios of 13. At Fe/As ratios above 13, the total As concentrations can be even below the newest WHO recommendation of 10 µg L^{-1}. This is an appropriate solution that can be applied in rural areas with decentralized water supply and high Fe and As concentrations in water due to the simple operation (coagulant and oxidant agents could be added together and the color change could give a good indication while adding the solution). This solution is highly reliable in operation, uses minimum energy and requires low levels of investment in the plant. The reagents are easily available in developing countries and they are well known by villagers. The addition of Al could improve the filterability due to the formation of bigger particles. There is no evidence that potassium levels in municipally treated drinking water, even water treated with potassium permanganate, are likely to pose any risk to the health of consumers. The daily generation of As contaminated sludge is very low; however, care should be taken in disposal of the sludge and it should not be disposed near children's playing areas or near edible crops. A suitable way of disposal would be to bury the sludge, dispose of it with other solid wastes, solidify it in concrete or discharge it in sanitary latrines. This solution may be applied also in industrialized countries because it does not involve expensive upgrading in small- to medium-sized water treatment plants that already have either a coagulation or filtration unit.

5. ACKNOWLEDGMENT

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