

## Article

# H<sub>2</sub>O<sub>2</sub>-Enhanced As(III) Removal from Natural Waters by Fe(III) Coagulation at Neutral pH Values and Comparison with the Conventional Fe(II)-H<sub>2</sub>O<sub>2</sub> Fenton Process

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**Abstract:** Arsenic is a naturally occurring contaminant in waters, which is toxic and adversely affects human health. Therefore, treatment of water for arsenic removal is very important production of safe drinking water. Coagulation using Fe(III) salts is the most frequently applied technology for arsenic removal, but is efficient mostly for As(V) removal. As(III) removal usually requires the application of a pre-oxidation step, which is mainly conducted by chemical or biological means. In this study, we show that Fe(III) coagulation in the presence of H<sub>2</sub>O<sub>2</sub> can be a very efficient treatment process for As(III) removal, which has been never been shown before in the literature. The results showed that addition of 8.7–43.7 mM hydrogen peroxide to Fe(III) coagulation process was able to increase the effectiveness of As(III) removal in synthetic groundwater by 15–20% providing residual concentrations well below the regulatory limit of 10 µg/L from initial As(III) concentrations of 100 µg/L, at pH 7. The enhanced coagulation process was affected by the solution pH. The removal efficiency substantially declined at alkaline pH values (pH > 8). Addition of EDTA in the absence of H<sub>2</sub>O<sub>2</sub> had a strong inhibiting effect where the As(III) removal was almost zero when 88.38 µM EDTA were used. Radical quenching experiments with 50, 100 and 200 mM DMSO, methanol and 2-propanol in the H<sub>2</sub>O<sub>2</sub>-coagulation process had a slightly adverse effect on the removal efficiency. This is considered as indicative of an adsorption/oxidation of As(III) process onto or very near the surface of iron oxide particles, formed by the hydrolysis of Ferric iron ions. In practice, the results suggest that addition of H<sub>2</sub>O<sub>2</sub> increases the As(III) removal efficiency for Fe(III) coagulation systems. This is an important finding because the pre-oxidation step can be omitted with the addition of H<sub>2</sub>O<sub>2</sub> while treating water contaminated with As(III).

**Keywords:** arsenic; hydrogen peroxide; coagulation; ferric iron; radical scavengers

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## 1. Introduction

Arsenic contamination of ground waters used for drinking purposes is a problem of global concern. Reports are referring to different parts of the world such as Bangladesh [1], India [2], United States [3] and Greece [4]. Arsenic levels in these areas are much higher than the World Health Organization recommended standard of arsenic in drinking water of 10 µg/L. Typically, natural ground water contains higher concentrations of As than surface waters because of stronger water-rock interactions and favorable conditions induce arsenic release in the water [5]. Also, anthropogenic activities which include mining activities, combustion of fuels and the use of pesticides and crop desiccants that contain arsenic result in contamination of valuable water sources such as lakes and rivers [6].

Arsenic is present in groundwater mostly with its inorganic forms. Specifically, the dominant forms of arsenic found in groundwater at neutral pH values are arsenite As(III) as H<sub>3</sub>AsO<sub>3</sub> and arsenate As(V), as H<sub>2</sub>AsO<sub>4</sub><sup>−</sup> and HAsO<sub>4</sub><sup>2−</sup> [7]. Arsenic is a very toxic element. It is reported to cause health problems to humans such as cardiovascular problems and various forms of cancer [5]. As(III) is found to be more toxic than As(V). Also As(III) is

more mobile than As(V), which is mostly attributed to its presence in ground waters with its uncharged species of arsenious acid at circumneutral pH values. It is for this reason, that it is more difficult to adsorb on most relevant solid surfaces.

According to Hering et al., 2017 [6], the most commonly applied treatment technology for the removal of arsenic from groundwaters is coagulation using iron or aluminum salts [8–10]. Arsenic is removed by co-precipitating with the coagulants and/or adsorption on the surface of formed flocs [8–12]. As(V) removal is more efficient than As(III) removal because of the uncharged nature of  $\text{H}_3\text{AsO}_3$  and thus, it has lower affinity for the positively charged iron at neutral pH. For this reason, in full scale treatment plants pre-oxidation of arsenic before adding the coagulant salt is a widely used step [4].

Oxidants that are mostly used are ozone ( $\text{O}_3$ ), chlorine, [13] sodium permanganate ( $\text{NaMnO}_4$ ) [14], persulfate (PS), peroxymonosulfate [15], calcium peroxide (CP), sodium percarbonate (SPC) [16] and  $\text{H}_2\text{O}_2$  [17]. As(III) removal by biological oxidation and adsorption has also been studied and is a widely applied technology worldwide [6,18]. Fenton process is also able to oxidize As(III) to As(V) because of formation of hydroxyl radicals, and then the produced As(V) can be removed by adsorption of the formed iron oxides [19]. In a similar manner, use of ZVI (Zerovalent Iron) can also oxidize As(III) and cause the removal of As(V) [20]. The use of hydrogen peroxide simultaneously with Fe(III) has not been extensively investigated up to now [17,21].

The objective of the present work was to investigate the performance of Fe(III) coagulation towards As(III) removal in the presence or absence of  $\text{H}_2\text{O}_2$  and to compare the results with the traditional Fenton process for As(III) removal. The aim was to examine if by this way, it would be possible to avoid the use of an oxidation step, prior to the most commonly used technology, which is the Fe(III) coagulation. We examined the effect of initial concentration of the coagulant and the effect of pH in all the processes. The effect of EDTA (Ethylenediaminetetraacetic acid) on coagulation was also investigated in all processes. In order to study the mechanism of Fe(III)- $\text{H}_2\text{O}_2$  process for As(III) removal we performed quenching experiments with scavengers Dimethyl sulfoxide (DMSO), methanol and 2-propanol) testing for potential oxidants that can cause the oxidation of As(III) to As(V). The use of these scavengers is important to identify whether the oxidation of As(III) follows the adsorption/surface oxidation mechanism or the bulk oxidation/adsorption mechanism. Finally, the performance of the Fe(III)/ $\text{H}_2\text{O}_2$  system in treating an As(III) contaminated synthetic water was evaluated. In this paper, we show that addition of  $\text{H}_2\text{O}_2$  in the water prior to coagulation with Fe(III) increases the efficiency of As(III) removal and eliminates the need for an oxidation step. In practice, the Fe(III)- $\text{H}_2\text{O}_2$  system can be used as efficiently as the Fenton system and is a viable alternative to the Fenton process. We believe that the proposed double mechanism (adsorption/oxidation, oxidation/adsorption) of As(III) sequestration in the Fe(III) coagulation system is a very interesting approach. This is a highly innovative approach, since until to date, and to the best of our knowledge, no treatment plant in the world applies this strategy, i.e., use of Fe(III) coagulation with hydrogen peroxide. Turning running systems into such a treatment way is very simple for plants already applying coagulation, because the hydrogen peroxide can be added in the water to be treated in advance of the coagulation system. The only limitation that this technology shows is the possible effect of pH, with values outside of the range 6.5 to 8.

## 2. Materials and Methods

### 2.1. Materials

All chemicals were reagent grade and used as received. Ferric nitrate nonahydrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Ferrous sulfate heptahydrate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Calcium nitrate tetrahydrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , sodium bicarbonate  $\text{NaHCO}_3$  and DMSO were purchased from Merck. EDTA was purchased from Chem-Lab NV.  $\text{H}_2\text{O}_2$  (30% v/v) was from PanReac AppliChem. As(III) stock solution (1000 mg/L) was prepared by dissolving appropriate aliquots of  $\text{NaAsO}_2$  (VWR Chemicals). Fe(II) and Fe(III) stock solutions (1000 mg/L) were prepared by dissolution of appropriate aliquots of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  respectively.

Fe(II) stock solution was acidified to pH 2 using a stock solution of HCl (2N) to slow down Fe(II) oxidation, because the oxidation of ferrous iron by dissolved oxygen is much slower at acidic pH values [22].

## 2.2. Coagulation Experiments

All coagulation tests were performed using a flocculation jar tester (Velp Scientifica, Usmate Velate, Italy). Synthetic water used for the experiments was de-ionized spiked with 2 mM NaHCO<sub>3</sub> and 1 mM Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. Additional coagulation experiments were conducted in tap water to test if the method can remove efficiently arsenic from drinking water. In brief the procedure was as follows: 500 mL of water containing 100 µg/L As(III) were used in each of the 4 jars. Subsequently, the salts were added in such a dose to achieve the desirable salt concentrations in solution. The solution pH was adjusted before and after the addition of salts to achieve the initial pH value of 7 with stock solutions of HCl and NaOH (2, 1, 0.1 N) from concentrated 37% HCl solution and 50% NaOH solution (Merck, Taufkirchen, Germany). The pH values were measured again after the completion of the experiments and negligible pH changes were observed at the end of the experiment. After the addition of the Fe(II) and Fe(III) doses rapid mixing took place for 2 min followed by slow mixing at 40 rpm for 10 min and a settling period of 45 min followed to allow the flocs to precipitate. Afterwards, samples were filtered through a syringe filter with 0.45 µm PTFE (Polytetrafluoroethylene) membrane. Samples containing Fe(II) were acidified with 2N HCl. Speciation of arsenic was performed afterwards. Speciation of arsenic was performed by passing the sample through a disposable cartridge packed with 2.5 g of a selective aluminosilicate adsorbent that retains only As(V). Thus, the treated sample contains only As(III) which is measured by Atomic Absorption Graphite Furnace spectroscopy. Experiments with H<sub>2</sub>O<sub>2</sub> followed the same procedure as the experiments with a small difference. H<sub>2</sub>O<sub>2</sub> was added from the H<sub>2</sub>O<sub>2</sub> solution (30% v/v) just before the addition of the coagulants. Quenching experiments were performed with addition of the appropriate amounts of scavengers after the addition of arsenic and before the addition of coagulants and H<sub>2</sub>O<sub>2</sub>.

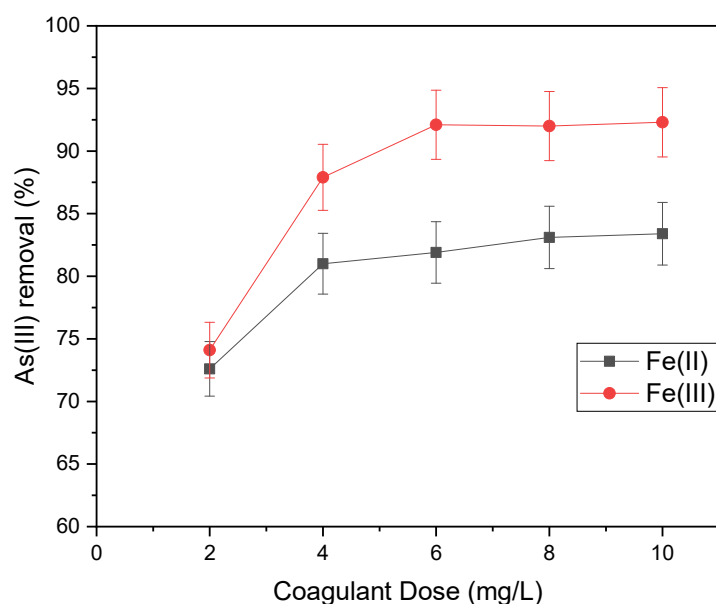
## 2.3. Analytical Determinations

The determination of ferrous and ferric iron was performed by 1,10-phenanthroline method. After filtration 5 mL of a sample were added in a falcon tube in both cases. For the determination of ferrous iron, the process is the following: 0.1 mL of 32% HCl solution, 1 mL of buffer solution (acetic acid-acetic ammonium) 0.5 mL of 1,10 phenanthroline and 3.4 mL of distilled water were added. After 10 min the iron absorption was measured using an UV-Vis spectrophotometer (model U-2000, Hitachi, Tokyo, Japan) at 510 nm. For the determination of total iron, the process is similar, but involves the addition of hydroxylamine, which reduces Fe(III) to Fe(II). The concentration of ferric iron is the difference between the concentrations of total and ferrous iron. Total arsenic was measured by Atomic Absorption Graphite Furnace spectroscopy (AAS-GF) (Varian Zeeman AA240Z with GTA 120, Mulgrave, VIC, Australia).

## 3. Results and Discussion

### 3.1. As(III) Removal by Fe(III) or Fe(II) Coagulation without the Use of H<sub>2</sub>O<sub>2</sub>

The first part of the experiments aimed at comparing the removal of As(III) by Fe(II) and Fe(III) in synthetic ground water. In the part, experiments were performed at pH 7, which remained almost constant during the experiments. Results from experiments with ferric nitrate, Fe(III), and ferrous sulfate, Fe(II), as coagulants in synthetic ground water are shown in Figure 1.



**Figure 1.** As(III) removal by ferrous and ferric coagulants in synthetic water. Initial concentration of As(III) was 100 µg/L, pH = 7.

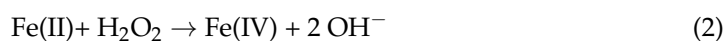
Figure 1 shows that under the applied experimental conditions and without the use of  $H_2O_2$ , Fe(III) coagulant removes more efficiently As(III) than Fe(II), with higher removal of arsenite across all the doses used. This is expected because ferrous iron is more soluble even at neutral pH than Fe(III) and does not create so efficiently the amorphous  $Fe(OH)_3$  flocs that are created from hydrolysis of ferric iron and are essential for As(III) removal by adsorption on the surface of the flocs. For the case of Fe(II) addition, As(III) removal takes place via Fe(II) oxidation by oxygen, which produces Fe(III) hydroxides, able to remove As(III). Final pH values in the two systems were almost unchanged. In particular, in the Fe(III) system when 2 mg/L was used the final pH was 7.1. Increase of the coagulant dose decreased the final pH. The final pH values were 7.05, 6.9, 6.85 and 6.8 for 4, 6, 8 and 10 mg/L respectively. Secondly, in the Fe(II) system the pH values were slightly higher for all coagulant doses used. The final pH values were 7.25, 7.2, 7.1, 7.05, 7.03 for 2, 4, 6, 8 and 10 mg/L Fe(II) respectively. Finally, increase in coagulant dose increased the sequestration, however up to a certain dose. For example, increasing the dose of ferric iron beyond 6 mg/L, had almost no effect. The same observation was made when ferrous iron was used. Therefore, it can be concluded that the optimal dose was 6 mg/L. This effect did not take place when solutions contained tap water and increase of removal was observed until the dose was 15 mg/L for both Fe(II) and Fe(III) (results not shown). Application of 20 mg/L slightly reduced the removal of As(III) in all conditions. It is reported that after the critical coagulation concentration, increase of the coagulant concentration has a negative effect on the coagulation process and lead to redissolution of amorphous  $Fe(OH)_3$  flocs [23]. A possible redissolution of the amorphous flocs could explain the drop of the As removal at 20 mg/L in experiments carried out in drinking water spiked with arsenic(III). It is also found in literature that in lower As(V) concentrations higher coagulant dose is required than in higher As(V) concentration to achieve the optimum coagulant dose [24]. This takes place when the arsenic concentration is so low (i.e., 100 µg/L) that the collisions between the molecules of the coagulant and the arsenic take place more than at higher As(III) concentrations [24].

### 3.2. Enhanced Coagulation with $H_2O_2$ as Oxidant

#### 3.2.1. Fe(III) Coagulation

In the present section, we investigated the effect of  $H_2O_2$  addition on As(III) removal in Fe(III) coagulation systems. In general, in most arsenic removal plants, when Fe(III)

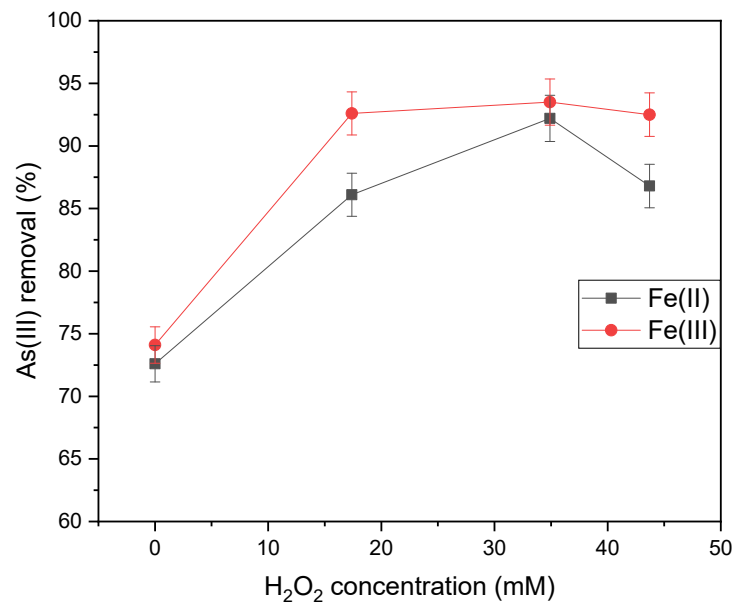
coagulation is applied and the water contains large amounts of As(III), an oxidation step is applied in order to oxidize arsenic(III) to As(V) and achieve efficient overall arsenic removal. The incorporation in the treatment train of an oxidation step prior to coagulation increases the operational costs and the complexity of the process. Therefore, it is of utmost importance to enable arsenic removal by Fe(III) coagulation, without the application of an oxidation step. The selected oxidant is H<sub>2</sub>O<sub>2</sub> which is proven to enhance the As removal in Fe(II) treatment systems [17,25,26]. It is reported in the literature, Fe(III) can react with H<sub>2</sub>O<sub>2</sub> to form superoxide radicals (O<sub>2</sub><sup>•-</sup>) and Fe(II) [27], which reacts rapidly with a molecule of hydrogen peroxide to create the aforementioned oxidants which oxidize As(III) to As(IV) [19,27]. As(IV) can react instantly with oxygen to form As(V) and As(V) can be subsequently removed by the iron oxides formed from Ferric hydrolysis (Equations (1)–(4)) [19,27]. These reactions can take place either on the surface of ferric iron or on the bulk solution assuming enough Fe is dissolved.



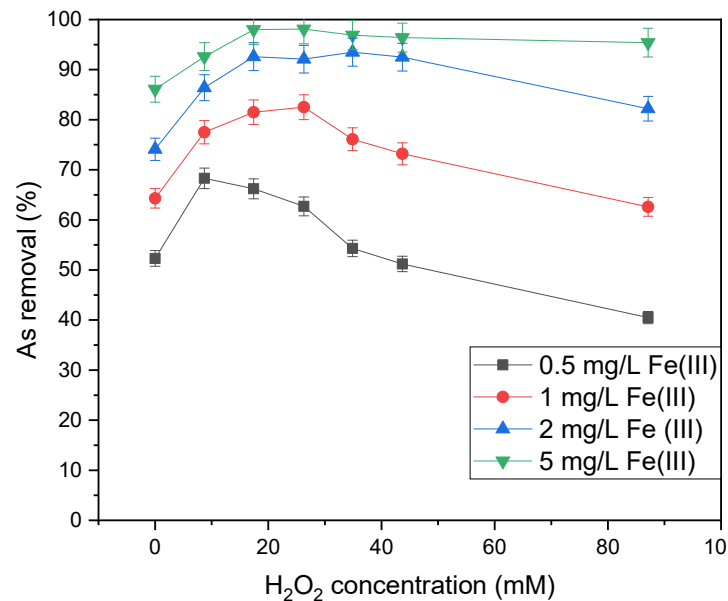
Therefore, the idea of this paper was to investigate in coagulation experiments the dominance of aforementioned reactions in Fe(III) coagulation for As(III) removal. Initially Ferric iron coagulation was tested with constant dose of 2 mg/L and variable concentrations of H<sub>2</sub>O<sub>2</sub>. The results showed a significant increase of As(III) when H<sub>2</sub>O<sub>2</sub> was used (Figure 2). As(III) removal by 2 mg/L of Fe(III) was about 75% and increased to about 90% in the presence of only 10 mM H<sub>2</sub>O<sub>2</sub>. While 75% removal is not sufficient enough to reduce 100 µg/L As(III) to below the limit of 10 µg/L, the Fe(III)-H<sub>2</sub>O<sub>2</sub> system could achieve this target, with a dose of only 2 mg/L of Fe(III). Compared with experiments done with Fe(III) alone, a dose of 6 mg/L or more is needed to reduce the concentration of As(III) by 90% (Figure 1). For comparison reasons, Fe(II) with H<sub>2</sub>O<sub>2</sub> was examined and the results are displayed in the same figure. Fe(II) with H<sub>2</sub>O<sub>2</sub> is the well-known Fenton process, which is known to generate oxidants, OH radicals and/or Ferryl species, which are able to oxidize As(III). Interestingly, the use of Fe(III) with H<sub>2</sub>O<sub>2</sub> gave better results than the use of Fe(II)-H<sub>2</sub>O<sub>2</sub>, which most likely means that the oxidation of As(III) is more efficient in this case. Indeed, the presence of solid surfaces, which are provided immediately after the addition of Fe(III) in water at neutral pH values, might act as catalyst for the faster oxidation of As(III) and thus more efficient removal of total arsenic is obtained. Further increase H<sub>2</sub>O<sub>2</sub> of concentration had a negligible effect or resulted in small decline of As(III) removal efficiency at 43.7 mM H<sub>2</sub>O<sub>2</sub>. Variation of H<sub>2</sub>O<sub>2</sub> concentration had the same effect in experiments with tap water (Figure 2).

Afterwards, the effect of initial dose of coagulant was examined. Doses of 0.5, 1 and 2 mg/L are evaluated. The effect of initial Fe(III) dose is shown in Figure 3. Increase of initial dose increases the removal efficiency of As(III). When the dose increased from 0.5 to 1 mg/L we observed a positive effect and better removal percentages. The increase fluctuated from 9 to 22% depending on H<sub>2</sub>O<sub>2</sub> concentration. Further increase to 2 mg/L greatly improved the As(III) removal where removal over 90 percent was achieved at 17.4–43.7 mM H<sub>2</sub>O<sub>2</sub>. Use of 5 mg/L Fe(III) showed excellent results in removing As(III) at all H<sub>2</sub>O<sub>2</sub> dose used. The optimum H<sub>2</sub>O<sub>2</sub> concentration for the removal of arsenic was approximately 10 mM which is enough to achieve removal around 90–95% as shown in Figure 3. However, the increase of coagulant dose from 2 to 5 mg/L has small effect on the As(III) at 10 mM H<sub>2</sub>O<sub>2</sub>. The increase from 90% when 2 mg/L were used to around 95% with coagulant dose of 5 mg/L does not justify the use of more than double coagulant dose. An advantage of using lesser coagulant doses is the formation of smaller solid by-product which is created by precipitation of ferric iron. This is practically useful in full-scale water

treatment plants because formation of the solid precipitates in smaller quantities leads to less operating problems and less cost of removing it from filters.



**Figure 2.** Enhanced As(III) removal with H<sub>2</sub>O<sub>2</sub> in synthetic water. Initial As(III) concentration was 100 µg/L, [Fe(II)] = [Fe(III)] = 2 mg/L, pH = 7.



**Figure 3.** Effect of initial Fe(III) dose in enhanced coagulation process. Initial As(III) concentration was 100 µg/L, pH = 7.

A point of maximum removal efficiency was observed at all doses used. This point occurred at different H<sub>2</sub>O<sub>2</sub> concentrations. With 0.5 mg/L the highest removal efficiency was observed at 8.7 mM H<sub>2</sub>O<sub>2</sub>. When the dose was doubled maximum removal was observed at 26.3 mM H<sub>2</sub>O<sub>2</sub>. Further increase to 2 mg/L resulted in better removal at 43.7 mM H<sub>2</sub>O<sub>2</sub>. However, with applied dose of 5 mg/L maximum removal was achieved at 17.4 mM. Further increase of the H<sub>2</sub>O<sub>2</sub> concentration declined the As(III) removal. Decline of the effectiveness of the method was observed at all initial doses at high H<sub>2</sub>O<sub>2</sub> concentrations. Reduction of the removal effectiveness was significant especially at 87.1 mM where As(III) sequestration was lowered by 3–30% comparing the removal at 87.1 mM

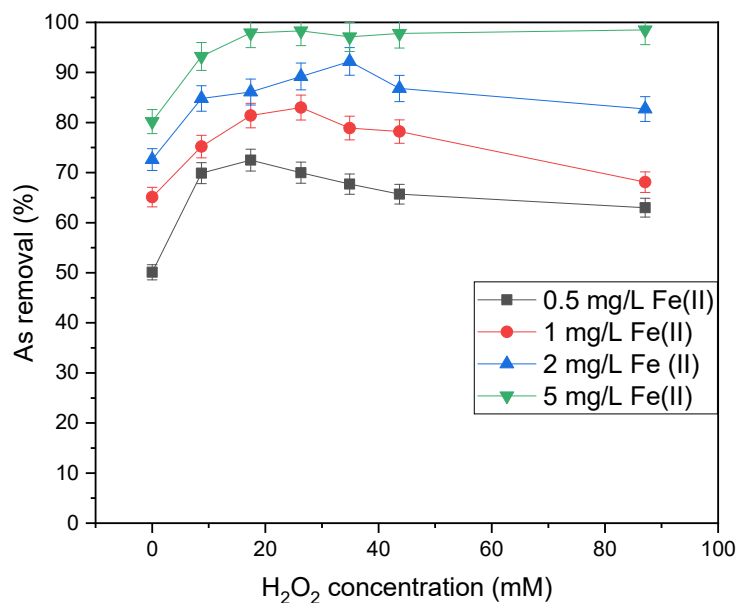
and at the points with maximum removal efficiency. Moreover, increase of initial dose seems to mitigate this effect. Smaller decline was observed when 2 mg/L were used. The positive effect of increased coagulant dose was confirmed by increasing the coagulant dose to 5 mg/L. This increase led to insignificant decline at high H<sub>2</sub>O<sub>2</sub> concentrations beyond the point of maximum removal efficiency (Figure 1).

Decline in removal effectiveness at bigger concentrations of H<sub>2</sub>O<sub>2</sub> can be attributed to the autooxidation of H<sub>2</sub>O<sub>2</sub>. At high H<sub>2</sub>O<sub>2</sub> concentration the quantity of OH• radicals are enough to react with H<sub>2</sub>O<sub>2</sub> to decompose H<sub>2</sub>O<sub>2</sub>. Therefore, the effective concentration of H<sub>2</sub>O<sub>2</sub> becomes smaller than expected. Moreover, it is reported that H<sub>2</sub>O<sub>2</sub> competes with the As(III) for the surface bound OH• radicals which is important if the oxidation of As(III) occurs in the surface of ferric iron [27]. This can explain the smaller decline of As(III) at higher concentration of H<sub>2</sub>O<sub>2</sub>. Since, increase of iron leads to more available surface sites for both H<sub>2</sub>O<sub>2</sub> and As(III) to react with surface-bound OH• radicals or/and potentially Fe(IV), competition between H<sub>2</sub>O<sub>2</sub> and As(III) is diminished significantly. Additionally, H<sub>2</sub>O<sub>2</sub> reacts with the As(IV) intermediate resulting in reducing its effective concentration therefore, less hydroxyl radicals are formed from the reaction with iron [27]. These H<sub>2</sub>O<sub>2</sub> consuming reactions along with autooxidation and auto-decomposition of H<sub>2</sub>O<sub>2</sub> at high concentration could explain the decline in As(III) removal efficiency.

### 3.2.2. Fe(II) Coagulation

The conventional Fenton process is a widely used method for removing arsenic from water [28,29]. Therefore it was important to compare the Fe(III)/H<sub>2</sub>O<sub>2</sub> coagulation process with the Fenton process to check if it is a viable alternative for As removal. The effect of initial Fe(II) dose is shown in Figure 4. As expected, the initial dose is very important, and its increase improves linearly arsenic removal. Increase of coagulant dose from 0.5 mg/L to 1 mg/L had a positive effect with rise in As(III) sequestration. Further increase of the coagulant dose from 1 to 2 mg/L had similar effect and the removal effectiveness rose by 4.5 to 14.6%. The effect of H<sub>2</sub>O<sub>2</sub> is clear and the As(III) sequestration was enhanced significantly by 18–22% depending on the concentration used. We also observed that maximum removal efficiency occurred at different H<sub>2</sub>O<sub>2</sub> concentrations. Moreover, as the coagulant dose increases the necessary H<sub>2</sub>O<sub>2</sub> concentration to achieve the maximum As(III) sequestration. When 2 mg/L were used, 34.9 mM of H<sub>2</sub>O<sub>2</sub> were added to maximize the efficiency. As the initial dose decreased to 1 mg/L the most efficient removal was observed at 26.3 mM H<sub>2</sub>O<sub>2</sub>. Further decrease of initial dose to 0.5 mg/L decrease the required H<sub>2</sub>O<sub>2</sub> concentration to achieve better As(III) removal to 17.4 mM. This did not apply in the experiments with coagulant dose of 5 mg/L, where the use of 26.3 mM achieved the best result. However, in further experiments the coagulant dose of 5 mg/L was not used despite achieving the best result. This was chosen because in the Fe(III) coagulation, it was stated that the difference in the As removal between 2 and 5 mg/L did not justify the use of more than double the coagulant dose. Since we use 2 mg/L in the Fe(III) coagulation system it was decided that for comparison reasons, the Fe(II) dose would be also 2 mg/L. Decline of As(III) removal is much smaller when Fe(II) was used. The reduction of removal effectiveness was similar for Fe(II) doses of 0.5–2 mg/L around 10–15% which was smaller than the decline observed in the Fe(III)/H<sub>2</sub>O<sub>2</sub> coagulation system. The mitigation of the decline by increased dose was apparent when 5 mg/L of Fe(II) were applied in the system where no decline was observed. The smaller decline at 0.5–2 mg/L takes place because hydrogen peroxide reacts with Fe(II) and decomposes rapidly. Theoretically, 1 mol of Fe(II) can catalyze the decomposition of up to 50 mol of hydrogen peroxide [30]. It was suggested that Fe(II) ions are involved in a cyclic process, perhaps oscillating between the Fe(II), Fe(IV), and Fe(III) oxidation states a number of cycles before final oxidation and precipitation of Fe(III) occurs. Additionally, 2 mol of hydrogen peroxide are destroyed in one cycle of oxidation of Fe(II) to Fe(III) [30]. Therefore, most of H<sub>2</sub>O<sub>2</sub> has reacted with Fe(II) to oxidize it and less H<sub>2</sub>O<sub>2</sub> is capable to compete with As(III) for the surface-bound

$\text{OH}^\bullet$  radicals on the surface of created Fe(III) assuming a part of the reaction takes place in the Fe(III) surface and/or Fe(IV) and with dissolved oxygen for the intermediate As(IV).



**Figure 4.** Effect of initial Fe(II) dose during coagulation treatment with  $\text{H}_2\text{O}_2$ . Initial As(III) concentration was  $100 \mu\text{g/L}$ ,  $\text{pH} = 7$ .

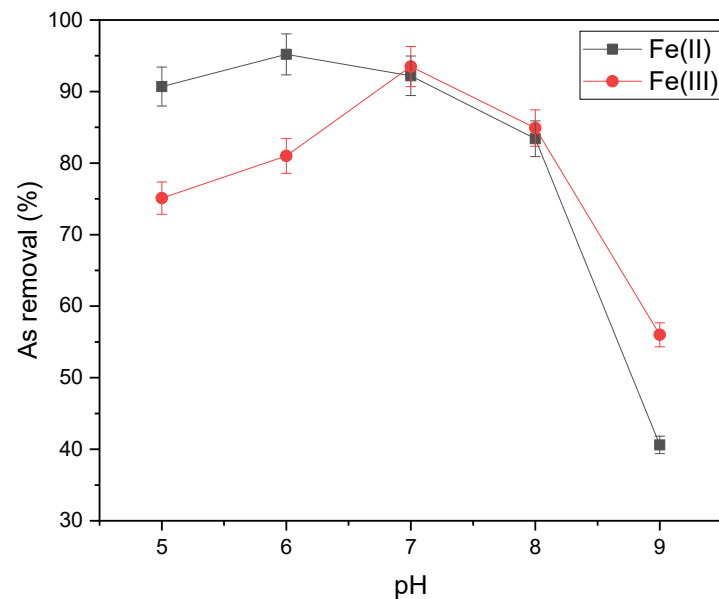
### 3.3. Effect of pH

After examining the effect of initial dose of iron and its implications in correlation with the concentration of hydrogen peroxide it is of critical importance to investigate the effect of pH on the As(III) removal. Typical pH values encountered in ground waters are in the range of 6–8 [31]. We decided to examine the effect of pH in a slightly bigger range of 5–9 to test if the method is capable of removing As(III) efficiently in a broader range of pH. We examined the effect of pH for both Fe(II) and Fe(III) treatment systems. The experiments were performed with the same initial concentration of As(III) at  $100 \mu\text{g/L}$  as all the previous experiments. From previous results, treatment of water with 2 mg/L and 43.7 mM  $\text{H}_2\text{O}_2$  gave the best results for the Fe(II) process and these conditions were chosen to perform the experiments examining the effect of pH. The results shown in Figure 5 indicated an excellent As(III) removal with Fe(II) application for pH values between 5–7. Under these conditions As(III) removal of above 90 percent was obtained, and the treated water had arsenic residual concentration below the regulation limit of  $10 \mu\text{g/L}$ . Increasing the pH to values above 8, we observed a great decline in the As(III) sequestration. At pH 9 only 40% of As(III) was removed in the Fe(II) system. The same effect was observed when Fe(III) was the coagulant with slightly more efficient removal especially at pH 9. This can be attributed to the fact that the solid iron surfaces that are formed have a negative overall surface charge at high pH values with the form of  $\text{FeOH}_4^-$  [21,32]. Its negative charge repulses the formed As(V) ( $\text{HAsO}_4^{2-}$ ), therefore, the adsorption of As(V) onto surface of ferric iron is diminished and as a result the removal of arsenic is also significantly lowered.

Hydrogen peroxide is known to be less stable at alkaline pH which results in auto decomposition and release of hydroperoxide ion ( $\text{HO}_2^-$ ) which is a powerful oxidant [33]. In fact, hydrogen peroxide was reported to have reacted with Orange G at pH 10.4 while at pH 6.0 no reaction was observed [33]. Better performance of the Fe(II)/ $\text{H}_2\text{O}_2$  system at pH 5.0 can be attributed to faster kinetics of  $\text{H}_2\text{O}_2$  decomposition by Fe(II) than Fe(III). Slightly better kinetics of the reaction of Fe(III) with  $\text{H}_2\text{O}_2$  at neutral pH explain the more similar removal effectiveness between ferrous and ferric iron when  $\text{H}_2\text{O}_2$  was utilized [30]. It is of great significance that this method can achieve higher As(III) removal compared to the



conventional coagulation, which As(III) removal around 60–75% for Fe(III) coagulation at neutral pH [8,21,34].



**Figure 5.** Effect of pH in enhanced coagulation process. Initial As(III) concentration was 100 µg/L [Fe(II)] = [Fe(III)] = 2 mg/L [H<sub>2</sub>O<sub>2</sub>] = 43.7 mM.

### 3.4. Effect of EDTA

After performing experiments testing the effect of pH, we investigated the effect of EDTA addition. EDTA is a very well-known organic ligand which is capable to form metal complexes and keep them in solution. As known, Fe(III) is insoluble at neutral pH and precipitates in the form of hydroxides. However, in the presence of EDTA, Fe(III) will form complexes, which will remain in solution and therefore, will prevent arsenic removal, because of less solid surfaces for adsorption. The EDTA test however, is conducted in order to see if As(III) is oxidized in the absence of solid surfaces by the presence of Fe(III) and H<sub>2</sub>O<sub>2</sub>. In the conventional treatment process, i.e., without H<sub>2</sub>O<sub>2</sub> addition, arsenic is adsorbed on the surface of Fe(III) hydroxides and is removed by precipitation of these hydroxides. However, the complexation of EDTA with ferric iron creates a stable complex which is soluble in water due to the strong complexation ability of EDTA with Fe(III) [30,35]. Therefore, the precipitation process does not take place and the removal of As declines greatly. This reasoning agrees with our results. In the Fe(III) process, the EDTA reduced the As(III) removal drastically. When water contained 44.19 µM EDTA the As(III) removal dropped to 28.5%. Increase of EDTA to 88.38 µM inhibited the removal almost completely. These EDTA concentration values were chosen in such a way that EDTA could be slightly above the stoichiometric concentration of the Fe(III)-EDTA complexes. It is known that 1 mol of Fe(III) reacts with 3 moles of EDTA. We decided that experiments would be conducted with a mol analogy of Fe(III)/EDTA 1:5 and 1:10. In the first case EDTA concentration is slightly above the stoichiometric concentration and in the second case it is in bigger excess. For the first set of experiments the appropriate concentration of EDTA was calculated to be 44.19 µM and for the second it was 88.38 µM. The results clearly show that EDTA has a negative effect on As(III) removal. This is attributed as aforementioned to the complexation of EDTA with ferrous and ferric iron and the excellent solubility of the complex and proves the importance of the solid surfaces on As(III) removal. Comparing these results with the Fe(II)-EDTA system we observed that the addition of 0.5 mg/L Fe(II) in water containing EDTA decreased the As(III) removal in a smaller degree for both EDTA concentrations used, from 50.1% to 44.9 when the concentration of EDTA in water was 44.19 µM and to 4.5% when EDTA concentration was doubled to 88.38 µM.

Residual As speciation results show that increase of initial EDTA concentration increases the oxidation of residual As(III) in absence of H<sub>2</sub>O<sub>2</sub> in the Fe(III) system. Comparing the Fe(III) system with initial concentration of EDTA at 44.19 μM and without EDTA we observed an increase in As(III) oxidation by around 35% with EDTA addition. Further increase of EDTA concentration at 88.38 μM increased the As(III) oxidation even further by 10% more. Moreover, decomposition of Fe(III)-EDTA by molecular oxygen could explain the fact that we observed oxidation of As(III) even when Fe(III) was used without hydrogen peroxide. EDTA in iron systems, can be decomposed. This takes place because the EDTA complexes react slowly with the molecular oxygen according to the literature. From this reaction H<sub>2</sub>O<sub>2</sub> is formed. Then, H<sub>2</sub>O<sub>2</sub> catalytically reacts with the Fe(III)-EDTA complex. As a result, hydroxyl radicals are created which promote the decomposition of EDTA. In the enhanced coagulation process the added H<sub>2</sub>O<sub>2</sub> is in excess compared to the EDTA and the creation of the hydroxyl radicals is very fast. The radicals formed afterwards react with the Fe(III)-EDTA complex resulting in breaking the complex and in decomposing EDTA.

In the Fe(III)-EDTA decomposition OH• radicals are released which can react with As(III) to form As(IV), which subsequently reacts with dissolved oxygen to form As(V). Decomposition of EDTA results in releasing iron in solution. Therefore a small part of Fe(III) was released which also explains the reason for observing oxidation and removal of As(III) in the Fe(III)/EDTA system in absence of hydrogen peroxide. When Fe(II) was added we observed a decrease of As(III) removal in contrast with the Fe(III) process with 44.19 μM EDTA. The decline in oxidating capability of the system was 30%. While, at 88.38 μM EDTA As existed as the trivalent form at 71% in the Fe(II) system. This takes place because of the consumption of OH• radicals created during the reaction of Fe(II)-EDTA with dissolved oxygen by the EDTA decomposition and the oxidation of Fe(II) to Fe(III) therefore, less OH• radicals and less Fe(II) are available to promote As(III) oxidation compared with the process of Fe(II) coagulation without EDTA.

Enhancement of the coagulation process with hydrogen peroxide increased the As(III) sequestration in EDTA containing water as shown in Figure 6. However, the EDTA still had an inhibiting effect, which increased when the EDTA concentration was doubled. This is expected for two reasons. Firstly, EDTA is known to be oxidized by oxygen and to have affinity for OH• radicals [36]. Secondly, the kinetics of hydrogen peroxide decomposition by chelated Fe(II) and Fe(III) with EDTA are 3 orders of magnitude greater than non-chelated Fe(II) at pH 7 which creates reactive oxygen species and mostly OH• radicals for which EDTA has great affinity [30]. Also, Fe(II)-EDTA reacts with molecular oxygen and in the process of oxidation to Fe(III)-EDTA it creates H<sub>2</sub>O<sub>2</sub> [37,38] which we believe it can induce decomposition of EDTA and oxidation of As(III) by OH• radicals. Therefore, reactive oxygen species are formed which react with EDTA and decompose it. This means that the iron is released and then can precipitate and subsequently remove arsenite. The release of OH• radicals during EDTA decomposition by dissolved oxygen can explain the fact that a small part of As(III) can be oxidized even when H<sub>2</sub>O<sub>2</sub> was not used (Figure 7).

### 3.5. Effect of Radical Scavengers on As(III) Removal

Three radical scavengers were applied to identify the reactive oxygen species which promote the As(III) oxidation and subsequently the removal of arsenic as As(V) during the enhanced coagulation process. As radical scavengers, 2-propanol, methanol and DMSO were applied. 2-propanol is capable to scavenge OH• radicals while DMSO and methanol are able to scavenge both OH• radicals and Fe(IV) species. The latter two scavengers have different affinity towards Fe(IV) with kinetics for the reaction of Fe(IV) (Fe=O<sup>2+</sup>) with methanol and DMSO are  $5.72 \times 10^2$  and  $1.26 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  respectively [39–41]. 50, 100 and 200 mM of scavengers were applied and their effect on the arsenic removal and on the As(III) oxidation was investigated. Fenton reaction is a well-known reaction with an established mechanism [15], therefore, we investigated the nature of the reactive oxygen species (ROS) only in the Fe(III)/H<sub>2</sub>O<sub>2</sub> system since it is not as well studied as the Fenton reaction. Initial dose of the coagulant was at all cases 2 mg/L. 2-propanol had a negligible

effect on both the As removal (Figures 8–10) and the As(III) oxidation (Figures 11–13) even when 200 mM were added which is a very high concentration relative to the coagulant dose used. This shows that most likely, hydroxyl radicals were not involved in arsenic uptake during coagulation with H<sub>2</sub>O<sub>2</sub>-Fe(III). Since 2-propanol proved that hydroxyl radicals did not oxidize As(III), methanol and DMSO could be considered as Fe(IV) scavengers. Methanol had a slightly negative effect on the As removal which can be attributed to the small affinity for Fe(IV) even at 200 mM (Figures 8–10). However, its effect increased slightly at very high H<sub>2</sub>O<sub>2</sub> concentration (87.1 mM). This was observed at all concentrations used. Methanol inhibited the As(III) oxidation since half of the residual arsenic remaining was As(III) (Figures 11–13). It is reported that at neutral pH in a Fe(II)/H<sub>2</sub>O<sub>2</sub> system Ferryl species is created as an oxidant that is highly selective towards As(III) [42]. This is in agreement with our findings because high concentrations of methanol relative to initial arsenic concentration were required to induce inhibition of oxidation.

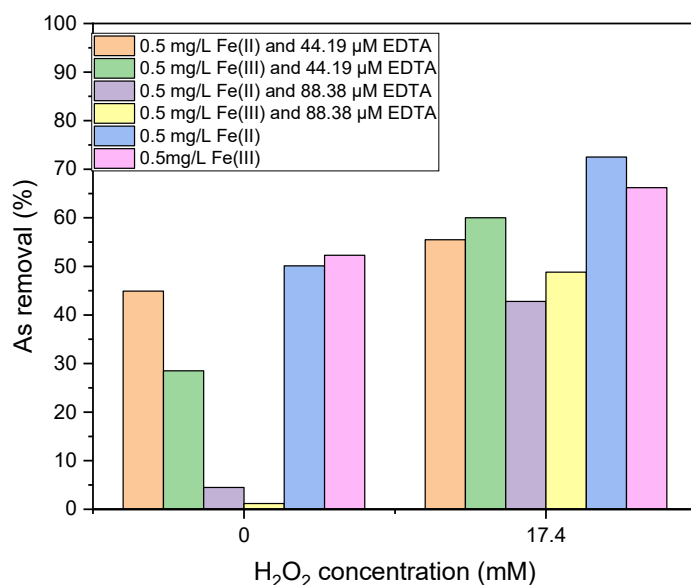


Figure 6. The effect of EDTA on As(III) removal and comparison with experiments without EDTA. Initial concentration of Fe(II) and Fe(III) was 0.5 mg/L, pH = 7.

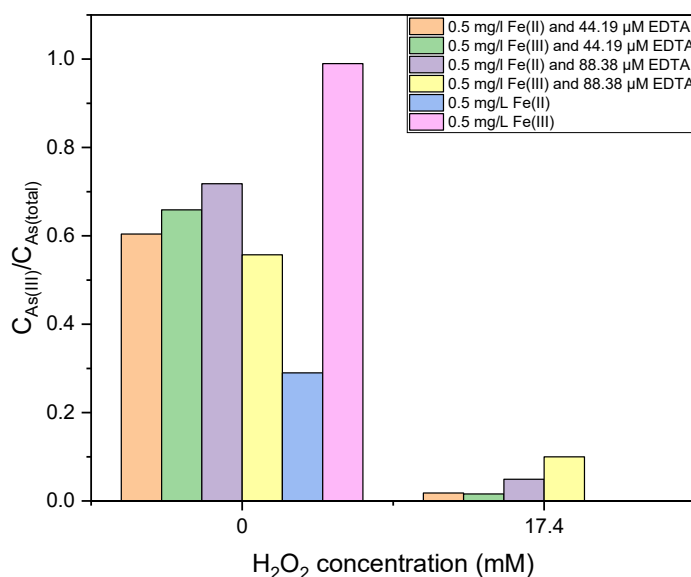
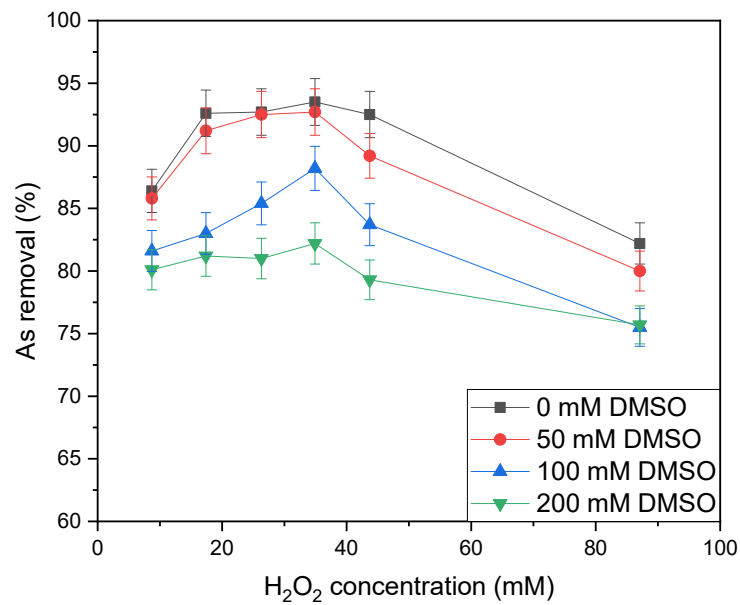
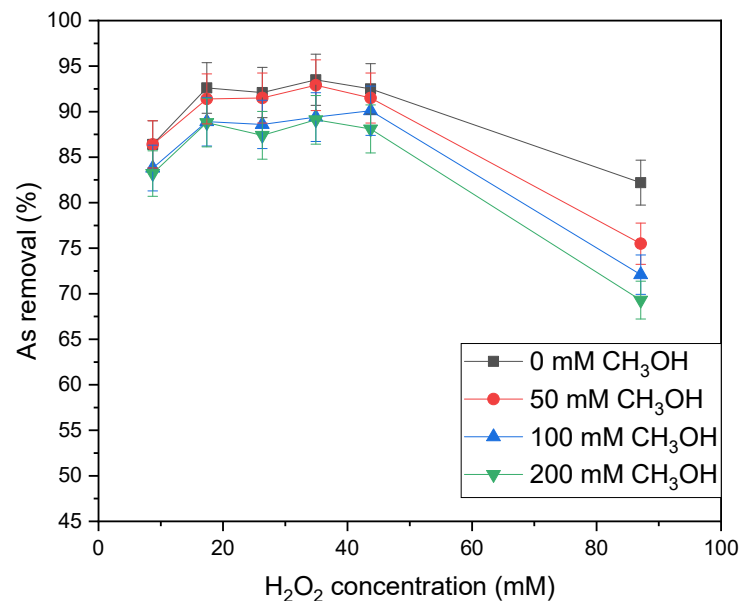


Figure 7. The effect of EDTA on residual As speciation and comparison with experiments without EDTA. Initial concentration of Fe(II) and Fe(III) was 0.5 mg/L, pH = 7.

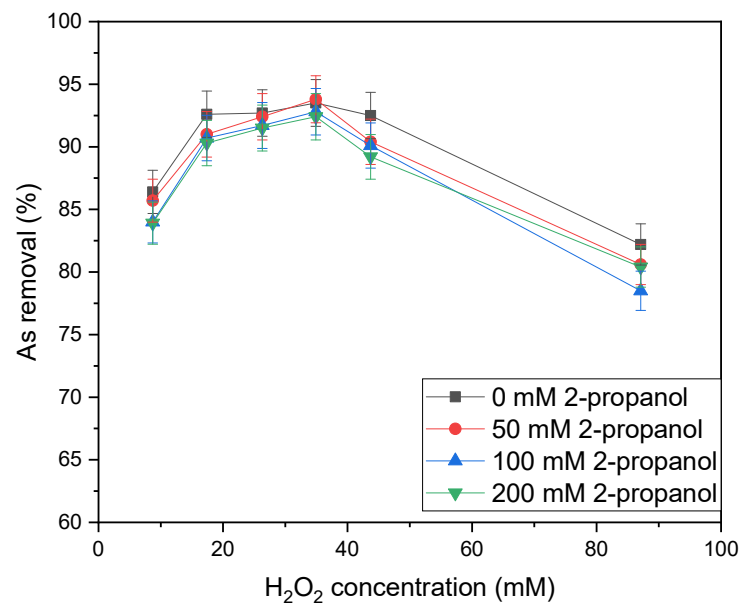


**Figure 8.** Effect of DMSO on As(III) removal. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.

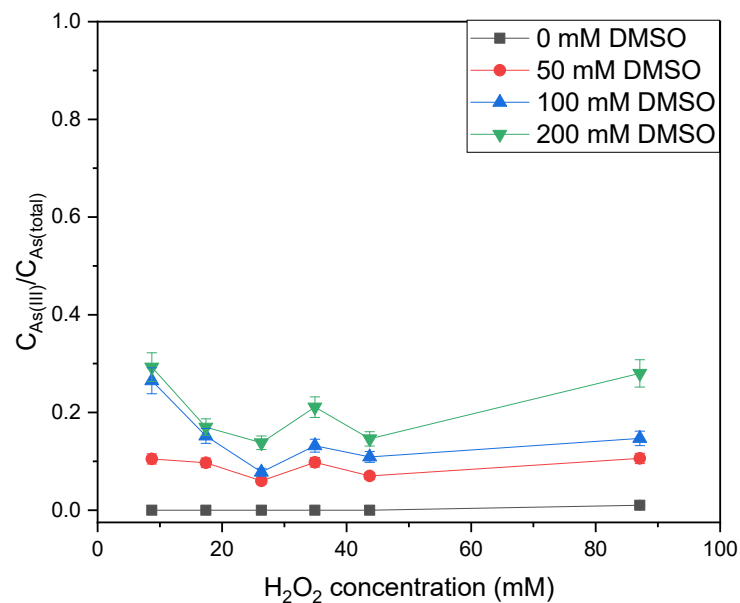


**Figure 9.** Effect of methanol on As(III) removal. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.

DMSO had a more evident adverse effect on As(III) removal which indicates that Fe(IV) is an important oxidant in this Fe(III)/H<sub>2</sub>O<sub>2</sub> system. The inhibition caused by the DMSO is a clear indication that Fe(IV) formed and react with As(III) to form As(V). Inhibition of the oxidation is also proved by the slight existence of As(III) in the residual arsenic solution. Therefore, it is our view that the hydroxyl radicals are not the main oxidants of As(III) in the solution under the conditions that the experimental work was carried out and the main oxidant could be Fe(IV). However, even at 200 mM DMSO used we observed a relatively small inhibition on removal of arsenic. Thus, we consider that there are two main pathways of oxidation and removal of As(III) in the Fe(III)-H<sub>2</sub>O<sub>2</sub> coagulation process. First, oxidation of As(III) can take place either in bulk solution by Ferryl species and then the formed As(V) is adsorbed on the surface of ferric iron.



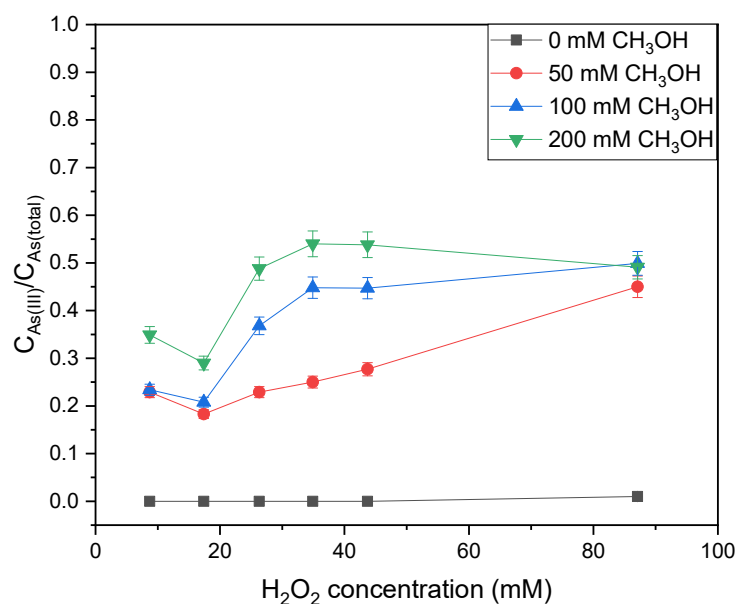
**Figure 10.** Effect of 2-propanol on As(III) removal. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.



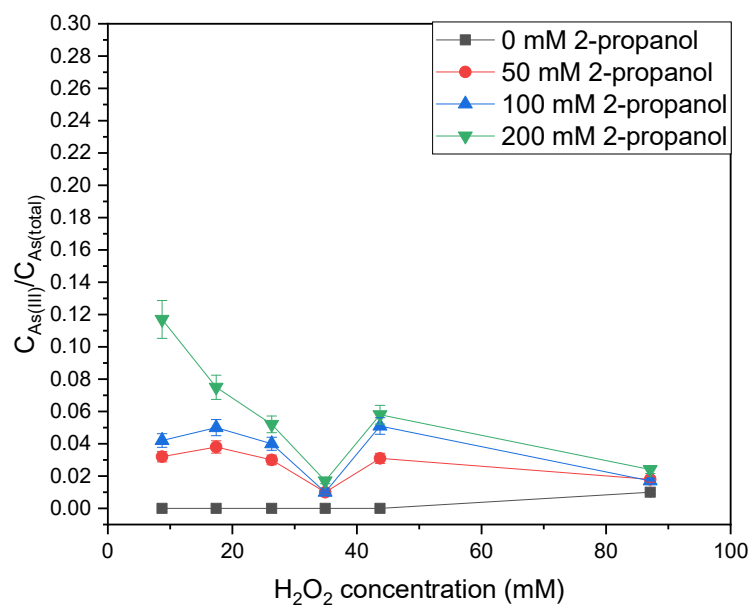
**Figure 11.** Effect of DMSO on residual As concentration. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.

The second mechanism could be that on the surface of ferric iron, adsorption of As(III) takes place first and subsequently As(III) is oxidized on the surface of Fe(III). Moreover, there are other reactive oxidants than free OH<sup>•</sup> radicals and Fe(IV) such as surface-bound OH<sup>•</sup> radicals which could explain the relatively small effect of scavengers in this enhanced coagulation process [43]. This combination of mechanisms could explain also the difference in As(III) removal when Fe(III) is applied without and with H<sub>2</sub>O<sub>2</sub> addition. In the absence of H<sub>2</sub>O<sub>2</sub>, As(III) removal takes place through the surface adsorption mechanism. In the presence of H<sub>2</sub>O<sub>2</sub>, the formation of Ferryl species contribute to the additional 15–25% As(III) removal that was shown in Figure 2. The proposed double mechanism of As(III) oxidation is illustrated in Figure 14. Before concluding, we should mention that this study has few limitations. The pH is the biggest limitation of this study as seen by the significant decline in removal at pH value above 8. Moreover, the initial concentration of H<sub>2</sub>O<sub>2</sub> is of great

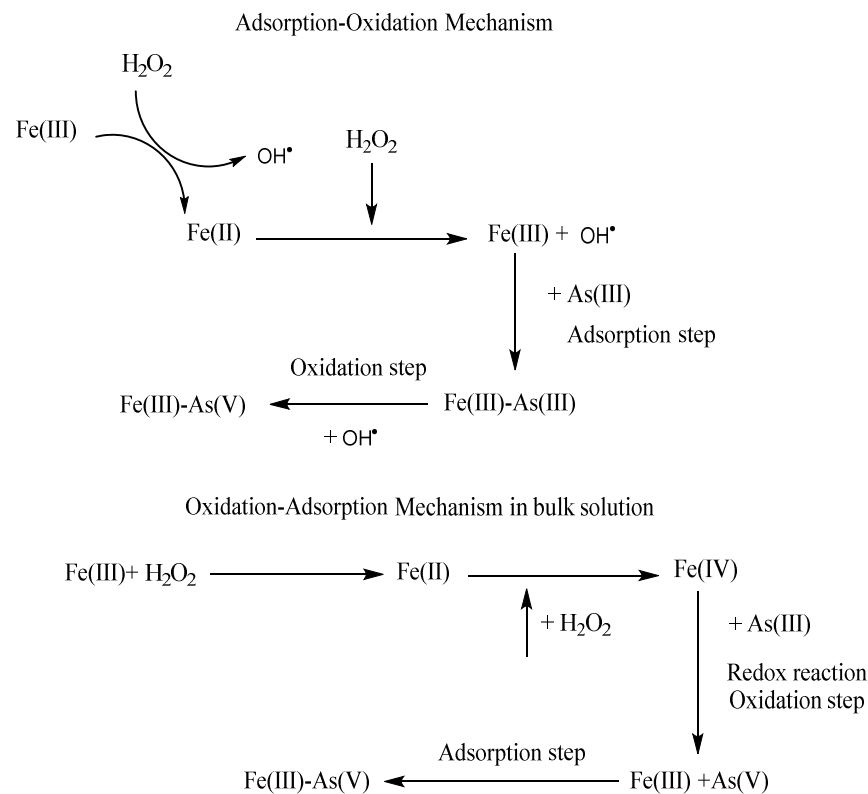
importance. We observed that the use of high concentration above 35 mM actually has a negative effect and is limiting the efficiency of the Fe(III)-H<sub>2</sub>O<sub>2</sub> system.



**Figure 12.** Effect of methanol on residual As concentration. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.



**Figure 13.** Effect of 2-propanol on residual As concentration. Initial concentration of As(III) was 100 µg/L. [Fe(III)] = 2 mg/L, pH = 7.



**Figure 14.** The proposed double mechanism of As(III) oxidation in the surface of Fe(III) and in bulk solution.

#### 4. Conclusions

The two coagulation systems (Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub>) and their performance were tested in synthetic ground water and tap water for As(III) oxidation and removal. The systems were able to achieve efficient As(III) removal in synthetic water with residual arsenic concentrations lower than 10 µg. Enhanced coagulation process, using H<sub>2</sub>O<sub>2</sub> before the addition of the coagulants achieved better results when compared to the conventional coagulation. Both systems showed high removal effectiveness at neutral and acidic pH values with similar kinetics of the H<sub>2</sub>O<sub>2</sub> decomposition by Fe(II) and Fe(III) at neutral pH. Alkaline pH (>8) significantly decreased the efficiency of the systems. While the addition of hydrogen peroxide enhances the coagulation process, the excess of hydrogen peroxide reduces the enhancement because of H<sub>2</sub>O<sub>2</sub> consuming reactions which self-scavenge the coagulation process by competing with As(III) for the surface hydroxyl radicals. Also, reaction with the intermediate As(IV) can reduce its effective concentration by a small margin.

Addition of EDTA showed clear inhibition of the coagulation process by forming a strong complex with Fe(II) and Fe(III), circumventing the flocculation of Fe(III), thus also the removal of As(III). A mechanistic study of the Fe(III)/H<sub>2</sub>O<sub>2</sub> system showed slight effect on the As(III) removal by radical scavengers (2-propanol, methanol, DMSO) and on As(III) oxidation which is shown by speciation of the residual arsenic concentrations. These are evidences of oxidation of As(III) in solution by Fe(IV) however, because of the relatively small effect of the scavengers even when high concentrations were applied, it was assumed that As(III) oxidation follows pathways: the majority of oxidation takes place on the surface of Fe(III) by surface-bound OH• radicals and a smaller part of oxidation takes place in bulk solution by Fe(IV).

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