Article

Use of Novel Composite Coagulants for Arsenic Removal from Waters—Experimental Insight for the Application of Polyferric Sulfate (PFS)

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Abstract: In the present study, several pre-polymerized coagulants of iron and aluminum were tested for their efficiency towards As(V) and As(III) removal from water sources. The results showed that the pre-polymerized coagulants of iron, such as poly-ferric sulfate and poly-ferric silicate chloride, were very efficient for As(V) removal. With regard to As(III) removal, among all examined coagulants, including the conventional ferric chloride, only the poly-ferric sulfate (PFS) was able to reduce As(III) to concentrations below the drinking water regulation limit of 10 µg/L. In contrast, all tested composite coagulants based on aluminum were not capable of removing efficiently both species of arsenic. PFS addition in water containing 4 mM of alkalinity and 25 µg/L of As(V) and As(III) (i.e., total arsenic concentration 50 µg/L) resulted in finished water with less than 5 µg/L arsenic, only by dosing 5 mg Fe-PFS/L at pH 7, whereas, simultaneously, the residual iron concentration was found well below its drinking water regulation limit of 200 µg/L. The use of PFS could provide a viable alternative for As(III) and As(V) removal at household treatment level for application in vulnerable communities, without the need of any additional treatment, such as oxidation of As(III) to As(V).

Keywords: arsenic removal; composite inorganic coagulants; poly-ferric-sulfate; alkalinity

1. Introduction

Arsenic contaminated groundwater is a major threat to human health when used as a drinking water source and concerns millions of people worldwide. Particularly, in Southeast Asia, more than 500 million people are exposed to arsenic concentrations over the WHO recommended concentration of 10 µg/L, and this was identified as a major cause of skin lesions and cancer. In Europe, significantly extended geogenic pollution of groundwaters with arsenic occurs in several countries, including Greece, Italy, Romania, Hungary, and Croatia [1–3]. The European Directive 98/83/EC lowered the limit of arsenic in drinking water from 50 to 10 µg/L, and since then, several treatment plants have been installed to tackle the arsenic pollution problem and to serve the affected population with safe drinking water [4]. However, there are still areas in several countries of Europe and several millions of people in Asia, who are still exposed to elevated arsenic concentrations, i.e., in remote areas without access to community piped treated drinking water [2,4].

Arsenic is usually present in polluted waters with both major inorganic forms of pentavalent arsenate—As(V)—or trivalent arsenite—As(III) [5]. In aerated waters, such as in surface water bodies or in swallow aquifers, the ionic species $H_2AsO_4^-/H_2AsO_4^{2-}$ of As(V) are the main existing forms. In contrast, in anoxic aquatic environments, such as those existing in several deep groundwaters, the As(III) predominates, which, in common pH values of most drinking waters (i.e., 6.5–8.2), usually exists as the non-dissociated form of H_3AsO_3 due to its pKa value of 9.2 [6]. Therefore, As(III) is more mobile (avoiding electrostatic interactions with other constituents) and thus, more difficult to be removed by the application of conventional treatment methods, which mainly involves the adsorption/binding onto appropriate charged surfaces. As a result, regarding the efficient As(III) removal, the pre-oxidation of As(III) to the As(V) form is always practiced, which is commonly performed by employing ozonation, chlorination, or manganese oxides [2,4].

However, the incorporation in water treatment processes for small urban settlements of an additional treatment step renders the treatment more complicated and expensive. Therefore, several efforts have been made to achieve effective arsenic removal in a one-step adsorption process, which incorporates an effective As(III) oxidation to As(V), without extra chemical reagent addition [7]. At the same time, the water treatment cost for arsenic removal with adsorption is several times higher than that of the corresponding chemical coagulation [8]. In this direction, if the groundwater contains sufficient concentrations of iron (i.e., 1 mg/L or more), then the simple aeration of it promotes the growth of indigenous iron oxidizing bacteria, which can oxidize iron, manganese, and As(III). The oxidized As(V) can be then effectively removed by sorption onto the co-produced iron or manganese hydrous oxides, which are simultaneously formed from the oxidation of dissolved iron or manganese [9]. However, if the groundwater does not already contain sufficient concentrations of (dissolved) iron, or if it contains elevated phosphate concentrations, acting as an inhibitor of this process, then—despite As(III) oxidation—the subsequent removal of As(V) by sorption onto iron oxides is not efficient enough due to the lack of sufficient adsorption sites [10]. In such cases, and in full-scale plants, coagulation with iron or aluminum salts is usually applied, which can diminish arsenic concentrations to below 5 μg/L [2].

Several studies have examined the direct removal of As(III), i.e., without the application of the pre-oxidation step, with a commercially available coagulant addition, such as ferric chloride, ferric sulfate, or aluminum sulfate. However, these studies have shown that the reduction of As(III) to concentrations below 10 μg/L is not feasible for pH values relevant to drinking water treatment and for realistically applied coagulant concentrations [11].

Pre-polymerized inorganic coagulants, such as poly-aluminum chloride (PACl) and poly-ferric sulfate (PFS), are extensively used across the world for water treatment with continuously increasing demand over the last two decades [12]. Recent study using PACl with high content of Al_{30} showed high efficiency for As(V) removal, while less than 40% As(III) removal was achieved [13]. On the contrary, poly-ferric sulfate was used for the removal of both As(III) and As(V) and it was found that As(III) removal was very efficient, with 90% of As(III) able to be removed together with more than 95% of As(V) [14]. However, this study was performed by using very high initial arsenic concentrations (i.e., 10 mg/L), which are not relevant for polluted waters, normally containing arsenic lower than 200 μg/L.

In a more recent study, Cui and co-authors [15] examined the use of ferric sulfate and poly-ferric sulfate and conducted a mechanistic study. However, they did not study the direct removal of As(III); instead, they firstly oxidized As(III) to As(V) by the application of $Ca(ClO)_2$ and then studied the mechanism of As(V) removal. Therefore, the investigation of the removal of both major aquatic arsenic species by the application of pre-polymerized iron coagulants still comprises an innovative approach.

In the present work, As(III) and As(V) removal from artificially polluted water was further investigated by the application of PFS, as well as by other pre-polymerized coagulants of iron and aluminum, in order to evaluate the possibility of removing both major species of arsenic (i.e., As(V) and As(III)) simultaneously without As(III) pre-oxidation. The composite coagulants that have been studied were (laboratory-synthesized) poly-ferric sulfate (PFS), poly-ferric silicate chloride (PFSiC),

and poly-aluminum ferric silicate chloride coagulants (PSiFACs) and their variables [16], and these were compared to conventional ferric chloride. To the best of our knowledge, this is the first study examining the removal of both As(III) and As(V) species by a variety of novel inorganic pre-polymerized iron-based coagulants and in the range of concentrations relevant to drinking water treatment.

2. Materials and Methods

2.1. Synthesis of Coagulants

The composite coagulants, PSiFAC (poly-aluminum ferric silicate chloride) and PFSiC (poly-ferric silicate chloride) were produced at room temperature under various experimental conditions—see also Tolkou and Zouboulis, 2014 [16]—and by using different ratios of components and (inorganic) polymerization modes. The initial metal solutions were 0.5 M $AlCl_3 \cdot 6H_2O$ (Merck) and 0.5 M $FeCl_3 \cdot 6H_2O$ (Merck), while the corresponding added-alkaline solutions were 0.5 M NaOH (Merck) and 0.5 M $NaHCO_3$ (Merck). The concentration of the poly-silicic acid solution (pSi) was also 0.05 M [17]. To evaluate our results, a typical commercially available Fe-based coagulant ($FeCl_3 \cdot 6H_2O$) was also examined. Table 1 summarizes the experimental conditions used for the synthesis of the selected pre-polymerized coagulants. In particular, for the preparation of PFS, the proposed method of Jiang and Graham (1998) [18] was followed, which was appropriately adapted. The selected concentrations of coagulants are based on the real applications, which use coagulant concentrations between 2–50 mg/L as metal (i.e., Fe or Al) [4] based on factors such as arsenic concentration, arsenic speciation, other components such as phosphates and silicates in the water to be treated, and the pH of the water [11].

Table 1. Preparation conditions of selected laboratory-prepared coagulants examined in the present study.

Coagulant Type	Molar Ratios	Description	Procedure
$PFS_{0.3}$	[OH]/[Fe] = 0.3	$Fe_2(SO_4)_3 + H_2SO_4 +$ $H_2O_2 + NaHCO_3$	Oxidation of ferrous sulfate to ferric sulfate in highly acidic conditions (H_2SO_4, 96 wt %). The oxidizing agent was H_2O_2 (30%) and then, the alkaline solution of $NaHCO_3$ was slowly added up to pH 1.3
$PFSiC_{1.5-15}$	[OH]/[Fe] = 1.5 [Fe]/[Si] = 15	$FeCl_3 + pSi + NaOH$	Appropriate amount of pSi solution was added in $FeCl_3$ solution under vigorous stirring and then, the alkaline solution of NaOH was slowly added up to pH 1.4
$PSiFAC_{1.5-10-15}$	[OH]/[Al] = 1.5 [Al]/[Fe] = 10 [Al + Fe]/[Si] = 15	$(AlCl_3 + FeCl_3) +$ $pSi + NaOH$	Appropriate amount of $FeCl_3$ solution was added in $AlCl_3$ solution under vigorous stirring. Then, the pSi solution was added to the resulted Fe/Al solution at desired ratios, followed by the alkaline solution of (NaOH) addition up to pH 3.5

2.2. Jar-Tests

Jar tests were applied for the examination of the coagulants' efficiency. A jar-test apparatus (Aqualytic) equipped with six paddles was used, employing 1 L glass beakers. Artificial water samples (1 L) polluted with arsenic were prepared by using de-ionized water with 4 mM of alkalinity (unless otherwise stated) and initial As(III) or As(V) concentrations of 100 μg/L (unless otherwise stated). The conditions used in the jar-test runs are shown in Table 2. Water samples were collected from the supernatant of each beaker, filtered through 0.45 μm nylon membrane filters, and acidified at a pH lower than 2 by an addition of 4 N HNO_3.

Table 2. Experimental conditions applied during the jar-test experiments.

Sample	Rapid Mixing Period	Slow Mixing Period	Sedimentation
Artificial water	2 min at 160 rpm	10 min at 45 rpm	45 min without mixing

2.3. Arsenic Speciation

Arsenic speciation was conducted in selected samples, using the technique of Meng and Wang (1998) [19]. Briefly, 50 mL of water sample were filtered through a disposable cartridge packed with 2.5 g of alumino-silicate adsorbent selective for As(V) removal. As(III) remained in the filtrate, which was acidified, and the arsenic concentration was later determined. Meng and Wang [19] reported that the average recovery of As(III) in the filtrate was 98% for total arsenic concentrations below 500 μg/L, which was also verified during this study.

2.4. Arsenic, Aluminum, and Iron Determination

Initial and residual arsenic concentration was determined by Hydride Generation-Atomic Absorption Spectrometry (HG-AAS, Perkin Elmer AAnalyst 400). The residual aluminum concentrations were determined by the eriochrome cyanine R standard method [20], where aluminum species react with eriochrome cyanine R dye at pH 6, resulting in a colored compound with a maximum absorbance at 535 nm. The residual iron concentration was determined by the phenanthroline standard method (3500 Fe B), where iron is reduced to the ferrous state by boiling in an acidic environment with hydroxylamine and treated with 1,10-phenanthroline addition at pH 3.2–3.3, producing a color with a maximum absorbance at 510 nm [20].

3. Results and Discussion

3.1. As(V) Removal by Pre-Polymerized Coagulants of Iron and Aluminum

The removal of As(V) by a variety of different pre-polymerized coagulants of iron and aluminum was examined, using an initial As(V) concentration 100 μg/L, with a coagulant dose resulting in constant metal (either aluminum or iron) concentration of 10 mg/L. The experiments have been performed in de-ionized water, spiked with 4 mM $NaHCO_3$, and at a pH value of 7 ± 0.2. The obtained results are shown in Figure 1, which shows the removal of arsenic by pre-polymerized coagulants or iron or aluminium, with a coagulant dose of 10 mg/L (as metal) at pH 7. It can be noticed that the use of pre-polymerized coagulants of iron are more efficient than the respective of aluminum. Several variables of laboratory-synthesized iron coagulants have been examined, such as poly-ferric chloride silicate (PFSiC), poly-ferric silicate (PFSi), and poly-ferric sulfate (PFS), noting that in some of these coagulants the basification medium (i.e., NaOH or $NaHCO_3$) was varied. Figure 1 shows that almost all coagulants of iron resulted in residual concentrations of As(V) lower than the limit of 10 μg/L and that the efficiency of PFS is better than the corresponding of ferric chloride. Moreover, the adsorption capacity of PFS is close to that calculated by the predicting equations based on the $FeClSO_4$ addition for As(V) removal [21].
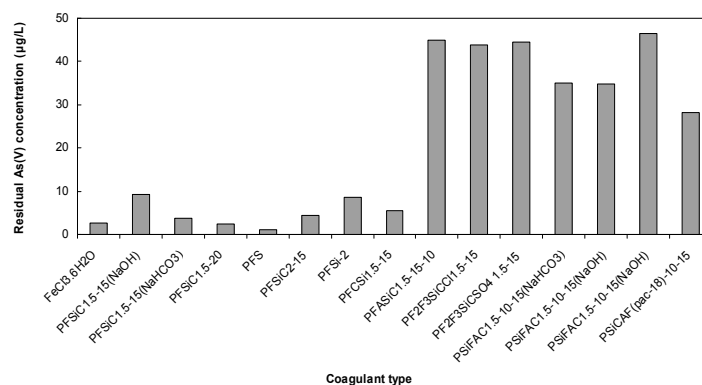

Figure 1. As(V) removal from deionized water buffered with 4 mM alkalinity by use of different (laboratory-prepared) pre-polymerized coagulants of iron and aluminum. Coagulant dose: 10 mg/L as metal Fe or Al concentration, water pH: 7 ± 0.2.

However, composite coagulants based on aluminum (i.e., PFASiC 1.5–15, PSiFAC 1.5–10, etc.) were not efficient enough for the removal of As(V), in comparison with the composite coagulants based on iron, despite the fact that poly-aluminum chloride has been shown in the literature to be very efficient towards As(V) removal [13]. Therefore, this study was further focused on the use of pre-polymerized coagulants of iron and the specific investigation on As(III) removal.

3.2. *As(III) Removal by Use of Pre-Polymerized Coagulants of Iron*

Further investigations were conducted using PFS, PFSi, and PFSiC for the examination of As(III) removal. These results were compared with the corresponding results obtained by the use of ferric chloride (commercially available coagulant), and the results are shown in Figure 2.
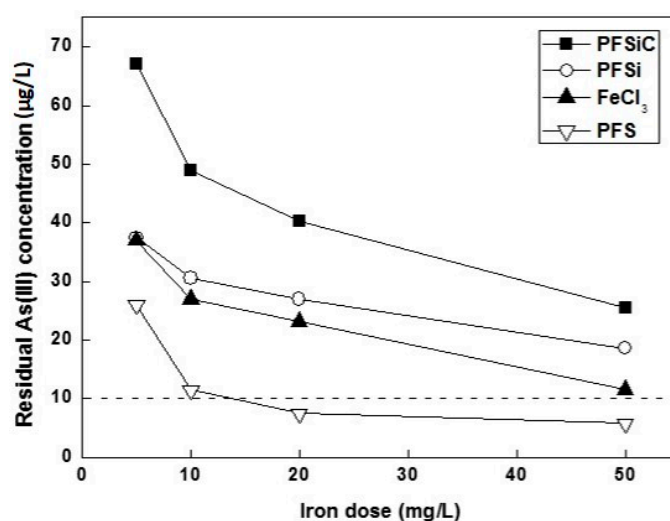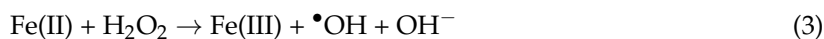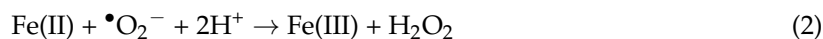

Figure 2. As(III) removal by three pre-polymerized coagulants of iron and by the conventional ferric chloride as a function of iron dose. Initial As(III) concentration 100 μg/L and water pH 7 ± 0.2.

As(III) removal was in all cases less efficient than that of As(V). PFSiC and PFSi were less efficient than the ferric chloride, whereas PFS was proved to be the most efficient among the coagulants tested and it was the only one to achieve As(III) concentrations below 10 μg/L from initial As(III) concentrations 100 μg/L with a dose close to 10 mg Fe-PFS/L. Concentrations of 10 mg/L for iron are considered relevant for drinking water treatment, especially for waters containing arsenic concentrations equal or higher than 100 μg/L. For example, in Guatemala, coagulation-filtration is used to treat around 4500 m^3/day of groundwater of average As concentrations of 150 μg/L, with 12 mg/L of FeCl$_3$. In Chilean plants, even higher doses of FeCl$_3$ (up to 56 mg/L) have been used in full-scale plants [4]. Therefore, the use of 10 mg Fe-PFS/L for 100 μg/L As(III) removal is considered as a viable coagulant dose. In contrast, ferric chloride, even when a high dose of 50 mg Fe-FeCl$_3$/L was used, did not manage to reduce As(III) concentration below the legislative imposed limit for arsenic in drinking water. However, the obtained results with ferric chloride are in good agreement with the corresponding results of a previous relevant study investigating As(III) removal with conventional coagulants [11]. Eventually, the residual iron concentrations in all experiments were well below the drinking water regulation limit of 200 μg/L.

In order to explain the increased removal of As(III) by PFS, the speciation of iron (Fe(II) or Fe(III)) in the structure of PFS was investigated. It was found that the PFS contained around 15% of Fe(II), whereas the other iron coagulants do not contain any Fe(II). The presence of Fe(II) in an oxygen-rich aquatic environment results in oxidation of Fe(II) to Fe(III), which in turn releases hydroxyl radicals

according to the mechanism proposed by Hug and Leupin (2003) [22] that oxidize As(III) to As(V), as described by the following reactions.

$$Fe(II) + O_2 \rightarrow Fe(III) + {}^{\bullet}O_2{}^{-} \tag{1}$$

$$Fe(II) + {}^{\bullet}O_2{}^{-} + 2H^{+} \rightarrow Fe(III) + H_2O_2 \tag{2}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^{-} \tag{3}$$

Hydroxyl radicals can then oxidize As(III) to As(V), following a step reaction scheme:

$$As(III) + {}^{\bullet}OH \rightarrow As(IV) \tag{4}$$

$$As(IV) + O_2 \rightarrow As(V) + {}^{\bullet}O_2{}^{-} \tag{5}$$
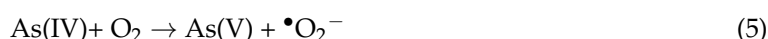
As(V) is then efficiently adsorbed on the ferric hydroxides $(Fe(OH)_3)$, formed during the hydrolysis of PFS. Moreover, to increased efficiency for As(III) removal might be contribute the gradual in situ oxidation of Fe(II), which results in short-chain oligomeric/polymeric species of $Fe(OH)_y{}^{z+}$ that favor in turn the surface complexes formation of As(III), as well of As(V). These two mechanisms are probably responsible for the reason of the increased PFS efficiency regarding the removal of As(III) compared to the conventional ferric chloride and the other examined pre-polymerized coagulants of iron.

3.3. As(III) and As(V) Removal by PFS

PFS proved to be efficient for the reduction of both forms of arsenic from aqueous solutions to concentrations below 10 μg/L. Therefore, the use of PFS was further examined for the removal of different initial As(III) concentrations and for the removal of an As(III) and As(V) mixture (Figure 3). Removal of initial As(III) concentrations of 15, 25, 50, and 100 μg/L were examined by 5 mg/L PFS (as metal), and the results were compared with the removal of a mixed solution containing 25 μg/L of As(III) and 25 μg/L of As(V), with a total arsenic concentration of 50 μg/L.
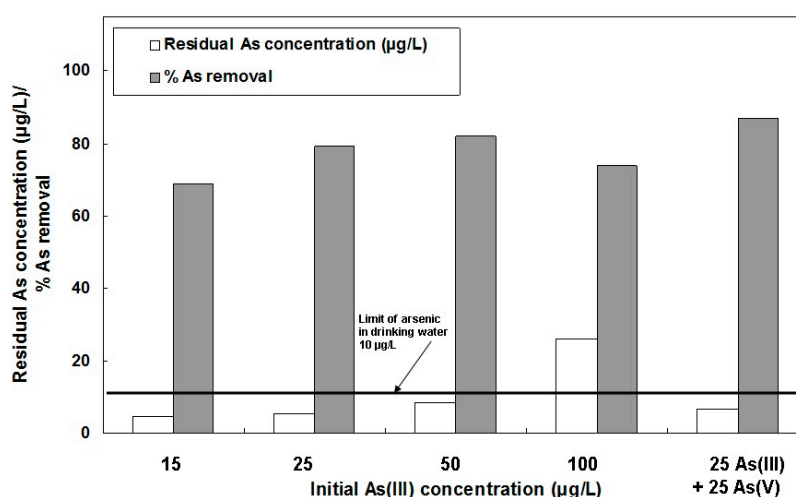

Figure 3. As(III) removal as a function either of initial As(III) or As(III)/As(V) concentration. Experimental conditions: PFS dose 5 mg Fe-PFS/L and water pH 7 ± 0.2.

The results indicated that, for an initial concentration of 50 μg As(III)/L or lower, the respective residual concentrations were below 10 μg/L, even when the smaller coagulant dose of 5 mg Fe-PFS/L was applied. Speciation analysis of residual arsenic concentrations showed that all arsenic left in water was in the trivalent form, most likely because the PFS quantity was not enough or the kinetics

were slower, in order to oxidize all the As(III) content. In a previous relevant work [11], the use of ferric chloride was found to be capable of reducing As(III) concentration to below 10 μg/L only when starting from an initial As(III) concentration of 25 μg/L and applying higher coagulant doses (i.e., 10 mg/L). Following previous experiments, water containing a mixture of 25 μg As(III)/L and 25 μg As(V)/L was treated with 5 mg Fe-PFS/L. A residual concentration of 4 μg/L was determined, while arsenic speciation analysis revealed the presence of only As(III) in the treated water, meaning that it removed around 85% of As(III) and all of the As(V) content. The latter verifies that PFS can efficiently treat water sources, which usually contain both arsenic species.

Conclusively, the experimental results indicate that the use of PFS could be an alternative to traditional treatment, providing treated water with very low arsenic concentrations, without the need of As(III) pre-oxidation treatment. Furthermore, the implementation of PFS in the water treatment process for small urban settlements can be practiced via pipe flocculation followed by direct filtration, which has been tested in the past for As(V) removal [23]. In addition, the use of PFS can have some benefits regarding the environmental footprint of the applied technology, since it has lower residual iron concentrations than conventional coagulants and does not require the use of chemical reagents for As(III) oxidation.

3.4. Effect of Carbonate Concentration on As(III) Removal by the Use of PFS

The previous section showed that the use of PFS can reduce As(III) from 50 μg/L to below 10 μg/L by applying a coagulant dose of 5 mg/L. These results are considered as efficient; however, they were obtained from waters containing an alkalinity of 4 mM (NaHCO$_3$) at pH 7. According to another study, where arsenic concentration in groundwaters of Northern Greece was investigated, this value is realistic and actually is at the lower end of values measured in the arsenic affected ground waters in this region [5]. Values of alkalinity ranged between 4 and 8 mM HCO$_3$ in this area, and similar or slightly higher concentrations were measured in other areas with arsenic polluted groundwaters, such as in Argentina [24], in the Pannonian basin [25], and in Pakistan [26]. Therefore, since alkalinity is known to affect the efficiency of coagulation, in the present study, alkalinity values from 1 to 8 mM were examined to evaluate the effect on As(III) removal. The results are shown in Figure 4.
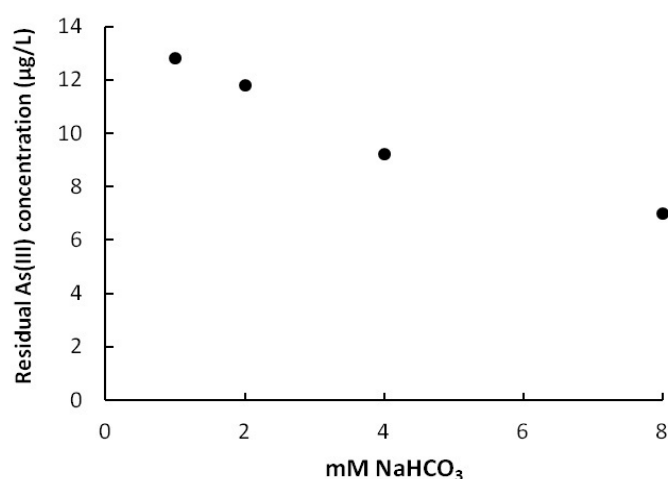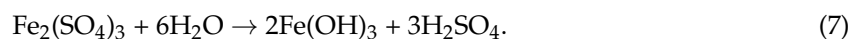

Figure 4. As(III) removal as a function of alkalinity concentration in artificially As-polluted water by the use of 5 mg Fe-PFS/L. Initial As(III) concentration 50 μg/L and water pH 7 ± 0.2.

These results indicate that, by increasing the alkalinity concentration, an increase in the efficiency of As(III) removal was also noticed. This is most likely attributed to the greater formation of flocs in the presence of alkalinity and the improved pH control. The following reactions take place in solution,

when ferric sulfate or PFS is introduced in aquatic solution in the presence (reaction (6)) or absence of alkalinity (reaction (7)):

$$Fe_2(SO_4)_3 + 6HCO_3^- \rightarrow 2Fe(OH)_3 + 6CO_2 + 3SO_4^{2-} \tag{6}$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4. \tag{7}$$

Therefore, alkalinity in general is a critical component in achieving efficient coagulation, and most arsenic-containing groundwaters have values within the range 4–8 mM of HCO_3^-. In addition, since PFS is a pre-polymerized coagulation reagent, it does not consume much alkalinity. Therefore, no significant pH changes were observed after the addition of PFS into the water; i.e., from an initial pH of 7, the final pH ranged between 6.8 and 6.9, which must increase to around 7.5 if water is to be served to the population.

4. Conclusions

The use of several newly prepared composite pre-polymerized coagulants of iron and aluminum was investigated in this study, aiming to identify their efficiency for As(III) and As(V) removal from water, which could be used as an alternative to conventional coagulants and circumvent the use of oxidizing reagents. Most of the iron-based coagulants were very efficient towards As(V) removal. In contrast, the pre-polymerized coagulants based on aluminum were not equally efficient. As(III) was found to be removed effectively only by PFS. A dose of 5 mg Fe-PFS/L, could reduce As(III) concentration from 50 to lower than 10 µg/L, covering a wide range of arsenic polluted groundwaters. In investigating the cause of this enhanced efficiency towards other coagulants, it was found that 15% of the iron of PFS was in the form of Fe(II), resulting in a mixed coagulant of Fe(II)/Fe(III) salts. The presence of Fe(II) most likely caused the As(III) oxidation and the removal of the resulting As(V) to concentration values below the drinking water regulation limit of 10 µg/L. Conclusively, this publication intends to show the increased efficiency of PFS for arsenic removal from groundwaters, and further research is scheduled in order to shed light on the responsible mechanisms of arsenic removal and to test the applicability of this reagent by its use in small scale pilot units, working under realistic conditions, i.e., with an NSF water matrix.

Author Contributions: Athanasia K. Tolkou conducted the experimental work, prepared the coagulants and wrote the materials and methods section. Nikolaos M. Tzollas conducted the analysis of arsenic in aquatic solutions. Ioannis A. Katsoyiannis, Anastasios I. Zouboulis, Manassis Mitrakas, Mathias Ernst, conceived, designed and supervised the experiments and contributed equally in writing the manuscript and providing careful explanations for the obtained results. Ioannis A. Katsoyiannis had the overall coordination of the project.

Conflicts of Interest: The authors declare no conflicts of interest.

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