

Article

Removal of Antimony Species, Sb(III)/Sb(V), from Water by Using Iron Coagulants

Manassis Mitrakas ¹, Zoi Mantha ², Nikos Tzollas ², Stelios Stylianou ², Ioannis Katsoyiannis ² and Anastasios Zouboulis ^{2,*}

¹ Laboratory of Analytical Chemistry, Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; manassis@eng.auth.gr

² Laboratory of Chemical & Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; zoi.mantha92@gmail.com (Z.M.); ntzollas@gmail.com (N.T.); s.stylianou@gmail.com (S.S.); yiank@yahoo.com (I.K.)

* Correspondence: zoubouli@chem.auth.gr

Received: 23 August 2018; Accepted: 20 September 2018; Published: 25 September 2018



Abstract: Antimony (Sb) is classified as a toxic pollutant of high priority, because its effects on human health (toxicity) are similar to those of arsenic. However, unlike arsenic, the removal of antimony from polluted waters is still not well understood. In the present study the removal of common antimony species in water, namely, Sb(III) and Sb(V), was investigated by the addition of iron-based coagulants. The applied coagulants were Fe(II), Fe(III), and equimolar mixed Fe(II)/Fe(III) salts and the experiments were performed with realistic antimony concentrations in the range 10–100 µg/L, by using artificially polluted tap water solutions. Sb(III) removal by Fe(III) provided better adsorption capacity at a residual concentration equal to the drinking water regulation limit of 5 µg/L, that is, $Q_5 = 4.7 \mu\text{g Sb(III)}/\text{mg Fe(III)}$ at pH 7, which was much higher than the value achieved by the addition of Fe(II) salts, that is, $Q_5 = 0.45 \mu\text{g Sb(III)}/\text{mg Fe(II)}$, at the same pH value. Similarly, Sb(V) was more efficiently removed by Fe(III) addition, than by the other examined coagulants. However, Fe(III) uptake capacity for Sb(V) was found to be significantly lower, that is, $Q_5 = 1.82 \mu\text{g Sb(V)}/\text{mg Fe(III)}$, than the corresponding value for Sb(III). The obtained results can give a realistic overview of the efficiency of conventionally used iron-based coagulants and of their mixture for achieving Sb concentrations below the respective drinking water regulation limit and therefore, they can be subsequently applied for the designing of real-scale water treatment units.

Keywords: antimony treatment; Sb(III); Sb(V); Fe-based coagulants; polluted waters

1. Introduction

Groundwater pollution by toxic oxyanions, such as As, Se, Sb, and so on, is considered as a major global concern, because of their adverse effects on human health; their presence in waters is mostly due to geogenic origin. Antimony is usually present in groundwaters as Sb(III) or Sb(V) species; Sb(III) was found to be 10 times more toxic than Sb(V) [1]. Antimony toxicity can accidentally occur either due to occupational exposure, or during medicinal therapy. Occupational exposure may cause respiratory irritation, pneumoconiosis, spots on the skin, and gastrointestinal symptoms, whereas as a therapeutic agent, antimony has been mostly used for the treatment of leishmaniasis and schistosomiasis [2]. The effects of antimony exposure depend on the duration of exposure, when humans are exposed at levels above the Maximum Concentration Limit (MCL). For relatively shorter periods of time U.S. E.P.A. has found that antimony can potentially cause nausea, vomiting, and diarrhea, whereas for longer periods of time antimony is considered as a human carcinogen, when the exposure exceeds constantly concentrations above MCL. Because of its toxicity, antimony concentrations are regulated

by both the European Commission Drinking Water Directive and the U.S. E.P.A., with the MCLs being 5 and 6 $\mu\text{g/L}$, respectively.

Antimony speciation and distribution in freshwaters (of surface or ground origin) have not been extensively studied. Total background-Sb dissolved concentrations in groundwater have been reported in the range 0.010–1.5 $\mu\text{g/L}$ [3], while anthropogenic and geothermal sources are responsible for much higher levels, in ranges of 0.7–170 $\mu\text{g/L}$ and 0.06–26 $\mu\text{g/L}$, respectively [4]. The most common source of antimony in drinking water sources is the dissolution from metal plumbing and fittings. Antimony leached from Sb-containing materials would be mostly in the form of Sb(V) oxy-anion. It is most likely for this reason, that even in anoxic groundwaters that is in a reductive environment, considerable Sb(V) concentrations can be also detected [5]. However, according to thermodynamic equilibrium predictions/diagrams, dissolved antimony in water exists mainly as Sb(V) in oxic (e.g., surface) waters and as Sb(III) in anoxic (e.g., ground) waters. In pH values relevant to most natural waters, that is, between 6–8, the Sb(III) is mainly present as Sb(OH)_3 , whereas Sb(V) exists as a negatively charged aqueous complex, Sb(OH)_6^- [6].

Several treatment processes have been applied for the removal of antimony from polluted water or wastewater streams, such as reverse osmosis [7], biosorption [8], electrocoagulation [9], adsorption [10,11] and coagulation [1,12]. Nevertheless, only a few studies have focused on removing antimony from drinking water sources, aiming to achieve the residual antimony concentrations below the respective regulation limits [11,13]. It is worth noting also that most of the proposed methods for the removal of antimony from waters, have adapted treatment approaches similar to that applied for arsenic removal [14], such as adsorption and coagulation [12].

The coagulation/precipitation process usually incorporates the use of relatively low-cost ferric or aluminum salts to successively capture/remove both Sb(III) and Sb(V) species [15]. Relevant studies indicated that the removal of Sb(III) is more favorable, than that of Sb(V), due to the higher mobility of the latter (pentavalent) species at pH values above 5 [12]. Guo and co-authors (2009) [12] reported 99% Sb(V) removal from a high initial concentration of 49.2 mg Sb(V)/L, by using a ferric chloride dosage of 6×10^{-4} mol/L. When compared to Sb(V), effective Sb(III) removal was achieved by using a significantly lower ferric dose at pH 6. Sb(III) removal became highly efficient when 4×10^{-4} mol/L of Fe(III) was used, producing treated water in compliance with the respective drinking-water standard. Therefore, the removal of reduced antimony species, that is, Sb(III), by coagulation-precipitation is more pronounced than that of the oxidized form Sb(V) [12,13,16], unlike what happens in the case of the As(III)/As(V) system [17]. Sb(III) removal was not found to be greatly affected by groundwater composition [12], whereas Sb(V) removal was adversely affected by the presence of other anions, for example, bicarbonates, sulfates, phosphates, or humic acids, commonly encountered in waters [16].

The main advantages of coagulation/precipitation process for the drinking water treatment are the relatively low capital costs, the effectiveness over a rather wide range of pH values, the applicability to large volume of waters, and the simplicity of operation [12]. However, the disadvantages of this process are the rather low expected removal of Sb(V) species and the demand of the addition of considerable high coagulant doses, which may result in the formation of large quantities of eventually toxic sludge, difficult to be disposed of.

The aim of this work was to examine systematically the major parameters that favor effective antimony removal (both major aqueous species) by Fe-based coagulants' addition, along with the estimation of uptake capacity at the residual concentration equal to the EU drinking water regulation limit (5 $\mu\text{g/L}$), by using appropriately polluted tap water, which may allow the direct use of obtained data for upscaling purposes. To the best of our knowledge, neither the application of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (a common coagulant agent), nor the application of mixed coagulants, such as the used equimolar $\text{Fe}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ reagents, has been previously reported, which comprises a new approach for antimony removal and opens the field for further improvements. Fe(II) was applied in order to examine its efficiency for Sb(V) removal, through the preliminary reduction to the less soluble (and more easily removed) species of Sb(III) and to compare the results with the case of Fe(III) use for

Sb(III) and Sb(V) removal. Furthermore, experimental trials by using a mixed equimolar coagulant of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were also conducted, in order to investigate the possible interactions between the applied coagulants, which might lead to increased overall antimony removal efficiency. To the best of our knowledge, there is no publication, estimating the Q_5 adsorption capacity (i.e., the necessary for lowering the concentration of Sb down to the MCL) for iron-based coagulants and for a variety of operational and physico-chemical parameters, which can provide essential data for enabling the upscale of antimony treatment/removal in drinking water treatment units.

2. Materials and Methods

2.1. Water Characteristics

Tap water of Thessaloniki city, Greece, after passing through a fixed bed of activated carbon for chlorine removal, was used in this study (Table 1). Water samples were daily spiked either with Sb(III) or Sb(V) and were used for the experiments at least 6 h after the respective antimony species addition, to allow sufficient time for them to be fully hydrolyzed, and form the species similar to those present in natural waters polluted with antimony.

Table 1. Major physicochemical characteristics of Thessaloniki tap water.

Parameter	Average Value
pH	7.30
Conductivity, $\mu\text{S}/\text{cm}$	590
Na, mg/L	35
Ca, mg/L	80
Mg, mg/L	24
HCO_3^- , mg/L	342
Fe, mg/L	<0.02
Mn, mg/L	<0.005
NO_3^- , mg/L	9
SO_4^{2-} , mg/L	8
Cl^- , mg/L	13
TOC, mg/L	0.4

2.2. Reagents and Materials

Deionized water was used to prepare stock solutions of used reagents. All glassware, polyethylene bottles, and sample vessels were immersed in 15% HNO_3 solution and rinsed three times with deionized water before use. The 100 mg/L stock solutions of Sb(V) and Sb(III) were prepared by the dissolution of $\text{KSb}(\text{OH})_6$ or Sb_2O_3 compounds (analytical grade) in 2 M HCl, respectively [12,18], whereas the initial antimony concentrations for the experiments were in the range of 100 $\mu\text{g}/\text{L}$ or lower.

2.3. Experimental Procedure

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used for preparing daily fresh 1000 mg Fe/L stock solutions. Treatment tests were performed on a program-controlled JJ-4A jar tester with six paddles/beakers. The water pH was adjusted with the addition of 0.1 M HCl or 0.1 M NaOH. Test water (1000 mL) was transferred into a 1000 mL beaker. Under initial rapid stirring (140 rpm), a predetermined dose ranging between 1–10 mg Fe/L was added. After 2 min of rapid mixing, the stirring speed reduced to 40 rpm (duration 45 min), followed by 15 min settling time. A 100 mL supernatant sample was collected and filtered through a 0.45 μm membrane filter for further analytical determinations [13]. To determine the surface charge of FeOOH precipitates, the Iso-Electric Point (IEP) was calculated by the zeta-potential curve at 20 ± 1 °C of solid adsorbent dispersion in 0.01 M NaNO_3 versus the respective pH of solution, by using a Micro-electrophoresis Apparatus (Mk II device, Rank Brothers).

2.4. Analytical Procedure

Initial and final (effluent) antimony concentrations were determined by Atomic Absorption-Hydride Generation unit and Flow Injection Analysis (FIAs). The method's detection limit was 0.4 $\mu\text{g Sb/L}$. The used instrument was a Perkin Elmer (HG-AAS, Perkin Elmer-A Analyst 400).

3. Results and Discussion

3.1. Antimony Speciation

According to thermodynamic equilibrium predictions (Figure 1), dissolved antimony in water matrixes exists mainly either as Sb(V) in oxic waters, or as Sb(III) in anoxic groundwaters. However, the partly presence of Sb(III) in oxic waters, as well as of Sb(V) in anoxic ones, has been often reported [19]. In pH values commonly encountered in natural waters, that is, between 6–8, the Sb(III) is mainly present as Sb(OH)_3 , whereas Sb(V) mostly exists as a negatively charged complex, Sb(OH)_6^- (Figure 1).

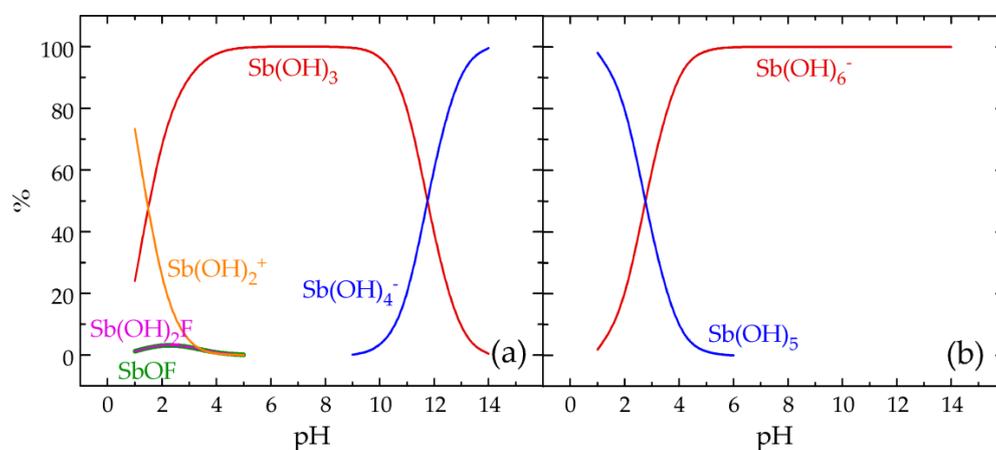


Figure 1. Percentage of (a) Sb(V) and (b) Sb(III) species at concentrations 100 $\mu\text{g/L}$ in tap water matrix and 20 $^{\circ}\text{C}$. Diagrams derived by Visual MINTEQ 3.0 (<http://vminteq.lwr.kth.se>).

3.2. Sb(III) Removal by Fe(III) or Fe(II) Coagulation

3.2.1. Fe(III) Addition

The adsorption isotherms of Sb(III) removal by Fe(III) addition and precipitation/coagulation (Figure 2) indicated a significantly higher removal efficiency at pH 5, while the effect of pH values at the commonly encountered in natural waters range (6–8) was insignificant. Therefore, it can be concluded that pH does not play an important role on Sb(III) removal from natural waters by Fe(III) coagulation, in accordance with previous studies [18], which however referred to much higher initial antimony concentrations (at least an order of magnitude greater).

Table 2. Freundlich fitting parameters for the Sb(III) adsorption isotherms ($Q = K_F C^n$).

Coagulant	pH	K_F ($\mu\text{g/mg}/(\mu\text{g/L})^n$)	n	R^2	Q_5 $\mu\text{g Sb(III)}/\text{mg Fe}$
Fe(III)	5	2.964	0.7900	0.989	10.5
Fe(III)	6	0.985	1.0019	0.997	4.9
Fe(III)	7	0.887	1.0265	0.999	4.7
Fe(III)	8	0.995	0.9877	0.993	4.8
Fe(II)	7	0.032	1.6354	0.994	0.45

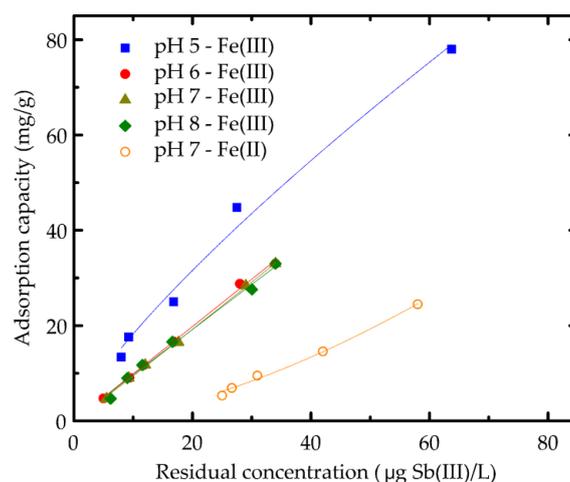


Figure 2. Fitting of Sb(III) adsorption (Freundlich model) onto FeOOH precipitates by using coagulation/precipitation with Fe(III) or Fe(II) salts at various water pH values; experimental conditions: $T = 22 \pm 1$ °C, initial antimony concentration $100 \mu\text{g Sb(III)/L}$, iron dose range $1\text{--}10 \text{ mg/L}$.

The better affinity of Sb(III) with the produced Fe(III) precipitate (FeOOH) at pH 5 is also clarified by the value of the n -parameter (0.79) of the Freundlich model, while the corresponding n -values at pH range 6–8 fluctuated at 1 ± 0.02 (Table 2). The latter is partially related to the isoelectric point (IEP) of FeOOH, which was ranged at 6.9 ± 0.3 ; that means a low surface density of FeOOH in the pH range (6–8) close to IEP, which along with the almost neutral surface of Sb(OH)_3 (Figure 1) results in low affinity. In contrast and at pH 5 (<IEP), where FeOOH present a higher positive surface density, the affinity ($n = 0.79$), as well the adsorption capacity, were significantly increased. Conclusively, the range (0.79–1) of n -value implies a weak chemisorption of Sb(OH)_3 onto FeOOH.

In the majority of relevant bench-scale experiments referred in literature, the efficiency of coagulants is evaluated through the percentage of removal capacity (e.g., [18]), while the residual concentrations of Sb(III) frequently fail to meet the regulation limit (e.g., [11]). In this study, however, the added coagulants and the main parameters of the procedure, influencing the removal of Sb species, are evaluated according to their efficiency to decrease the residual (final) concentration below the drinking water regulation limit (i.e., $5 \mu\text{g/L}$), along with their adsorption capacity, which will be abbreviated as Q_5 (mg/g), henceforth. The obtained adsorption data were fitted to Freundlich model ($Q = K_F C^n$) and showed that Fe(III) can achieve residual Sb(III) concentrations significantly lower, than the respective regulation limit at the pH range 5–8 (Table 2). Furthermore, the adsorption capacity, $Q_5 = 10.5 \mu\text{g Sb(III)/mg Fe(III)}$ at pH 5, was almost double in comparison to the corresponding at pH range 6–8, that is, $Q_5 = 4.8 \pm 0.1 \mu\text{g Sb(III)/mg Fe(III)}$, suggesting that the recommended dose for decreasing, for example, an initial concentration of $50 \mu\text{g Sb(III)/L}$ to the drinking water regulation limit of $5 \mu\text{g/L}$ at pH 7 is as follows:

$$\text{Fe(III) dose} = [50 - 5 \mu\text{g Sb(III)/L}] / [4.7 \mu\text{g Sb(III)/mg Fe(III)}] = 9.6 \text{ mg Fe(III)/L}$$

These results are in good agreement with relevant literature findings [12,16], although in these studies the results were expressed as percentage removal of antimony and, therefore, did not relate clearly with the adsorption capacity. Furthermore, the value $Q_5 = 4.7 \mu\text{g Sb(III)/mg Fe(III)}$ at pH 7 is significantly higher in comparison with the corresponding values of other commercially available Fe-based adsorbents (mainly used for As removal), such as

- GFH ($Q_5 = 1.4 \mu\text{g Sb(III)/mg GFH}$, or $2.5 \mu\text{g Sb(III)/mg Fe}$), which was supplied by SIEMENS and mainly consists of akaganeite with an iron content $55 \pm 1\% w/w$ at dry basis, and
- Bayoxide ($Q_5 = 0.6 \mu\text{g Sb(III)/mg Bayoxide}$, or $1.4 \mu\text{g Sb(III)/mg Fe}$) [11], which was supplied by Bayer and mainly consists of goethite with an iron content $52 \pm 1\% w/w$ [11].

Similarly, lower adsorption capacities of solid adsorbents in comparison to freshly precipitated FeOOH (as coagulation product) were also observed for the case of As(V) removal [20]. The apparent reason for this significantly higher removal capacity for the case of in situ formed FeOOH precipitates is the formation of short-chain polymers of $\text{Fe}(\text{OH})_y^{z\pm}$ with higher surface charge density, as they are gradually transformed from Fe(III) dissolved cations into FeOOH floc (solid) particles/precipitates.

3.2.2. Fe(II) Addition

The efficiency of Fe(II) addition on Sb(III) removal at pH 7 proved to be an order of magnitude lower, that is, $Q_5 = 0.45 \pm 0.1 \mu\text{g Sb(III)}/\text{mg Fe(II)}$, in comparison to Fe(III) (see Figure 2 and Table 2). This could be probably attributed to different hydrolysis path of iron species. The intermediate short-chain $\text{Fe}(\text{OH})_y^{z\pm}$ polymers formed during the Fe(III) hydrolysis to FeOOH precipitates favor the Sb(III) adsorption, while the gradual Fe(II) oxidation-hydrolysis restricts the surface charge density of formed FeOOH solids [11]. Furthermore, a partial Fe(II) oxidation was observed at pH 6 and 5, which in turn resulted in overpassing the respective iron regulation limit in the treated water, along with lower Sb(III) removal (additional disadvantage). Therefore, the experimental results in this case did not fit well with the main adsorption models, since the effectiveness of Fe(II) oxidation and the removal capacity were highly influenced by the dose, that is, by the initial Fe(II) concentration.

3.3. Sb(V) Removal by Fe(III) or Fe(II) Coagulation

3.3.1. Fe(III)

The Sb(V) coordination with oxygen atoms is different from the tetrahedral formation of As(V) oxy-anions, due to its larger ionic radius and lower charge density, which in turn may favor the octahedral geometry. Therefore, $\text{Sb}(\text{OH})_6^-$ is the dominant species in water pH values > 5 and thus, in pH range 6–8, commonly encountered in drinking water (Figure 1). Inversely to the case of Sb(III), the water pH was found to influence significantly the Sb(V) removal by the addition of Fe(III), as shown in Figure 3, which depicts that the Sb(V) removal efficiency by Fe(III) is decreasing linearly as pH rises from 5 to 7 and diminishes at pH value 8.

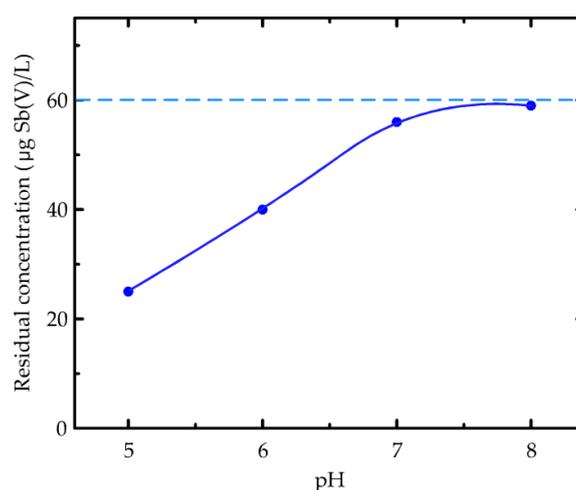


Figure 3. Influence of water pH on Sb(V) removal (experimental conditions: initial antimony concentration $C_0 = 60 \mu\text{g Sb(V)}/\text{L}$, Fe(III) dose $2.5 \text{ mg}/\text{L}$, $T = 22 \pm 1 \text{ }^\circ\text{C}$).

Since the isoelectric point of FeOOH precipitates was ranged at 6.9 ± 0.3 , at $\text{pH} < \text{IEP}$ the positive charge density dominates, due to iron species $\text{Fe}(\text{OH})_2^+/\text{Fe}(\text{OH})_2^+$, as illustrated in Figure S1 of supporting information, thus resulting in better uptake of negatively charged $\text{Sb}(\text{OH})_6^-$ species. Inversely, at water pH values $> \text{IEP}$ the dominating negatively charged $\text{Fe}(\text{OH})_4^-$ species repulses the similar charged $\text{Sb}(\text{OH})_6^-$ species, thus diminishing the Sb(V) uptake capacity.

The octahedral geometry of $\text{Sb}(\text{OH})_6^-$ species results also in significantly lower effectiveness, regarding Sb(V) removal by Fe(III) coagulants, in comparison to the relevant case of As(V). The fitting attempts to the main sorption models of adsorption isotherms data at pH 7 (Figure 4) has shown that the obtained results were best described by the BET multilayer model (Table 3), whereas the attempts to fit the data according to common Freundlich or Langmuir adsorption models did not produce reasonable predictions. Noting also that the fitting according to the BET model suggests a multilayer adsorption (physisorption), where the adsorption enthalpy is the same for any layer and a new layer can start forming before the previous one is finished [21]. Nevertheless, these results are in contradiction to most published results, such as those of Ali Inam et al., 2018 [18], due to the fact that they referred to equilibrium concentrations around two orders of magnitude higher or even more than those examined in the current study. In this study the adsorption data of Figure 4 favor the accurate determination of Fe(III)-solids uptake capacity at residual concentration equal to the drinking water regulation limit (Table 3).

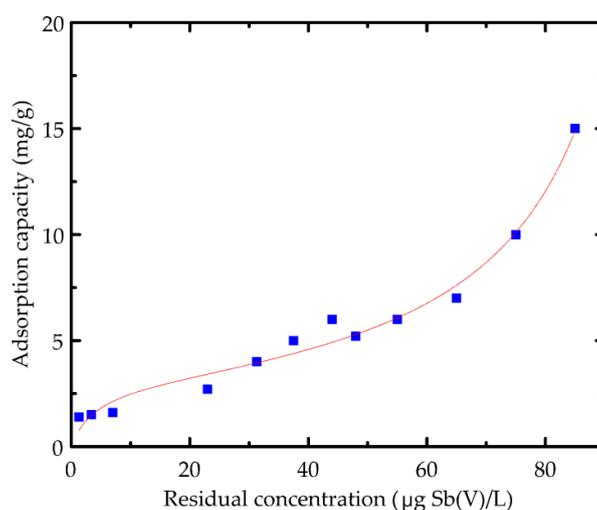


Figure 4. Fitting of Sb(V) adsorption onto FeOOH precipitates (BET model) by using coagulation/precipitation with Fe(III); experimental conditions: pH 7, $T = 22 \pm 1$ °C, initial concentrations range 15–100 µg Sb(V)/L, Fe(III) dose range 1–10 mg/L.

Table 3. BET fitting parameters for Sb(V) adsorption isotherms at pH 7 (according to the equation: $Q = aC/(1 + bC + dC^2)$).

Coagulant	a	b	c	R ²	Q ₅ µg Sb(V)/mg Fe
Fe(III) (Figure 4)	0.7732	0.2357	−0.0023	0.981	1.82
Fe(II) (Figure 6)	0.2239	0.0102	−0.0002	0.997	1.30
[Fe(III)]/[Fe(II)] = 1 (Figure 7)	0.4164	0.1251	−0.0014	0.985	1.31

The uptake capacity of FeOOH-precipitates formed for the case of Sb(V) removal at the drinking water regulation limit, that is, $Q_5 = 1.82$ µg Sb(V)/mg Fe(III), proved to be equal to 39% of the corresponding value for the relevant case of Sb(III) removal, that is, $Q_5 = 4.7$ µg Sb(III)/mg Fe(III). Noting also that the uptake capacity of Fe(III) for Sb(V) is almost equal to 2.5% of the corresponding value of As(V) oxy-anions of tetrahedral geometry (i.e., in the latter case $Q_5 = 44$ µg As(V)/mg Fe(III)) [22]. Therefore, by using an initial iron coagulation dose of e.g., 10 mg/L, which is usually at the highest end for most applications in full-scale drinking water treatment plants, the maximum initial concentration of Sb(V) that can be diminished (i.e., effectively treated) down to drinking water regulation limit at pH 7 is as follows:

$$10 \text{ mg Fe(III)/L} = [C_0 - 5 \text{ µg Sb(V)/L}] / [1.82 \text{ µg Sb(V)/mg Fe(III)}] \rightarrow C_0 = 23 \text{ µg Sb(V)/L}$$

While the recommended dose for decreasing an initial concentration of, for example, 50 $\mu\text{g Sb(V)/L}$ below the drinking water regulation limit is too high:

$$\text{Fe(III) dose} = [50 - 5 \mu\text{g Sb(V)/L}] / [1.82 \mu\text{g Sb(V)/mg Fe(III)}] = 24.7 \text{ mg Fe(III)/L}$$

Finally, from a techno-economical point of view, these results verify that Sb(V) removal by Fe(III) precipitation seems to be not an attractive process.

3.3.2. Fe(II) or Equimolar Fe(II)/Fe(III) Additions

The application of Fe(II) coagulant aimed at investigating the influence on Sb(V) uptake capacity through a preliminary chemical reduction to Sb(III) and subsequent easier removal. The redox potential of used tap water samples spiked with Sb(V) ranged at $+0.27 \pm 0.01 \text{ V}$ (Figure 5a), which can verify the stability of Sb(OH)_6^- species (Figure 5b). Figure 5a indicates the immediate change in the redox potential values, when introducing in this solution the Fe(II) coagulant, whereas a smaller redox potential reduction is taking place, when using the mixed coagulants addition. More specifically, the redox potential became significantly lower than $+0.1 \text{ V}$, where antimony is thermodynamically stable as Sb(OH)_3 (Figure 5b), even at the smaller applied Fe(II) dose (1 mg/L). In contrast, the Fe(III) addition does not provoke any significant changes in the redox potential values of the solution, as it is expected.

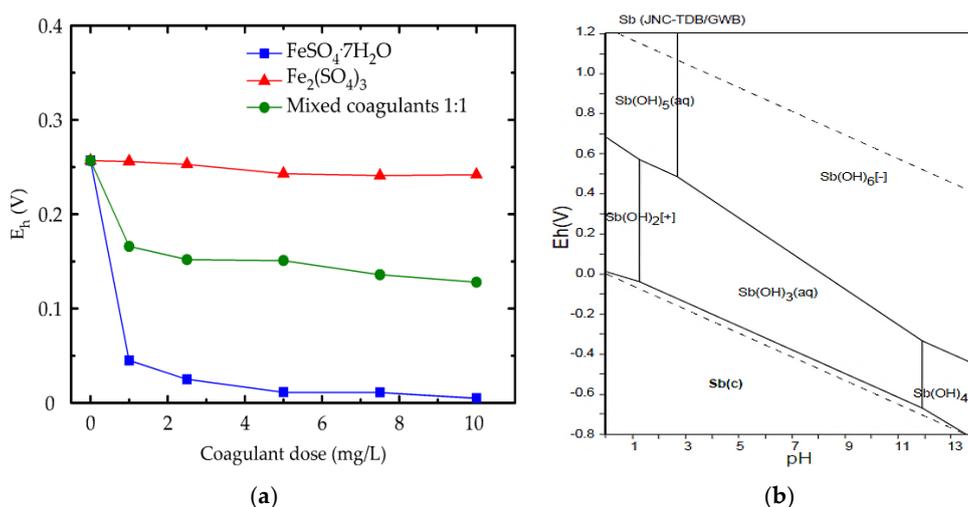


Figure 5. (a) Redox potential as a function of coagulant dose (at pH 7 and $C_0 = 50 \mu\text{g Sb(V)/L}$), (b) Eh-pH diagrams of the system Sb-O-H, according to Geological Survey of Japan Open File Report No. 419 (2005).

The redox potential changes can be considered as indications that reducing conditions prevail and thus, Sb(V) reduction can eventually take place. However, the oxidation–reduction reactions are a matter of kinetics as well. The fact that the use of Fe(II) as a coagulant agent increased the uptake capacity of Sb(V) by almost three times, that is, $Q_5 = 1.30 \mu\text{g Sb(V)/mg Fe(II)}$ (Table 3), in comparison to Sb(III) $Q_5 = 0.45 \mu\text{g Sb(III)/mg Fe(II)}$ (Table 2), can be probably attributed to Sb(V) reduction. The mechanism of gradual electron transfer from oxidized Fe(II) to reduced Sb(V) probably can favor the affinity between them and increase the respective uptake capacity. The fitting attempts of adsorption isotherms' data of Fe(II), as well as of equimolar Fe(II)/Fe(III) addition, at pH 7 to the main sorption models showed that they were also best fitted by the BET multilayer model (Figures 6 and 7), similarly to corresponding of Fe(III) addition. The achieved uptake capacities by Fe(II) addition, that is, $Q_5 = 1.30 \mu\text{g Sb(V)/mg Fe(II)}$, and by Fe(II)/Fe(III) addition, that is, $Q_5 = 1.31 \mu\text{g Sb(V)/mg Fe(II)/Fe(III)}$, were equal and by 30% lower in comparison to the corresponding of Fe(III) addition.

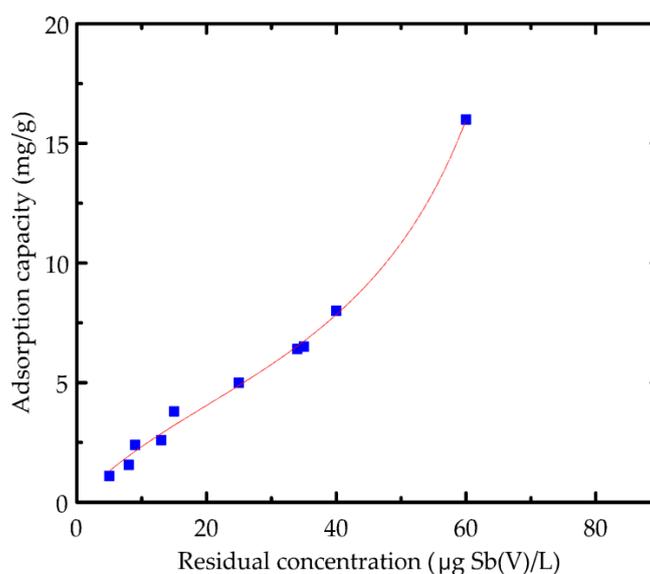


Figure 6. Fitting of Sb(V) adsorption onto FeOOH precipitates (BET model) by using coagulation/precipitation with Fe(II); experimental conditions: pH 7, $T = 22 \pm 1$ °C, initial concentrations range 15–100 µg Sb(V)/L, Fe(II) dose range 1–10 mg/L.

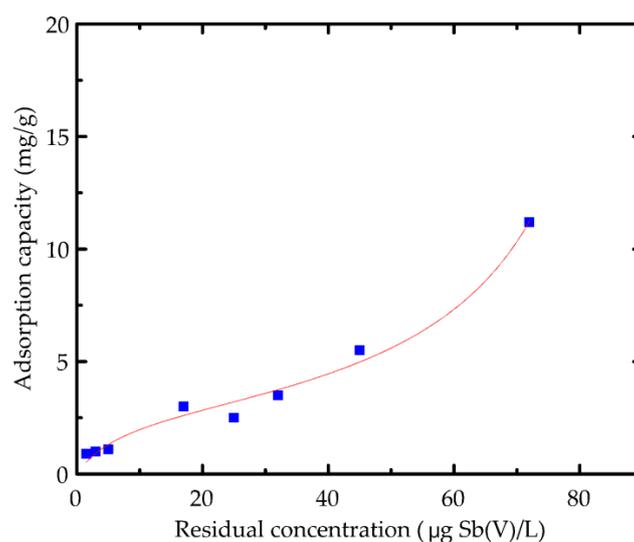


Figure 7. Fitting of Sb(V) adsorption onto FeOOH precipitates (BET model) by using coagulation/precipitation with equimolar Fe(III)/Fe(II); experimental conditions: pH 7, $T = 22 \pm 1$ °C, initial concentrations range 15–100 µg Sb(V)/L, total iron dose 1–10 mg/L.

Conclusively, although the reducing conditions prevailed in this case, the kinetics of reduction-coagulation/precipitation reactions seems to be rather slow and could not complete the reduction of Sb(V) to Sb(III) within the reasonable allowed time for reaction, which is relevant to drinking water treatment (in the range of several min and not of hours). Therefore, under these conditions Fe(III) proved to be more effective also for the case of Sb(V) removal in comparison to Fe(II) and Fe(II)/Fe(III) coagulants, noting however that this uptake capacity is equal to 39% of the corresponding value for the case of Sb(III).

4. Conclusions

- ✓ Coagulation is generally an effective treatment technique for antimony removal from polluted aqueous sources, with much more efficient Sb(III) removal induced by Fe(III) coagulant, that is, $Q_5 = 4.7 \mu\text{g Sb(III)}/\text{mg Fe(III)}$, than by Fe(II), that is, $Q_5 = 0.45 \mu\text{g Sb(III)}/\text{mg Fe(II)}$ at pH 7. Furthermore, Fe(III)-based coagulant addition proved also more efficient than the Fe(II) or Fe(III)/Fe(II) coagulants for Sb(V) removal. However, the Fe(III) uptake capacity for Sb(V), that is, $Q_5 = 1.82 \mu\text{g Sb(V)}/\text{mg Fe(III)}$, was found almost equal to 39% of the corresponding value for the case of Sb(III) and 2.5% of the corresponding value for the tetrahedral geometry As(V) oxy-anions (i.e., $Q_5 = 44 \mu\text{g As(V)}/\text{mg Fe(III)}$).
- ✓ Fe(II) coagulant seems to contribute to Sb(V) reduction to Sb(III), since its adsorption capacity for Sb(V), that is, $Q_5 = 1.3 \mu\text{g Sb(V)}/\text{mg Fe(II)}$, was found to be almost three times higher than the corresponding for Sb(III), that is, $Q_5 = 0.45 \mu\text{g Sb(III)}/\text{mg Fe(II)}$.
- ✓ The water pH value does not influence Sb(III) removal by the Fe(III) addition at pH range 6–8, commonly encountered in most natural waters with $Q_5 = 4.8 \pm 0.1 \mu\text{g Sb(III)}/\text{mg Fe(III)}$, because Sb(III) is present mainly as a neutral molecule in the form of Sb(OH)_3 . However, at pH 5 the uptake capacity proved to be significantly higher, that is, $Q_5 = 10.5 \mu\text{g Sb(III)}/\text{mg Fe(III)}$, due to the increase of positive surface charge density of FeOOH precipitates.
- ✓ By lowering the water pH below the IEP value of FeOOH precipitates, the uptake of Sb(OH)_6^- was gradually increased, due to the increase of positively charged $\text{Fe(OH)}^{2+}/\text{Fe(OH)}_2^+$ hydrolysis species of Fe(III), for example, for $C_0 = 60 \mu\text{g Sb(V)}/\text{L}$ and iron dose $2.5 \text{ mg Fe(III)}/\text{L}$ the residual concentrations at water pH 8, 7, 6, 5 were found to be 59, 56, 40, 25 $\mu\text{g Sb(V)}/\text{L}$, respectively.
- ✓ The fitting of adsorption isotherms data to sorption models, regarding the equilibrium antimony concentrations in the range of 5–100 $\mu\text{g}/\text{L}$, showed that the Sb(III) data were better fitted to the Freundlich model, while the corresponding data for Sb(V) were better fitted to the BET model.
- ✓ Finally, the experimental data of this study were focused in antimony concentrations commonly found in polluted natural waters (around or lower than 100 $\mu\text{g}/\text{L}$), hence allowing the accurate determination of respective adsorption capacities by the coagulation produced precipitates-solids at the drinking water regulation limit (Q_5), and therefore, supplying the fundamental information for upscaling the results of this study.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/10/10/1328/s1>, Figure S1: Fe(III) speciation as a function of water pH.

Author Contributions: Z.M. and S.S. conducted the experimental work. Z.M. and N.T. conducted the analysis of antimony by HG-AAS in aqueous solutions. I.K., A.Z., M.M., conceived, designed, and supervised the experiments and contributed equally in writing the manuscript and providing careful explanations for the obtained results. A.Z. had the overall coordination of the project and is the corresponding author of this paper.

Funding: This research received no external funding

Conflicts of Interest: The authors declare no conflicts of interest

References

1. Du, X.; Qu, F.; Liang, H.; Li, K.; Yu, H.; Bai, L.; Li, G. Removal of antimony(III) from polluted surface water using a hybrid coagulation–flocculation–ultrafiltration (CF–UF) process. *Chem. Eng. J.* **2014**, *254*, 293–301. [[CrossRef](#)]
2. Sundar, S.; Chakravarty, J. Antimony toxicity. *Int. J. Environ. Res. Public Health* **2010**, *7*, 4267–4277. [[CrossRef](#)] [[PubMed](#)]
3. Filella, M.; Belzile, N.; Chen, Y.-W. Antimony in the environment: A review focused on natural waters I. Occurrence. *Earth-Sci. Rev.* **2002**, *57*, 125–176. [[CrossRef](#)]
4. Aksoy, N.; Simsek, C.; Gunduz, O. Groundwater contamination mechanism in a geothermal field: A case study of Balcova, Turkey. *J. Contam. Hydrol.* **2009**, *103*, 13–28. [[CrossRef](#)] [[PubMed](#)]

5. WHO. Antimony in Drinking-water Background Document for Development of WHO Guidelines for Drinking-Water Quality. WHO/SDE/WSH/03.04/74. 2003. Available online: http://www.who.int/water_sanitation_health/dwq/chemicals/antimony.pdf (accessed on 23 March 2018).
6. Xi, J.; He, M.; Lin, C. Adsorption of antimony(III) and antimony(V) on bentonite: Kinetics, thermodynamics and anion competition. *Microchem. J.* **2011**, *97*, 85–91. [[CrossRef](#)]
7. Kang, M.; Kawasaki, M.; Tamada, S.; Kamei, T.; Magara, Y. Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination* **2000**, *131*, 293–298. [[CrossRef](#)]
8. Uluozlu, O.D.; Sar, A.; Tuzen, M. Biosorption of antimony from aqueous solution by lichen (*Physcia tribacia*) biomass. *Chem. Eng. J.* **2010**, *163*, 382–388. [[CrossRef](#)]
9. Zhu, J.; Wu, F.; Pan, X.; Guo, J.; Wen, D. Removal of antimony from antimony mine flotation wastewater by electrocoagulation with aluminum electrodes. *J. Environ. Sci.* **2011**, *23*, 1066–1071. [[CrossRef](#)]
10. Zhao, X.Q.; Dou, X.M.; Mohan, D.; Pittman, C.U.; Ok, Y.S.; Jin, X. Antimonate and antimonite adsorption by a polyvinyl alcohol stabilized granular adsorbent containing nanoscale zero-valent iron. *Chem. Eng. J.* **2014**, *247*, 250–257. [[CrossRef](#)]
11. Simeonidis, K.; Papadopoulou, V.; Tresintsi, S.; Kokkinos, E.; Katsoyiannis, I.A.; Zouboulis, A.I.; Mitrakas, M. Efficiency of iron-based oxy-hydroxides in removing antimony from groundwater to levels below the drinking water regulation limit. *Sustainability* **2017**, *9*, 238. [[CrossRef](#)]
12. Guo, X.; Wu, Z.; He, M. Removal of antimony(V) and antimony(III) from drinking water by coagulation–flocculation–sedimentation (CFS). *Water Res.* **2009**, *43*, 4327–4335. [[CrossRef](#)] [[PubMed](#)]
13. Kang, M.; Kamei, T.; Magara, Y. Comparing poly-aluminum chloride and ferric chloride for antimony removal. *Water Res.* **2003**, *37*, 4171–4179. [[CrossRef](#)]
14. Hering, J.G.; Katsoyiannis, I.A.; Theoduloz, G.A.; Berg, M.; Hug, S.J. Arsenic removal from drinking water: Experiences with technologies and constraints in practice. *J. Environ. Eng.* **2017**, *143*, 0311700. [[CrossRef](#)]
15. Gregor, J. Arsenic removal during conventional aluminum-based drinking water treatment. *Water Res.* **2001**, *35*, 1659–1664. [[CrossRef](#)]
16. Wu, Z.; He, M.; Guo, X.; Zhou, R. Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: Competing ion effect and the mechanism analysis. *Sep. Purif. Technol.* **2010**, *76*, 184–190. [[CrossRef](#)]
17. Ouzounis, K.; Katsoyiannis, I.A.; Zouboulis, A.I.; Mitrakas, M. Is the coagulation-filtration process with Fe(III) efficient for As(III) removal from groundwaters? *Sep. Sci. Technol.* **2015**, *50*, 1587–1592. [[CrossRef](#)]
18. Inam, M.A.; Rizwan, K.; Du, R.P.; Yong-Woo, L.; Ich, T.Y. Removal of Sb(III) and Sb(V) by Ferric Chloride Coagulation: Implications of Fe Solubility. *Water* **2018**, *10*, 418. [[CrossRef](#)]
19. Niedzielski, P.; Siepak, M. The occurrence and speciation of arsenic, antimony and selenium in ground water of Poznań city (Poland). *Chem. Geol.* **2005**, *21*, 241–253. [[CrossRef](#)]
20. Tresintsi, S.; Simeonidis, K.; Zouboulis, A.; Mitrakas, M. Comparative study of As(V) removal by ferric coagulation and oxy-hydroxides adsorption: Laboratory and full scale case studies. *Desalin. Water Treat.* **2013**, *51*, 2872–2880. [[CrossRef](#)]
21. Ebadi, A.; Soltan Mohammadzadeh, J.S.; Khudiev, A. What is the correct form of BET isotherms for modeling liquid phase adsorption? *Adsorption* **2009**, *15*, 65–73. [[CrossRef](#)]
22. Mitrakas, M.; Panteliadis, P.; Keramidas, V.; Tzimou-Tsitouridou, R.; Sikalidis, C. Predicting Fe³⁺ dose for As(V) removal at pHs and temperatures commonly encountered in natural waters. *Chem. Eng. J.* **2009**, *155*, 716–721. [[CrossRef](#)]

