

Article

An Effective Method to Remove Antimony in Water by Using Iron-Based Coagulants

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Abstract: The effectiveness of antimony (Sb) removal by using iron-based coagulants was investigated in this study. The effects of pH, coagulant types and dose, equilibrium concentration, co-existing humic acid (HA) and anions, and oxidation process were studied. Effective Sb removal was achieved by using Fe(III)-based coagulants. However, the removal efficiency of Sb by using Fe(II)-based coagulants was very low. The removal capacity of Sb fitted the Sips adsorption isotherm well, which revealed that the heterogeneous adsorption process onto the formed hydrous ferric oxide played an important role in Sb removal, and the mechanism was further supported by Fourier transform infrared spectrum analysis. Sb removal was inhibited by the presence of HA and phosphate, as well as oxidation and aeration. Therefore, coagulation by using Fe(III)-based coagulants without oxidation is an effective and promising method for removing Sb in aqueous solution.

Keywords: antimony removal; iron-based coagulant; polymeric ferric sulfate; oxidation

1. Introduction

Increasing antimony (Sb) contaminations pose a great threat to the environment and human beings, and have attracted increasing attention worldwide [1]. Besides natural activities, human activities, especially mining, dyeing, and textile industries, have aggravated the pollution and spread of Sb. Sb is highly toxic to human health, causing damage to the skin, eyes, lungs, stomach, liver, kidneys, heart, and nervous system [2]. Sb has been declared a high-priority pollutant of interest by the United States Environmental Protection Agency (USEPA) and European Union (EU). The maximum allowable concentration of Sb in water is regulated as 6, 10, and 5 $\mu\text{g}\cdot\text{L}^{-1}$ by the USEPA, EU, and the World Health Organization (WHO), respectively [3–5].

Given the high toxicity and severe pollution of Sb, many technologies have been developed to remove Sb from water in recent years, such as coagulation [6,7], adsorption [8,9], membrane [10], and electro-coagulation [11] related technologies. For example, many adsorbents were applied to remove Sb, such as goethite, diatomite, and Fe-Mn binary oxide [12]. Peatlands and constructed wetlands were investigated in regard to the removal of Sb from mining waste water via adsorption processes [13,14]. Among the developed technologies, the coagulation method remains popular worldwide due to its low cost, high efficiency, simple design and operation, and good matching with other water treatment equipment [15,16]. In addition, coagulation can achieve in situ removal of Sb in the case of emergency pollution incidents. Sb removal by coagulation with iron salts and aluminum salts was investigated, and the results revealed that ferric chloride (FC) exhibited better performance than poly-aluminum chloride for Sb removal, indicating that iron-based coagulants exhibited good performance in Sb removal [17]. Additionally, iron-based coagulants were demonstrated to exhibit good performance in Sb removal. The adsorption of formed hydrous ferric oxide (HFO) was found

to play an important role in Sb removal [18,19]. However, the performance of different iron-based coagulants for Sb removal, such as polymeric ferric sulfate (PFS), FC, and ferrous sulfate (FeSO_4), still remains to be explored.

Sb is a metalloid, the fourth element of Group VA in the periodic table. Given its natural and anthropogenic activities, Sb has been found in soil and water environments. Sb(III) and Sb(V) are the predominant states of Sb that exist in aerobic environments [20–22]. Under mildly acidic, neutral, and alkaline conditions, $\text{Sb}(\text{OH})_3$ and $\text{Sb}(\text{OH})_6^-$ are the dominant species for Sb(III) and Sb(V), respectively. Sb(III) is more toxic than Sb(V), but the solubility of the latter is higher than that of the former [2]. Guo et al. found that Sb(III) was easier to remove by coagulation with FC than Sb(V) [18]. In natural aqueous environments, many co-existing matters, including competing ions and organic matters, could interfere with the removal of Sb by coagulation. Moreover, the oxidization process can affect the state and removal of Sb in water by coagulation [23]. For example, the addition of KMnO_4 and aeration process, the common water treatment process, can oxidize Sb(III) to Sb(V) [24,25].

In the present work, the effects of solution pH, coagulant types, and dose on the removal of Sb by Fe(III)- and Fe(II)-based coagulants were investigated. In addition, the effects of competing matters, as well as oxidation, for Sb removal by coagulation were explored. The adsorption isotherms and mechanisms were also studied.

2. Materials and Methods

2.1. Reagents

Potassium pyroantimonate ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$), L-antimony potassium tartrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), FC ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and potassium permanganate (KMnO_4) were analytical grade reagents. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and PFS ($[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$) were used as coagulants in this work. All chemical agents in the experiments were purchased from (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Sb(V) and Sb(III) stock solutions were prepared from potassium pyroantimonate ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$) and L-antimony potassium tartrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2$) in water.

2.2. Coagulation Procedure

2.2.1. Instrumental Analysis

The Sb concentration in water was measured by inductively coupled plasma mass spectrometry (ICP-MS) (iCAP RQ ICP-MS, (Thermo Fisher Scientific Inc., Waltham, MA USA)) to evaluate the efficiency of coagulation. The pH was measured with a pH electrode (PHB-3 pH Pocket Tester, Shanghai San-Xin Instrumentation Inc. Shanghai, China). Fourier transform infrared (FTIR) spectrum were obtained in the range of 4000 to 400 cm^{-1} on a Thermo Scientific Nicolet IS10 using KBr pellets (Thermo Fisher Scientific Inc., Waltham, MA USA). The zeta potential was measured by Zeta potential analyzer (Zetasizer Nano ZS 90, Malvern Panalytical Ltd., Malvern, UK).

2.2.2. Batch Experiments

PFS, FC, and FeSO_4 were selected as coagulants for Sb removal, and the coagulant concentration was calculated as Fe. Sb samples were prepared by diluting Sb stock solution into water to obtain Sb synthetic aqueous samples of Sb(III) or Sb(V). Coagulation experiments were performed with jar tests at room temperature ($\sim 20\text{ }^\circ\text{C}$). The coagulation experiments were rapidly stirred at 200 rpm for 3 min and then slowly stirred at 40 rpm for 20 min, followed by settling down for 30 min. Subsequently, the clear supernatants were collected and filtrated with a $0.22\text{-}\mu\text{m}$ pore size membrane filter before analysis. The pH of each sample was adjusted with 0.1 M HCl or 0.1 M NaOH. The experiments on the effects of pH and dosage were duplicated three times, and the average results are reported in this paper.

To determine the optimum pH, the removal efficiencies of Sb(III) or Sb(V) (with initial Sb concentration of about $200 \mu\text{g}\cdot\text{L}^{-1}$) were investigated by using Fe-based coagulants (dose of $10 \text{ mg}\cdot\text{L}^{-1}$ as Fe) at pH values ranging from 3 to 10. At the optimum pH, the Sb removal efficiencies of three coagulants (PFS, FC, and FeSO_4) were investigated at a coagulant dose of 5, 10, 15, 20, 30, and $40 \text{ mg}\cdot\text{L}^{-1}$. The adsorption isotherm experiments of Sb(III) and Sb(V) were conducted with batch experiments at initial Sb loading in the range of $30 \mu\text{g}\cdot\text{L}^{-1}$ to $4 \text{ mg}\cdot\text{L}^{-1}$ and with a coagulant dose of $10 \text{ mg}\cdot\text{L}^{-1}$. To study the interference of co-existing substances in natural water, the effects of humic acid (HA, $2 \text{ mg}\cdot\text{L}^{-1}$) and competing ions ($2 \text{ mmol}\cdot\text{L}^{-1}$), including Cl^- , F^- , NO_3^- , HCO_3^- , SO_4^{2-} , and PO_4^{3-} , were investigated. Approximately 1, 5, and $10 \text{ mg}\cdot\text{L}^{-1}$ of KMnO_4 were applied to pre-oxidize samples prior to the coagulation process with $10 \text{ mg}\cdot\text{L}^{-1}$ of PFS. In addition, the aeration process was conducted for 20, 40, and 60 min prior to coagulation with PFS to investigate the effect of oxidation.

The concept of adsorption capacity was applied to analyze the removal performance of iron coagulants. The adsorption capacity here referred to the amount of Sb removed per unit mass of iron coagulants.

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where Q_e ($\text{mg}\cdot\text{g}^{-1}$) is the amount of Sb adsorption capacity per unit of the coagulant, C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial concentration of Sb, C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of Sb after coagulation, V (L) is the volume of the solution, and M (g) is the amount of coagulants added in the experiments.

The adsorption behavior of Sb by HFO flocs in the coagulation was described with Freundlich and Sips isotherms. The Freundlich isotherm is presented by

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (2)$$

where K_f is the Freundlich constant ($(\text{mg}\cdot\text{g}^{-1}) (\text{L}\cdot\text{mg}^{-1})^{-1/n}$), and n is the Freundlich exponent. The Sips isotherm is derived from the Langmuir and Freundlich isotherms. The Sips adsorption isotherm is presented by

$$Q_e = Q_m \frac{K_S C_e^\gamma}{1 + K_S C_e^\gamma} \quad (3)$$

where Q_m ($\text{mg}\cdot\text{g}^{-1}$) is the maximum adsorption capacity calculated by the equation, K_S is the Sips model isotherm constant ($\text{L}\cdot\text{g}^{-1}$), and γ is the Sips model exponent, which describes the heterogeneity of adsorbents.

3. Results and Discussion

3.1. Effects of pH

As shown in Figure 1a, 84%, 88%, and 15% of Sb(III) was removed by PFS, FC, and FeSO_4 , respectively at a pH of 3. When the pH was increased to 5, the highest removal rates of Sb(III) by using PFS, FC, and FeSO_4 were obtained (95%, 94%, and 60%, respectively). The Sb(III) removal rate by using PFS and FC remained higher than 85% within a wide pH range of 3 to 9. However, for FeSO_4 , the removal rate decreased remarkably when the pH was increased from 5 to 10. As shown in Figure 1b, the highest removal rate of Sb(V) was 92% and 93% at pH 5 with PFS and FC, respectively, and 79% at pH 6 with FeSO_4 . When the pH was increased from 3 to 5, the removal rate of Sb(V) increased slightly by using PFS and FC; however, a steep increase of the Sb(V) removal rate was obtained (4% to 75%) by using FeSO_4 . When the pH values increased from 5 to 6, the removal rate of Sb(V) by using the three coagulants changed slightly. When the pH was further increased from 6 to 10, the removal rate of Sb(V) decreased to 12%, 15%, and 7% for PFS, FC, and FeSO_4 , respectively. The optimum pH value was set at pH 5 for other batches.

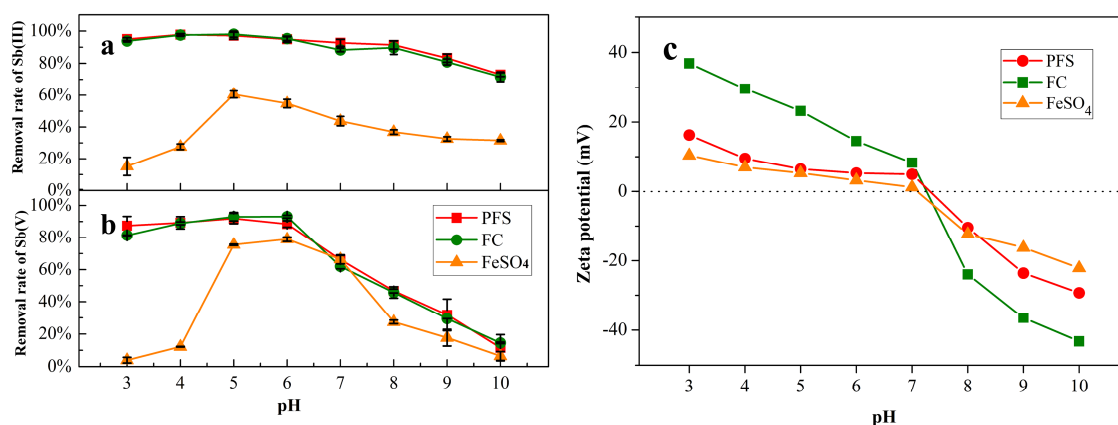


Figure 1. Effects of pH on (a) Sb(III) and (b) Sb(V) removal with $10 \text{ mg}\cdot\text{L}^{-1}$ of PFS, FC, and FeSO_4 (initial Sb(III) and Sb(V) concentrations: $200 \text{ }\mu\text{g}\cdot\text{L}^{-1}$). (c) Zeta potential of PFS, FC, and FeSO_4 (PFS, FC, and FeSO_4 concentrations: $30 \text{ mg}\cdot\text{L}^{-1}$ as Fe). PFS: polymeric ferric sulfate; FC: ferric chloride.

Within a broad pH range of 3 to 9, effective Sb(III) removal was obtained with PFS and FC. However, the optimum pH value for Sb(V) removal ranged from 5 to 6. For PFS and FC, the removal efficiency of Sb(III) was higher than that of Sb(V). However, for FeSO_4 , the removal efficiency of Sb(III) was lower than that of Sb(V). As the pH value increased, the zeta potential of PFS, FC, and FeSO_4 decreased (Figure 1c). When the pH value was below 7, the formed flocs was positively charged. When the iron-based coagulants were added into water at the optimum pH of 5, Fe(III) ions were hydrolyzed to form HFO. During agitation, the positively charged HFO adsorbed the neutrally charged Sb(III) or negatively charged Sb(V), resulting in the electrical neutralization and compression of the electric double layer for colloids. As a result, the HFO colloid became unstable and larger HFO flocculates were formed, precipitated, and separated from water, achieving the removal of antimony. The electrostatic interaction between the positively charged flocs and negatively charged $\text{Sb}(\text{OH})_6^-$ promoted the removal of Sb(V). However, when the pH value was below 3, the hydrolysis of iron-based coagulants decreased, which inhibited the removal of Sb.

In the coagulation process for Sb removal with iron-based coagulants, the active HFO flocs with many adsorption sites were formed due to the hydrolysis of iron ions in solution [10]. The pH value of the solution affected the properties of HFO flocs and the state of Sb in solution, which further affected the removal of Sb by coagulation. At pH 5, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_2^{2+}$ were the predominant Fe(III) species other than $\text{Fe}(\text{OH})_3$. With the further increase of pH, the cationic Fe species decreased, and anionic Fe species such as $\text{Fe}(\text{OH})_4^-$ increased [17]. In solution, Sb(V) existed as soluble anion $\text{Sb}(\text{OH})_6^-$. The electrostatic interaction between $\text{Sb}(\text{OH})_6^-$ and Fe(III) species facilitated the combination of HFO–Sb(V), which was affected by the pH value. Hence, the removal of Sb(V) by coagulation was affected. However, Sb(III) existed as a neutral molecule in water. The interaction between neutral Sb(III) and HFO flocs was due to chemical bonding, which was affected slightly by pH values of the solution. The low solubility of Sb(III) species facilitated Sb(III) removal [10]. Contrary to the effective Sb removal by using PFS and FC, the removal efficiency by using FeSO_4 was relatively low. Although the removal efficiency of Sb(V) with FeSO_4 was higher than that of Sb(III), it was still lower than that of Sb(V) with Fe(III)-based coagulants.

3.2. Effects of Coagulant Dose

Figure 2 shows that as the coagulant concentration increased, the removal rates of Sb(III) and Sb(V) increased until equilibrium was reached. Both PFS and FC exhibited better removal performance for Sb than FeSO_4 . Approximately $20 \text{ mg}\cdot\text{L}^{-1}$ of PFS and FC were required to reduce the concentration of Sb(III) below $5 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, in compliance with the WHO drinking water quality standard. Approximately $30 \text{ mg}\cdot\text{L}^{-1}$ of PFS and FC were required to decrease the concentration of Sb(V) below $5 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, indicating

that Sb(V) was more difficult to remove than Sb(III) by using PFS and FC. By coagulating with FeSO_4 , the remaining concentrations of Sb(III) and Sb(V) were higher than $5 \mu\text{g}\cdot\text{L}^{-1}$, which did not meet the standard.

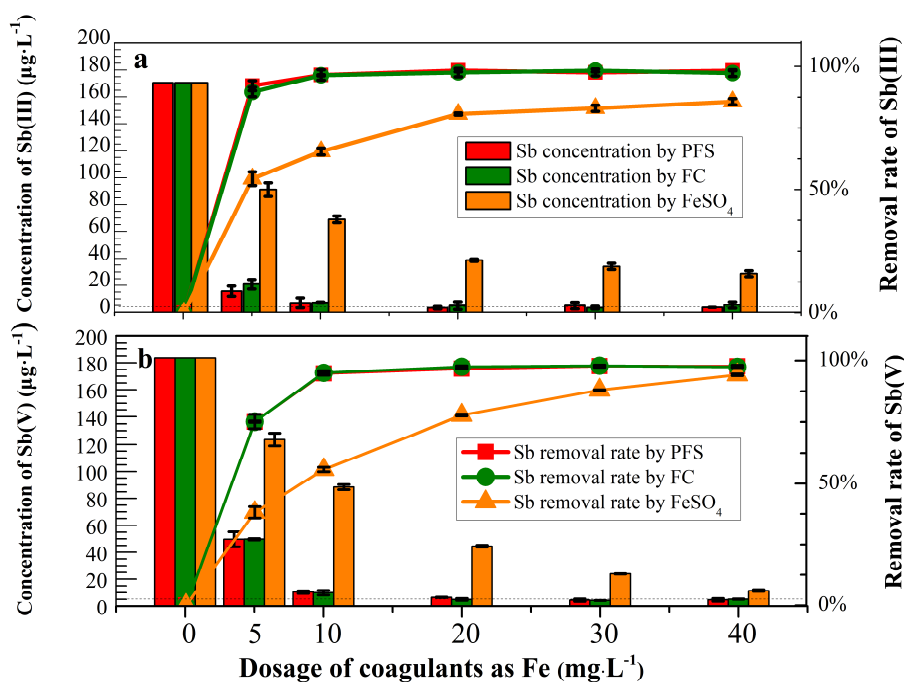


Figure 2. Effects of concentrations of coagulants on the removal of (a) Sb(III) and (b) Sb(V) by using PFS, FC, and FeSO_4 respectively (initial concentration of Sb(III): $176 \mu\text{g}\cdot\text{L}^{-1}$; Sb(V): $185 \mu\text{g}\cdot\text{L}^{-1}$).

Furthermore, Sb removal experiments were carried out using natural water obtained from Taihu Lake, Jiangsu Province, China (Figure S1). The Chemical Oxygen Demand (COD) in water was $42 \text{mg}\cdot\text{L}^{-1}$. PFS was applied to remove Sb, and the initial concentrations of Sb(III) and Sb(V) were 104 and $116 \mu\text{g}\cdot\text{L}^{-1}$. Both Sb(III) and Sb(V) were effectively removed at the PFS dosage of $20 \text{mg}\cdot\text{L}^{-1}$, and the concentration of residual Sb was below $5 \mu\text{g}\cdot\text{L}^{-1}$, meeting the WHO drinking water standard.

After coagulation, there were possibly some iron ions left in the water. Most iron ions could be precipitated as $\text{Fe}(\text{OH})_3$ in neutral water or removed in the subsequent treatment steps. The low toxicity and biocompatibility of iron-based coagulants ensured the safety of the treated water.

For the practical emergency treatment of Sb pollution in a lake, there are two main ways of using coagulation, namely, in-situ emergency treatment and off-site emergency treatment. The in-situ treatment involves adding chemicals into the lake directly. The pollutants will be deposited along with the sediment at the bottom of the lake, but there is a risk that the sediments will possibly be stirred up again. The off-site treatment involves pumping lake water into a sewage treatment station or facility for treatment. The treated water can be discharged back into the lake. The resulting sludge can be separated through a sedimentation tank, and then tested, treated, or comprehensively utilized.

3.3. Adsorption Isotherms

Adsorption by the formed HFO flocs during the coagulation process was the main routine for Sb removal [18]. The adsorption isotherms were applied to describe the adsorption behavior of Sb by HFO flocs in the coagulation, including Langmuir, Freundlich, and Sips isotherms. The Langmuir isotherm illustrates the adsorption behavior of an ideal adsorption system with homogeneous surface of the adsorbent. However, the results of simulated data via Langmuir isotherm were unreasonable. The Freundlich isotherm explains heterogeneous adsorption behavior, which indicates that different adsorption energies exist in different surface sites [26]. The Sips isotherm is derived from the Langmuir

and Freundlich isotherms. The result of adsorption capacity for Sb fitted well with the Sips adsorption isotherm. All the parameters of equations, as shown in Table 1, were derived from the nonlinear least-squares regression of the experimental data.

Table 1. Constants of Freundlich and Sips isotherms for Sb(III) and Sb(V) adsorption on hydrous ferric oxide flocs.

Isotherms	Constants	Sb(III)			Sb(V)		
		PFS	FC	FeSO ₄	PFS	FC	FeSO ₄
Freundlich	K_F ($\text{mg}\cdot\text{g}^{-1}$) ($\text{L}\cdot\text{mg}^{-1}$) ^{-1/n})	13.481	2.201	0.01	1.829	0.834	0.683
	n	1.735	1.146	0.698	1.809	1.542	1.95
	R ²	0.799	0.882	0.963	0.948	0.983	0.918
Sips	Q_m ($\text{mg}\cdot\text{g}^{-1}$)	350.56	356.05	60.84	264.39	306.04	43.29
	K_s ($\text{L}\cdot\text{mg}^{-1}$)	2.52×10^{-8}	4.54×10^{-4}	1.99×10^{-5}	2.29×10^{-4}	4.54×10^{-5}	1.99×10^{-5}
	γ	4.1263	0.923	1.676	1.103	0.923	1.677
	R ²	0.974	0.976	0.99	0.970	0.983	0.995

Figure 3a shows that with the increase of residual Sb concentration, the adsorption capacity increased until reaching an equilibrium. The fitted Sips isotherms revealed that the behavior of Sb adsorption was related to heterogeneous adsorption at low concentration but was similar to the homogenous adsorption at high concentration [26]. The maximum simulated adsorption capacity was 350 $\text{mg}\cdot\text{g}^{-1}$ with PFS, 356 $\text{mg}\cdot\text{g}^{-1}$ with FC, and 61 $\text{mg}\cdot\text{g}^{-1}$ with FeSO₄ for Sb(III), and 264 $\text{mg}\cdot\text{g}^{-1}$ with PFS, 306 $\text{mg}\cdot\text{g}^{-1}$ with FC, and 43 $\text{mg}\cdot\text{g}^{-1}$ with FeSO₄ for Sb(V), which were higher than many other iron-based adsorbents [27,28]. It indicates that the coagulation is potential at removing Sb at high initial concentrations. As shown in Figure 3b, PFS and FC exhibited similar maximum adsorption behavior. The removal performance of Sb(V) with both PFS and FC was better than that with FeSO₄. The adsorption capacities for Sb(V) with iron-based coagulants were much lower than those of Sb(III), and the equilibrium concentration of Sb was higher than that of Sb(III).

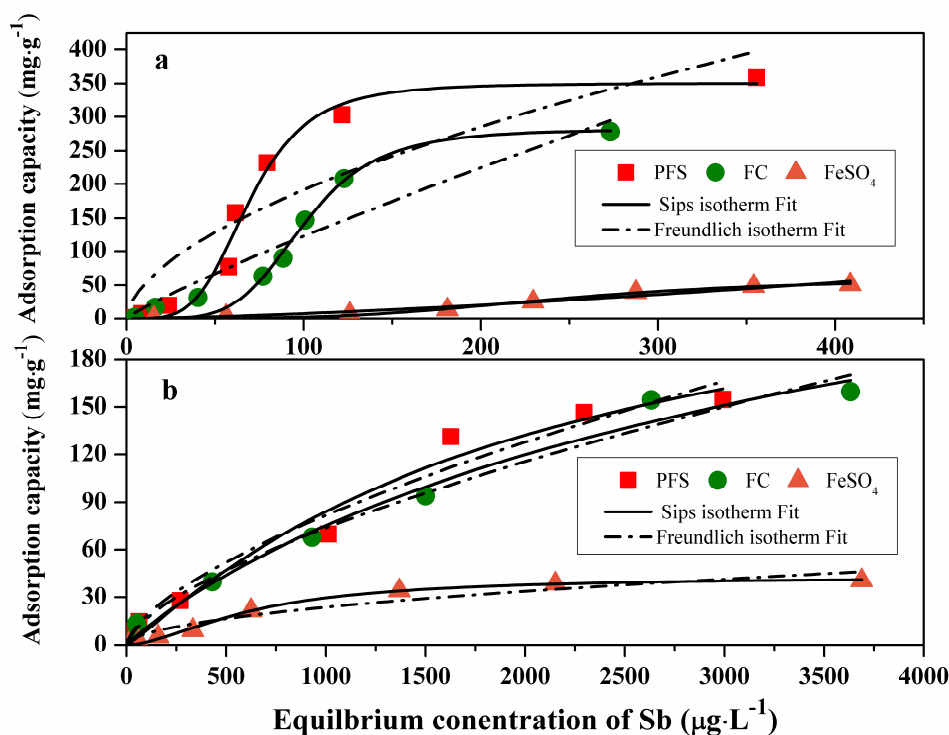


Figure 3. Coagulation of (a) Sb(III) and (b) Sb(V) by PFS, FC, and FeSO₄ fitted with Freundlich and Sips isotherms (dosage of coagulants as Fe: 10 $\text{mg}\cdot\text{L}^{-1}$).

3.4. Effects of Co-Existing Substances

In a natural aqueous system, many constituents may affect the removal of Sb, such as HA and anions [16]. The HA is connected with many functional groups, such as carboxyl and hydroxyl groups, which commonly exist in the natural environment. Figure 4 shows the effects of HA, Cl^- , F^- , NO_3^- , HCO_3^- , SO_4^{2-} , and PO_4^{3-} on the removal of Sb by coagulation with PFS. In the presence of Cl^- , F^- , NO_3^- , and SO_4^{2-} , the effects on the removal rate of Sb by coagulation with $10 \text{ mg}\cdot\text{L}^{-1}$ of PFS were negligible. With the presence of HCO_3^- , the removal rate of Sb(V) by coagulation was slightly decreased because the hydrolysis of HCO_3^- decreased the pH of the solution and affected the removal of Sb(V). However, with the presence of PO_4^{3-} , the removal of Sb(III) and Sb(V) was decreased remarkably, which was ascribed to the competition of adsorption sites between Sb and phosphate ions due to the similar tetrahedral structure and s^2p^3 outer electronic orbit [29]. HA also inhibited the removal of Sb(III) and Sb(V) remarkably. With the presence of HA, the removal rates of Sb(III) by using PFS, FC, and FeSO_4 decreased by 21.01%, 27.13%, and 19.79%, respectively, and those of Sb(V) decreased by 31.67%, 36.10%, and 31.75% respectively. On the one hand, HA was competitive with Sb on the adsorption sites of coagulants. On the other hand, reactive functional groups of HA, such as phenolic and carboxylic acid, facilitated the combination of Sb and HA, which increased the solubility of Sb and hence inhibited the removal of Sb [16,18].

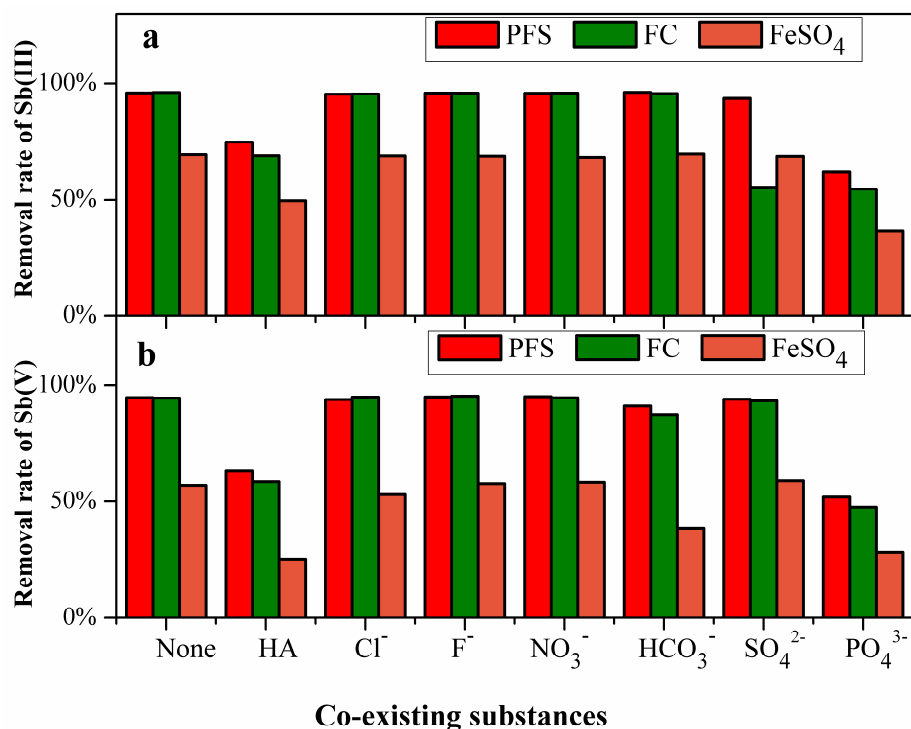


Figure 4. Effects of co-existing substances on the removal of (a) Sb(III) and (b) Sb(V) (the initial concentrations of Sb(III) and Sb(V): 192 and $205 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, respectively; dosage of PFS as Fe: $10 \text{ mg}\cdot\text{L}^{-1}$).

3.5. Effects of Oxidation on Sb Removal

In a naturally aerobic environment, many oxidizing substances may oxidize Sb(III) to Sb(V), which affects the mobility and removal of Sb [25,30]. In this study, the effects of KMnO_4 and aeration on the removal of Sb by coagulation with PFS of $10 \text{ mg}\cdot\text{L}^{-1}$ were investigated. Before coagulation, different concentrations of KMnO_4 were applied for pre-oxidation, and the aeration process was conducted for different times.

Figure 5a shows that the removal efficiency of Sb(III) decreased remarkably from 95% to 35% with the presence of $1 \text{ mg}\cdot\text{L}^{-1}$ KMnO_4 , which was ascribed to the oxidization of Sb(III) by KMnO_4 and interference of MnO_4^- on the competition for the adsorption sites. When the KMnO_4 concentration

was further increased, the removal rate reached a plateau. Additionally, the removal rate of Sb(V) with PFS coagulation decreased from 94% to 51% with the presence of $1 \text{ mg}\cdot\text{L}^{-1}$ KMnO_4 and further decreased to 29% with the presence of $10 \text{ mg}\cdot\text{L}^{-1}$ KMnO_4 .

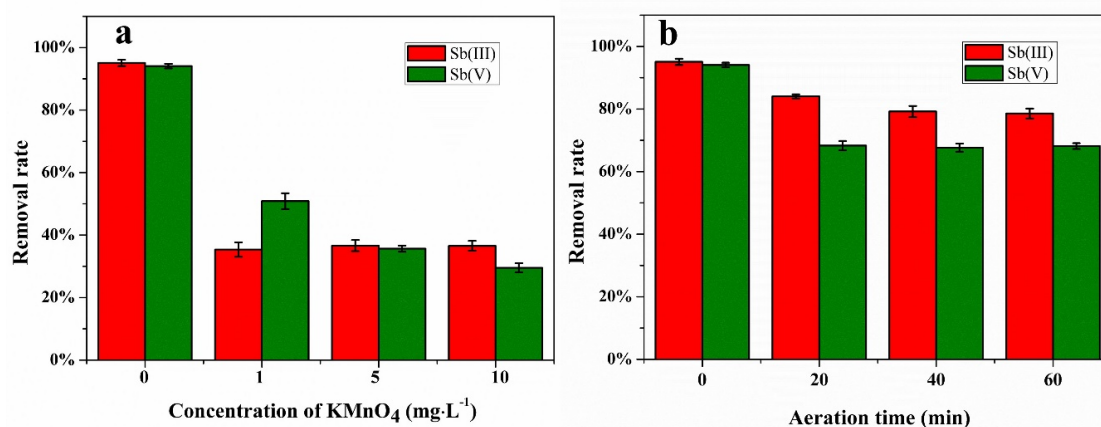


Figure 5. (a) Effects of the concentration of KMnO_4 in oxidation on the removal of Sb, and (b) effects of aeration time on the removal of Sb (the initial concentrations of Sb(III) and Sb(V): $200 \mu\text{g}\cdot\text{L}^{-1}$; dosage of PFS as Fe:10 $\text{mg}\cdot\text{L}^{-1}$).

Figure 5b shows that when the aeration time was increased from 0 min to 40 min, the removal rate of Sb(III) decreased from 94% to 79%. However, when the aeration time was further increased, the reduction in the Sb(III) removal rate was negligible. The removal rate of Sb(V) also decreased by 36% with aeration for 60 min. Besides the oxidation role of aeration, the decrease in Sb removal rate was ascribed to formed bubbles having affected the characteristics and affinity of the flocs, thereby inhibiting the adsorption of Sb onto the flocs [25].

3.6. Mechanisms

There were many possible mechanisms for the removal of Sb(III) and Sb(V) with iron-based coagulants, such as adsorption, precipitation, and coprecipitation. However, previous studies have demonstrated that precipitation and coprecipitation were negligible, which was in accord with our results [18,19]. Thereby, we attributed the removal of Sb by coagulation to the adsorption of HFO flocs, and we analyzed the mechanism and function of adsorption onto formed HFO flocs in the removal of Sb.

The combination of in situ formed HFO and Sb(III) or Sb(V) was investigated via FTIR spectra analysis (Figure 6). The spectral bands that appeared at around 3509 and 1641 cm^{-1} were attributed to the stretching and bending vibrations of $-\text{OH}$ groups, respectively, for the adsorption of water on the surface of precipitates [31]. Peaks at 1402 cm^{-1} were ascribed to the bending vibrations of $-\text{OH}$ groups connected to Sb and iron [32]. Peaks near 646 cm^{-1} were assigned to the $\text{Fe}-\text{OH}$ bonds of precipitates, and the small shift of those bands was attributed to the adsorption of Sb(III) and Sb(V) [33]. The small peaks at 590 and 487 cm^{-1} of HFO-Sb(V), which were observed for the precipitates produced by coagulation of Sb(V) with PFS and FC, were due to the symmetric stretching and bending vibrations of Sb(V)-O bonds, respectively [32]. In addition, the Sb(V)-O bonds did not appear in the spectrum of precipitates produced by the coagulation of Sb(III), which indicates that no oxidation of Sb(III) appeared on the surface of iron hydrolytic precipitates.

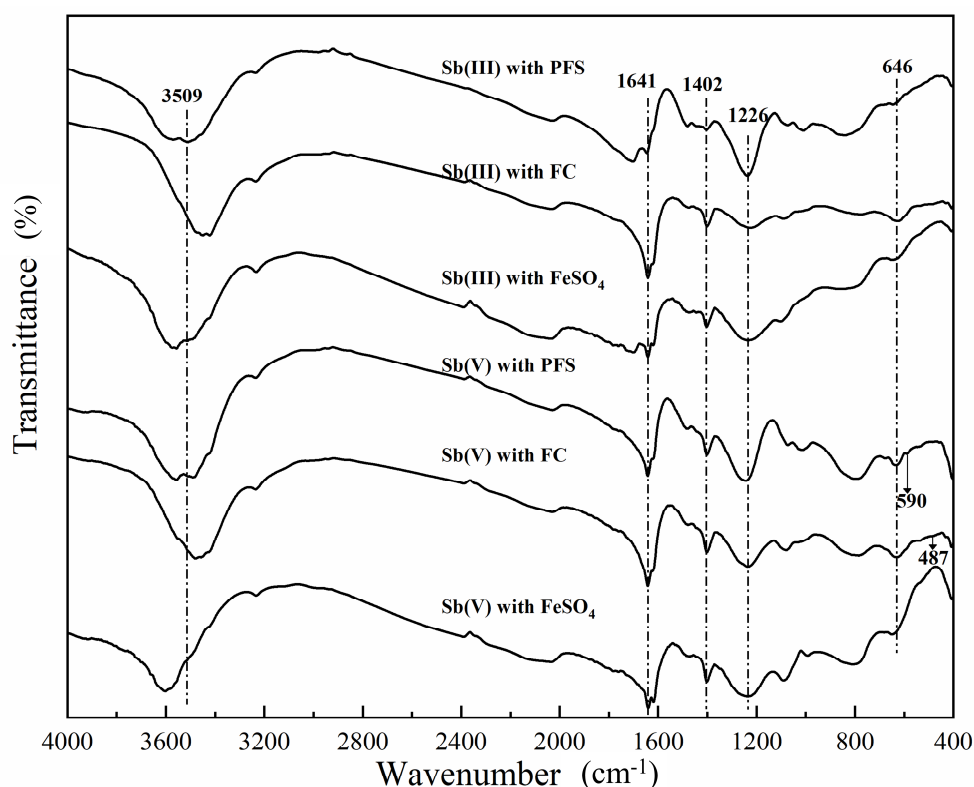


Figure 6. FTIR spectra for the precipitates of PFS, FC, and FeSO₄ after reaction with Sb(III) and Sb(V).

The in situ formed HFO by iron-based coagulation was highly active, but it was also unstable and easy to turn into ferric hydroxide precipitation of low activity. PFS, with the molecular formula of $(\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2})_m$, was much more complex than FC (FeCl_3). The hydrolyzed and polymerized iron ions in the aqueous solution formed more stable HFO flocs, and the addition of hydroxyl content facilitated the chemical bonding between HFO flocs and Sb. In the coagulation process with FeSO₄, flocs formed by the hydrolysis of Fe^{2+} ions were simple mononuclear complex, and their adsorption capacity was poorer than that of flocs formed by the hydrolysis of PFS and FC. In addition, the electrostatic interaction between the positive HFO flocs and negative $\text{Sb}(\text{OH})_6^-$ facilitated the removal of Sb(V).

4. Conclusions

The performance of Fe(III)-based (PFS, FC) and Fe(II)-based (FeSO₄) coagulants on the removal of Sb(III) and Sb(V) was investigated. The removal efficiency of Fe(III)-based coagulants (PFS and FC) was higher than that of the Fe(II)-based coagulant (FeSO₄). At the optimum pH of 5, by using Fe(III)-based salts with coagulant dose of $10 \text{ mg}\cdot\text{L}^{-1}$ at the initial Sb loading of $200 \mu\text{g}\cdot\text{L}^{-1}$, the removal rate of Sb(III) (97% with PFS and 98% with FC) was higher than that of Sb(V) (91% with PFS and 93% with FC), but the opposite was true with Fe(II)-based salts, wherein 61% of Sb(III) and 76% of Sb(V) were removed. The adsorption capacities by using PFS, FC, and FeSO₄ fit the Sips adsorption isotherms well, and the simulated maximum adsorption capacities were $350 \text{ mg}\cdot\text{g}^{-1}$ for Sb(III) and $264 \text{ mg}\cdot\text{g}^{-1}$ for Sb(V) by coagulation with PFS. The results indicated that the removal of Sb was attributed to the heterogenous adsorption of HFO at low initial Sb loadings, which was supported by the results of FTIR spectrum analysis. Oxidation inhibited the removal of Sb(III) remarkably. KMnO_4 , with its strong oxidizing property, remarkably decreased the removal efficiency of Sb. Moreover, the aeration process reduced the removal rate of Sb. In practical applications, Fe(III)-based coagulants have great potential in the treatment of Sb contaminations in rivers or lakes due to their effective and efficient performance, as well as advantages of conveniences and low cost. Furthermore, the oxidation process could be avoided in the removal of Sb(III).

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/12/1/66/s1>: Figure S1: Removal of Sb from Taihu lake water by coagulation using PFS (initial concentration of Sb(III): 104 $\mu\text{g}\cdot\text{L}^{-1}$; Sb(V): 116 $\mu\text{g}\cdot\text{L}^{-1}$).

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