



# Synergistic process using Fe hydrolytic flocs and ultrafiltration membrane for enhanced antimony(V) removal



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## ABSTRACT

Antimony (Sb) is harmful to human health, and Sb(V) is much more difficult to remove from water than other toxic elements such as arsenic (As). Theoretical studies have suggested that in situ flocs have stronger adsorption ability toward heavy metals than pre-made adsorbents. We believe that rational design of in situ flocs and the associated device structure will enable a floc-based device to be utilized in the removal of heavy metals. Based on this concept, we developed an integrated process taking advantage of the strong adsorption abilities of in-situ Al or Fe hydrolytic flocs and excellent separation properties of ultrafiltration (UF) membranes. We found that flocs could be well dispersed in a membrane tank with aeration from the bottom, and Fe-based flocs performed better in removing Sb(V) and alleviating membrane fouling than Al-based flocs. We also demonstrated that higher Sb(V) removal efficiency was induced with continuous injection, and lower solution pH. By controlling the aeration rate, injection frequency and the solution pH, membrane fouling was alleviated, especially under weakly acidic conditions. Additionally, owing to the higher rejection efficiency of the UF membrane, the effluent quality was improved, including the iron concentration, turbidity, and chromaticity. This innovative separation method shows promising potential for application in removing heavy metals in water treatment.

## 1. Introduction

Antimony (Sb), which is similar to arsenic (As), has received great attention due to its high toxicity and carcinogenicity towards humans after long-time exposure [1–3]. The maximum contaminant level (MCL) in drinking water for Sb is 5.0 and 6.0 µg/L in the USA and Europe, respectively [4,5]. In China, the MCL is 5.0 µg/L [6]. Sb(III) and Sb(V) are the two main species, of which Sb(III) is dominant under anoxic conditions with the main species of Sb(OH)<sub>3</sub>, while Sb(V) is dominant in oxic surface waters with the main species of Sb(OH)<sub>6</sub><sup>-</sup> over a wide pH range [1,3]. In comparison with As, the removal of Sb is much more difficult. Previous study has compared the behaviors between As and Sb during coagulation, and referred to the following order of the removal efficiency for As and Sb with Fe-based coagulants at neutral pH condition: As(V) > Sb(III) > As(III) > Sb(V) [7].

To remove Sb effectively, various technologies have been investigated, such as coagulation/flocculation [8], membrane separation [9], electrochemical methods [10], adsorption [11], etc. Most studies have found that adsorption is still the most promising method to remove antimony, after considering the cost and practical operation [12–14].

Up to now, many adsorbents have been investigated to remove antimony, such as metal oxides [6,15], sorbents based on waste materials [16], etc. However, the adsorption ability of these aforementioned adsorbents toward Sb is relatively low, and their use in actual operations is inhibited to a large extent by the need for frequent regeneration.

In fact, the synthetic adsorbents always showed reduced adsorption abilities after drying and granulation procedures [1]. To overcome this problem, the freshly prepared adsorbents may be advantageous regarding their adsorption capability due to maintaining the activity of adsorption sites as much as possible. The surface adsorption activity and amorphous structure of the freshly prepared adsorbents can lead to higher affinity for adsorbents. It has been demonstrated that freshly prepared Al hydrolytic flocs significantly improved the removal efficiency of fluoride (F) compared to AlCl<sub>3</sub> coagulation, and showed a maximum adsorption ability above 110.0 mg F/g Al from pH 5.0–7.0 [17]. To remove trace concentrations of Sb in drinking water, Fe hydrolytic flocs were freshly prepared and the removal efficiency of Sb(V) was significantly increased after filtration. The maximal adsorption capacity of Sb(V) is as high as 10.2 mM/g Fe at pH 5.0 [1].

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Although the in situ Al or Fe hydrolytic flocs have higher adsorption ability than other adsorbents owing to alleviating the loss of active surface [17], most of these materials are used with a filter bed by loading onto porous carriers during actual operations. Here, a noticeable problem is that the corresponding loading efficiency is always lower due to the properties of the carriers [1]. As a result, the flocs have a large potential to release during filtration, leading to higher concentrations of Al or Fe in the effluent. In addition, the in situ Al or Fe hydrolytic flocs easily form a cake layer and cannot be fully utilized due to the nature of the flocs. Furthermore, microorganisms would tend to grow after long-time operation, resulting in the need for frequent cleaning and disinfection in the subsequent operations, especially when the influent temperature is high.

It is well known that aluminum salts and iron salts are commonly used coagulants in water treatment, and ultrafiltration (UF) membranes have also been widely applied because of the superior effluent quality achieved, even with variable feed-water properties [18–21]. To overcome the disadvantages mentioned above, we developed an integrated progress based on the strong adsorption ability of in situ flocs and the excellent rejection efficiency of UF membranes. Although previous studies reported that iron salts exhibited strong affinity toward Sb [22–24], aluminum salts were also investigated in this work after considering the corresponding membrane fouling degree. In this integrated system, flocs were totally suspended in the membrane tank by aeration from the bottom, so that they could be fully utilized. On one hand, the negatively charged Sb(V) ( $\text{Sb}(\text{OH})_6^-$ ) could be easily adsorbed by the freshly prepared flocs, especially under lower pH conditions with positively charged surface. On the other hand, the flocs could be well separated from the solution by the UF membrane. Furthermore, although the UF membrane pore diameter is relatively large (from several nanometers to dozens of nanometers), it can also remove heavy metals partially due to adsorption by the membrane pores [9], leading to an increase in the Sb(V) removal efficiency.

To fully investigate the feasibility of the integrated progress, our current research was carried out in a drinking water plant in Hunan province, located in central China (N:27.7°; E:111.2°). Due to mining operations, the concentration of Sb is relatively high in the surface water, dominated by Sb(V). However, the traditional water treatment process cannot remove Sb(V) effectively in the local drinking water plant, resulting in high concentrations of Sb(V) in effluent. Here, the feasibility of the integrated progress was tested with the effluent as feed water. Some factors responsible for determining the antifouling properties of the integrated process were also investigated, such as the injection frequency, aeration rate, solution pH, etc.

## 2. Materials and methods

### 2.1. Characteristics of feed water

The specific characteristics of the feed water (before upgrading) are listed in Table 1. Due to the dissolved oxygen in surface water, the main species of antimony in effluent was Sb(V), of which the proportion of concentration was as high as  $99 \pm 1\%$ .

**Table 1**  
The characteristics of feed water.

Parameters	Feed water
Water temperature (°C)	27.2–29.8
pH	7.3–7.9
Residual chlorine (mg/L)	0.4–1.0
Turbidity (NTU)	0.3–1.0
Chromaticity	1.0–7.0
Concentration of Sb ( $\mu\text{g/L}$ )	5.4–19.8
Dissolved organic matter (mg/L)	0.6–3.3
UV <sub>254</sub> (1/cm)	0.01–0.013

### 2.2. Preparation of flocs

All chemical reagents used were analytical grade except when specified. Four commonly used coagulants ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ) were chosen in this study. The coagulants were dissolved into 400 mL deionized (DI) water each time and the corresponding flocs were prepared by adjusting the solution pH to 7.5 with 1 M NaOH, which was similar to that of the feed water (pH 7.3–7.9). To prevent a high concentration of aluminum and iron in effluent after membrane filtration, the prepared flocs were washed by DI water three times before injecting. It was shown that almost 60% of aluminum species were solid hydrolysis products at pH 7.5 [25], while almost 100% of iron species were solid hydrolysis products [26]. Thus, the concentration of Al-based flocs was almost 60% of the concentration of Al-based coagulants, while the concentration of Fe-based flocs was almost equal to the concentration of Fe-based coagulants.

### 2.3. Filtration progress

A schematic illustration of the integrated membrane process is shown in Fig. S1. The height of the membrane tank was 800 mm, and the inner diameter was 64 mm. Feed water was fed into the UF membrane tank, comprising a polyvinylidene fluoride (PVDF) hollow-fiber membrane module (Litree, China) with the average pore size of 30 nm (provided by the manufacturer). The effluent from the membrane module was continuously withdrawn by a peristaltic pump (1 L/h), which was operated in a cycle of 30 min filtration and 1 min backwashing (2 L/h). The water level was controlled by a water level gauge and a ceramic aeration device (diameter: 40 mm) was set in the bottom of the membrane tank. The flocs were prepared before injecting each time to maintain the activity [27]. All flocs were suspended in the membrane tank with aeration from the bottom. The total concentration of flocs (calculated as Al or Fe, the same below) was 50 mM during the whole filtration (running for 10 days) and the flocs were directly injected into the membrane tank in batches (once every 2 days and once per day) or continuous injection with a peristaltic pump. The trans-membrane pressure (TMP) was monitored by pressure sensors and recorded every day. The hydraulic retention time (HRT) was 2.2 h and the accumulated sludge was not released during the whole filtration. All samples were taken before the next injection, except in the continuous injection mode.

### 2.4. Characteristics of flocs

During the filtration at day 1, floc samples were taken from below the water surface to minimize impurities. Floc images were captured by a microscope with a CCD camera (GE-5, Aigo, China) after transferring the sample onto a microscope slide. The images were finally analyzed by Image J software and the corresponding floc diameters were determined by the floc area. The average pore size of the pre-deposited membrane was also analyzed by Image J software [28]. The specific surface area of flocs was measured by the Brunauer-Emmett-Teller method (BET, ASAP2020HD88).

### 2.5. Measurements of extracellular polymeric substances (EPS) in sludge

The fouled membrane modules were carefully taken out from the membrane tank at the end of the experiment (day 10). A modified heating method was used to extract the EPS from the sludge [29]. The sludge suspension was first dewatered by centrifugation (Model 5417C, Eppendorf, Germany) in a tube (50 mL) at 4000 rpm for 5 min. The sludge pellet in the tube was re-suspended in phosphate buffer saline (20 mL) solution, sheared by a vortex mixer (Vortex-Genie 2, Mo Bio Laboratories, Inc, USA) for 10 min, then treated by ultrasonication (Nusonic, USA) for 5 min, and finally heated to 80 °C for another

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