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)₃, while Sb(V) is dominant in oxic surface waters with the main species of Sb(OH)₆[−] 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 AlCl₃ 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 ₂₅₄ (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

30 min. The mixture was centrifuged at 10,000 rpm for 15 min, and then the supernatant was used for EPS analysis.

A modification of the Bradford method was used to qualify the absolute concentrations of protein, using bovine serum albumin as the standard [30]. The absolute concentration of polysaccharide in EPS was measured by the phenol-sulfuric acid method, using glucose as the standard [31].

2.6. Other analytical measurements

Water temperature was obtained by a thermometer. pH was measured by an Orion benchtop pH meter. Water samples were filtered (0.45 μm) and placed into a quartz cuvette to measure the UV absorbance at 254 nm using an ultraviolet/visible spectrophotometer (U-3010, Hitachi High Technologies Co., Japan). The total organic matter (TOC) was measured by the total organic matter analyzer (TOC-Vcph, SHIMADZU, Japan). Surface charges of flocs before and after adsorption were measured by a nano-particle sizing & zeta potential analyzer (BECKMAN COULTER Ltd., USA). The antimony, aluminum and iron concentrations in effluent were measured by inductively coupled plasma mass spectrometry (ICP-MS, 7500a, Agilent Technology, USA). Images of the layered membrane surface were obtained using scanning electron microscopy (SEM, JSM-7401F, JEOL Ltd., Japan).

3. Results

3.1. Effects of Al-based and Fe-based flocs

To investigate the removal efficiency of Sb(V) and the effects of flocs on membrane behavior, the prepared flocs were injected into the membrane tank with the injection rate of once every 2 days (Fig. 1). The results showed that the removal efficiencies of Sb(V) were only 7.3% and 10.7% at day 2 and day 6 (before washing by feed water) without flocs. However, the removal efficiency of Sb(V) increased in the presence of flocs. In comparison with other flocs, flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ performed better, for which the removal efficiency of Sb(V) was as high as 40.7% after 10 days.

Fig. 1b shows that TMP significantly increased in the absence of flocs, and was 74.6 kPa after running for 7 days with the higher water temperature (Table 1). At day 8, the TMP was dramatically reduced to 14.8 kPa after washing with the feed water, indicating serious cake layer fouling. When flocs were suspended in the membrane tank, most particles could be removed/rejected by flocs during filtration. As a result, the corresponding TMP slowly increased. It was shown that Fe-based flocs also performed better in alleviating membrane fouling, especially with flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The corresponding TMP

was 17.9 kPa at day 10, while it was 35.1 kPa, 61.3 kPa and 77.9 kPa in the presence of flocs formed by $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, respectively.

3.2. Effect of injection frequency

It has been demonstrated that a high residual aluminum in drinking water may lead to some neurological problems, such as Alzheimer's disease [32,33]. Moreover, owing to the higher removal efficiency of Sb(V) and lower TMP development, flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was further investigated (the same below). To investigate the behaviors of flocs, three different injection frequencies were chosen to understand the membrane performance (Fig. 2).

Fig. 2a shows that the removal efficiency of Sb(V) was higher with the continuous injection mode, being 53.6% at day 10. This was higher than the value obtained with the injection rate of once every 2 days (40.7%). However, more serious membrane fouling occurred when flocs were continuously injected into the membrane tank, so that TMP was 31.2 kPa after 10 days. The corresponding TMP values were 26.8 kPa and 17.9 kPa with the injection rates of once per day and once every 2 days, respectively.

3.3. Effect of aeration rate

The characteristics of flocs were significantly affected by aeration rate, such as the particle size, the attachment ability to the membrane surface, etc. It is well known that the larger the aeration rate, the smaller the particle size and the larger the specific surface area, which might influence the adsorption ability toward Sb(V). Furthermore, less affinity of flocs to the membrane surface was induced with larger aeration rate. Therefore, three different aeration rates (0.1, 0.2 and 0.5 L/min) were investigated to understand the removal efficiency of Sb(V) and the TMP development (Fig. 3).

As seen from Fig. 3a, aeration rate had little effect on the removal efficiency of Sb(V). The removal efficiency of Sb(V) was 40.7% with the aeration rate of 0.1 L/min and 37.3% with the higher aeration rate of 0.5 L/min. However, it was also clearly shown that lower TMP development occurred in the presence of a higher aeration rate, due to the smaller attachment ability of flocs to the membrane surface. After running for 10 days, the TMP increased to 17.9 kPa when the aeration rate was 0.1 L/min, while increasing to 15.6 kPa and 10.3 kPa with the aeration rates of 0.2 L/min and 0.5 L/min, respectively.

3.4. Effect of solution pH

Characteristics of flocs could also be dramatically influenced by solution pH, especially the surface charge and the particle size. To

Fig. 1. Effect of flocs on (a) the removal efficiency of Sb(V) and (b) the development of TMP. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h; aeration rate: 0.1 L/min.

Fig. 2. Effect of injection frequency on (a) the removal efficiency of Sb(V) and (b) the development of TMP. Other experimental conditions: dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h; aeration rate: 0.1 L/min.

understand the membrane performance in the presence of Fe-based flocs, the removal efficiency of Sb(V) and the development of TMP were investigated under different pH conditions as shown in Fig. 4.

As seen from Fig. 4a, the removal efficiency of Sb(V) was as high as 92.8% at pH 6.0 after running for 10 days, which was much higher than that at pH 9.0 (only 15.9%). Table S1 shows that the concentration of Sb(V) in effluent was lower than 1.0 µg/L at pH 6.0, which was significantly lower than the MCL of the United States, European Union, and China. In addition, the iron concentration in the effluent was almost the same (depending on the iron concentration of the influent: 0.02–0.08 mg/L) before and after the membrane filtration, due to the larger particle size of flocs and the weakly acidic condition [26]. Fig. 4b shows that the TMP increased much more slowly at pH 6.0 than that at pH 9.0. The TMP at pH 6.0 was only 3.7 kPa after running for 10 days. However, the development of TMP increased with rising solution pH. The corresponding TMP values were 17.9 kPa and 22.3 kPa at pH 7.5 and pH 9.0 at day 10, respectively.

4. Discussion

Owing to the high water temperature (Table 1), microorganisms easily proliferated in the membrane tank without disinfection (Fig. S2). Thus, the morphology of the membrane surface was investigated in the absence/presence of flocs before and after filtration (Fig. 5). In contrast with the virgin membrane surface (Fig. 5a), it is clearly shown that a dense cake layer was formed by EPS in the absence of flocs after running for 7 days (Fig. 5b).

For the removal of Sb(V), although Sb(V) could be adsorbed by

membrane pores during filtration [9], the removal efficiency is low because of the relatively large pore diameter (average pore diameter: 30 nm). Fig. 1a shows that the removal efficiency of Sb(V) by the UF membrane alone was 7.3% at day 2, while rising to 10.7% at day 6. This meant that both the UF membrane and the corresponding EPS could not remove Sb(V) effectively. However, the removal efficiency of Sb(V) was higher when injecting flocs, being 27.2% and 40.7% in the presence of flocs formed by $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at day 10, respectively. This was consistent with the previous studies, which have demonstrated that iron salts had a strong adsorption ability toward Sb(V) due to the formation of an inner-sphere complex [23]. With increasing concentration of flocs, the removal efficiency of Sb(V) slowly increased (Fig. 1a).

Previous studies have reported that EPS always cause severe membrane fouling due to the dense cake layer formed [34–37]. Therefore, the TMP significantly increased to 74.6 kPa at day 7 in the absence of flocs. However, the TMP was dramatically reduced to 14.8 kPa at day 8 by washing the membrane surface carefully with feed water, indicating that cake layer formation was the main fouling mechanism. When the loose flocs were injected, they were well dispersed and in the membrane tank, and were also easily attached to the membrane surface during filtration. As a result, most EPS was wrapped into the flocs first (Fig. 5c), reducing the possibilities getting to the membrane surface directly and alleviating membrane fouling dramatically.

To further understand the variation of TMP, the concentrations of protein and polysaccharide in the sludge were investigated at day 10 in detail (Fig. 6). The results showed that the concentration of protein or polysaccharide was lower in the presence of Fe-based flocs compared

Fig. 3. Effect of aeration rate on (a) the removal efficiency of Sb(V) and (b) the development of TMP. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h.

Fig. 4. Effect of solution pH on (a) the removal efficiency of Sb(V) and (b) the development of TMP. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h; aeration rate: 0.1 L/min.

with the Al-based flocs. A possible reason was that microorganisms did not easily proliferate in the presence of the corrosive Fe-based flocs [38]. Thus, the membrane fouling was more severe with suspended Al-based flocs (Fig. 1b). In addition, the concentration of protein was much higher than that of polysaccharide, indicating that the major components of EPS were protein-like substances.

When Fe-based flocs were directly injected into the membrane tank with the frequency of once every 2 days, most adsorption sites of flocs could not be fully utilized owing to the presence of sludge. Moreover,

the characteristics of flocs gradually became inactive as a function of time [27]. Thus, the removal efficiency of Sb(V) was only 40.7%, and 53.6% with the continuous injection. In addition, the inhibition of microorganism development was greater with the injection mode of once every 2 days due to the stronger corrosive properties [38]. The total concentrations of protein and polysaccharide were $16.7 \pm 1.4 \mu\text{g/g}$ (injection every 2 days) and $19.8 \pm 2.1 \mu\text{g/g}$ with the continuous injection. As a result, membrane fouling was relatively severe with the continuous injection (Fig. 2b).

Fig. 5. SEM of membrane surface: (a) the virgin membrane surface; (b) after running for 7 days in the absence of flocs; and (c) after running for 10 days in the presence of flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h; aeration rate: 0.1 L/min.

Fig. 6. Concentration of (a) protein and (b) polysaccharide in the sludge after running for 10 days. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h; aeration rate: 0.1 L/min.

Fig. 7. Images of the flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in membrane tank: (a) pH 7.5 with aeration rate of 0.1 L/min; (b) pH 7.5 with aeration rate of 0.5 L/min; (c) pH 6.0 with aeration rate of 0.1 L/min; (d) pH 9.0 with aeration rate of 0.1 L/min. Other experimental conditions: injection frequency: once every 2 days; dose of flocs: 10 mM/injection; water treatment capacity: 1 L/h; HRT: 2.2 h.

The integrated UF membrane process was also influenced by the aeration rate to some extent (Fig. 3). The images in Fig. 7a and b show the floc sizes at different aeration rates. The average particle size was $273.3 \pm 14.8 \mu\text{m}$ with the aeration rate of 0.1 L/min, while it was $219.5 \pm 21.6 \mu\text{m}$ with the aeration rate of 0.5 L/min. Although the specific surface area of flocs produced with the aeration rate of 0.1 L/min ($312.1 \pm 9.7 \text{ m}^2/\text{g}$) was larger than that with the aeration rate of 0.5 L/min ($288.6 \pm 13.4 \text{ m}^2/\text{g}$), the removal efficiency of Sb(V) was influenced little by aeration rate. The main reason was that the electrostatic attraction effect between Fe-based flocs and Sb(V) played an important role [1,23], while the zeta potentials of Fe-based flocs varied little (data not shown) with changes in aeration rate. In addition, the electrostatic attraction force between Sb(V) and Fe-based flocs was

much stronger than the shearing force induced by aeration, even with the aeration rate of 0.5 L/min. Thus, the removal efficiency of Sb(V) was influenced little by aeration rate. Furthermore, the total concentrations of protein and polysaccharide were almost the same (about $16.7 \pm 1.4 \mu\text{g/g}$) with different aeration rates, and greater aeration rate resulted in flocs with less attachment ability. Accordingly, the corresponding TMP was 17.9 kPa when the aeration rate was 0.1 L/min, while it was 10.3 kPa when the aeration rate was 0.5 L/min at day 10.

Solution pH was another important factor in the performance of flocs. The zeta potential of flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was $9.7 \pm 2.1 \text{ mV}$ at pH 6.0, while the values were $2.5 \pm 0.8 \text{ mV}$ at pH 7.5, and $-3.1 \pm 0.9 \text{ mV}$ at pH 9.0, respectively. It is known that Sb(V) is negatively charged ($\text{Sb}(\text{OH})_6^-$) between pH 3–10 [4,5], so that it is

easily adsorbed by the positively charged Fe-based flocs under lower pH conditions. Fig. 7c and 7d show the images of the flocs formed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ under different pH conditions, illustrating that the average particle size was $114.1 \pm 9.2 \mu\text{m}$ at pH 6.0, and $306.7 \pm 22.4 \mu\text{m}$ at pH 9.0. Smaller particles have larger specific surface area. The specific surface areas were $337.9 \pm 10.3 \text{ m}^2/\text{g}$ at pH 6.0, and $276.3 \pm 18.4 \text{ m}^2/\text{g}$ at pH 9.0. In fact, the average pore diameter of the floc cake layer analyzed by Image J software was $4.8 \pm 0.3 \text{ nm}$ (pH 6.0) and $5.6 \pm 0.7 \text{ nm}$ (pH 9.0), as shown in Fig. S3. For the aforementioned reasons, much higher removal efficiency occurred at pH 6.0. This was also consistent with a previous study, which reported that the variation of Sb removal efficiency varied significantly as a function of solution pH in the presence of ferric hydroxide [4].

Furthermore, the activity of microorganisms would be inhibited under acidic conditions [39]. In comparison with the total concentration of protein and polysaccharide ($16.7 \pm 1.4 \mu\text{g}/\text{g}$) at pH 7.5, the total concentration of protein and polysaccharide was only $9.4 \pm 0.5 \mu\text{g}/\text{g}$ at pH 6.0. As a result, lower development of TMP occurred (Fig. 4b). Owing to the weakly acidic conditions, the concentration of iron and chromaticity in the effluent were almost unchanged before and after the filtration. Although the activity of microorganisms would also be inhibited under alkaline conditions (the total concentration of protein and polysaccharide was $12.6 \pm 1.8 \mu\text{g}/\text{g}$ at pH 9.0), the floc particle size was larger and the specific surface area was smaller, leading to worse membrane performance (Fig. 4b).

In view of the foregoing observations, the process combining flocs and UF membrane behaved well, especially in the presence of Fe-based flocs. Continuous injection performed better in the removal efficiency of Sb(V), while a little worse in alleviating membrane fouling. However, the aeration rate had little effect on the removal efficiency of Sb(V), while playing an important role in the development of TMP. Both Sb(V) removal efficiency and TMP development were better under acidic conditions. Further research will be focused on the long-time filtration properties with different sludge discharge frequencies and in situ chemical cleaning with disinfection.

5. Conclusions

Inspired by the favorable characteristics of in situ flocs and UF membrane, we developed a novel process for Sb(V) removal. We found that the in situ flocs could be well suspended in the membrane tank with aeration from the bottom, and could thus be fully utilized. The integrated membrane process performed better in removing Sb(V) and less severe membrane fouling was induced, especially with Fe-based flocs. Continuous injection has great potential for removing Sb(V) owing to the freshness of the flocs. Aeration rate had little effect on the removal efficiency of Sb(V), while playing an important role in reducing membrane fouling, especially for the highest aeration rate.

Moreover, Fe-based flocs had higher positive charge and larger specific surface area under acidic conditions, resulting in stronger adsorption/rejection ability toward Sb(V). The activity of microorganisms was also inhibited, leading to alleviation of the development of TMP during filtration. In addition, the introduction of Fe-based flocs had little effect on the iron concentration, turbidity and chromaticity in the effluent.

Specifically, this study highlights the advantages of in situ flocs combined with an UF membrane in removing Sb(V), including stronger adsorption ability, lower cost and better rejection efficiency than other comparable techniques. This innovative separation method, initially developed for separation of Sb(V) in aqueous solution, has potential for broader applications in water treatment.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2017.05.022>.

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