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Enhanced antimony(V) removal using synergistic effects of Fe hydrolytic flocs and ultrafiltration membrane with sludge discharge evaluation

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ABSTRACT

The integration of adsorbents with ultrafiltration (UF) membranes is a promising method for alleviating membrane fouling and reducing land use. However, a number of problems have become apparent concerning the granular adsorbents used currently, such as high running cost, high chance of causing membrane surface damage, low in situ chemical cleaning efficiency, etc. Herein, to overcome these disadvantages, loose in situ hydrolyzed flocs were directly injected into the membrane tank, providing strong adsorption ability at low cost. To test the feasibility of this method, the heavy metal pollutant antimony (Sb (V)) in a water plant was chosen at a test case, which is similar to arsenic and difficult to remove. We found that Fe-based flocs integrated with an UF membrane showed a large potential advantage in removing Sb(V), even after running for 110 days. We demonstrated that the observed slow transmembrane pressure development could be ascribed to the loose floc cake layer formed, even though some extracellular polymeric substances were induced during operation. We also found that the floc cake layer was easily removed by washing with feed water or dissolved by in situ chemical cleaning under strongly acidic conditions, and many primary membrane pores were clearly observed. In addition, a relative long sludge discharge interval was feasible for this technology and the effluent quality was good, including the turbidity, chromaticity and iron concentration. Based on the excellent performance, these flocs integrated with UF membranes indeed show potential for application in water treatment.

1. Introduction

Drinking water treatment technology has been significantly developed in the past few decades, mainly due to developments in materials science (Ajmani et al., 2012). The risks of water quality are of great concern because of the serious water pollution due to increased industrialization, and new methods of guaranteeing water quality are urgently needed. Here, most studies have focused on the application of new materials, aiming to improve the traditional water treatment process with novel technologies. As a result, membrane technology has been widely used in water treatment (Huang et al., 2009; Drioli et al., 2011), and has even been predicted to become the main water treatment technology in the next few decades (Shannon et al., 2008).

However, researchers have demonstrated that membrane fouling is inevitable as a function of time due to the accumulated pollutants in membrane pores or on the membrane surface (Wang and Tarabara, 2008; Wu et al., 2011). To alleviate membrane fouling, different pretreatment technologies have been investigated to combine coagulation/adsorption and membrane filtration: pre-adsorption, direct-filtration and integrated filtration. Owing to the better membrane performance and smaller land use, more studies have been focused on integrated filtration in recent years (Kim et al., 2010; Cai and Benjamin, 2011; Zhang et al., 2016).

Up to now, various kinds of adsorbents have been used in the integrated filtration process to test their antifouling properties, such as heated iron oxide particles (Zhang et al., 2003), heated aluminum oxide particles (Kim et al., 2008), carbon nanotubes

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(Ajmani et al., 2012), powdered activated carbon (Cai et al., 2013), nanoscale zerovalent iron (Ma et al., 2015), etc. Although these granular adsorbents showed good performance, many problems were found during filtration, including relatively high operation cost, high chance of causing membrane surface damage due to shearing force, and low in situ chemical cleaning efficiency due to the dense cake layer formed by extracellular polymeric substances (EPS). It is known that inexpensive aluminum salts and iron salts are widely used in water treatment, whose flocs exert little shearing force on membranes. Flocs formed in situ, which maintain the adsorption sites as much as possible, were found to have stronger adsorption ability than pre-made adsorbents (Liu et al., 2011; He et al., 2015). To overcome the abovementioned problems, in situ prepared flocs were directly injected into the membrane tank in the current research, which were fully suspended in the membrane tank by aeration from the bottom.

In addition, the sludge discharge interval is one of the main running conditions, which is also crucial to UF membrane fouling (Ozdemir and Yenigun, 2013). It has been reported that sludge discharge could benefit different reversible and irreversible fouling behaviors because of the various compositions of retentate solution in the membrane tank (Bai et al., 2013; Yu et al., 2015). For the water plant, a longer sludge discharge interval not only means a higher water production rate, but also means a smaller amount of sludge produced and lower running cost. However, little is known about the effect of sludge discharge frequency on the integrated membrane process. Furthermore, most research has been focused on the behavior of organic pollutants during membrane filtration (Abdelrasoul et al., 2013; Tabatabai et al., 2014; Meng et al., 2015), while fewer studies have paid attention to the removal of smaller molecular weight (MW) organic matter, especially heavy metals (Barakat and Schmidt, 2010).

Here, to fully investigate this integrated membrane process, antimony (Sb) was chosen, which is similar to arsenic and is also difficult to remove (He et al., 2015). It has caused great concern due to its potential toxicity and carcinogenicity towards humans after long-time exposure (Wilson et al., 2010). The maximum contaminant level (MCL) in drinking water for Sb is 5 μg/L in the USA and China (Filella et al., 2002a, 2002b; Xu et al., 2011). 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 (Filella and May 2005; He et al., 2015).

The current test was carried out in a drinking water plant in the province of Hunan, located in central China (N: 27.7°; E: 111.2°). The concentration of Sb is relatively high in the surface water of the local area owing to mining, and even in the effluent of the water plant. Fe flocs hydrolyzed in situ were used in this study due to the strong adsorption affinity toward Sb of iron salts, especially under acidic conditions (Leuz et al., 2006; He et al., 2015). To understand the membrane behavior in detail, the effect of sludge discharge frequency was evaluated. Some factors responsible for the membrane performance were also investigated, such as the running time, the in situ chemical cleaning efficiency, etc.

2. Materials and methods

2.1. Characteristics of feed water

Table 1 presents the specific characteristics of the feed water. The main species of antimony in the effluent was Sb(V) because of the dissolved oxygen in the surface water. Owing to the low removal efficiency of traditional water treatment, the concentration of Sb(V) in effluent was higher than the MCL before upgrading the plant. To enhance the removal efficiency toward Sb(V), the final solution pH in the membrane tank was maintained at 6 with 1 M HCl by using a peristaltic pump, and no additional disinfection was used during the experiment.

Table 1
The characteristics of feed water.

Parameters	Feed water
Water temperature (°C)	8.9–28.5
pH	7.3–7.9
Concentration of Sb (V, μg/L)	4.1–13.7
Turbidity (NTU)	0.2–2.1
Chromaticity	1.0–8.0
Residual chlorine (mg/L)	0.3–0.9
Total organic matter (TOC, mg/L)	0.5–3.8
UV_{254} (cm^{-1})	0.01–0.16

2.2. Preparation of flocs

All chemical reagents were analytical grade except when specified, and $FeCl_3 \cdot 6H_2O$ (Sinopharm chemical regent Beijing Co., Ltd, China) was used. The coagulants were dissolved in 400 mL deionized (DI) water each time and the corresponding flocs were prepared by adjusting the solution pH to 6 with 1 M NaOH. To prevent a high concentration of iron in effluent, the prepared flocs were washed by DI water three times before using. The concentration of Fe-based flocs was almost equal to the concentration of Fe-based coagulants, because Fe hydrolytic flocs are the dominant iron species around neutral pH conditions (Eilbeck and Mattack, 1987).

2.3. Adsorption kinetics of Sb(V) on flocs and EPS

Deionized (DI) water and potassium antimony tetrahydrate ($KSbO_3 \cdot 3H_2O$) were used for all the adsorption kinetic experiments. In order to obtain a proper dose of flocs during the test afterward, 20 μg/L Sb(V) was chosen according to the highest concentration observed (18.9 ± 0.9 μg/L) in the effluent. The prepared Sb(V) solution was added into a 1 L beaker with magnetic agitation (100 rpm) in the presence of 0.01 M NaCl to provide background ionic strength at pH 6. The prepared flocs were dosed with the concentrations of 1, 2, 5, 10, 15 mg/L as Fe.

To fully understand the adsorption kinetics of Sb(V) on EPS, bovine serum albumin (BSA) and polysaccharide (SA) were used to simulate EPS (Coseza et al., 2013). The adsorption kinetic experiment procedures were similar to those used for the adsorption kinetics of Sb(V) on flocs. The BSA, SA or their 1:1 mixture were dosed with the concentrations of 0.5, 1, 5, 10, 20, 50, 100 mg/L. All adsorption kinetic experiments were conducted at room temperature.

2.4. Filtration process

Fig. S1 shows the specific schematic illustration of the integrated membrane process. Feed water was continuously fed into the membrane tank, in which a hollow-fiber membrane module (polyvinylidene fluoride, Litree, China) was immersed. The membrane module was composed of 30 membranes, each one being 53 cm long. The inner diameter of the membrane tank was 64 mm, and the height was 800 mm. The effluent from the membrane was pumped by a peristaltic pump (1 L/h), which was operated in a cycle of 30 min filtration and 1 min backwashing (2 L/h). A ceramic aerator (diameter: 40 mm) was placed in the bottom, allowing flocs to be suspended in the membrane tank. The flocs were freshly prepared before injecting to maintain their activity (Chen et al., 2015).