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GRAPHICAL ABSTRACT

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- Figure 1 illustrates the adsorption of alginate molecules onto iron and alum flocs under various conditions. The legend identifies the components: red circles represent alginate molecules, tan shapes represent iron flocs, and grey star-like shapes represent alum flocs. The diagrams are arranged in two rows: the top row for iron flocs and the bottom row for alum flocs. Each row contains five diagrams corresponding to different experimental conditions: Low dose of iron/alum, High dose of iron/alum, High dose of iron/alum + Sodium, High dose of iron/alum + Calcium, and High dose of iron/alum + Sodium + Calcium. The diagrams show that the adsorption of alginate molecules is most pronounced in the 'High dose of iron/alum + Calcium' condition and least in the 'Low dose' condition.

ABSTRACT

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[1]. However, membrane fouling is the main limitation for a broader application of membrane technology [2,3]. Polysaccharides, which dominate the extra-cellular polymeric substances (EPS), are produced by microorganisms [4]. In comparison with the fouling behavior of humic acids or proteins, polysaccharides could cause much more serious flux decline in natural waters due to its wide molecular weight distribution [5,6]. Alginate is a hydrophilic polysaccharide and has been extensively studied as a model by many researchers [1,7,8]. It consists of a linear

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copolymer with varying proportions of 1,4-linked β -D-mannuronic acid, C-5 epimer and α -L-guluronic acid [4].

The physical properties of alginate are influenced by ionic strength (NaCl) [9]. At higher ionic strength, the electric double layer around the negatively charged alginate molecules was compressed [10]. As a result, alginate molecules become more coiled due to the reduced electrostatic repulsion [11,12]. Up to now, many studies have reported that alginate could accelerate membrane fouling at high ionic strength, owing to more chances of alginate molecules depositing onto the membrane surface even blocking the membrane pores [13,14].

In addition to decreasing the particle size of alginate molecules in the presence of high ionic strength, calcium ions are well known as “bridging agents” with alginate molecules for many years, where calcium ions bind preferentially with carboxylic functional groups and the adjacent alginate molecules are linked [15,16]. It has been found that membrane flux can be improved by increasing the concentration of calcium ions, which is possibly due to the larger particle size (resulting in a lower resistance) or a highly permeable alginate gel layer induced by calcium ions [17–19].

Coagulation is the most common process to remove turbidity and natural organic matter (NOM) in drinking or waste water treatment, and iron/alum salts are widely used as coagulants for pretreatment, which is advantageous on improving permeate flux [20–22]. The extent of improvement on the performance of membrane filtration is greatly dependent on the properties of coagulants, dosages, pH, etc. [23,24]. Barbot et al. [24] presented that alum species played an important role on the characteristics of coagulant flocs, which could influence the behavior of the downstream membrane filtration. Yu et al. [25] found that a much lower trans-membrane pressure (TMP) was caused by alum salt compared to that induced by iron (III) salt in the UF system, and Konieczny et al. [26] demonstrated that membrane fouling was much more reduced by $\text{Al}_2(\text{SO}_4)_3$ than that by $\text{Fe}_2(\text{SO}_4)_3$ or FeCl_3 in the “in-line” coagulation-ultrafiltration hybrid process. According to Qiao et al. [27], FeCl_3 was better for membrane fouling in a large-scale UF process in comparison with polyaluminum chloride (PACl).

Herein, in order to understand the different performance of UF membrane caused by alginate in the presence of iron/alum salt, iron (III) chloride hexahydrate (iron salt) or aluminum chloride (alum salt) was added into the feed. To further probe into the fouling mechanism, sodium chloride, calcium chloride and their combinations were added into the solution in the presence of iron salt or alum salt. The corresponding membrane flux decline and the alginate concentration after filtration were systematically investigated. In addition, a schematic model was proposed based on the findings from this study to better illustrate the fouling phenomena.

2. Experimental methods

2.1. Materials

All chemicals were analytical reagent except specific illustration. Deionized (DI, Millipore Milli-Q) water was used to prepare stock solutions. Sodium alginate, sodium chloride, iron (III) chloride hexahydrate and aluminum chloride were obtained from Sinopharm Chemical Regent Co., Ltd (China). A stock solution of sodium alginate was prepared at a concentration of 10 g/L using DI water. Sodium alginate working solution was used within one week to prevent the growth of microgram. The solution was stored in prewashed glass bottle in the dark at 4 °C and was brought to room temperature immediately prior to use.

2.2. Ultrafiltration experiments

The polyvinylidene fluoride (PVDF, Ande membrane separation technology & engineering (Beijing) Co., Ltd, China) flat sheet UF membrane (100 kDa) was used in all experiments. Fresh membranes were

placed in DI water for 24 h to remove impurities. All membranes were filtrated with 300 ml DI water first in order to keep the membrane flux constant. The stirred cell (Millipore, Amicon 8400) was driven by nitrogen gas and the pressure was maintained stable (0.1 MPa) during filtration. J/J_0 as a function of time was used for the flux variation from the stirred cell experiments, where J_0 was the initial membrane flux.

During the test, pH of the final solution was maintained at 7.0 by prior addition of a predetermined amount of 0.1 M/1 M NaOH. To understand the membrane fouling under different conditions, sodium chloride, calcium chloride and their combinations were added. Then NaHCO_3 and iron/alum salt stock was diluted into the feed. Afterward 10 mg/L SA was formed by adding the corresponding stock solution to working solution. Rapid mixing speed of 200 rpm was maintained for 1 min and slow mixing speed of 50 rpm was maintained for another 14 min to allow floc growth. All experiments were conducted at room temperature.

2.3. Jar test

A 0.5 L beaker with a flocculator device (ZR4-2, Zhongrun, China) was used for the jar test, which can provide comparative information. The selected dose of iron salt or alum salt (1.2 mM) was added with solution pH at 7.0. The stirring speed was simultaneously increased to 200 rpm. The speed was maintained for 1 min, and then reduced to 50 rpm for 14 min to allow floc growth to occur. Dynamic floc size and fractal dimension (D_f) were measured by a laser diffraction instrument (Mastersizer 2000, Malvern, UK) as the coagulation and flocculation processes proceeded. Floc size measurement was taken every 30 s and logged by computer while fractal dimension was measured by small-angle light scattering. Detailed method has been described extensively by other studies [28,29].

2.4. Analytical measurements

Membrane flux was recorded by data logger. pH was tested by Orion pH Benchtop while zeta potential was measured by Nano particle sizing & Zeta potential analyzer (Delsa Nano C, Beckman Coulter Ltd, USA). Membrane pore size was analyzed by IB-FT, GmbH (POROLUX 1000, Germany). Images of the surface of the fouled membrane were obtained using scanning electron microscopy (SEM) which was carried out with a JSM-7401F Field Emission equipped with a cold Field Emission Gun in SEI mode at 3 kV accelerating voltage (JEOL Ltd., Tokyo, Japan). Total polysaccharide concentration was measured by the phenol sulfuric acid method [30].

3. Results

3.1. In the presence of iron/alum salt

To investigate the flux decline caused by alginate coagulated with iron/alum salt, different doses of iron/alum salt were added into the feed. The flux–decline curves obtained during each fouling run are compared with the alginate concentration after filtration in Fig. 1. A much lower flux decline caused by alginate was observed in the presence of 1.2 mM iron salt or alum salt compared to that in the presence of 0.1 mM salt. Similar trend of the concentration of alginate after filtration was also found (Fig. 1b). The concentration of alginate after filtration was 1.83 ± 0.19 mg/L in the absence of iron salt or alum salt, while that was decreased with increasing the dose of coagulants in the feed, especially for the 1.2 mM alum salt (alginate concentration after filtration was 0.45 ± 0.07 mg/L).

Many studies show that pore blockage of UF membrane plays an important role in the case of fouling by polysaccharides [1,31]. It is reported that the diameter of alginate molecule is in the range of 50–137 nm [32,33], while the average pore diameter of the UF membrane used in our experiment was 43.8 ± 5.3 nm. Thus, adsorption and pore blocking

Fig. 1. Effect of different doses of iron/alum salt on (a) flux decline during fouling and (b) concentration of alginate after filtration. Other experimental conditions during the fouling runs: pH = 7.0.

were occurred during the filtration, leading to severe membrane fouling in the absence of coagulants (final $J/J_0 = 0.27$). When the dose of iron salt or alum salt was low (0.1 mM), the chance of alginate molecules depositing onto the membrane surface was still large because most alginate molecules could not be “captured” by the iron flocs or alum flocs. As a result, the concentration of alginate after filtration was only a little lower than that in the absence of iron/alum salt. When high dose of coagulant was applied (1.2 mM), more alginate molecules could be adsorbed or “trapped” by the iron/alum flocs. Thus, membrane flux was increased and the corresponding concentration of alginate after filtration was low (Fig. 1b). It was also observed that alum salt behaved better than iron salt during the filtration.

Fig. 2 shows the surface morphology of membrane after the filtration of 10 mg/L alginate coagulated with 1.2 mM iron salt or 1.2 mM alum salt. It was clearly shown that the cake layer formed by iron salt coagulating with alginate was less compact compared with that formed by alum salt, indicating that more chances of non-captured alginate molecules getting to the membrane surface and passing through the membrane.

3.2. In the presence of iron/alum salt with ionic strength

Owning to the dramatic variation of the flux decline caused by alginate in the absence/presence of 1.2 mM iron salt or alum salt (Fig. 1a), the dose of 1.2 mM was chosen. The influence of ionic strength (calculated as NaCl, the same below) on the flux–decline behavior during alginate fouling in the presence of 1.2 mM iron/alum salt and the corresponding concentration of alginate after filtration are presented in Fig. 3. It was shown that the flux decline as well as alginate

concentration after filtration became more substantial with increasing ionic strength.

These results can be ascribed to the following reasons. Firstly, the electric double layer around negatively charged alginate molecules was compressed at higher ionic strength, resulting in the decreased electrostatic repulsion between alginate molecules and membrane surface [6,11]. Secondly, alginate molecules became more coiled at higher ionic strength because of the reduced interchain electrostatic repulsion, reducing the size of the molecules in solution [12]. Thus, more alginate molecules could not be “captured” by the 1.2 mM iron flocs or alum flocs. It was easier for the coiled alginate molecules getting to the membrane surface even blocking the membrane pores. In contrast, the relatively strong electrostatic repulsion between alginate molecules and the membrane surface prevented the alginate molecules getting to the membrane surface and a lower concentration of alginate after filtration was found. Similar trends of accelerating membrane fouling by increasing ionic strength have been observed in other studies [9,11]. They found that the membrane flux decline was increased with increasing ionic strength when there was alginate alone even when there were humic acids alone. In addition, the membrane flux decline caused by alginate coagulated with 1.2 mM alum salt was still lower than that coagulated with 1.2 mM iron salt in the presence of ionic strength.

3.3. In the presence of iron/alum salt with calcium ions

To investigate the flux decline caused by alginate coagulated with 1.2 mM iron/alum salts in the presence of calcium ions, different doses of calcium ions were added into the feed. The permeate flux behavior during fouling and the corresponding measured concentration of

Fig. 2. Images of the fouled membrane surface after filtration: (a) membrane fouled by alginate in the presence of iron salt and (b) membrane fouled by alginate in the presence of alum salt. Experimental conditions during the fouling runs: alginate = 10 mg/L, iron salt = 1.2 mM, alum salt = 1.2 mM and pH = 7.0.

Fig. 3. Effect of ionic strength in the presence of iron/alum salt on (a) flux decline during fouling and (b) concentration of alginate after filtration. Other experimental conditions during the fouling runs: alginate = 10 mg/L and pH = 7.0.

alginate after filtration are presented in Fig. 4. The results showed that the membrane flux caused by alginate coagulated with 1.2 mM iron/alum salt in the presence of calcium ions was precipitously increased, especially when coagulated with 1.2 mM alum salt. For the 1.2 mM iron salt, the final J/J_0 caused by alginate in the presence of 0.1 mM Ca^{2+} was increased from 0.29 (alginate alone) to 0.46, while that caused by alginate in the presence of 1 mM Ca^{2+} was increased to 0.52. For the 1.2 mM alum salt, the final J/J_0 caused by alginate in the presence of 0.1 mM Ca^{2+} was increased from 0.29 (alginate alone) to 0.70, while that caused by alginate in the presence of 1 mM Ca^{2+} was increased to 0.75. Similar trend was found about the concentration of alginate after filtration (Fig. 4b).

Lee et al. [8,12] demonstrated that calcium ions could bind with carboxylic groups, which could form “bridges” between adjacent alginate molecules. Listiari et al. [17] showed that the average particle diameter of alginate molecules was increased in the presence of calcium ions. Thus, more alginate molecules could be “captured” by the high dose of iron flocs or alum flocs during coagulation and the chance of alginate molecules getting to the membrane surface was decreased dramatically. As a result, membrane flux was significantly improved and the concentration of alginate after filtration was also decreased. Although calcium ions played an important role on the membrane flux in the presence

of iron/alum salts, alum salt was still performed much better than that of iron salt.

3.4. In the presence of iron/alum salt with the combination of ionic strength (NaCl) and calcium ions

In view of the foregoing observations it was evident that ionic strength could accelerate membrane fouling while calcium ions could mitigate membrane fouling in the presence of iron/alum salts. In order to look further into the fouling behavior caused by alginate coagulated with 1.2 mM iron/alum salts when there was the combination of ionic strength (NaCl) and calcium ions, different ratios of sodium ions to calcium ions were added into the feed (Fig. 5). The results showed that the fouling was more serious with simultaneously increasing the concentration of sodium ions compared to that caused by alginate coagulated with 1.2 mM iron/alum salts in the presence of only 1 mM calcium ions (Fig. 4a). Similarly, the concentration of alginate after filtration was also increased (Fig. 4b).

It has been reported that there is a competition between monovalent and divalent cations for the binding sites on alginate molecules [20,34]. On one hand, alginate molecules became more coiled in the presence of high ionic strength, resulting in more chances of alginate molecules

Fig. 4. Effect of calcium ions in the presence of iron/alum salt on (a) flux decline during fouling and (b) concentration of alginate after filtration. Other experimental conditions during the fouling runs: alginate = 10 mg/L and pH = 7.0.

Fig. 5. Effect of the combination of ionic strength and calcium ions in the presence of iron/alum salt on (a) flux decline during fouling and (b) concentration of alginate after filtration. Other experimental conditions during the fouling runs: alginate = 10 mg/L and pH = 7.0.

depositing onto the membrane surface or blocking the membrane pores. On the other hand, calcium ions bound preferentially with carboxylic groups and formed “bridges” between adjacent alginate molecules, leading to the capture of more alginate molecules by iron/alum flocs. Therefore, the flux decline caused by alginate coagulated with 1.2 mM iron/alum salt in the presence of the combination of ionic strength and calcium ions was more serious than that caused by alginate coagulated with 1.2 mM iron/alum salt in the presence of calcium ions alone, while that was decreased compared to that caused by alginate coagulated with 1.2 mM iron/alum salt in the presence of ionic strength alone. In addition, fouling caused by alginate coagulated with 1.2 mM alum salt was still less serious than that coagulated with 1.2 mM iron salt. The concentration of alginate after filtration was correlated well with the flux decline (Fig. 5b).

4. Discussion

Wang and Tarabara [35] demonstrated that pore blocking could cause serious flux decline for the porous microfiltration and ultrafiltration membranes. To understand the fouling mechanism caused by alginate in the presence of iron salt or alum salt, iron chloride hexahydrate or aluminum chloride was added into the solution with/without ionic strength, calcium ions and their combinations. It was shown that alum salt behaved better than iron salt on improving membrane flux.

The diameter of alginate molecules (50 to 137 nm) was close to the average pore diameter of the UF membrane used (average pore diameter: 43.8 ± 5.3 nm). When there was low dose of iron/alum salt

(0.1 mM) in the feed, most alginate molecules could not be “captured” by the iron flocs or alum flocs. Thus, more alginate molecules still deposited onto the membrane surface and blocked membrane pores. However, more flocs formed gradually with increasing the dose of iron/alum salt, which could “capture” more alginate molecules. In comparison with the membrane flux decline caused by alginate coagulated with high dose of iron salt (1.2 mM), the membrane flux decline caused by alginate coagulated with high dose of alum salt (1.2 mM) was greatly decreased.

To understand the different membrane behavior caused by alginate in the presence of 1.2 mM iron/alum salt, the properties of flocs were investigated. It is well known that the characteristics of flocs play an important role on reducing membrane fouling, due to the fact that the properties of the cake layer were determined by the properties of flocs [25]. The formation of flocs and their fractal dimensions were investigated in the jar test (Fig. 6). A rapid rise in the median size (d_{50}) of both 1.2 mM iron flocs and 1.2 mM alum flocs were occurred during the rapid mixing/early flocculation period (<3 min), and the d_{50} values of both iron salt and alum salt reached a maximum value after approximately 6 min (Fig. 6a). The d_{50} of the alum flocs was smaller (548 ± 25 μm) than that of iron flocs (786 ± 39 μm). Furthermore, the fractal dimension of flocs formed by 1.2 mM alum salt ($D_f = 2.71 \pm 0.07$) was larger than that formed by 1.2 mM iron salt ($D_f = 2.48 \pm 0.03$), resulting in a more compact cake layer formed by alum flocs (Fig. 2). According to Listiarini et al., the cake formation resistance ($1.73 \times 10^{13} \text{ m}^{-1}$) caused by alginate in the presence of alum (30 mg/L, calculated as Al) was much lower than that in the absence of alum

Fig. 6. Comparison of iron/alum floc characteristics at pH = 7.0: (a) formation of flocs and (b) fractal dimension of flocs.

Fig. 7. Schematic diagram of the membrane fouling mechanism caused by alginate under different conditions at pH 7.0.

($6.28 \times 10^{13} \text{ m}^{-1}$), which was conducted in nanofiltration [17]. As a result, membrane flux was significantly improved by high dose of alum salt.

In addition, the zeta potential of 1.2 mM iron flocs was $2.32 \pm 0.57 \text{ mV}$ while that was $7.59 \pm 1.15 \text{ mV}$ of 1.2 mM alum flocs. After coagulating with the 10 mg/L alginate, the zeta potential of 1.2 mM alum flocs was $-16.58 \pm 1.13 \text{ mV}$, and that was $-20.44 \pm 2.21 \text{ mV}$ for the 1.2 mM iron flocs. The zeta potential indicated that alum flocs could adsorb a little more alginate molecules during flocculation compared to that of iron flocs. Furthermore, the sedimentation rate of the 1.2 mM iron flocs was much faster than that of the 1.2 mM alum flocs after coagulation. Therefore, the chance of alginate molecules depositing onto the membrane surface or blocking into the membrane pores was much less in the presence of 1.2 mM alum salt than that in the presence of 1.2 mM iron salt. In other words, membrane flux decline caused by alginate coagulated with alum salt was significantly decreased compared to that coagulated with iron salt.

Lee et al. [9] showed that alginate molecules could become more coiled at high ionic strength due to the reduced interchain electrostatic repulsion. Thus, the flux decline caused by alginate in the presence of iron/alum salt with ionic strength was more serious than that without ionic strength because the chance of alginate molecules blocking the membrane pores was larger, especially for the less compact iron flocs. Lee et al. [6] and Nataraj et al. [8] demonstrated that calcium ions could bind with carboxylic groups, forming “bridges” between adjacent alginate molecules. As a result, when calcium ions and high dose of iron/alum salt were presented together in the solution, membrane flux decline was significantly decreased, of which a more compressible layer was formed on the membrane surface after “capturing” most alginate molecules during the filtration, especially for alum salt [17]. In addition, this formed cake layer reduced the chance of alginate molecules depositing onto the membrane surface or blocking into the membrane pores, leading to the membrane fouling reduced. When iron/alum flocs, ionic strength and calcium ions were all in the system, the flux decline caused by alginate under this condition was greater than that in the presence of iron/alum flocs and calcium ions, while smaller than that in the presence of the combination of iron/alum flocs and ionic strength. However, owing to the smaller average diameter, larger fractal dimension, and stronger adsorption capacity of alum flocs, the membrane fouling caused by alginate was less serious in the presence of alum flocs than that in the presence of iron flocs, whether ionic strength, calcium ions and their combinations were in the system or not. Detailed fouling mechanism was shown in Fig. 7.

5. Conclusions

Coagulation pre-treatment could enhance the performance of membrane filtration by decreasing the chance of pollutants getting to the membrane surface and blocking the membrane pores. Fouling caused by alginate coagulated with iron/alum salt on UF membrane was investigated with/without ionic strength, calcium ions and their combinations in the system. The overall findings of the study are as follows:

1. UF membrane fouling caused by alginate was significantly reduced only in the presence of high dose of iron/alum salt, due to most alginate molecules could still be adsorbed onto the membrane surface or blocked into the membrane pores with low dose of iron/alum salt in the solution.
2. Membrane flux decline was increased by increasing ionic strength in the presence of high dose of iron/alum salt while that was significantly decreased in the combination of calcium ions and high dose of iron/alum salt. When ionic strength and calcium ions were presented together with high dose of iron/alum salt, the flux decline caused by alginate was lower than that with only ionic strength and high dose of iron/alum salt, but higher than that with only calcium ions and high dose of iron/alum salt.
3. Alum salt behaved better than iron salt with/without ionic strength, calcium ions, and their combinations in the feed. The measured alginate concentration after filtration was correlated well with the flux decline. Membrane flux decline was much more decreased at coagulation conditions, which resulted in a lower concentration of alginate after filtration, especially in the combination of calcium ions and alum salt.

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