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Improving pollutant removal and membrane performance via pre-treatment with a specific formulation of polysilicato-iron

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ABSTRACT

The effectiveness of a specific formulation of polysilicato-iron coagulant, designated as AS1, in removing pollutants from raw water and in mitigating membrane fouling during subsequent microfiltration tests has been investigated using two water sources from South Australia (Happy Valley and Myponga). The results showed that for both water sources, AS1 was as effective as ferric chloride in removing organic matter (60–65% removal), but better than alum (45–55% removal). AS1 pretreatments produced large flocs, which settled more efficiently, resulting in pretreated waters with much lower turbidity (0.12–0.15 NTU), compared to ferric chloride and alum pretreatments (0.35–2.53 NTU). The turbidity of alum-pretreated waters had values similar or even higher than those of corresponding raw waters. Under the current experimental conditions, ferric chloride and alum pretreatments of both water sources gave rise to significant decreases in flux during microfiltration. This is attributed to the small flocs generated by these pretreatments which could deposit on the membrane surface and/or penetrate and block the membrane pores. In contrast, AS1 pretreatments resulted in a relative flux of unity for Happy Valley water, and of 0.8 for Myponga water, whereas the corresponding ferric chloride and alum pretreatments resulted in lower relative flux values ranging from 0.4 to 0.7. The better performance of AS1 in controlling membrane fouling is attributed in part to the much diminished effects of the pore blocking mechanism.

Keywords: Microfiltration; Water treatment; Membrane; Fouling; Coagulant; Polysilicato-iron

1. Introduction

A major problem in membrane filtration processes in water treatment plants is membrane fouling, which causes deterioration of both the quantity and quality of treated water, reduces membrane life and consequently results in higher treatment costs [1–4]. A common method to mitigate membrane fouling is coagulation which aims to reduce pollutants in raw water prior to filtration [5–7]. Aluminium-based or iron-based coagulants are often used, but these conventional coagulants preferentially remove hydrophobic rather than hydrophilic substances [8–10], charged rather than neutral substances [11,12] and larger-sized rather than smaller-sized substances [8,13]. The selectivity of pollutant removal by conventional coagulants is a major factor limiting their effectiveness. As well, these coagulants generate small-sized flocs that may readily penetrate and block the membrane pores. Increasing coagulant dose to improve the removal of pollutants may result in an increase in the amount of the small flocs, leading to more pore blocking and increased membrane fouling [14].

In response to the need for better coagulants, CSIRO has developed specific formulations of polysilicato-iron coagulant for the treatment of raw water prior to membrane filtration processes. Essentially, the coagulation performance of polysilicato-iron is a combination

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of both the charge neutralisation property as exhibited by metal salt coagulants and the strong bridging properties arising from the higher chain length of polysilicic acid. The latter properties have the effect of strengthening the structure of flocs [15,16]. Our previous research has shown that the performance of polysilicato-iron coagulant in removing pollutants and in mitigating membrane fouling depends in part on the formulation of the polysilicato-iron and on the chemistry of the raw water [14].

The present study investigates the performance of a specific formulation of polysilicato-iron coagulant, designated as AS1, which was optimised for two different water sources from South Australia, Australia (Happy Valley and Myponga). The effectiveness of AS1 in removing pollutants from the raw waters and in mitigating membrane fouling during subsequent microfiltration tests is reported and compared with those of conventional aluminium sulphate (alum) and ferric chloride. Parameters used to assess the coagulating efficiencies include the removal of turbidity, total organic carbon (TOC) and dissolved organic carbon (DOC). Membrane performance was assessed using single hollow fibre hydrophilic membranes (PVDF-2) with nominal pore size of 0.1 µm in constant pressure filtration tests with periodic backwashing.

2. Experimental

2.1. Water sources

The water quality characteristics of Happy Valley and Myponga waters are summarised in Table 1. Compared to Happy Valley water, Myponga water had high values of TOC, DOC and turbidity.

2.2. Coagulants

Conventional coagulants aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were supplied by BDH Laboratory and Chem-Supply, respectively. The synthesis of AS1 was essentially similar to the method described previously [14]. In the present study, certain modifications of the synthesis method were adopted and the concentrations of Fe and Si were optimised and fixed at particular values to suit the chemistry of Myponga and Happy Valley waters.

Table 1
Characteristics of waters

Water	TOC (mg/l)	DOC (mg/l)	Turbidity (NTU)
Myponga	11.1	11.0	2.71
Happy Valley	5.1	5.1	0.91

2.3. Jar test

The standard jar tests were carried out using AS1, ferric chloride and alum. The pH of the water was maintained at pH 6 using sulphuric acid or sodium hydroxide. After adding appropriate coagulant dose to the water, the solution was flash mixed for 1 min at 190 rpm. The speed was then reduced to 60 rpm for 15 min, after which the treated water was left to settle for 15 min. After settling, the supernatant solution was collected for analysis of TOC, DOC and residual turbidity. The supernatant solution obtained after pretreatment with an optimal coagulant dose was selected for filtration experiments.

2.4. Turbidity and floc size

The turbidity of the waters was monitored using a HACH 2100N IS turbidimeter. To investigate the floc size, samples of the coagulated waters were taken at different settling times up to 15 min and filtered through a 0.2 µm filter paper (Gelman Sciences). The filtrate was then observed using an Olympus BHSM Metallographic Optical Microscope.

2.5. TOC and DOC analyse

TOC and DOC were measured using an O/I Analytical Aurora Model 1030 Wet Oxidation TOC analyser with an autosampler. Prior to analysis for DOC, each sample was filtered through a 0.45 µm polycarbonate membrane filter (Poretics Corporation).

2.6. Membrane filtration

Filtration experiments for water samples pretreated with optimal coagulant doses were carried out in dead-end mode using single hollow fibre hydrophilic polyvinylidene fluoride (PVDF-2) membranes (Memcor). The membrane characteristics are given in Table 2.

The water was pumped from the outside to the inside of the hollow fibres at a constant pressure of 0.5 bar. The filtrate was weighed on a balance and a data acquisition system was used to record the filtrate mass with time and the ambient air temperature. Liquid backwashing of the membrane was achieved via pressurised water and a series of valves. The data acquisition and control system were used to control the filtration pressure and the backwash sequence. The backwashing regime was a 10 s liquid backwash (0.8 bar)

Table 2
Properties of the PVDF-2 membrane

Fibre dimensions		Surface area (m^2)	Nominal pore size (µm)	Clean Water Flux (l/h.bar.m^2)	Polarity
Inner diameter (mm)	Outer diameter (mm)				
0.39	0.65	1.225×10^{-3}	0.1	1700 ± 300	Hydrophilic

every 40 min. All results are expressed as relative flux (membrane flux at 20°C/flux with Milli-Q water at 20°C) versus filtrate mass.

3. Results and discussion

3.1. Coagulating efficiency

The results showed that the extent of TOC and DOC removal for each individual experiment was similar. Therefore, for brevity, only results for TOC are discussed. Figs. 1a and b compare the TOC removal for Happy Valley and Myponga waters, respectively, by different coagulant pretreatments.

It can be seen that the TOC removal for Myponga water was more effective compared to that for Happy Valley water. In particular, the maximum levels of TOC removed by AS1 and ferric chloride for Myponga water were about 65%, whereas those for Happy Valley water were about 60%. The difference in TOC removal was more pronounced in the case of alum pretreatment with 55% removal for Myponga water and 45% removal for Happy Valley water. Also, TOC removal efficiencies of AS1 and ferric chloride were similar for both water sources, and were higher than those of alum. The difference in TOC removal between AS1/ferric chloride and alum was about 15% for Happy Valley water and 10% for Myponga water. In addition, a dose of 526 µmol/l Fe^{3+} or Al^{3+} was required to achieve optimal TOC removal for Myponga water, whereas a lesser dose of 321 µmol/l Fe^{3+} or Al^{3+} was needed for Happy Valley water. The higher coagulant dose for Myponga water is likely because this water had higher TOC content.

Table 3 shows the turbidity values of the supernatant solution collected following the coagulant pretreatments at the optimal doses. For Happy Valley water, the AS1 pretreatment was the most effective in removing turbidity with a residual turbidity of the pretreated water of 0.12 NTU, whereas the turbidity of the water pretreated with ferric chloride and alum had values of 0.35 and 1.69 NTU, respectively. It is noted that the turbidity of the alum pretreated water was higher than that of the raw water. Similar effectiveness of AS1 in removing turbidity was also observed for raw Myponga water. In particular, AS1 was the most effective in removing turbidity from Myponga water with a residual turbidity of 0.15 NTU, whereas the corresponding ferric chloride and alum pretreatments resulted in turbidity values of 1.92 and 2.53 NTU, respectively.

The superior performance of AS1 in removing turbidity is most likely due to rapid settling of flocs generated by the AS1 pretreatment. Figs. 2 and 3 show

Table 3
Turbidity (NTU) of raw and coagulant pretreated water

Water	Raw	AS1	Ferric chloride	Alum
Happy Valley	0.91	0.12	0.35	1.69
Myponga	2.71	0.15	1.92	2.53

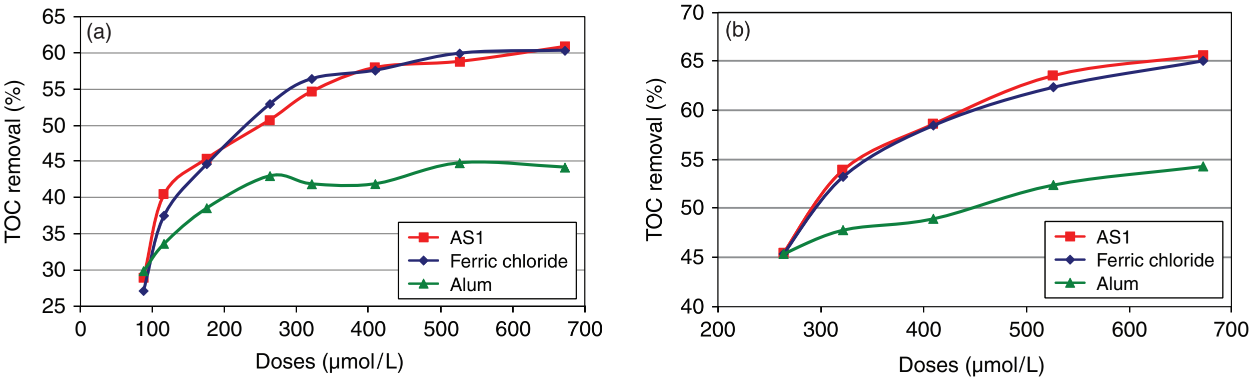

Fig. 1. TOC removal (%) for Happy Valley (a) and Myponga (b) waters by different coagulant pretreatments.

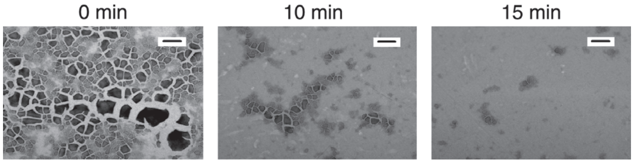

Fig. 2. Optical images of AS1 flocs as a function of settling time after pretreatment of raw Myponga water with AS1 (bar = 60 μm).

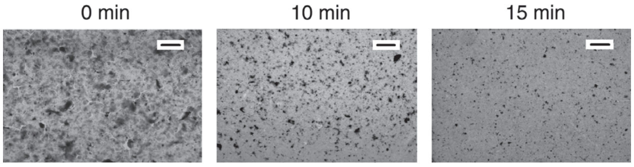

Fig. 3. Optical images of alum flocs as a function of settling time after pretreatment of raw Myponga water with alum (bar = 60 μm).

optical images of the flocs remaining in the supernatant solution following different settling times for Myponga water pretreated with AS1 and alum, respectively, at the optimal doses.

It can be seen from these Figures that AS1 flocs were much larger than alum flocs. This is most likely due to the strong bridging properties associated with polysilicic acid. As settling time increased, the flocs remaining in the supernatant solution decreased in size and in amount, presumably because more of larger flocs have settled. After 15 min, at which time the supernatant solution was collected as feed for subsequent filtration experiments, most AS1 flocs ranged between 10 and 30 μm, whereas alum flocs were mostly in the range 0.1–1 μm or less.

3.2. Membrane filtration

Fig. 4 shows the relative flux through the PVDF-2 membrane as a function of filtrate mass for Happy Valley water pretreated with various coagulants at the optimal doses. Also included in Fig. 4 is the relative flux of the raw water for purpose of comparison. It can be seen that the AS1 pretreatment resulted in better membrane performance compared to ferric chloride and alum. In particular, a relative flux of unity was achieved for the water pretreated with AS1, whereas the pretreatments with ferric chloride and alum gave rise to relative flux values even worse than those for the raw water, especially at higher throughputs.

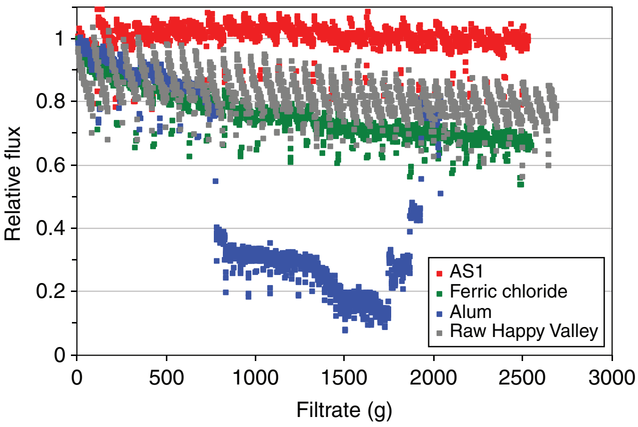

Fig. 4. Relative flux as a function of filtrate mass for raw and coagulant treated Happy Valley water.

A possibility for the dramatic decrease in the flux of alum pretreated water at about 0.8 kg throughput is that large particulate matter remaining in the water could settle in the tubing of the filtration apparatus and block the flow of water. Alternatively, this flux decline represents real membrane fouling caused by the small flocs produced by the alum pretreatment. To investigate these possibilities, second and third filtration runs were carried out for the alum pretreated water using the filtrate collected at the end of the first run as the feed for the second run, and the filtrate of the second run as the feed for the third run. A fresh membrane was used in each run.

The membrane performance for these consecutive runs is shown in Fig. 5. Although less dramatic compared to the first run, significant drops in the flux for the second and third runs at about 0.8 and 0.5 kg throughput, respectively, were also observed. These results strongly suggest that large particulate matter was not responsible for the flux decline. This is consistent with the small size of alum flocs (0.1–1 μm or less) as observed by optical microscopy. It is possible that the small flocs generated by the alum pretreatment could

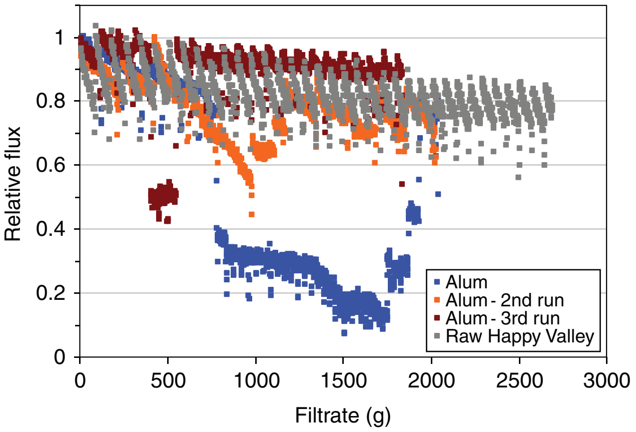

Fig. 5. Relative flux as a function of filtrate mass for consecutive filtration runs for alum pretreated Happy Valley water.

deposit on the membrane surface and/or penetrate and block the membrane pores. The pore blocking mechanism could have a major role in causing the rapid flux decline. These flocs were partly removed during subsequent backwashing operations, and higher flux values were obtained as a result. The progressive decrease in the fouling effects of small flocs for the second and third runs is likely due to lesser amounts of flocs present in the respective feeds following the consecutive runs.

Although the membrane performance of the ferric chloride pretreated water was better compared to the alum pretreated water, it was worse than that of the raw water, especially at higher throughputs. Presumably, the flocs generated by the ferric chloride pretreatment could result in fouling effects similar to those discussed for the alum case and thus contribute to the high fouling potential of the pretreated water. On the contrary, the relative flux of unity in the case of AS1 pretreatment indicates that AS1 flocs did not have the adverse fouling effects as suggested for alum and ferric chloride flocs. Indeed, AS1 pretreatment produced quite large flocs, which settled more efficiently as observed by microscopy, resulting in pretreated water with much lower turbidity compared to alum and ferric chloride pretreatments. Pretreatment with AS1 may also cause beneficial changes in the pretreated water which reduce membrane fouling. In a previous study [14], we suggested that the carried-over AS1 may deposit on the membrane and act as a “protective layer”. The foulants would deposit on the top of this layer, rather than directly on the membrane surface. Both the deposited AS1 and foulants may then be effectively removed by backwashing, thus minimising the fouling effects.

Similar to the case of Happy Valley water, the AS1 pretreatment of Myponga water resulted in better membrane performance compared to the ferric chloride and alum pretreatments. As can be seen in Fig. 6, whilst all the flux curves show a decrease in flux with throughput, the flux of the AS1 pretreated water was always higher than those of ferric chloride and alum pretreated waters throughout the duration of the experiment.

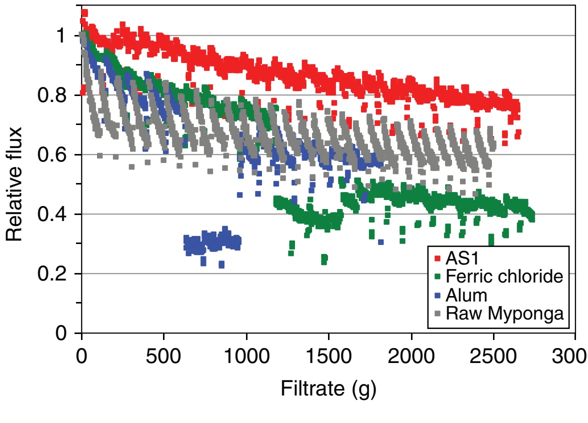

Fig. 6. Relative flux as a function of filtrate mass for raw and coagulant treated Myponga water.

Compared to the raw water, the flux values for ferric chloride and alum pretreated waters were better in the early phase, but they later experienced significant drops at about 1.2 and 0.7 kg throughput, respectively. Such drops in the flux values are similar to those observed for alum pretreated Happy Valley water, and are thus likely due to the small ferric chloride and alum flocs which could deposit on the membrane surface and/or enter and block the membrane pores. As discussed previously, the membrane pore blocking mechanism could have a major role in causing the rapid flux decline. Whilst subsequent backwashing operations could remove parts of these entrapped flocs and improve the fluxes, they were not very effective as suggested by the low flux values at higher throughputs.

4. Concluding remarks

In this study, the effectiveness of AS1, which comprises a specific formulation of polysilicato-iron, in removing pollutants from raw water and in mitigating membrane fouling during subsequent microfiltration tests has been investigated using Happy Valley and Myponga water sources. The results showed that for both water sources, AS1 was as effective as ferric chloride, but better than alum, in removing organic matter. In all cases, the removal of organic matter from Happy Valley water was more difficult than from Myponga water. AS1 pretreatments produced large flocs, which settled more efficiently, resulting in pretreated waters with much lower turbidity compared to ferric chloride and alum pretreatments. The turbidity of alum-pretreated waters had values similar or even higher than those of corresponding raw waters.

The AS1 pretreatments resulted in better membrane performance. Under the current experimental conditions, the ferric chloride and alum pretreatments of both water sources gave rise to significant drops in flux values during the filtration runs. This is most likely due to the small flocs generated by these pretreatments which could deposit on the membrane surface and/or penetrate and block the membrane pores (pore blocking mechanism). In contrast, the AS1 pretreatments resulted in a flux of unity for Happy Valley water, and highest flux for Myponga water compared to corresponding ferric chloride and alum pretreatments. The better performance of AS1 in controlling membrane fouling is attributed in part to the much diminished effects of the pore blocking mechanism. AS1 may also deposit on the membrane and act as a “protective layer”. The foulants would deposit on the top of this layer, rather than directly on the membrane surface. Both the deposited AS1 and foulants may then be effectively removed by backwashing, thus minimising the fouling effects.

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