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Effect of granular activated carbon filter on the subsequent flocculation in seawater treatment

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HIGHLIGHTS

- Effect of GAC filtration was evaluated through Jar test and membrane hybrid system.
- GAC filtration removed majority of hydrophobic and LMW organics from seawater.
- GAC filtration helped to reduce flocculant dose significantly (from 2–3 to 1 mg/L).
- The subsequent flocculation can remove biopolymers (not effectively removed by GAC).
- Combination of GAC filtration & flocculation can be a technical, economical solution.

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ABSTRACT

In this study, a granular activated carbon (GAC) filter was used to remove organics from seawater. The effect of GAC filtration on the subsequent treating of seawater by flocculation was evaluated through Jar test experiments and submerged membrane coagulation hybrid system (SMCHS). GAC filtration removed 70% of low molecular weight (LMW) neutrals and acids from seawater which helped to reduce the biofouling of membrane. GAC filtration also helped to reduce flocculant dose significantly. Relatively high doses of ferric chloride ($FeCl_3$ 3 mg/L) and poly-ferric sulfate (PFS 2 mg/L) were normally needed to obtain high organic removal when flocculation was used without the pretreatment of GAC filter adsorption. The use of GAC filtration prior to the application of SMCHS reduced the flocculant dosage to 1 mg/L to achieve the same removal. The subsequent flocculation by different flocculants such as ferric chloride ($FeCl_3$) and poly-ferric sulfate (PFS) was found to be able to remove biopolymers which were not effectively removed by the pretreatment (GAC filtration). The technical and cost analyses made showed that a combination of GAC filtration and flocculation with low flocculant dose can be a superior technical and economical solution for seawater pretreatment.

1. Introduction

The application of Reverse Osmosis (RO) in desalination is considered as a promising solution to solve the water shortage problem in many regions of the world. However, membrane fouling is a major challenge as it decreases both the quality and quantity of product water, increases the energy consumption and cleaning requirement as well as shortens membrane life [1]. In order to reduce membrane fouling, pretreatment of seawater is widely applied. The pretreatment of seawater reduces both colloidal and organic matter which otherwise can penetrate into the membrane pores and cause biofouling in RO membrane.

Flocculation has proved to be an effective and economical method for seawater pretreatment in desalination. A number of researchers have coupled low pressure membrane based pretreatment with coagulation/flocculation [2–6] to improve the treatment efficiency. Previous studies showed that the submerged membrane coagulation hybrid system (SMCHS) could help to increase the permeate flux of the membrane and modify the characteristics of the deposit on the membrane [6,7]. Ferric chloride is a commonly used metal flocculant as its trivalent ferric ions (Fe^{3+}) readily undergoes hydrolysis, complexation and precipitation in solution [8,9]. However, one main drawback of flocculation as pretreatment is the use of a relatively high amount of flocculant and as a consequence a larger amount of chemical sludge is formed. The sludge needs to be treated or disposed and results in higher operation cost. Also flocculation cannot remove all different dissolved organics in seawater.

Granular activated carbon (GAC) has been used extensively as an adsorbent to remove organic compounds from wastewater because it has a strong affinity to the organics even at low concentration [10]. Its performance has been proven better than other media such as sand

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and anthracite [11]. One of the major advantages of using granular activated carbon (GAC) is the availability of large surface areas for adsorbing organic matter. The application of a GAC filter prior to the application of SMCHS can be a solution for reducing the chemical dose while still maintaining same or even more organic and colloidal removal [12,13]. Recent results of Naidu et al. [13] showed that GAC filter can be used as a biofilter in seawater desalination pretreatment. It could reduce organic compounds, especially the low molecular weight organics through adsorption and biodegradation.

In this study, GAC filter was applied as an effective pre-treatment to remove organics and suspended solids from seawater prior to the application of flocculation. The effect of GAC filtration on the subsequent flocculation treatment was evaluated through Jar test experiments (batch test) and submerged membrane coagulation hybrid system (SMCHS) (continuous test) with raw seawater and GAC pretreated seawater. The emphasis is on the reduction of flocculant (chemical) dose through the application of GAC filter. The organics in seawater before and after treatment was characterized through various analytical methods such as three dimension-fluorescence excitation emission matrix (3D-FEEM) and liquid chromatography-organic carbon detector (LC-OCD). Modified fouling index with ultrafiltration (UF-MFI) and nanofiltration (NF-MFI) was used to determine the fouling potential of raw and preadsorbed seawater. In this study, five different flocculants namely ferric chloride ($FeCl_3$), poly-ferric sulfate (PFS), titanium tetrachloride ($TiCl_4$), poly-aluminum chloride (PACl), and aluminum sulfate $Al_2(SO_4)_3$ were used and their relative merits was compared.

2. Material and methods

2.1. Material

2.1.1. Seawater

Seawater used in this study was collected from Chowder Bay, Sydney, Australia. It was filtered through a centrifuge to remove large particles prior to the experiments. The characteristics of the seawater are presented in Table 1.

2.1.2. Membrane

The hollow fiber micro-filtration (MF) module from Mann + Hummel Ultra-Flo Pty. Ltd. (Singapore) was used. This membrane was made of hydrophilic modified PAN and had an average pore size of 0.10 μm and surface area of 0.1 m^2. The inner and outer diameters of fiber were 1.1 and 2.1 mm, respectively.

2.1.3. Flocculants

Five different inorganic flocculants namely ferric chloride ($FeCl_3$), poly-ferric sulfate (PFS), titanium tetrachloride ($TiCl_4$), poly-aluminum chloride (PACl) and aluminum sulfate ($Al_2(SO_4)_3$) were used. $FeCl_3$, $TiCl_4$ and $Al_2(SO_4)_3$ were reagent grade and were used without any purification. PACl and PFS were commercial products of Orica Chemicals and contain 10.5% w/w Al_2O_3 and 42.5% $Fe_2(SO_4)_3$ respectively. The basicity of PACl was 50% whereas this value of PFS was 10%.

Table 1
Characteristics of seawater used in this study.

Analysis category	Concentration	Analysis category	Concentration
pH	7.65–8.14	Se (μg/L)	<25
Salinity (g/L)	35.5–38.2	Cr (μg/L)	<25
Conductivity (ms/cm)	51.8–54.3	Fe (mg/L)	<0.05
TSS (mg/L)	2–13	Mn (μg/L)	2–3
Turbidity (NTU)	0.3–0.42	Ni (μg/L)	<10
DOC (mg/L)	1.41–1.64	Cu (μg/L)	<10
BOD_5 (mg/L)	<1	As (μg/L)	<25
Coliforms (/100 mL)	<2	Cd (μg/L)	<0.1
Total phosphorus (mg/L)	<0.01–0.06	Hg (μg/L)	<1
NO_3-N (mg/L)	0.01	Zn (mg/L)	<25
NH_4-N (mg/L)	0.02	Alkalinity	66–80
NO_2-N (mg/L)	<0.01	(mg/L as $CaCO_3$)	(Mostly bicarbonate)

2.1.4. Granular activated carbon

A commercial coal based GAC MDW4050CB (James Cumming & Sons Pty Ltd.) was used in the GAC filter. It was cleaned by distilled water and dried at 103 °C before use in the study. The particle size of GAC used in this study was 0.42–0.6 mm. Bulk density and specific surface of GAC are 748 kg/m^3 and 1000 m^2/g, respectively.

2.2. Experimental methods

2.2.1. GAC filter

GAC filter is an open filter. A perspex column (internal diameter of 20 mm) was packed with GAC to an effective height of 1 m. The adsorption column experiments were run at a constant filtration rate of 10 m/h (corresponding to an empty bed contact time (EBCT) of 6 min) for 4 days (at a down-flow mode).

2.2.2. Jar test

Predetermined doses of flocculants were added into 1 L seawater samples. The samples were then stirred rapidly (120 rpm) for 2 min followed by a slow mixing (30 rpm) for 20 min, and then allowed to settle for 30 min. The supernatant was filtered through a 0.45 μm microfilter and the filtrate was used for further organic analysis.

2.2.3. Floc strength and recoverability

At different flocculation conditions were determined using the procedure of Yang et al. [14] in which floc breakage occurred at 200 rpm for 5 min and floc regrowth was performed at 40 rpm for a further 15 min.

2.2.4. Submerged membrane coagulation hybrid system

The schematic diagram of the SMCHS set-up is shown in Fig. 1. Peristaltic pumps were used for pumping raw seawater, flocculants and permeate. The reactor volume was 3 L and the aeration rate was kept constant throughout this study (1 L/min). The trans-membrane pressure (TMP) was recorded automatically by a data logger.

2.3. Measurement

- *Organic fractions of seawater* were measured using a size exclusion liquid chromatography (for separating classes of dissolved organic materials) with a carbon detector (liquid chromatography-organic carbon detection, LC-OCD Model 8 developed by DOC Labor, Dr Huber, Germany).
- *Modified fouling index* (*MFI*) was determined at a standard reference pressure (207 ± 3 kPa) and feed water temperature (20 °C). The ultrafilter (UF) with a molecular cut-off of 17.5 kDa was used for the Jar test study whereas a nanofilter (NF) with a molecular cut-off of 700 Da was used for SMCHS.
- *Floc size* in the Jar test study was monitored by drawing the sample through the Mastersizer 2000 and back to the Jar by a peristaltic pump placed downstream of the Mastersizer [14].
- *Three dimensional-fluorescence excitation emission matrix* (*3D-FEEM*): fluorescence measurements of dissolved organic matter in seawater samples were carried out using a Varian Eclipse Fluorescence Spectrophotometer. EEMs were recorded by scanning emission wavelengths from 250 to 500 nm repeatedly at excitation wavelengths scanned from 220 to 400 nm [15].

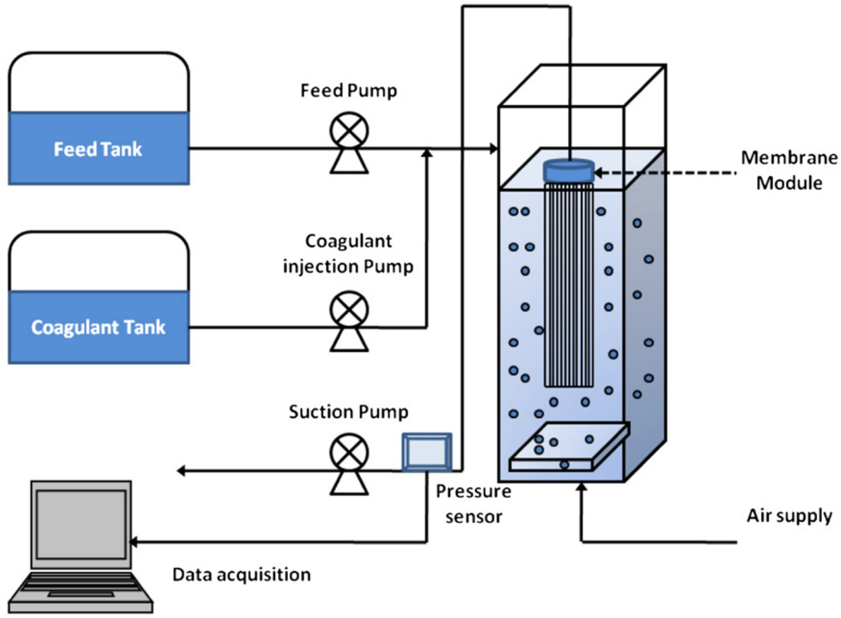

Fig. 1. Schematic diagram of SMCHS.

3. Results and discussion

3.1. Jar test

3.1.1. Organic removal

3.1.1.1. Liquid chromatography–organic carbon detector (LC–OCD). The Jar test was firstly carried out with raw seawater in order to determine the optimum dose of flocculant. In this experiment, the initial DOC of raw seawater was 1.41 mg/L. The organic removal by different flocculants is presented in Fig. 2. The results show that the organic removal of raw seawater by flocculation depends both on the type of flocculants and its dose.

Generally the removal efficiency of organics increased with larger flocculant doses. For PFS, PACl, and $TiCl_4$, a flocculant dose of 2 mg/L (as Fe^{3+}, Al^{3+} and Ti^{4+}, respectively) was enough to get the maximum organic removal whereas a slightly higher dose of 3 mg/L (as Fe^{3+} and Al^{3+}, respectively) was required for $FeCl_3$ and $Al_2(SO_4)_3$ to obtain the maximum organic removal efficiency. The DOC removal efficiency was found to decrease slightly when the dose of flocculants continue to increase above these values. The reduction of pH to below 7–7.5 (depend on flocculants) and the re-stabilization of the colloidal particles in this condition may be the reasons of this phenomenon [5]. The pH of the seawater in this Jar test study was 7.81.

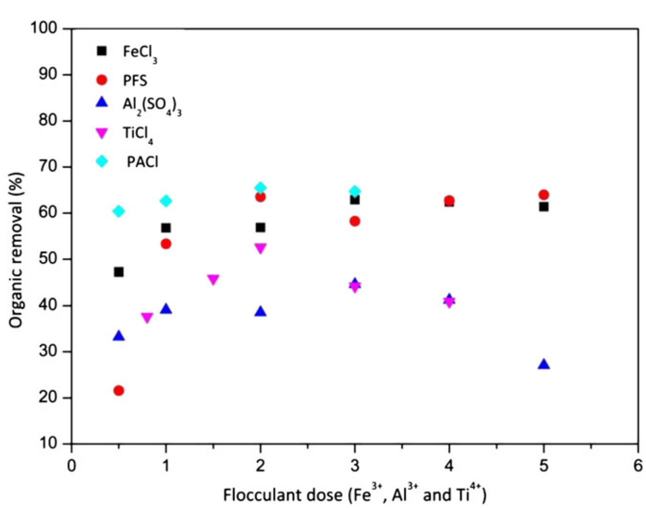

Fig. 2. DOC removal efficiency as a function of concentrations of five different flocculants (initial organic matter concentration of seawater was 1.41 mg/L).

Among the five flocculants, the highest organic removal was obtained with PACl and PFS at doses of 2 mg/L (as Al^{3+}) and 2 mg/L (as Fe^{3+}), respectively. The organic removal efficiency with the above two flocculants was 65.5% and 63.5%, respectively. This value was slightly higher than the maximum removal efficiency (62.9%) obtained with $FeCl_3$ at 3 mg/L (as Fe^{3+}). The $Al_2(SO_4)_3$ resulted in the lowest organic matter removal (44.7%) as such it was not used in subsequent experiments.

To evaluate the effect of GAC filtration on flocculation in organic removal, raw seawater was first filtered through the GAC column and the effluent was flocculated using a Jar test. The DOC of seawater during the experiment was 1.64 mg/L. The flocculation results with preadsorbed seawater showed that there was no visible floc when the flocculant dose was below 1.0 mg/L. The removal efficiency of organic matter fractions after GAC filtration and subsequent Jar test at flocculant dose of 1 mg/L is presented in Table 2.

The results from LC-OCD showed that raw seawater contained 70% of hydrophilic substances in which humic (molecular weight ≈ 1000 Da) was significant (38%) of the total organic. The biopolymer (large molecular weight 20,000 Da), building blocks (300–500 Da) and LMW neutrals and acids (below 350 Da) accounted for 12, 11, and 9%, respectively.

GAC filtration was found to remove 63% of DOC. This removal efficiency was similar to that of flocculation at optimum doses. The GAC filter adsorbed a majority (83%) hydrophobic organic matter from seawater. In addition to that, a significant amount of LMW neutrals and acids was also removed. Penru et al. [16] and Tansakul et al. [17] reported that LMW organic compounds are mainly responsible for biofouling of membrane. The result suggests that the application of GAC filter can help to reduce membrane fouling. However, experimental results also showed that GAC filtration was not effective in removing biopolymers (only achieved 20%, Table 2). Here the principal mechanism by which GAC removes organic contaminants from seawater is adsorption. Organic in seawater exists from large, high-molecular weight compounds such as biopolymer (molecular weight 20,000 Da) or humic (molecular weight ≈ 1000 Da, non-polar weak acids) to smaller

Table 2
Removal efficiency (%) of organic matter fractions after GAC filter and Jar test.

Samples	DOC (%)	Hydro-phobic (%)	Hydro-philic (%)	Bio-polymers (%)	Humic substances (%)	Building blocks (%)	LMW organics (%)
Preadsorbed seawater	63	83	52	20	40	42	70
Preadsorbed seawater with $FeCl_3$ (1 mg/L)	73	99	58	40	49	42	72
Preadsorbed seawater with PFS (1 mg/L)	72	98	57	40	46	50	72
Preadsorbed seawater with PACl (1 mg/L)	71	93	56	50	40	50	74
Preadsorbed seawater with $TiCl_4$ (1 mg/L)	75	95	63	40	46	42	87

molecular weight acids (less than 350 Da). GAC has high surface area and adsorptive property which favor the organics' removal. It can adsorb organic material as the attractive forces between the carbon surface (non-polar) and the organic contaminant (non-polar) are stronger than the forces keeping the components dissolved in seawater (polar).

Following GAC-filter, flocculation improved the removal of the remaining biopolymers and humics. As a result, the combination of GAC followed by flocculation with a lower flocculant dose (1 mg/L) led to a better DOC removal in comparison to flocculation alone even at higher doses (2–3 mg/L).

3.1.2. Modified fouling index

The modified fouling index of the effluent was measured following GAC filtration and following flocculation using an ultrafilter (UF) membrane with a molecular cut-off is 17.5 kDa. The reduction of UF-MFI was found to be higher after GAC filtration. The UF-MFI of raw seawater was 21,870 s/L^2 and that of GAC filter effluent was only 7720 s/L^2. This was further reduced to 5830 and 4385 s/L^2 after $FeCl_3$ and PFS flocculation, respectively (with a dose of 1 mg/L). The values were nearly similar to that of flocculation of raw seawater by higher dose of $FeCl_3$ (5040 s/L^2 with 3 mg/L as Fe^{3+}) and PFS (4446 s/L^2 with 2 mg/L as Fe^{3+}).

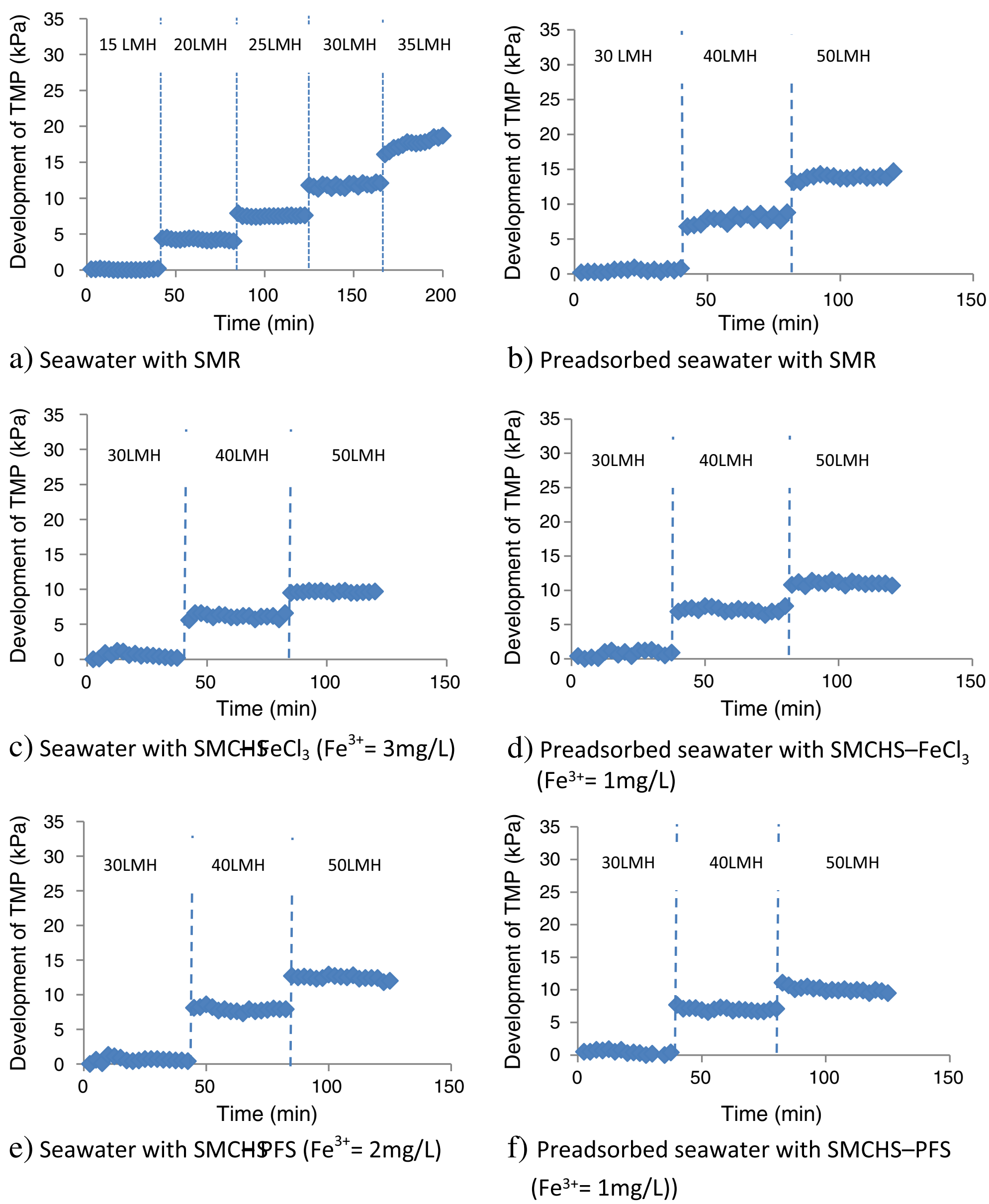

Fig. 3. TMP variation of SMR and SMCHS with $FeCl_3$ as flocculants.

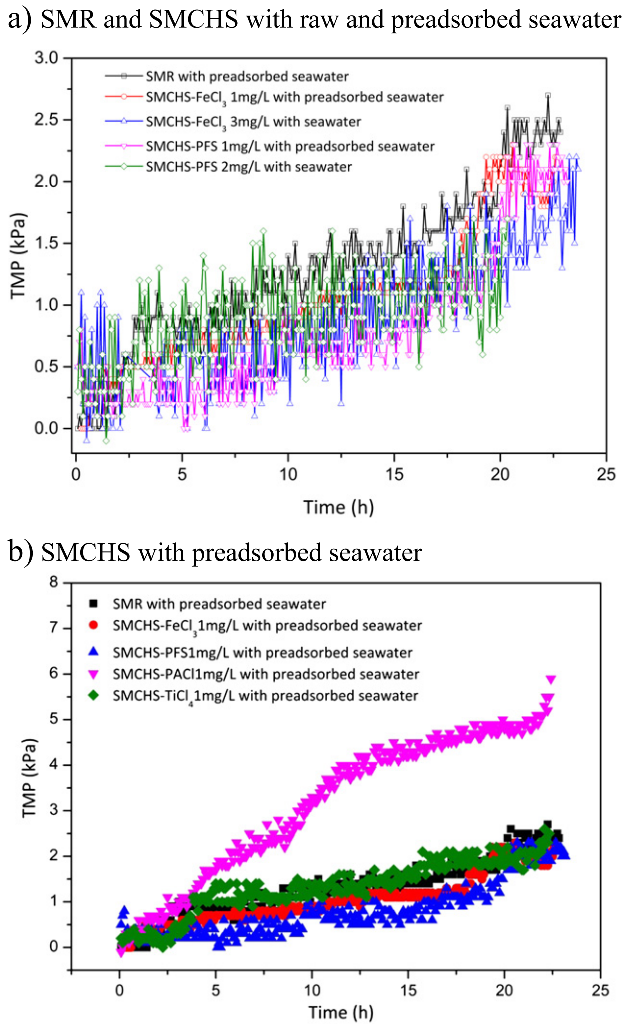

Fig. 4. Variation of TMP values.

3.2. Submerged membrane coagulation hybrid system

The SMCHS was used to test the flocculation and floc separation in a continuous mode. Both seawater and preadsorbed seawater were used as feed to SMCHS.

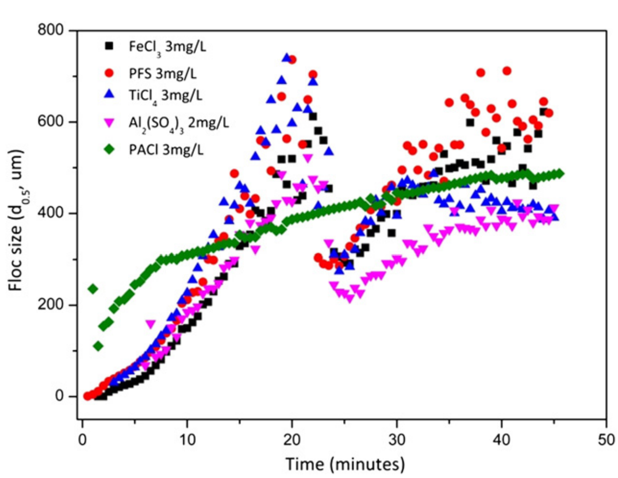

Fig. 5. Floc breakage and regrowth with different flocculants.

Table 3
The nanofilter-modified fouling index of seawater before and after adsorption by GAC filter and by SMCHS with different flocculants.

	NF-MFI ($\times 10^5$ s/L^2)
Raw seawater	202
Raw seawater with SMCHS–$FeCl_3$ 3 mg/L	17
Preadsorbed seawater with SMR	24
Preadsorbed seawater with SMCHS–$FeCl_3$ 1 mg/L	9.9

3.2.1. Critical flux

The effect of pre-adsorption of seawater by GAC filter on the performance of SMCHS was firstly evaluated through the variation of critical flux. The critical flux is the maximum flux where there is no transmembrane pressure (TMP) increase with time. Here, the critical flux was measured quantitatively by the "flux stepping" method in which a predetermined flux was applied in the reactor for 40 min and the TMP was monitored simultaneously. The flux was then increased and the system was operated at the increased flux while the TMP was measured for another 40 min and so on. The critical flux was the flux where the TMP started to become unsteady and increase with time.

As expected, the critical flux increased after pre-adsorption of seawater by the GAC filter. The critical flux of submerged membrane reactor (SMR) increased from 35 L/m^2·h with raw seawater to more than 50 L/m^2·h with preadsorbed seawater (Figs. 3a and b). The removal of organic compounds, especially the LMW organics (MW below 350 Da) and some part of building blocks (MW from 300 to 500 Da) from the hydrophilic compounds led to an increase of the critical flux as the deposition of these organic fractions was the main cause of irreversible fouling of MF [6]. The use of $FeCl_3$ and PFS as in-line flocculants in SMCHS also led to a further increase of the critical flux of the system to more than

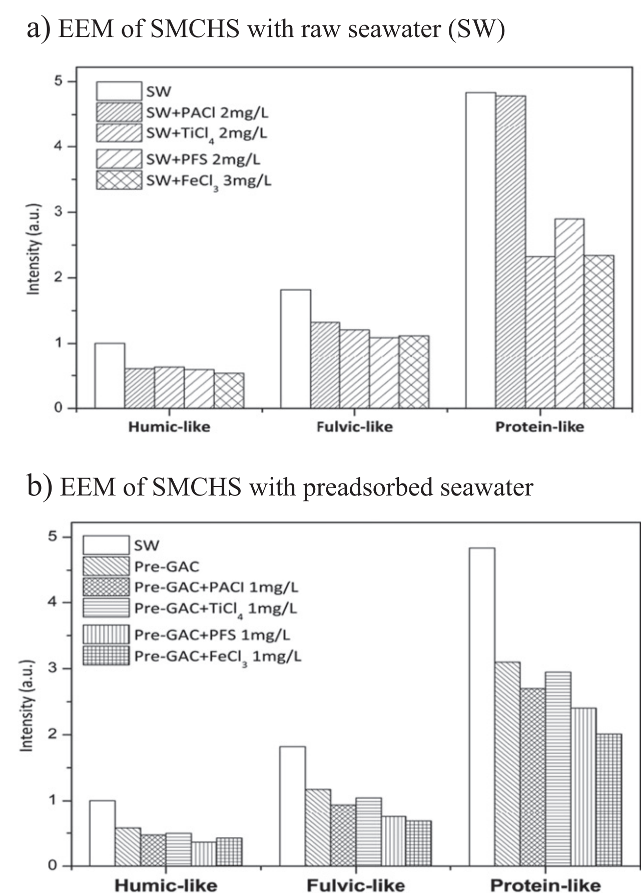

Fig. 6. EEM of different flocculants with raw and preadsorbed seawater by SMCHS.

Table 4
Amount of flocs (mg/L) formed with different flocculants with raw and preadsorbed seawater.

Flocculant	Dose (mg/L as Fe^{3+}, Al^{3+}, or Ti^{4+})		
	Raw seawater 2 mg/L	Raw seawater 3 mg/L	Preadsorbed seawater 1 mg/L
$FeCl_3$	26	28	20
PFS	25	28	18
$TiCl_4$	20	26	19
PACl	23	28	16

50 $L/m^2 \cdot h$ (Figs. 3c to f). It should be noted that lower flocculant dose (1 mg/L) was used for preadsorbed seawater.

3.2.2. Trans-membrane pressure

Following the critical flux experiments, longer term SMCHS experiments were conducted. The effect of GAC preadsorption of seawater on TMP development is shown in Fig. 4. Our previous study [5] showed that TMP development of SMR with raw seawater was much higher than that of SMCHS (in-line flocculation with Fe^{3+} dose of 3.0 mg/L). In this study, the TMP development of SMR with preadsorbed seawater (by only GAC filter and without any in-line flocculation) was similar to that of SMCHS with raw seawater flocculated $FeCl_3$ of 3 mg/L and PFS of 2 mg/L. This shows that preadsorption by GAC filter alone helped in reducing membrane fouling to a similar extent as in-line flocculation with SMR. It was also found that in-line flocculation using a lower dose of $FeCl_3$ (1 mg/L instead of 3 mg/L) and PFS (1 mg/L instead of 2 mg/L) followed by SMCHS also led to similar TMP development (Fig. 4a).

The application of lower dose (1 mg/L) of PFS and $TiCl_4$ as flocculants in the SMCHS with preadsorbed seawater also led to similar TMP development. However, there was a significant development of TMP when PACl at a dose of 1 mg/L was used instead (Fig. 4b).

A floc breakage and re-growth in the reactor was simulated through experiments with modified mastersizer. A procedure adopted by Yang et al. [14] was used in this study. The profiles of floc breakage and re-growth of SMR with raw seawater is presented in Fig. 5. The results show that $TiCl_4$ led to slightly larger floc sizes than that of $FeCl_3$ and PFS. The similar pattern of floc breakage and re-growth was observed with $FeCl_3$ and PFS. The floc size of PACl was smaller than the other three flocculants but the floc formed was very strong and was not broken at high shear. These strong flocs formed by PACl contribute to the formation of cake layer on the membrane surface and resulted in a higher fouling. This may be the reason for the rapid development of TMP when PACl was applied in SMCHS.

3.2.3. Modified fouling index

Effect of GAC preadsorption on fouling potential of seawater is given in Table 3. The reduction of the fouling potential of seawater by GAC filtration was studied using modified fouling index with nanofilter membrane with molecular weight cut-off of 700 Da. The results showed that the preadsorption by GAC led to a significant reduction of NF-MFI. The NF-MFI was reduced by about 9 times, from 202×10^5 s/L^2 to less than 24×10^5 s/L^2. It was further reduced to 9.9×10^5 s/L^2 when SMCHS was used with the lower dose (1 mg/L as Fe^{3+}) of $FeCl_3$.

3.2.4. Excitation–emission matrix

Different category of organics such as humic-like, fulvic-like and protein-like substances can be identified and measured by EEM. The comparison of performance of different flocculants with raw and preadsorbed seawater is presented in Fig. 6. The results showed that there was no much difference among different flocculants in removing humic-like and fulvic-like compounds from raw seawater. $TiCl_4$ and $FeCl_3$ were better than PFS and PACl in removing protein-like compounds. The removal efficiency of the two flocculants with protein-like reached about 52%.

GAC filtration followed by SMCHS gave rise to higher organic removal. $FeCl_3$ and PFS showed better organic removal efficiency in comparison with the other two flocculants. The removal of humic-like and fulvic-like compounds by the combined treatment of GAC filter-SMCHS achieved 63.7% and 62.4% with lower doses of PFS and $FeCl_3$, respectively.

3.2.5. Floc amount

The amount of floc generated by different flocculants with raw and preadsorbed seawater was estimated and presented in Table 4. Here the floc amount was estimated by measuring the weight change of filter papers after filtering 1 L of flocculated seawater. As expected, the higher flocculant doses led to higher amount of flocs. The amount of flocs generated by $FeCl_3$ and PFS at their optimum doses was 28 mg/L and 25 mg/L. The application of 1 mg/L of these flocculants for treating preadsorbed seawater significantly reduced the amount of floc formed (26.9–42.8%). The reduction in the amount of floc helps reduce the sludge treatment cost and make the treatment process economical.

3.3. Cost estimation

A typical cost estimation was made to show the feasibility of these pretreatments. In this cost analysis, the savings in applying pre-adsorption with GAC filtration to flocculation (at a lower dosage) against flocculation alone was calculated. The comparison of cost with different flocculants with and without GAC preadsorption was made based on 10,000 m^3/d of desalinated water production capacity and is presented in Tables 5 and 6. Here the optimal dose given in Table 6 is calculated in terms of Fe^{3+}, Ti^{4+} and Al^{3+} (of all five flocculants) whereas the amount of required flocculant was made using molecular weight of flocculant used ($FeCl_3 \cdot 6H_2O$ = 270.3 g/mol, $TiCl_4$ = 189.7 g/mol, $Al_2(SO_4)_3 \cdot 18H_2O$ = 666.4 g/mol, polyferric silicate = 339.94 g/mol and polyaluminium chloride = 221.65 g/mol).

Table 5
Comparison of cost with different flocculants (based on 10,000 m^3/d of seawater treatment).

	$FeCl_3$	PFS	$Al_2(SO_4)_3$	PACl	$TiCl_4$
Optimal dose (mg/L)	3.0	2.0	3.0	2.0	2.0
Flocculant price (US $/ton)	200	180	200	260	1950
Flocculant required (ton/d)	0.145	0.167	0.190	0.126	0.079
Cost of flocculant (US $/d)	29.1	30.0	38.0	32.7	154.5
Sludge production (ton/d)	0.280	0.250	0.350	0.230	0.200
Sludge treatment price (US $/ton)	37	37	37	37	37
Cost of sludge treatment (US$/d)	10.4	9.3	13.0	8.5	–
Incineration (US $/d)	–	–	–	–	8.8
By-product (US $/d)	–	–	–	–	−120
Total cost (US $/d, US $/$m^3$ of treated water)	39.5 (0.00395)	39.3 (0.00393)	51.0 (0.00515)	41.2 (0.00412)	43.3 (0.00433)

Table 6
Cost saving on flocculation with GAC pre-adsorption (based on 10,000 m^3/d of seawater treatment).

	$FeCl_3$	PFS	$Al_2(SO_4)_3$	PACl	$TiCl_4$
Optimal dose (mg/L)	1.0	1.0	1.0	1.0	1.0
Flocculant price (US $/ton)	200	180	200	260	1950
Flocculant required (ton/d)	0.048	0.083	0.063	0.063	0.040
Cost of flocculant (US $/d)	9.7	15.0	12.7	16.4	77.3
Sludge production (ton/d)	0.200	0.180	0.230	0.160	0.200
Sludge treatment price (US $/ton)	37	37	37	37	37
Cost of sludge treatment (US $/d)	7.4	6.7	8.5	5.9	–
Incineration (US $/d)	–	–	–	–	+6.6
By-product (US $/d)	–	–	–	–	−90.0
GAC operation (see Table 7) (US $/d)	13.5	13.5	13.5	13.5	13.5
Total cost (US $/d, US $/$m^3$ of treated water)	30.6 (0.00306)	35.2 (0.00352)	34.7 (0.00347)	35.8 (0.00358)	7.4 (0.00074)
Cost saving (US $/d)	9.9	5.0	17.8	6.3	35.9

3.3.1. Cost estimation of flocculation alone

The cost of flocculation as pretreatment was calculated for different flocculants. Five different flocculants including $FeCl_3$; PFS; $Al_2(SO_4)_3$; PACl; and $TiCl_4$ were used in the calculation. The optimal dose of each flocculant was determined using Jar test in terms of organic removal.

In this cost estimation, the price of flocculant (at optimal dose) and the treatment cost of chemical sludge (37 US $/ton of sludge) [18] were used. In the case of $TiCl_4$, valuable by-product of TiO_2 (price is 10,000 US $/ton, incineration cost 44 US $/ton) can be recovered [19]. In order to produce TiO_2, $TiCl_4$ flocculated sludge was required to undergo incineration process. This cost was included in the cost calculation. Here, TiO_2 recovery rate from flocculated sludge is 6%, which was estimated based on the previous study of Shon et al. [19].

3.3.2. Cost estimation of GAC preadsorption and flocculation

The cost saving was also estimated for preadsorption (GAC filtration) followed by flocculation. When preadsorption using GAC adsorption was used, the amount of flocculant required reduced (from 3 or 2 mg/L to 1 mg/L). Similarly the amount of chemical sludge produced was also reduced. This led to a cost reduction (or saving) in flocculation process.

The GAC column was operated at a filtration velocity of 10 m/h (empty bed contact time: 6 min). A filter run time of 1 day and a filtration velocity of 10 m/h were assumed in the economic calculation based on our earlier study [13]. In the initial stage, DOC removal by GAC is by adsorption. The adsorption capacity of GAC will gradually be reduced but the DOC removal capacity of GAC filter will be improved by biodegradation through the development of microbial community on the medium. The formation of biodegradable products in GAC column stimulates biological activities in the subsequent filtration [13]. In order to maintain its adsorption capacity, however, the optimal (minimum but sufficient) backwashing should be provided to GAC column. After 15 days of GAC filter operation, the DOC removal remained constant. In the cost estimation of GAC column operation, the following were assumed: (i) GAC cost over its life-time, (ii) GAC column is required to be backwashed once a day (at 20 m/h for 10 min), and (iii) GAC is regenerated once a year [20]. In calculating the cost, potential cost saving of less frequent replacement of RO membrane through the introduction of pretreatment was not included. The cost estimation for GAC column operation is given in Table 7.

Table 7
GAC column operation cost (based on 10,000 m^3/d of seawater treatment).

	GAC	Note
Filtration velocity	10.0 m/h	Rapid filter
Column depth (m)	1.0 m	
Bed volume	41.7 m^3	
GAC packing density	425 kg/m^3	Measured value after packing into the column
GAC required amount (total)	17.7 ton	
GAC operation cycle	20 years	Assumed value
GAC required amount (yearly basis and daily basis)	0.9 ton/year and 0.0024 ton/d	
GAC price	900 US $/ton	
GAC price (daily basis)	2.1 US $/d (1)	
Back washing (Energy requirement, US $/d)	0.3 US $/d (2)	6.9 kWh required to backwash at 20 m/h for 10 min. 1 kWh is 0.25$.
Regeneration	11.1 US $/d (3)	230 US $/ton is required for re-generation of GAC (once a year).
Total cost	13.5 US $/d	(1) + (2) + (3)

The calculation shows that although the preadsorption by GAC filter will require initial investment for GAC filter but the running cost of the treatment system can be reduced through reduction of the amount of flocculant needed as well as decreasing the need of sludge treatment. The cost for treatment of a cubic meter of seawater can reduce from 39.3–51.0 US $/$m^3$ to 7.4–35.2 US $/$m^3$. A big saving can be achieved especially for flocculation by $TiCl_4$. The payback time for flocculation by $TiCl_4$ and $FeCl_3$ will be 15 months and 53 months, respectively.

4. Conclusions

Preadsorbed seawater by GAC filtration reduced the organic compounds as well as fouling potential. Significant amounts of hydrophobic and low molecular weight of hydrophilic parts were reduced by adsorption with GAC. The GAC filter also can adsorb humic-like, fulvic-like and protein-like organic compounds. As a result, fouling potential decreased significantly after GAC preadsorption (nearly 3 times of UF-MFI and 9 times of NF-MFI). High molecular weight (biopolymer) substances which were not removed effectively by GAC filtration can then be removed through flocculation. The GAC preadsorption helps to reduce the flocculant dose needed for SMCHS in order to achieve high critical flux. After GAC preadsoption, there was also no need for higher dose of flocculants for organic removal. The combination of GAC filter and SMCHS can be an effective and economical solution for pretreating seawater.

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