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Abdullah H. Alshahri , Luca Fortunato*, NorEddine Ghaffour , TorOve Leiknes

Water Desalination and Reuse Center (WDRC), Division of Biological & Environmental Science & Engineering (BESE), 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*Corresponding author: Tel. +966 12 808 2289; Email: Luca.Fortunato@kaust.edu.sa

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*Corresponding author: Tel. +966 12 808 2289; Email: Luca.Fortunato@kaust.edu.sa

Abstract

Harmful algal blooms (HABs) are considered a major threat for seawater reverse osmosis (SWRO) plants. The presence of HABs in the raw feed water can cause increase of chemical consumption within the desalination plant, increase membrane fouling rate and might lead to plant shutdown. The removal of Algal Organic Matters (AOMs) during the pretreatment will help in increasing the membrane lifetime, reduce operation cost and increase the plant reliability. In this study, the efficiency of liquid ferrate and ferric chloride during coagulation on the removal of AOMs was investigated. The liquid ferrate was generated *in-situ* by wet oxidation of ferric iron using hypochlorite in a caustic medium. Two seawater models were employed, the first one contains 10 mg c/L of sodium alginate and the second one contains also 10 mg c/L of *Chaetoceros Affinis* algae (CA). During the advanced coagulation, liquid ferrate proved to be more effective in removing AOM than ferric chloride, with an overall DOC removal of 90%, enabling 100% algal removal and the inactivation of 99.99% of the

microorganisms. The results presented in this study highlights the efficiency of liquid ferrate as seawater pretreatment during the HABs events.

Keywords: Coagulation, SWRO pretreatment, AOMs, Fouling, HABs, Desalination.

1. Introduction

In arid regions with limited fresh water resources, water supply through seawater desalination is often the only viable solution to meet increasing water demand due to population growth, economic growth, and urbanization. In recent years, seawater desalination by reverse osmosis (SWRO) has become the dominant technology for desalination as it provides a high quality product, at lower cost, and with less environmental impact compared to conventional thermal desalination processes (Ghaffour et al., 2013; Jones et al., 2019). Increasingly large SWRO desalination plants have been constructed over the past twenty years to meet the growing demand of fresh water. The MENA region accounts for about 45% of the global desalination production, where Saudi Arabia is the largest producer of desalinated water in the world (Alharbi et al., 2012). Although the number and capacity of SWRO plants is increasing, a major challenge to this technology is membrane fouling which affects the process by increasing the cost of the water produced (Jiang et al., 2017).

Fouling mitigation and control is a major activity in all desalination plants where several approaches and strategies are applied (Fortunato and Leiknes, 2017; Kennedy et al., 2008; Valladares Linares et al., 2016). Fouling occurs as a function of the feedwater quality and operating conditions used, and depending on the dominant type of fouling, leads to an increase in operating costs due to more frequent chemical cleaning needed, increasing pressure required to compensate flux reduction from fouling, and increase in energy consumption (Fortunato et al., 2017). Biofouling in particular is considered a major challenge and occurs when a biofilm forms on the RO membranes, eventually resulting in an

increase in membrane resistance and reduction in permeability and solute rejection. Biofilm development and growth is related to the feed water quality and depends on the concentration of bioavailable organic compounds and the presence of biofilm-forming bacteria in the feed (Jeong et al., 2012). Effective pretreatment is often considered as the only strategy able to reduce the fouling potential by decreasing the amount of organic matter and inactivating the microorganisms in the feed (Henthorne and Boysen, 2015). Conventional SWRO pretreatment consists of coagulation/flocculation with sedimentation followed by conventional rapid dual media filtration and cartridge filters (Al-Mashharawi et al., 2013; Guo et al., 2005; Lin et al., 2019; Shon et al., 2009).

Algal blooms are a major threat to SWRO desalination plant operations (Alizadeh Tabatabai et al., 2014; Villacorte et al., 2017, 2015), and can occur unexpectedly without any early detection warnings. The algae can invade SWRO desalination plants and cause temporary shut down of the plant (Berkday, 2011). Algal blooms can be non-toxic or toxic (defined as harmful algal blooms, HABs), and independent of toxicity represent a severe challenge to SWRO plants and their pretreatment systems (Caron et al., 2010). Several case studies of such events are reported in the literature. The tendency of algal bloom events along the coast of Oman has increased from 1976 to 2018, where reports show that the Gulf of Oman turns green twice a year during such events, with the blooms being the size of Mexico and spreading across the Arabian Sea all the way to India (Al-Azri et al., 2012). A recent event reported in the Arabian Sea began in November 2017, lasting for almost five months, and during its peak in January covered an area three times the size of Texas. In another recent event along the coast of Florida (USA), an algal bloom caused the death of thousands of

marine animals and later on caused health problems for humans (Lapointe et al., 2017). Red tides (caused by algal blooms) along the Florida coast typically last around 3-5 months, however, the most recent one in 2018 extended for more than 9 months, considered the longest on record since 2006 (Karki et al., 2018).

Many efforts have been made to improve and enhance pretreatment options for SWRO processes to reduce fouling potentials and optimize the overall production of fresh water. Particularly during algal blooms this becomes a major challenge. Conventional pretreatment options commonly used have been demonstrated to not be fully effective in mitigating biological fouling (Kennedy et al., 2005; Lee et al., 2008). Although coagulation and flocculation reduce colloidal particles and dissolved organics in seawater, fouling still occurs. Traditional coagulants based on ferric salts are commonly used, such as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (Jiang et al., 2002; White and Franklin, 1998).

The use of ferrate (FeO_4^{2-}) as an alternative coagulant has been tested in both drinking water and wastewater treatment, where beneficial effects such as advanced oxidation and disinfection compared to traditional coagulants has been highlighted (Mackul'ak et al., 2016; Wilde et al., 2013). Ferrate is a powerful oxidant and also considered an environmentally friendly or green disinfectant, however, disinfection and advanced oxidation processes in marine waters (e.g., ballast water treatment, marine aquaculture) have mainly focused on ozone and UV based technologies. Most studies on ferrate reported in the literature focus on ferrate's oxidation efficiency in surface water and wastewater treatment, and where only a few studies investigated the potential disinfectant capabilities of ferrate (Bandala et al., 2009).

The objective of this study is to evaluate the suitability of liquid ferrate as an advanced coagulant in SWRO pretreatment during algal blooms. The efficiency of *in-situ* generation of liquid ferrate (FeO_4^{2-}) (Fe(VI)) as a coagulant was investigated. The liquid ferrate performance was compared to standard ferric chloride (FeCl_3) (Fe(III)) commonly used for seawater pretreatment for coagulation and flocculation. The biocidal effect of liquid ferrate on algae was also assessed. The efficiency of the coagulants was tested on raw seawater and two seawater analogs representing conditions observed during severe algal blooms.

2. Materials and methods

2.1 Feed water quality

The effect of liquid ferrate on three different feed water qualities was investigated in this study. Raw Red Sea seawater was collected from the intake line of the full-scale reverse osmosis (SWRO) desalination plant at KAUST (Thuwal, Saudi Arabia) (Fortunato et al., 2018). The content in organic carbon is one of the main parameters used to assess the seawater quality, where the Red Sea water is generally considered to be of high quality with low TOC and DOC concentrations (Dehwah et al., 2015). Hence, to assess the impact of changing feed water qualities during harmful algal blooms, two analog seawater conditions were prepared. One was prepared by enriching the raw seawater with sodium alginate (SA), and the other by cultivating *Chaetoceros Affinis* (CA) algae, which is a bloom forming algae. Characteristics of the raw seawater and the two analogs are summarized in Table 1.

Table 1 Characteristics of feed waters used in the study.

Parameters	Raw Red Sea water	Analog seawater	
		Sodium alginate	Cultivated Algae
Temperature	23.5 ± 0.5 °C	23.5 ± 0.5 °C	23.5 ± 0.5 °C
pH	8.00 ± 0.20	8.00 ± 0.20	8.00 ± 0.20
TDS	40000 ± 2100 mg/L	40000 ± 2100 mg/L	40000 ± 2100 mg/L
Conductivity	59 ± 1 mS/cm	59 ± 1 mS/cm	59 ± 1 mS/cm
Turbidity	1.27 ± 0.52 NTU	2.50 ± 0.50 NTU	12.00 ± 1.00 NTU
TOC	1.0 ± 0.2 mg/L	10.0 ± 0.2 mg/L	10.0 ± 0.4 mg/L
DOC	0.8 ± 0.1 mg/L	9.0 ± 0.1 mg/L	8.5 ± 0.8 mg/L
Total alkalinity	118 ± 2 mg/L	118 ± 2 mg/L	118 ± 2 mg/L

Sodium alginate model (SA): sodium alginate is commonly used as a surrogate to mimic algal blooms in seawater (Lee and Mooney, 2012). Sodium alginate (VWR Prolab Chemicals) was used to make the analog feed water by mixing 1 g of sodium alginate in 1 L of Milli-Q water. The stock solution was designed to have a desired TOC concentration of 10 mg/L. A Shimadzu TOC analyzer was used to determine the concentration of sodium alginate solution.

Algal organic matter (AOM) model: the bloom-forming algae species *Chaetoceros Affinis* (CA) was cultivated to produce natural biopolymers found during algal blooms. The marine diatom species (*Chaetoceros Affinis*, CCAP 1010/27, imported from Culture Collection of Algae and Protozoa (CCAP) company, Oban, Scotland) was cultivated in Red Sea water spiked with Guillard's medium (CCAP, 2010) under controlled laboratory conditions. The cultures

were aerated with filter-sterilized air to ensure nutrient distribution and to avoid settling of cells. Cultures were exposed to 12h dark / 12h light cycles using mercury fluorescent lamps (average photon flux density $40 \mu\text{mol m}^{-2} \text{s}^{-1}$) at a constant growth temperature of 20°C , as per the method developed by Myklestad (1995) (Myklestad, 1995). The culturing protocol starts with a 2 ml inoculum of new strain in a 50 ml sterile culture tube enriched with marine nutrients based on Guillard F/2 medium, and incubating it in an environmental chamber. Strain cultures were renewed every week by taking an inoculum of 0.1-0.2 ml (from test tubes) or 0.5 to 1 mL (from Erlenmeyer flasks), using the best old culture which is free of contamination, to inoculate three to four new vessels of the same size to start a new strain. The total algal concentration and cell viability was measured using a flow cytometer (Accuri C6, BD Biosciences) based on a standard protocol proposed for drinking water analysis (Prest et al., 2013).

2.2 Liquid Ferrate preparation

A cost-efficient way of generating ferrate is by aqueous chemical oxidation (wet oxidation) of ferric iron using chlorine in a caustic medium (Thompson et al., 1951). Ferric chloride (FeCl_3) is oxidized to ferrate (FeO_4^{2-}) by sodium hypochlorite (NaOCl) in the presence of sodium hydroxide (NaOH), as shown in Eq. (1).

When added to aqueous systems, liquid ferrate is a powerful oxidant that readily decomposes to ferric iron $\text{Fe}(\text{OH})_3$ and oxygen (Goff and Murmann, 1971),

Ferrate concentrations were measured using the spectroscopy method, where the absorbance of a ferrate solution at 510 nm can be converted to the ferrate concentration using a coefficient, defined as the ratio of the ferrate absorbance at 510 nm (cm^{-1}) to the ferrate concentration. Concentrations were determined for a given amount of ferrate diluted in a given volume of phosphate buffer (5mM phosphate/ 1mM borate, at pH 9.1) and absorbance measured at the 510 nm wavelength, as given by Eq. (3)

$$\epsilon = A/BC \quad (3)$$

where “A” is UV/Vis absorbance by sample, “B” represents Fe (VI) concentration (M) in the examined sample, and “C” is light path (cm) of the quartz cell used in this study. The molar absorption coefficient (ϵ) at 510 nm is determined to be equal to $1150 \text{ M}^{-1}\text{cm}^{-1}$.

2.3 Analytical Method

The pH measurements were conducted by using a CyberScan 6000 series meter (pH6000, Eutech instruments). The turbidity analysis, performed without filtering the samples, was carried out with a HACH-Lange turbidity meter (Germany). TOC analysis was carried out with a Shimadzu TOC analyzer (TOC-V CPH, Shimadzu, Japan). DOC analysis was conducted using liquid chromatography with an organic carbon detection (LC-OCD), from (LC-OCD-OND Model 8, DOC-Labor, Germany), after filtering the samples (0.45 μm filter pore size). 3000 μL samples were injected for analysis with 180 min of retention time and a flow rate of

1.1 mL/min. Organic matter can be divided into five fractions defined as biopolymers, humic substances, building blocks, low molecular weight (LMW) neutrals and LMW acids (Alshahri et al., 2017; Huber et al., 2011). Active biomass in the samples was determined through ATP analysis using a Celsis ATP-Analyzer and analysis reagent kit (Celsis, USA), based on firefly luciferin-luciferase bioluminescence reaction. Interference by salts was minimized by diluting the sample 50 times with milli-Q water (100 μ L of each sample was added to 1500 μ L of milli-Q water) with a final volume of the measured sample of 50 μ L. Algae concentrations were measured using a BD Accuri® C6 flow cytometer, based on laser excitation of unstained auto-fluorescent algal cells. The samples were analyzed at a medium flow setting (35 μ L/min) with an injection volume of 50 μ L. All samples were measured in triplicate to ensure accuracy (Van der Merwe et al., 2014).

2.4 Experimental Procedure

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (98% pure, anhydrous, Sigma- Aldrich) was used to prepare 1 M of stock solution. Liquid ferrate was produced in the laboratory by wet oxidation (as described above) by mixing components according to the following method (Goff and Murmann, 1971); adding 21.4 g NaOH into 103 mL of NaOCl to obtain a pH value >10, and intensive mixing with a stirrer (1200 rpm) to achieve a homogeneous solution; adding 2.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ into the solution and mixing for 60 minutes to get the final product.

Standard jar tests were conducted on a six-place stirrer, and utilized to simulate various

mixing, flocculation and settling conditions in order to obtain the optimum dose and pH. During the Jar test, 2 L beakers with the same treatment programs using different feed waters and different coagulant dosages were run. Jar tests were conducted by adding 10 mg C/L of sodium alginate stock or AOM into 2 L of seawater. After that, an appropriate volume of ferric chloride and liquid ferrate stock solutions (according to the desired dose) were added. After mixing the coagulant for one minute, the mixing rate was reduced to 35 rpm (regular mixing, 35 s^{-1}) to maintain completely stirred conditions for 20 min. (Fig. 1). The solution was then left to settle for 1 hour before samples of the supernatant were taken to measure the water quality parameters.

A TOC concentration of 10 mg C/L for the two analog feedwaters was chosen as this represents severe fouling conditions. Jar test experiments were conducted for pH values varying between 5–9 and liquid ferrate dosages range between $1\text{--}3\text{ mg L}^{-1}$ as Fe. The pH range represents the region of best performance for iron-based coagulants, and also allows assessing liquid ferrate performance at pH ranges of natural seawaters (8–9). The pH was adjusted by adding predetermined quantities of 0.5 N NaOH or HCl.

FEED WATERS

Fig. 1. Experimental procedure for the pretreatment of SW, SA, and AOM

3. Results and discussions

3.1 Liquid ferrate synthesis

Ferrate can be synthesized through oxidation to convert ferrous or ferric iron to a higher valence. The oxidation step can be performed in different ways, a dry state utilizing heat with an oxidant, by using electricity, or by wet oxidation. Pure ferrate can only be obtained through a separation process where it is isolated from other reaction byproducts. It is important to note that while the oxidation step is simple and inexpensive, the purification of ferrate is time consuming and expensive. Liquid Ferrate can be generated by wet oxidation of ferric iron using chlorine in a caustic medium. The production cost is lower compared to commercial dry ferrate, moreover, it is environmentally friendly and inexpensive in terms of operation and maintenance. In fact, in producing ferrate by wet oxidation, the pure reagents are the only contributors to the cost (Lee, 2003). Since no purification step is involved, wet oxidation enables the generation of liquid ferrate, where the ferrate is present in solution mixed with "unreacted" ferric chloride.

In this study, liquid ferrate was obtained by wet chemical oxidation of ferric chloride by sodium hypochlorite in alkaline conditions. A 12% yield was obtained, which is in agreement with the maximum achievable yield at the concentration of NaOH and NaOCl applied. These conditions were chosen to minimize the use of chemicals and costs. Therefore, the liquid solution employed in this study contained a Fe(III) to Fe(VI) ratio of almost 9:1. Other yields are reported in the literature that are very high, however, the maximum yield of liquid ferrate can be achieved by wet oxidation is 35% by using excessive amounts of NaOH and NaOCl (Sun et al., 2013).

3.2 Comparative performance of liquid ferrate (VI) and ferric chloride (III)

The efficiency of SWRO pretreatment is commonly assessed by measuring the turbidity and organic removals in the feedwater. Practically, SDI is used to quantify the suspended solids removal efficiency (Rachman et al., 2013). DOC is considered a collective parameter used to quantify the concentration of organic matter in the seawater. The performance of RO membranes has been correlated to DOC content in the feedwater, where concentrations greater than 2 mg/L have been shown to impact membrane fouling and likely lead to biofouling (Edzwald and Haarhoff, 2011). During algal blooms, DOC in the raw seawater can reach up to 12 mg/L (Anderson et al., 2017) thus causing major operational challenges. Performance of the pretreatment process under these conditions is critical to prevent biofouling of the RO membranes. The performance of liquid ferrate as an advanced coagulant was compared to conventional ferric chloride for pretreatment of seawater, applied to raw seawater and two analogs simulating algal bloom conditions (e.g. 10 mg C/L SA, and 10 mg C/L AOM).

Turbidity removal efficiencies are summarized in Fig. 2. For raw seawater, turbidity removal varied between 1-24% for Fe(III) and 44-60% for Fe(VI). For the AOM analog seawater, removal was around 27% for Fe(III) compared to 63% for Fe(VI). It is worth to notice that no improvement was observed with increasing Fe dose.

Results show that the 12% yield of liquid ferrate as used in this study was more effective in turbidity removal compared to ferric chloride in all cases tested. Other studies have reported that low doses of sodium ferrate helped in removing the turbidity in wastewater samples, removing suspended particles and color from feed water during the coagulation process.

Indeed, the percentage of turbidity removal using sodium ferrate was found to be much higher than for other types of coagulants used (Jiang et al., 2015; Talaiekhosani et al., 2017).

Fig. 2. Turbidity removal by using ferric chloride vs. liquid ferrate on raw seawater, and algae seawater model.

3.3.1 Performance of Fe (III) and Fe (VI) for DOC, and AOM removal

The removal of dissolved organic matter (DOC) with ferric chloride and liquid ferrate coagulants is summarized in Fig. 3. Fe (III) showed a slightly lower DOC removal (~85 %) compared to Fe (VI) (~90%) in raw seawater. For the SA analog seawater, the two coagulants showed a similar performances on DOC removal. For the seawater analogs mimicking algal bloom conditions, Fe (VI) led to a DOC removal of 88-93%, while for Fe (III) a lower removal of around 58-87% was observed (Fig. 3A). The effect of pH was tested for the AOM analog at pH's 5, 7, and 9, where DOC removal was generally less than 30% under acidic and neutral pH while around 93% was observed for alkaline conditions (Fig. 3B). The higher DOC

removal achieved at pH 9 is due Fe (VI) being more stable in alkaline conditions, thus facilitating the oxidation reactions before decomposition to ferric species takes place. Results presented in this study confirm the positive effect of liquid ferrate in removing the organic matter due to its oxidation ability. This is in agreement with previous studies that reported a 20% higher removal of DOC in drinking water treatment when using liquid ferrate as coagulant compared to an equivalent dose of ferric sulfate (Goodwill et al., 2016). In fact, ferrate enables the oxidation of organic compounds through a radical reaction with the formation of hydrogen bonds and facilitates removal by coagulation / precipitation (Huang et al., 2001). Results in this study are in agreement with reported values from previous coagulation studies (20-67%)(Goodwill et al., 2016; Liu et al., 2017), where the removal efficiency of liquid ferrate on the raw seawater and the two seawater analogs was found to be even slightly higher (60-93%).

Fig. 3. DOC removal by ferric chloride vs. liquid ferrate (A) for raw seawater, sodium alginate (SA) seawater analog, and algae seawater analog (AOM), and (B) impact of pH on liquid ferrate doses on algae (AOM) seawater analog.

3.3.2 Performance of Fe (III) and Fe (VI) for NOM removal

The organic matter in seawater consists of a mixture of different organic compounds including aquatic humic and fulvic acids and products generated from bacterial and algal activity (*i.e.* microbial and algal organic matter) (Edzwald and Haarhoff, 2011). A more detailed assessment of DOC organic fractions was performed using LC-OCD analysis (Fig. 4). A similar removal in DOC for the two coagulants was observed in raw seawater. Around 95% removal was observed for the bio-polymers and building blocks. The removal of these compounds is mainly due to the coagulation effect of both the coagulants. As reported in

literature, the fluvic and humic acids are highly removed by using ferrate. In fact, by using liquid ferrate, the ferrate decomposition from Fe (VI) to Fe (III), leads to the formation of Fe(OH)_3 which enables the removal of fluvic acid through adsorption and coprecipitation (Qu et al., 2002). While the LMW acids showed a similar removal of 98-100%, a higher removal was observed for LMW neutrals, 14-29% for Fe (III) vs. 38-65% for Fe (VI) (Fig. 4A, B). While the two coagulants showed similar performances in the treatment of the SA seawater analog, a significant difference was observed for the AOM seawater analog. For the latter, biopolymer removal by Fe (III) was ~74% while the removal was higher, 97-100%, for the Fe (VI) coagulant (Fig. 4E, F). In seawater the biopolymer fraction is composed of acids, proteins, simple sugars, anionic polymers, negatively charged and neutral polysaccharides, which are a major concern for biofouling of RO membranes. All these compounds are present as well in the algal organic matter (AOM) (Edzwald and Haarhoff, 2011). The liquid ferrate completely removes the biopolymers through adsorption and enmeshment in ferric hydroxide, forming large Fe-biopolymer aggregates (Alizadeh Tabatabai et al., 2014). The removal in concentration of building blocks was similar, with 86% for Fe(VI) and 81% Fe(III). Due to ferrate's oxidation ability, a significantly higher removal of LMW acids (73%) was observed compared to ferric chloride, which showed an adverse effect of increasing the LMW acids concentration with increasing ferric chloride dose. Indeed, the high oxidation potential of ferrate enables oxidation of small molecules like LMW acid and neutrals. Results suggest that Fe (VI) had a lower removal of LMW neutrals compared to Fe (III), 4% vs. 52%, however, in the case of the liquid ferrate LMW neutrals are formed during oxidation of the bio-polymers. Applying liquid ferrate on the AOM analog seawater showed a higher concentration of LMW neutrals compared to the feedwater tested.

Based on the same Fe dose, the liquid ferrate option showed a better performance compared to a conventional ferric chloride coagulant. The enhanced performance is accounted by the liquid ferrate having a combined oxidation and coagulation effect from the two different oxidation states. Ferrate acts as a strong oxidant, and combined with the formation of ferric hydroxide as ferrate decomposes, improved conditions for coagulation and removal of metals, non-metals and humic acids can be observed (Potts and Churchwell, 1994).

Fig. 4. Impact of ferric chloride vs. liquid ferrate on the NOM fraction. Raw seawater (SW) with ferric chloride (A) and liquid ferrate (B); Alginate seawater (SA) with ferric chloride (C) and liquid ferrate (D); Algae seawater (AOM) with ferric chloride (E), and liquid ferrate (F).

3.3 Biocidal effect and algae removal with liquid ferrate

Algal blooms are responsible for producing large amounts of organic matter in the seas and oceans (Field et al., 1998). From the perspective of seawater desalination, AOM produced by the algal cells can cause significant operational problems and membrane fouling in RO plants. The biocidal effect of liquid ferrate and potentially enhanced algae removal was also assessed.

Higher algae removal was observed for liquid ferrate for all concentrations tested. Equivalent dosages of 1, 2 and 3 mg Fe/L was applied, at pH 9. With liquid ferrate 94-100% removal in the algae concentration was observed compared to 48-72% with ferric chloride (Fig. 5A). The effect of the pH on the liquid ferrate efficiency was tested at pH 5, 7, and 9, resulting in increasing removal with increasing pH for all doses applied (Fig. 5B). The highest algae removal achieved at pH 9 is due to the stability of ferrate in alkaline conditions. In general, liquid ferrate enhances the removal efficiencies of algae in the seawater as demonstrated by the AOM analog seawater used. The positive effect is due to the multiple capabilities of ferrate that include oxidation, coagulation, and biocidal properties (Kanari et al., 2005). Results presented in this study highlighted the ability of liquid ferrate to inactivate algae.

Reports in the literature have documented the strong oxidation capacity of ferrate and its potential as an alternative disinfectant to inactivate microorganisms (viruses, bacteria, algae). Studies have shown that ferrate is effective in treating bacteria such as *Staphylococcus aureus*, *Streptococcus faecalis*, *Escherichia coli* and *Salmonella typhimurium* and can inactivate the microorganisms over a wide range of pH and salinities at relatively low dosages and short contact times (Murmah and Robinson, 1974). Liquid ferrate is

considered an environmentally friendly biocide compared to other disinfectants such as chlorine, chlorine dioxide, ozone and chloramines as it is reduced to ferric iron in the process without the formation of any toxic byproducts (Dong et al., 2019; V K Sharma, 2007; Wang et al., 2015). The ferrate action as disinfectant is mainly due to the loss in activities of both polymerase and nuclease. Conventional coagulation with ferric chloride can only remove a small amount of microorganisms through adsorption on precipitates and does not have a biocidal effect. Microorganisms will therefore remain in the feedwater using conventional ferric coagulants and can enter the RO membrane pressure vessels and contribute to biofouling development (Khan et al., 2019). The biocidal capabilities of liquid ferrate therefore represent an additional benefit of using liquid ferrate as an alternative coagulant in the pretreatment stage. Previous studies have documented the high biocidal efficiency of ferrate in bacterial inactivation in wastewater treatment (Bandala et al., 2009; V. K. Sharma, 2007).

The biocidal efficiency of liquid ferrate was assessed by measuring ATP to evaluate the microbial activity in the seawater. ATP measurements have been reported to correlate with biomass and bacterial growth potential in SWRO membrane processes (Abushaban et al., 2018). Tests conducted on the raw seawater showed that ATP removal was between 87-99.99% for liquid ferrate compared to 16-41% for ferric chloride (Fig. 6). In the AOM analog seawater using cultivation of CA algae, a 98-99.99% removal was achieved with liquid ferrate compared to 38-57 % with ferric chloride (Fig. 6). These findings confirm the potential efficiency of liquid ferrate as an advanced pretreatment option in SWRO to also control bacterial activity during algal blooms, thereby further reducing biofouling potential during algal blooms.

Fig. 5. Algal removal in AOM analog sweater; (A) varying doses of Fe from ferric chloride vs. liquid ferrate, (B) impact of pH with liquid ferrate doses.

Fig. 6. Impact of ferric chloride vs. liquid ferrate on ATP of raw seawater, and algae seawater model.

4. Conclusion

In this study, the efficiency of liquid ferrate as seawater pretreatment during high turbidity events (i.e. algal bloom) was investigated. Results from this study showed that liquid ferrate achieved better removals in terms of organic carbon and microorganism content compared to conventional ferric chloride using equivalent dose range of iron (Fe).

Based on the findings of this study, the main conclusions are as follows:

- Liquid ferrate was generated *in-situ* through wet oxidation of ferric chloride by hypochlorite in caustic media
- Higher removals of DOC, NOM and AOM (particularly biopolymers) were observed using liquid ferrate compared to conventional ferric chloride in all feedwaters tested.
- Removal efficiencies by liquid ferrate increased with increasing pH due to the increase in ferrate stability at alkaline conditions.
- Liquid ferrate was able to fully inactivate microorganisms in the feed waters and enhance the removal of algal cells.

Overall, jar test results from this study demonstrate that liquid ferrate coagulant provides better pretreatment than conventional ferric chloride for seawater with high organic content typically found during algal blooms. High yields for liquid ferrate were achieved through an *in-situ* wet oxidation process that can relatively easily be adapted to conventional processes using ferric chloride as a coagulant. The use of liquid ferrate for the coagulation and flocculation pretreatment was found to be more effective in removing organic carbon in seawater under algal bloom conditions, and also provided an added biocidal effect through

efficient inactivation of microorganisms in the feedwater. Therefore, liquid ferrate is therefore considered an excellent alternative option for coagulation/flocculation pretreatment in SWRO processes, especially during algal bloom events.

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Highlights

- Liquid Ferrate was tested as SWRO pretreatment during algal bloom.
- Liquid ferrate was generated in-situ by wet oxidation of ferric chloride in alkaline medium.
- The removal performances of liquid ferrate were compared with ferric chloride.
- Liquid ferrate achieved higher Algal Organic Matter removal compared to ferric chloride.
- Liquid ferrate enabled the complete inactivation of bacteria and algae.

FEED WATERS

Figure 1

Figure 2

Figure 3

Ferric Chloride

Liquid Ferrate

Raw Seawater (SW)

Alginate Seawater (SA)

Algae Seawater (AOM)

Figure 4

Figure 5

Figure 6