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Synthetic
AOM in
saline water

Coagulation at 120 rpm for 1 min,
flocculation for 20 min,
followed by 30 min sedimentation

Fe(III) + NaOCl

In situ
Fe (VI)

Fe(III) + NaOCl

Algae cell
concentration

Sample
after filter
through
0.45 μm

LC-OCD
analysis

DOC

Real AOM
extarcted from
CA & *Hym*

Mitigation of algal organic matter released from *Chaetoceros affinis* and *Hymenomonas* by *in situ* generated ferrate

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ABSTRACT: This study demonstrates the application of *in situ* ferrate (Fe(VI)) for the efficient removal of dissolved algal organic matter (AOM) from seawater. Sodium hypochlorite (NaOCl) and ferric (Fe(III)) were used to produce *in situ* Fe(VI) by wet chemical oxidation. First, the removal efficiencies of model AOM compounds, humic acid (HA), and sodium alginate (SA) were evaluated in the presence of sodium chloride with an initial influent dissolved organic carbon (DOC) concentration of 5.0 mg C L⁻¹ at different pH levels to establish the optimal doses for *in situ* Fe(VI) generation. The concentration of Fe(VI) was determined by the 2,2-Azino-bis

(3-ethylbenzothiazoline-6-sulfonic acid) ultraviolet-visible spectrophotometry method. In the case of HA, 72% DOC removal was recorded when applied with 1.5 mg L⁻¹ of Fe(III) and 1.5 mg L⁻¹ of NaOCl (*in situ* Fe(VI) concentration of 1.46 mg L⁻¹) while 42% DOC removal was observed for SA. Subsequently, the removal of AOM extracted from two bloom-forming algal species, *Chaetoceros affinis* (CA) and *Hymenomonas* (Hym), cultivated in seawater from the Red Sea, were tested with *in situ* generated Fe(VI) at the established optimum condition. *In situ* Fe(VI) recorded superior performance in removing AOM extracted from CA and Hym, showing 83% and 92% DOC removal when the influent DOC concentrations were 2.48 and 2.63 mg L⁻¹, respectively. A detailed AOM characterization was conducted using liquid chromatography–organic carbon detection.

Keywords: Algal organic matter; coagulation; ferrate; oxidation; seawater desalination

List of Abbreviations

AOM	algal organic matter
BB	Building blocks
BP	Biopolymers
CA	<i>Chaetoceros affinis</i>
DOC	Dissolved organic carbon
EOM	Extracellular organic matter
HMW	High molecular weight
Hym	<i>Hymenomonas</i>
HA	Humic acid
HS	Humic substances

LC–OCD Liquid chromatography–organic carbon detection

LMW Low molecular weight

MW Molecular weight

NOM natural organic matter

SA sodium alginate

1. INTRODUCTION

Seawater reverse osmosis (SWRO) is a well-established desalination technology for the production of potable water, however, its cost-effective application depends on the ability to control membrane fouling, which mainly occurs due to the deposition of particles, colloids, inorganic matter, organic matter and biological products (Guo et al., 2018). In particular, the emerging threat of harmful algal blooms (HABs) poses a new challenge for SWRO since HABs cause membrane fouling that is not easily managed by using conventional pretreatments (Edzwald and Haarhoff, 2011). Severe HABs can debilitate SWRO operations – in 2008 and 2009, intense HABs in the Oman and Arabian Gulf forced the shutdown of several SWRO plants due to the blockage of pretreatment systems (mostly applying granular media filtration), poor-quality influent water for reverse osmosis (RO), and the fear of causing irreversible damage to RO membranes (Richlen et al., 2010; Villacorte et al., 2015a).

Generally, algal blooms occur when colonies of marine algae proliferate at exponential rates, subsequently producing toxic or harmful effects on humans and marine life. Algae-derived compounds, collectively known as algal organic matter (AOM), are comprised mainly of biopolymers (e.g., extracellular polysaccharides and proteins) which take up more than 80% of AOM. Other components of AOM are refractory organic matters (e.g., humic-like substances)

and low molecular weight biogenic substances (e.g., lipids, nucleic acids, other dissolved organic substances). Certain algae generate very high amounts of sticky extracellular polysaccharides. The dominance of polysaccharides and proteins in AOM enhances its hydrophilicity and stickiness, and as such, dissolved AOM may lead to severe fouling of membranes and produce a variety of harmful disinfection by-products (Fang et al., 2010; Li et al., 2012; Plummer and Edzwald, 2001; Zainudin et al., 2018; Zhou et al., 2014).

For the smooth operation of SWRO plants, attention has been given to develop effective pretreatment technologies to control RO membrane fouling during harmful algal blooms. Conventional pretreatment systems for turbidity removal and surface loading rate optimization applied at SWRO plants include coagulation, granular media filtration, dissolved air flotation, and low-pressure membrane based pretreatment methods such as ultrafiltration and microfiltration (Jeong et al., 2012; Lee et al., 2016a; Löwenberg et al., 2015). In particular, one of the more common methods used is granular media filtration, but its performance suffers significantly from harmful algal blooms. Therefore, we propose an advanced oxidation-coagulation system based on the *in situ* generation of Fe(VI) by wet chemical oxidation for enhancing the quality of seawater before granular media filtration. Ferrate has recently been reported as a potential agent for the water treatment (Deng et al., 2018; Fan et al., 2018; Rai et al., 2018; Shin et al., 2018) due to its multifunctional, environmentally-friendly properties for oxidation, disinfection, coagulation, and odor removal (Diak and Örmeci, 2017; Ding et al., 2012; Golovko et al., 2011; He et al., 2018; Manoli et al., 2017). The redox potential of ferrate ions is 2.2 V, which is much higher than other regularly used oxidizing agents such as chlorine (1.358 V), hypochlorite (1.482 V), and ozone (2.076 V) (Hernández et al., 2017; Jiang, 2014; Jiang and Lloyd, 2002). However, to-date, there has been few assessments or reports on the *in*

91 *situ* generation of ferrate (Fe(VI)) by wet chemical oxidation for the removal of AOM from
92 seawater.

93 The disinfectant properties of Fe(VI) for inactivating *Escherichia coli* (*E. coli*) were
94 found to be dependent on contact time and dose (Cho et al., 2006). Fe(VI) at dosages less than
95 0.5 mg L⁻¹ can achieve complete inactivation of bacteria, viruses and pathogens, and total
96 coliform, irrespective of the original microbial count (Cho et al., 2006; Jiang et al., 2015). In
97 another research finding, Fe(VI) was reported as a highly efficient disinfectant (95% removal of
98 *E. coli*), showing significant bacteria removal at doses below 1 mg L⁻¹, compared to the poor
99 removal (less than 20%) by a ferric/aluminum based coagulant (Jiang, 2014; Li et al., 2018).
100 Compared to NaOCl disinfection, Fe(VI) is also superior as it is less affected by pH. Moreover,
101 Fe(VI) can be reduced to ferric species, including ferric hydroxide, which can facilitate the
102 flocculation process and minimize the production of disinfection by-products or hazardous by-
103 products in pre-oxidation (e.g., trihalomethanes, bromates, and haloacetic acid) (Dobosy et al.,
104 2016; Golovko et al., 2011; Sun et al., 2016; Talaiekhosani et al., 2016; Zheng and Deng, 2016).
105 Therefore, Fe(VI) is considered a green chemical for water treatment, and treatments using
106 Fe(VI) have been termed as green technology (Sun et al., 2016). Nevertheless, several challenges
107 remain in realizing the practical application of Fe(VI) technology, mainly concerning its high
108 cost and stability issues (Rai et al., 2018; Wacławek et al., 2017).

109 In this study, we use sodium hypochlorite (NaOCl) and ferric (Fe(III)), which are widely
110 used as an oxidant and coagulant pair (Lee et al., 2016b; Sharma et al., 2008), to produce *in situ*
111 Fe(VI) by wet chemical oxidation. Various doses of Fe(III) with NaOCl at different pH values
112 are investigated for the optimization of *in situ* Fe(VI) production in the presence of model AOM

compounds such as humic acid (HA) and sodium alginate (SA) (Lee et al., 2017). A mechanistic study of the *in situ* generated Fe(VI)'s performance in removing real AOM harvested from algal bloom species *Chaetoceros affinis* (CA) and *Hymenomonas* (Hym), which are common in the Red Sea, was conducted based on the optimum conditions identified for the model compounds.

2. MATERIALS AND METHODS

2.1 Chemicals

The coagulant stock solution was prepared by dissolving ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98% pure, anhydrous, Sigma-Aldrich) in Milli-Q water to reach a final concentration of $1,000 \text{ mg L}^{-1} \text{ Fe(III)}$ and was used immediately after preparation. Sodium hypochlorite (NaOCl , reagent grade, available chlorine 10–15%, Sigma-Aldrich) was used as an oxidant and diluted with Milli-Q water to obtain a final stock concentration of $1,000 \text{ mg L}^{-1} \text{ OCl}^-$, which was stored at 4°C prior to use. Two different model AOM compounds were used: sodium-alginate (SA) sodium salt (Sigma-Aldrich) and humic-acid (HA) sodium salt (Sigma-Aldrich). The stock solutions were prepared by dissolving HA and SA separately in Milli-Q water, then filtering with a $0.45 \mu\text{m}$ filter to exclude undissolved salts. The pH was controlled using 0.1 N hydrochloric acid (HCl , ACS reagent, 95.0–98.0%, Sigma-Aldrich) and 0.1 N sodium hydroxide (NaOH , 98% pure, anhydrous, Sigma-Aldrich). Sodium chloride (NaCl) purchased from Sigma-Aldrich (ACS reagent, $\geq 99.0\%$) was used for changing the salinity.

2.2 Algae cultivation and AOM production

Two bloom-forming species of algae, *Hymenomonas* (*Hym*) and *Chaetoceros affinis* (*CA*), were cultivated in batch cultures to simulate an algal bloom event in the Red Sea. *Hym* samples were collected from the Oceanological Observatory of Banyuls-sur-Mer, France, and *CA* samples (CCAP 1010/27) were obtained from the Culture Collection of Algae and Protozoa at the Scottish Association for Marine Science in Oban, Scotland. *Hym* is a marine coccolithophorid which can cause blooms at mild temperatures in nutrient-deficient water, i.e., during spring. The diameter of *Hym* cells, which are spherical and have calcareous walls, ranges between 8–30 µm. *CA* is a marine diatom frequently observed in temperate regions and is responsible for early spring bloom formations, during which it releases extracellular polymeric substances. *CA* cells are oval-cylindrical in shape, have silicate cell walls, and range from 8–25 µm in diameter and 15–30 µm in height.

The algal cultures were inoculated into 5 L of Red Sea water that was previously filtered through a 0.45 µm-cellulose acetate filter, then were autoclaved at 121 °C for 20 min and spiked with an F/2 medium as shown in **Fig. 1**. During algal inoculation, the 5 L culture media was filled in 10 L bottles to allow good air circulation and light penetration. During the incubation period, the temperature was maintained at 20 ± 2 °C, and the culture media was applied with continuous aeration and a 12-12h light-dark cycle (Rehman et al., 2017; Tabatabai et al., 2014; Villacorte et al., 2015b). All glassware and other materials used in the experiments were sterilized. The average cell counts and AOM concentrations (based on DOC concentrations) of the batch cultures were monitored every 2–4 d. The algal culture growths of both species were monitored immediately after sampling on specific incubation days. The cultures were agitated prior to sampling to ensure homogeneity.

Isolation, composition, and structure characterization of AOM

Figure 1. Experimental setup for algae cultivation.

2.3 Experimental procedure

HA and SA are well-known model compounds that represent the humic substances and biopolymer of algal or natural organic matter (Kislenko and Oliynyk, 2004; Xu et al., 2018, 2016) as shown in Fig. S1. As per the LC-OCD data for both algae species *CA* and *Hym*, it was found that humic substances and polysaccharides were the predominant components in the AOM. Therefore, an in-depth study was conducted with the model humic acid (HA) (representing humic substances-like AOM) and sodium-alginate (SA) (representing high molecular weight (HMW) polysaccharides or biopolymer-like AOM) compounds to find the optimum dose condition for *in situ* Fe(VI) generation before applying to AOM obtained from real algal species. Jar test experiments were conducted in a standard jar test apparatus (PB-900TM, Phipps and Bird, USA) to evaluate the efficiency of oxidation-coagulation on the model

AOM compounds at different doses. Accordingly, we measured the amounts of *in situ* Fe(VI) generated with the different combinations of NaOCl and Fe(III), their respective dosages ranging between 0–1.5 mg L⁻¹, as shown in Fig. 2. Coagulation only, without oxidation, served as the control. The tests were conducted in two parts: one using model AOM compounds and the other testing real AOM. Based on the optimum dose condition observed for model compounds, the real AOM extracted from algae species *Hym* and *CA* were examined for DOC removal. The pH of the feed solution was adjusted with 0.1 N NaOH or 0.1 N HCl as necessary. NaOCl was injected into the solution while mixing at 120 rpm for 1 min. Subsequently, Fe(III) was added in the following sequence: rapid mixing at 120 rpm for 1 min, flocculation at 30 rpm for 20 min, and settling for 30 min. Samples were then taken from 3 cm below the surface of the water and filtered through 0.45 µm filters to check the DOC concentration and perform liquid chromatography with organic carbon detection (LC–OCD) analysis.

Figure 2. Experimental procedure for the pre-treatment of AOM.

2.4 Analytical methods

2.4.1 Liquid chromatography - Organic carbon detection (LC-OCD)

AOM was quantified in terms of DOC concentration and measured with a Shimadzu TOC-L analyzer (precision $\pm 2\%$, Shimadzu, Japan) after filtering through a $0.45\ \mu\text{m}$ filter according to the non-purgeable organic carbon (NPOC) measurement procedure. AOM stocks of both algae species were quantified and fractionated using LC-OCD (DOC-Labor, Germany). The LC-OCD measurements were performed in duplicate, and the mean value was reported (variation less than 5%). The samples were carried to the dual chromatographic columns by a mobile phase

(phosphate buffer, 12.5 g KH_2PO_4 (Fluka, USA) + 7.5 g $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ (Fluka, USA) to 5 L) at a flow rate of 1.5 mL min^{-1} . In the LC–OCD, the injection volume and retention time were maintained at 2,000 μL and 180 min, respectively, for all samples. Using the area integration method, the chromatographs were analyzed using a customized software program (ChromCALC) (Huber et al., 2011; Tabatabai et al., 2014). The relative responses of organic carbon, ultraviolet (UV) absorption, and organic nitrogen at different retention times were measured with an online organic carbon detector, UV detector, and organic nitrogen detector. The fractions and concentration of biopolymers (BP), humic substances (HS), building blocks (BB), and low molecular weight (LMW) acids and neutrals were determined on the basis of peaks and retention times observed in the chromatographs (Villacorte et al., 2015b).

2.4.2 Monitoring culture growth

A BD Accuri C6 flow cytometer (Ann Arbor, MI) with 488 nm excitation from a blue solid-state laser was used to measure the concentration of algal cells. Green emission was collected in the FL1 channel ($533 \pm 30 \text{ nm}$ (with excitation at 488 nm)) and red fluorescence in the FL3 channel ($>670 \text{ nm}$) (Rehman et al., 2017). Following the SYBR green propidium iodide (SGPI) staining procedure (Van der Merwe et al., 2014), an individual 495 μL sample was filled in a sterile Eppendorf tube, incubated at 35°C for 10 min, stained with Invitrogen SYBR[®] Green I (SGI) with propidium iodide (PI) (final stain concentration $1 \times \text{SGI} + 10 \mu\text{g mL}^{-1} \text{ PI}$), vortexed for a second time, then incubated for 15 min. 200 μL of the sample was transferred to 96-well plates (with white flat bottoms) for measurement. All sample analyses were performed in triplicate. No dilutions were necessary, as the events did not exceed the performance limit with regard to data acquisition rate ($< 4,000$ events recommended).

2.4.3 Calculation of *in situ* ferrate concentration

The *in situ* generation of Fe(VI) was detected by adding colorless 2,2-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, MP Biomedicals) to the solution containing Fe(VI) to form characteristic green ABTS^{•+} radicals at 415 nm (Noorhasan et al., 2008). The Fe(VI) concentration was measured using indirect ABTS UV-Vis method (UV-VIS spectrophotometer, UV-2600, Shimadzu). As the absorbance at 415 nm is directly proportional to the concentration of Fe(VI), aqueous Fe(VI) concentration can be calculated using the following equation:

$$\text{Concentration of Fe(VI)} = \frac{\Delta A_l^{415} \cdot V_{\text{final}}}{\epsilon \cdot l \cdot V_{\text{sample}}} \quad (\text{Eq. 1})$$

where ΔA_l^{415} is the absorbance at 415 nm after path length correction for blank in cell of l,

ϵ = molar extinction coefficient

l = path length of optical cell,

V_{final} = final volume after addition of all reagents

V_{sample} = volume of original sample

The molar extinction coefficient (ϵ) was considered as $3.40 \pm 0.05 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Hernández et al., 2017; Lee et al., 2005).

3. RESULTS AND DISCUSSION

3.1 Characteristics of AOM produced by *CA* and *Hym*

The changes in the algal cultures' cell concentrations and dissolved AOM, monitored over a 10 d cultivation period, are presented in **Figs. 3a** and **3b**, respectively.

Figure 3. Changes in (a) algal cell concentration and (b) AOM concentration during the batch culture incubation of *CA* and *Hym* for 10 d.

Both species underwent a lag or induction phase during the initial 3 d, followed by an exponential (most active) growth phase from day 4 onwards. During the exponential growth phase, continuous increases in cell density were observed because the algal cells multiplied in the presence of nutrients in the culture medium. *CA* grew relatively faster than *Hym*. On day 10, the cell concentrations of *CA* and *Hym* were $1.81 \times 10^6 \text{ cells mL}^{-1}$ and $8.49 \times 10^5 \text{ cells mL}^{-1}$, respectively (**Fig. 3a**).

244 **Table 1.** LC–OCD data for both algal species.

Species	Days of incubation	Hydrophilic DOC (mg C L ⁻¹)	BP (mg C L ⁻¹)	PS (mg C L ⁻¹)	PN (mg C L ⁻¹)	HS (mg C L ⁻¹)	BB (mg C L ⁻¹)	LMW neutrals (mg C L ⁻¹)
<i>CA</i>	Day 0	7.64	0.09	0.09	-	2.84	1.19	3.52
	Day 1	10.07	0.29	0.29	-	2.71	2.35	4.72
	Day 2	8.58	0.18	0.18	-	3.24	1.11	4.05
	Day 4	10.82	1.34	1.23	0.11	4.42	0.86	4.20
	Day 6	11.51	1.40	0.73	0.67	5.03	0.94	4.14
	Day 10	10.41	1.26	1.2	0.06	5.59	0.31	3.25
<i>Hym</i>	Day 0	7.60	0.11	0.1	0.01	2.25	1.24	4.00
	Day 1	9.20	0.53	0.41	0.12	2.42	1.99	4.27
	Day 2	7.81	0.22	0.22	-	2.86	0.84	3.91
	Day 4	10.24	1.050	1.04	0.01	4.14	0.76	4.29
	Day 6	10.72	0.68	0.61	0.07	4.16	0.70	5.17
	Day 10	10.19	1.49	1.3	0.19	4.46	0.35	3.88

245

246 Using LC–OCD, the components of the dissolved AOM produced from *CA* and *Hym*

247 were analyzed. As shown in Table 1, the AOM mostly consisted of BP (or HMW) AOM, HS,

248 and LMW neutrals (or LMW–AOM). The initial concentrations (at day 0) of BP, HS, and LMW

249 neutrals may be attributed to the specific compounds in the medium in which the algae species

250 were inoculated (Villacorte et al., 2015b); however, from day 4, which marked the exponential

251 growth period, significant increases in the concentrations of HS and LMW neutrals were

252 observed. Also, considerable increases in BP production for both *CA* and *Hym* were observed

253 compared to the initial period, which is mainly due to increase in the production of
 254 polysaccharides (PS). The amount of AOM increased as well, owing to the higher BP and HS
 255 concentrations during the cultivation period. On day 10 of incubation, *CA* recorded relatively
 256 higher levels of HS (54%) and PS (95%) production whereas *Hym* produced relatively less HS
 257 (44%) and PS (87%).

258

259 **Figure 4.** Ratio of BP to DOC (BP/DOC %) over incubation time.

260 **Fig. 4** plots the ratio of the relative concentrations of BP to DOC over time for both algal
 261 species. On day 6, the hydrophilic DOC concentrations for *CA* and *Hym* were 11.51 and 10.72
 262 mg C L⁻¹, respectively, and a higher BP:DOC ratio was observed for *CA* (12%) compared to
 263 *Hym* (6%); this was consistent with other studies (Merle et al., 2016; Rehman et al., 2017).

264

3.2 Comparison of Fe(III) and *in situ* Fe(VI) for the removal of AOM model compounds

Various combinations of oxidant NaOCl and coagulant Fe(III) dosages were used to generate *in situ* Fe(VI) at pH 5, 8, and 12 in saline water (35 g L⁻¹ NaCl). The initial DOC concentration of the influent solution was maintained at 5 mg C L⁻¹ for both HA and SA.

3.2.1 Performance of Fe(III) vs *in situ* Fe(VI) for HA removal

Table 2 demonstrates higher HA removal by *in situ* generated Fe(VI) in the presence of NaCl at all pH conditions. At pH 5, compared to when only Fe(III) was added as a coagulant, the combinations of 1.5 mg L⁻¹ of NaOCl with 1.5 mg L⁻¹ of Fe(III) and 0.5 mg L⁻¹ of NaOCl with 0.5 mg L⁻¹ of Fe(III) showed superior HA removal by 41% and 36%, respectively, via *in situ* Fe(VI) generation. Notably, the highest performance of HA removal was observed at pH 8 via *in situ* generated Fe(VI); 70% removal achieved by 1.5 mg L⁻¹ NaOCl with 1.5 mg L⁻¹ Fe(III), and 35% by 0.5 mg L⁻¹ NaOCl with 0.5 mg L⁻¹ Fe(III). In comparison, coagulation by Fe(III) at the doses of 1.5 mg L⁻¹ and 0.5 mg L⁻¹ showed only 47% and 17% removal, respectively. At alkaline conditions (i.e., at pH 12), coagulation by Fe(III) was ineffective for HA removal but *in situ* Fe(VI) maximized HA removal by 25% even when 0.5 mg L⁻¹ NaOCl with 0.5 mg L⁻¹ Fe(III) was added.

Table 2. Performance of Fe(III) vs *in situ* Fe(VI) for HA removal at different pH levels.

Influent condition	pH	Coagulant	Doses (mg L ⁻¹)	DOC removal %
HA mixed with Milli-Q water in the presence of NaCl (35 g L ⁻¹), initial DOC equivalent to 5 mg C L ⁻¹	5	Fe(III)	Fe(III): 0.5 mg L ⁻¹	22.96
			Fe(III): 1.5 mg L ⁻¹	34.68
		<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	35.79

		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	41.57
8	Fe(III)	Fe(III): 0.5 mg L ⁻¹	17.07
		Fe(III): 1.5 mg L ⁻¹	47.10
	<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	35.05
		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	69.77
12	Fe(III)	Fe(III): 0.5 mg L ⁻¹	8.93
		Fe(III): 1.5 mg L ⁻¹	11.78
	<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	25.26
		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	21.11

282

283 HA dissolves and then diffuses into water in the form of a humate complex with ions.
 284 Humate complexes are formed by dissociating hydrogen ions from the carboxyl (COOH) and
 285 hydroxyl (OH) groups of HA, resulting in a negatively charged anion (COO⁻ or -CO⁻) (Illés and
 286 Tombácz, 2003). The diffusivity of HA increases with lower pH and higher NaCl concentration
 287 (Esmaeili et al., 2012), which can be explained by the compaction of HA molecules at low pH
 288 and high ionic strength. As reported in a previous study (Takahashi et al., 1999), the behavior of
 289 Fe(III) is greatly affected by HA at various pH levels, forming complex compounds such as
 290 humate at pH ranging from 3.5–8.5, while under alkaline conditions, absorption and hydrolysis
 291 predominate. Significant absorption of HA was observed in the presence of NaCl (Esmaeili et
 292 al., 2012). Therefore, the removal of HA was most effective at pH values 5 and 8, where HA
 293 deprotonated to a higher negative charge, potentially due to the formation of humate. In high
 294 salinity, Fe(III) hydrolyses to various species with different charges at various pH values.

Iron was more efficient in neutral and alkaline mediums ($6 < \text{pH} < 9$). In cases of pH levels higher than 9.0–9.5, monomeric anions, $\text{Fe}(\text{OH})_4^-$, were generated by consuming OH^- ions instead of $\text{Fe}(\text{OH})_3$, causing a slight decrease in the final pH and an overall decrease in removal efficiency (Koby et al., 2014). Furthermore, during wet oxidation (Talaiekhosani et al., 2017), Fe(III) salt is oxidized under alkaline conditions, by either hypochlorite or chlorine oxidants as shown in Equations 2 and 3.

Also in line with previous studies (Cook and Olive, 2012; Ghosh et al., 2014; Lee et al., 2005; Sharma et al., 2015), ferric hydroxide formed when the pH value was nearer to neutral where the concentration of iron is the lowest, leading to higher Fe(VI) production through the consumption of the generated ferric hydroxide. Therefore, at pH 8, the significant formation of aqueous Fe(VI) was visually verified by the ABTS method. The colorless ABTS solution reacts with Fe(VI) to form green $\text{ABTS}\cdot^+$ radicals (Noorhasan et al., 2008).

According to a previous study (Sharma et al., 2015), approximately 38% removal of fulvic acid was observed when using $10\text{ }\mu\text{M}$ Fe(VI) with an initial concentration of 6 mg L^{-1} . Another study demonstrated that Fe(VI) could remove an additional 10-20% of DOC compared to ferric sulfate and that 100% inactivation of *E. coli* could be achieved at lower doses of ferrate

316 compared to NaOCl with ferric sulfate at pH 8 with 30 min contact time (Jiang et al., 2007).
317 Compared to Fe(III) or aluminum coagulants, Fe(VI) has superior removal efficacy in terms of
318 turbidity, COD, color, and bacterial inactivation removal. Among the various oxidants used in
319 water treatment, Fe(VI) was demonstrated to be one of the powerful oxidant to treat organic and
320 inorganic pollutants from water. It has also been reported that the TOC removal efficiency for
321 grey water using Fe(VI) is higher at pH 8 compared to pH 5 and pH 12 (Song et al., 2017).
322 Overall, *in situ* Fe(VI) has been noted for performing a dominant and proactive role for HA
323 removal in saline conditions at pH 8, which is around the natural pH of most seawaters.
324 Therefore, a more detailed study was conducted for HA removal at various doses of oxidant and
325 coagulant at pH 8.

326 **Fig 5** illustrates the DOC removal of HA using various doses of Fe(III) against *in situ*
327 Fe(VI) produced by multiple combinations of NaOCl and Fe(III) at pH 8 (Table S1). The
328 different concentrations of *in situ* generated Fe(VI) were measured by indirect ABTS UV-Vis
329 method and are presented in **Fig. 6**. *In situ* generated 1.46 mg L^{-1} Fe(VI) at combined doses of
330 1.5 mg L^{-1} Fe(III) with 1.5 mg L^{-1} NaOCl appeared to have the highest DOC removal efficiency
331 (72%).

Figure 5. Performance of Fe(III) vs *in situ* Fe(VI) for HA removal at pH 8.

Figure 6. *In situ* generation of Fe(VI) at pH 8 in the presence of AOM model compound (HA).

3.2.2 Performance of Fe(III) vs *in situ* Fe(VI) for SA removal

The removal of SA was studied at different pH conditions (Table 3). At pH 5, higher SA removal (37%) was observed with coagulation alone by Fe(III) at the dose of 1.5 mg L⁻¹, whereas 29% SA removal was observed for *in situ* Fe(VI) generation by 1.5 mg L⁻¹ NaOCl with 1.5 mg L⁻¹ Fe(III). At pH 8, the control coagulation by 1.5 mg L⁻¹ Fe(III) showed a 29% SA removal, but for *in situ* generated Fe(VI) by 1.5 mg L⁻¹ NaOCl with 1.5 mg L⁻¹ Fe(III) exhibited a higher removal efficiency (42%). At pH 12, very low SA removal was observed for both Fe(III) and *in situ* Fe(VI), compared to pH 5 and 8.

Table 3. Performance of Fe(III) vs *in situ* Fe(VI) for SA removal at different pH levels.

Influent condition	pH	Coagulant	Doses (mg L ⁻¹)	DOC removal %
SA mixed with Milli-Q water in the presence of NaCl (35g L ⁻¹), initial DOC	5	Fe(III)	Fe(III): 0.5 mg L ⁻¹	13.52
			Fe(III): 1.5 mg L ⁻¹	37.07

equivalent to 5 mg C L ⁻¹	<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	12.89
		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	28.62
8	Fe(III)	Fe(III): 0.5 mg L ⁻¹	17.30
		Fe(III): 1.5 mg L ⁻¹	29.12
	<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	7.59
		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	42.38
12	Fe(III)	Fe(III): 0.5 mg L ⁻¹	16.30
		Fe(III): 1.5 mg L ⁻¹	17.50
	<i>In situ</i> Fe(VI)	Fe(III): 0.5 mg L ⁻¹ , NaOCl: 0.5 mg L ⁻¹	6.96
		Fe(III): 1.5 mg L ⁻¹ , NaOCl: 1.5 mg L ⁻¹	19.08

A previous study (Chekli et al., 2017) on coagulated organic compounds characterized by LC-OCD also reported a lower removal of HMW biopolymer such as alginate by ferric coagulants compared to LMW aromatic organic compounds such as humic substances. In another research finding (Kislenko and Oliynyk, 2004), a higher removal rate of humic acid was observed, which was attributed mainly to the formation of intermolecular bindings between metal ions and acidic groups of humic acid (Gogoi et al., 2016). In addition, the generation of *in situ* ferrate was relatively higher for HA compared to SA. Interestingly, as shown in Table S2, DOC removal was effective at dosages of 1.5 mg L⁻¹ NaOCl and 1.5 mg L⁻¹ Fe(III) at pH 8, which we attribute to the *in situ* generation of Fe(VI). Thus, to find the optimal dosage, SA removal was further investigated at pH 8 in saline conditions.

Figure 7. Performance of Fe(III) vs *in situ* Fe(VI) for SA removal at pH 8.

Figure 8. *In situ* generation of Fe(VI) at pH 8 in the presence of AOM model compound (SA)

The removal of SA by *in situ* Fe(VI) was in good agreement with that of HA, with 1.26 mg L⁻¹ Fe(VI) generated *in situ* from 1.5 mg L⁻¹ NaOCl with 1.5 mg L⁻¹ Fe(III) at pH 8 showing the highest DOC removal efficiency (42%) as presented in **Fig. 7**. The *in situ* generation of Fe(VI) was also observed in various combinations of NaOCl and Fe(III) doses, with the colorless ABTS solution creating the characteristic green color. The Fe(VI) concentration was measured using indirect ABTS UV-Vis method, and the results are shown in **Fig. 8**.

For both model HA and SA compounds, DOC removal was most efficient when applying 1.5 mg L⁻¹ NaOCl and 1.5 mg L⁻¹ Fe(III) for *in situ* Fe(VI) generation at pH 8. As can be seen from **Fig. 5 & 7**, *in situ* Fe(VI) generation varied with respect to different organic species, resulting in 1.46 mg L⁻¹ and 1.26 mg L⁻¹ of Fe(VI) concentration for HA and SA, respectively. The same optimum NaOCl and Fe(III) dose conditions for *in situ* Fe(VI) generation was applied

to AOM obtained from two bloom-forming algae species to examine its performance in removing real AOM produced by algae.

3.3 Performance of *in situ* Fe(VI) for the removal of AOM produced by algae

The AOM produced by *CA* and *Hym* was collected to study the removal efficiency at the optimum condition for generating the maximum *in situ* Fe(VI), i.e., the application of 1.5 mg L⁻¹ NaOCl with 1.5 mg L⁻¹ Fe(III). The DOC concentrations of the extracted AOM from *CA* and *Hym* were 15.4 mg L⁻¹ and 17.6 mg L⁻¹, respectively, and the initial pH of the extracted AOM was about 8.1. For the *in situ* Fe(VI) performance study, the extracted AOM stocks were diluted to 50, 20, and 10% with Red Sea water that was previously filtered through a 0.45 µm cellulose acetate filter, followed by autoclaving at 121 °C for 20 min to mimic actual AOM released during algal bloom events in seawater (Chekli et al., 2017). The DOC concentration of the Red Sea water was recorded as 0.82 ± 0.05 mg L⁻¹. **Fig. 9** demonstrates the DOC removal for *CA* and *Hym* at different AOM concentrations. Enhanced AOM removal performance was observed for both *CA* and *Hym* with respect to varying AOM concentrations and compositions, which was consistent with a previous study (Sharma et al., 2015). Comparatively higher DOC removal was found for *Hym* (92%) and *CA* (83%) under *in situ* Fe(VI) when their initial feed AOM concentrations were 2.63 and 2.48 mg L⁻¹, respectively. *In situ* Fe(VI) removed AOM extracted from *Hym* relatively better than AOM extracted from *CA*. This can be attributed to the fact that on day 10, *Hym* had a lower BP:HS ratio of 3.0, compared to *CA*'s 4.4, which is in good agreement with the model compound study. As per previous research findings (Song et al., 2016; Yang et al., 2012), Fe(VI) has a high affinity for oxidizing compounds such as HS that contain C = C double bonds or an aromatic structure. Also, on day 10, the HS for *CA* was 5.59 C mg L⁻¹ whereas for *Hym* it was only 4.46 C mg L⁻¹. Therefore, the *in situ* generated Fe(VI) handled

relatively fewer dissolved organic matters fractions for oxidation in the case of *Hym* than *CA*, resulting in higher DOC removal for *Hym*. DOC removal can be attributed to the removal of BP through the formation of Fe-BP aggregates (Tabatabai et al., 2014). Even at very high AOM concentrations of *CA* (8.52 mg L⁻¹) and *Hym* (9.62 mg L⁻¹), *in situ* generated Fe(VI) was able to achieve removal efficiencies of 66% and 74%, respectively.

Figure 9. DOC removal (%) by *in situ* generated Fe(VI) at various initial feed AOM concentrations of *CA* and *Hym*.

The dissolved AOM of *CA* and *Hym* contained significant amounts of BP (> 20,000 Da) including medium molecular weight compounds (HS~1000 Da and BB 350~500 Da) and LMW substances (neutrals and acids < 350 Da). In a recent study, high levels of fouling and flux decline in MF membranes were attributed to the existence of BP compounds in dissolved AOM (Zhang et al., 2013). BP mainly consists of surface-active polysaccharides which have metal-binding carboxyl and hydroxyl groups (Kenney and Fein, 2011). Furthermore, BP could have a strong affinity for interacting with trivalent metal Fe(III) to form large-sized colloidal Fe-BP complexes. *In situ* generation of ferrate, which is a strong disinfectant that oxidizes and

facilitates the flocculation process, has a proactive role in AOM removal. The high removal efficiency observed at low AOM concentrations may be due to complete charge neutralization. Moreover, the use of oxidant (NaOCl) and coagulant Fe(III) facilitated the *in situ* generation of Fe(VI), which possesses powerful disinfecting properties to control algal cells and AOM. Overall, it is concluded that a superior AOM removal efficiency can be achieved by *in situ* generated Fe(VI) over coagulation by Fe(III).

4. Conclusions

This study provides insight into the *in situ* generation and performance of aqueous Fe(VI) for removing real AOM produced from harmful algal blooming species as well as model AOM compounds such as HA and SA. The major conclusions are as follows.

- Two algal bloom-forming species, *Hym* and *CA*, were cultivated in batch cultures. Cell concentrations of *CA* and *Hym* reached 1.81×10^6 cells mL⁻¹ and 8.49×10^5 cells mL⁻¹, respectively. AOM extracted from *CA* consisted of 12% BP (e.g., polysaccharides and proteins) compounds, 53% HS (refractory organic), and 31% LMW neutral compounds; while AOM extracted from *Hym* consisted of 14% BP compounds, 44% HS, and 38% LMW neutral compounds.
- AOM removal by *in situ* Fe(VI) was superior to that by Fe(III). At the optimum saline condition at pH 8, 72% of HA was removed by *in situ* Fe(VI) at 1.46 mg L⁻¹ concentration compared to only 47% removal by coagulation by Fe(III) alone at 1.5 mg L⁻¹ concentration. Moreover, SA removal increased up to 42% using *in situ* generated Fe(VI) coagulation at 1.26 mg L⁻¹ concentration, compared to 29% when using only Fe(III) coagulation.

- For AOM extracted from *CA* and *Hym*, excellent DOC removal (92% and 83%, respectively) was achieved by *in situ* generated Fe(VI) when the influent AOM concentrations of *CA* and *Hym* were 2.48 and 2.63 mg L⁻¹ (in terms of DOC), respectively. This could be attributed to the high affinity of Fe(VI) for oxidizing HS and for removing BP by forming Fe-BP aggregates compared to conventional coagulation.

■ ASSOCIATED CONTENT

Supporting Information

■ AUTHOR INFORMATION

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Notes

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Highlights:

1. In situ ferrate was generated by combined dosages of sodium hypochlorite and ferric.
2. Ferrate concentration was determined using indirect ABTS UV-Vis method.
3. Algal Organic Matter removal by *in situ* ferrate was superior to that by ferric.
4. *In situ* generated ferrate showed high affinity for oxidizing humic substances.
5. *In situ* generated ferrate removed biopolymers by forming aggregates.