

## Comparison of liquid ferrate and ferric chloride coagulants for humic acid removal in a seawater reverse osmosis desalination plant

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### ABSTRACT

This study investigates the removal of humic acid from seawater through coagulation–flocculation–sedimentation treatment. Liquid ferrate Fe(VI) and ferric chloride Fe(III) coagulants were used to oxidize humic acids. The experimental results demonstrated that Fe(VI) has a superior performance compared to Fe(III) in terms of removal of dissolved organic carbon (DOC), turbidity, and natural organic matter (NOM). DOC removal was up to 95% with Fe(VI) and up to 58% with Fe(III). NOM fractions removal was higher with Fe(VI) compared to Fe(III). Biopolymers removal was up to 80% for Fe(VI) and up to 60% for Fe(III). Humic substances removal was up to 97% for Fe(VI) and up to 68% for Fe(III). The removal of low molecular weight (LMW) compounds showed a different pattern in which Fe(VI) achieved up to 98% removal for LMW neutrals and up to 88% removal of LMW acids while Fe(III) increased the concentration of LMW-neutrals and LMW-acids. The results of this research demonstrates that liquid ferrate can perform better than ferric chloride in the coagulation–flocculation–sedimentation process for treating seawater containing humic acids in terms of removing turbidity, total organic carbon and DOC fractions. Therefore, liquid ferrate is a potential coagulant to enhance seawater treatment during high humic substances conditions.

*Keywords:* Desalination; Pretreatment; Ferrate; Coagulation; Humic acid; Natural organic matters

### 1. Introduction

The use of seawater reverse osmosis (SWRO) desalination technology has been significantly increasing around the world but membrane fouling still remains an operational obstacle [1]. One of the main challenges that impacts the operation of SWRO desalination plants is natural organic matter (NOM), such as humic substances (HS), which react with chlorine and form disinfection by-products (DBPs) and bioactive organic compounds during the chlorination–dechlorination process [2]. NOM contains HS, proteins, amino acids, polysaccharides, carbohydrates, aldehydes, ketones and alcohols, where it is the dominant fraction. Humic substances (HS) are divided into fulvic acids (FA) and humic acids (HA) according to their aqueous solubility.

FA are hydrophilic acids soluble under all pH conditions, while HA is soluble at a higher pH. The molecular weight of HA is greater than 100,000 Daltons [3]. Feed water with a high load of NOM can cause irreversible fouling of membranes due to clogging and poor effluent quality of the pretreatment processes [4]. Evaluation of different pretreatment options to reduce the content of humic substances can help in reducing the impact of biofouling [5].

There are different treatment methods used to reduce humic acids in raw seawater such as use of subsurface intake systems to reduce NOM concentrations [6–10]. The most commonly used pretreatment option in SWRO desalination plants is the coagulation–flocculation–sedimentation (CFS) process. Increasing the coagulant doses in conventional coagulation leads to an increase in sludge production and

the chemical use and storage requirements in a water treatment facility [11]. Previous study showed that the polyaluminum chloride (PACl) and polyaluminum ferric chloride (PAFCl) as green coagulants has high potential to remove humic acid from surface water, but PAFCl had a better performance regarding the treatment of aluminum residuals [12]. According to a previous study, the surfactant-modified nanozeolite (SMNZ) had high potential as a low-cost sorbent for the removal of humic acid in water and wastewater treatment processes [13].

In this study, it was attempted to improve this conventional treatment method and make it more robust for removal of NOM and more specifically humic acids with the use of a new coagulant. This work aims to evaluate liquid ferrate coagulant performance in treating humic acid in comparison with a conventional ferric chloride coagulant for seawater treatment. Advanced coagulation with the use of liquid ferrate (Fe(VI)) is believed to have a significant role in seawater treatment, as an oxidant, disinfectant and coagulant. It has been recognized as a promising alternative pretreatment of SWRO for biofouling reduction [14–17]. This study paves the way to use CFS pretreatment with liquid ferrate coagulant to remove the humic acids in SWRO desalination plants. The use of liquid ferrate as a coagulant for humic acid removal in SWRO desalination plants would contribute to lower rates of RO membrane biofouling.

## 2. Material and methods

### 2.1. Feed water quality

Feed water was prepared using synthetic seawater by mixing Red Sea water with humic acids. Red Sea water quality characteristics are presented in (Table 1).

The good quality of Red Sea water requires higher organic concentration to conduct the required study. To clearly study the effect of liquid ferrate on humic acids in seawater, a humic acid sodium salt (Humic Acid Sodium Salt, Technical Grade, Black Color and Granules, Sigma-Aldrich, USA) enriched solution was prepared by diluting humic acid stock solution with Milli-Q water to the desired concentration of 13 mg/L as dissolved organic carbon (DOC). The synthetic seawater was passed through a 0.45  $\mu\text{m}$  syringe filter and the concentration of humic acid was measured by using a liquid chromatography–organic carbon detection (LC-OCD) (DOC Labor, Germany) device. The feed water characteristics are identical to Red Sea water except

for the increased concentration of DOC which is 13 mg/L and it mainly contains humic substances. Humic substances concentrations were measured by using the LC-OCD.

### 2.2. Coagulation test

The coagulation effectiveness of ferric chloride Fe(III) vs. liquid ferrate Fe(VI) on pretreatment of seawater containing a high humic acid concentration was evaluated. Liquid ferrate(VI) was produced *in-situ* through wet oxidation by adding ferric chloride ( $\text{FeCl}_3$ ) to a mixture of sodium hydroxide (NaOH) and sodium hypochlorite (14%) ( $\text{NaOCl}$ ) [14]. A dose of (1–3 mg-Fe/L) liquid ferrate and ferric chloride was added separately to the seawater which contained humic acid and the performance was compared using standard jar tests.

A pH range was selected to represent regions of best performance for iron-based coagulants, as well as to allow investigation of liquid ferrate(VI) performance in different pH ranges of synthetic seawater (8–9). The pH was adjusted by adding a predetermined quantity of 0.5 N NaOH or HCl. Coagulation conditions were set at rapid mixing for 1 min at 200  $\text{s}^{-1}$ ; flocculation for 20 min at 40  $\text{s}^{-1}$ ; and quiescent settling for 60 min [14,16]. A bench scale experiment was set up for the pretreatment system, which included CFS processes as presented in Fig. 1.

### 2.3. Measurements

Removal of organic carbon was evaluated by LC-OCD (DOC Labor, Germany), which was used to determine the

Table 1  
Red Sea water quality characteristics

Parameter	Value
Temperature, °C	23–24
pH	7.9–8.2
Total dissolved solids, mg/L	36,000
Conductivity, mS/cm	58–60
Turbidity, NTU	0.75–1.8
Total organic carbon, mg/L	0.75–1.2
Dissolved organic carbon, mg/L	0.7–0.9
Total alkalinity, mg/L	118

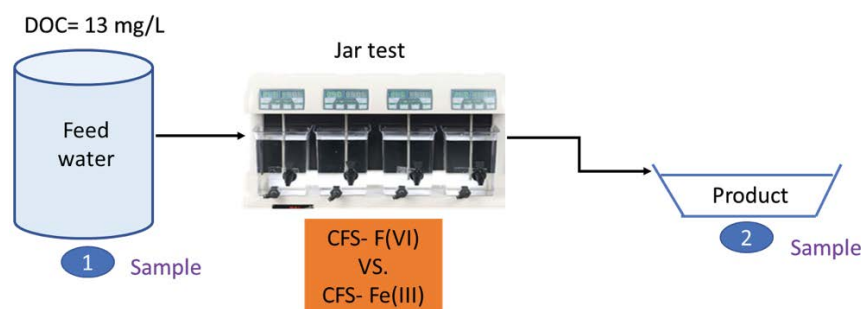


Fig. 1. Schematic diagram of the pretreatment system which includes coagulation–flocculation–sedimentation processes, 1 and 2 indicate sampling locations.

DOC and natural organic matter fractions (NOM). The components of the NOM measured, included biopolymers (BP), building blocks (BB) humic substances (HS), low molecular weight acids (LMW-A) and low molecular weight neutrals (LMW-N) [18]. For the DOC and NOM fractions, a calibration curve was established for both molecular masses of humics and detector sensitivity prior to the sample measurements. For the molecular mass calibration, humic acid and fulvic acid standards (Suwannee River Standard II) were used. Potassium hydrogen phthalate and potassium nitrate ( $\text{KNO}_3$ ) were used for sensitivity calibration [19,20].

Turbidity removal was measured using a HACH-Lange turbidity meter (Germany). Three different calibrations standards were used to calibrate the device before use, including 0, 1, 10, and 100 NTU. Standard water quality parameters (e.g., turbidity, DOC, NOM fractions) were measured before and after CFS treatment.

### 3. Results and discussion

In the presence of HA in seawater with a concentration of 13 mg/L, a general trend of turbidity removal increases with the increase in the Fe(VI) dose. The turbidity of seawater containing humic acid was measured without filtering. The Fe(VI) coagulant proved to be more efficient by reducing the turbidity up to 92% (Fig. 2A) compared to 81% reduction with the use of the Fe(III) coagulant (Fig. 2B). Fe(VI) has an ability to remove the suspended particles, thereby reducing turbidity in the feed water [21]. The removal efficiency of turbidity using Fe(VI) was higher than the other coagulant types [22]. CFS treatment with low dosage of Fe(VI) was able to achieve a greater degree of floc formation. This

was attributed to the enmeshment of turbidity by large flocs formation with the use of CFS-Fe(VI) which enhance the sedimentation process [23].

The removal of DOC concentration after using Fe(VI) coagulant was 85%–97% (Fig. 2C) while use of Fe(III) reduced DOC concentration in the range of 24%–58% (Fig. 2D). In this case, with an initial DOC concentration of 12.8 mg/L, an increase of DOC removal was observed with the increase of the Fe used for Fe(VI) and Fe(III). Generally, DOC removal achieved by the Fe(VI) coagulant is greater than that achieved with the Fe(III) coagulant [15,16]. Fe(VI) coagulant, which decomposes to Fe(III), is capable of decreasing DOC and NOM concentration [24]. CFS-Fe(VI) can enhance the seawater quality by increasing organic matter removal. This is attributed to degradation of the organic matter by using Fe(VI) to smaller dissolved organic matter fractions. These degraded organics with Fe(VI) are easily removed by CFS process. The kinetics and extent of oxidation and charge interaction between cationic Fe hydrolysis species and  $\text{Fe}(\text{OH})_3$  precipitation are the main mechanisms of organics removal by Fe(VI) [25]. Fe(VI) effectively reduces the DOC due to the overall effect of oxidation, coagulation and sedimentation on the removal of organic carbon compounds.

The NOM of seawater consists of different organic compounds, such as biopolymers (BP), building blocks (BB), humic substances (HS), low molecular weight acids (LMW-A) and low molecular weight neutrals (LMW-N) [26].

Fe(III) removed 60% of the biopolymers (BP) while Fe(VI) removed 60%–80% of the BP (Fig. 3). The removal is due to biopolymers adsorption in the precipitated ferric hydroxide and the formation of Fe-large biopolymer aggregates [27].

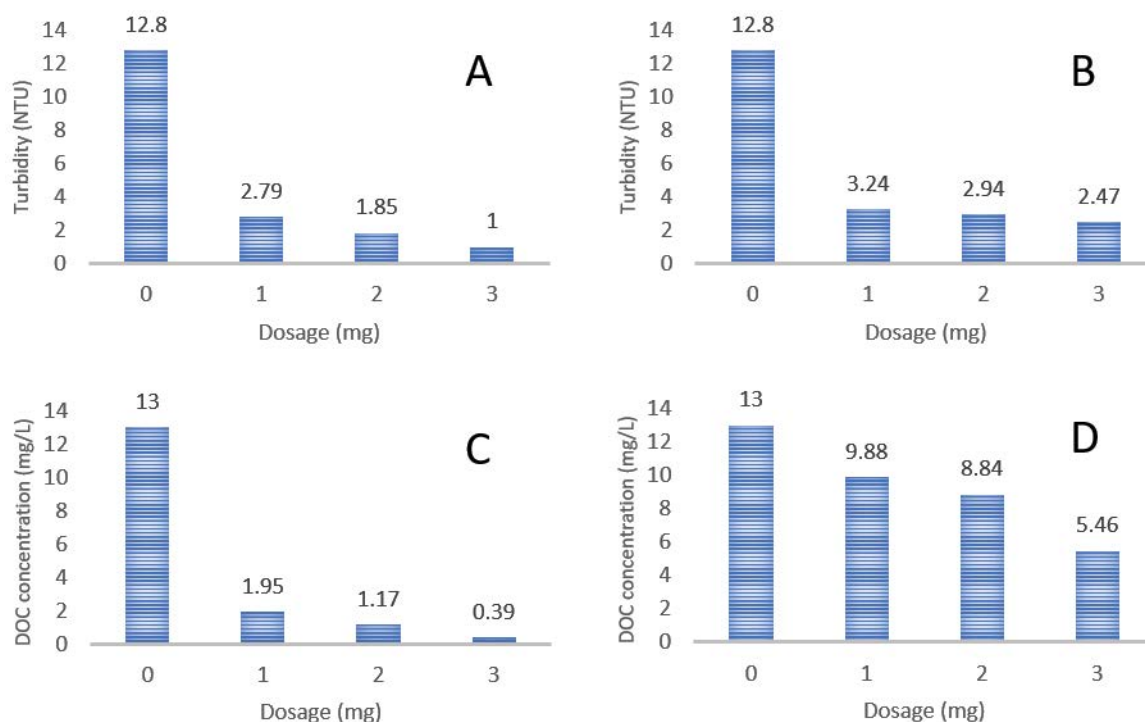


Fig. 2. (A) Turbidity removal by using Fe(VI), (B) turbidity removal by using Fe(III), (C) dissolved organic carbon removal by using Fe(VI), and (D) dissolved organic carbon removal by using Fe(III).

Fe(VI) showed higher performances in removing humic substances such as humic acids (HA) with a removal of 88%–97% compared to 33%–68% for Fe(III) (Fig. 3). It was also demonstrated in the literature that humic substances such as humic acids were reduced significantly by using Fe(VI) [25]. In fact, Fe(VI) reduction from Fe +6 to Fe +3, leads to the formation of  $\text{Fe}(\text{OH})_3$ , which enhances the removal of humic acid through the adsorption and coprecipitation [28].

For building blocks (BB), a similar concentration reduction compared to the trend for HS was observed for the two coagulants with the removal percentage from 86% to 96% for the Fe(VI) and 57% to 93% for Fe(III) (Fig. 3).

A different pattern was observed for LMW compounds in which Fe(VI) removed 65% to 98% of LMW neutrals (LMW-N) while Fe(III) increased the concentration of (LMW-N). Similarly, Fe(VI) removed up to 88% of LMW

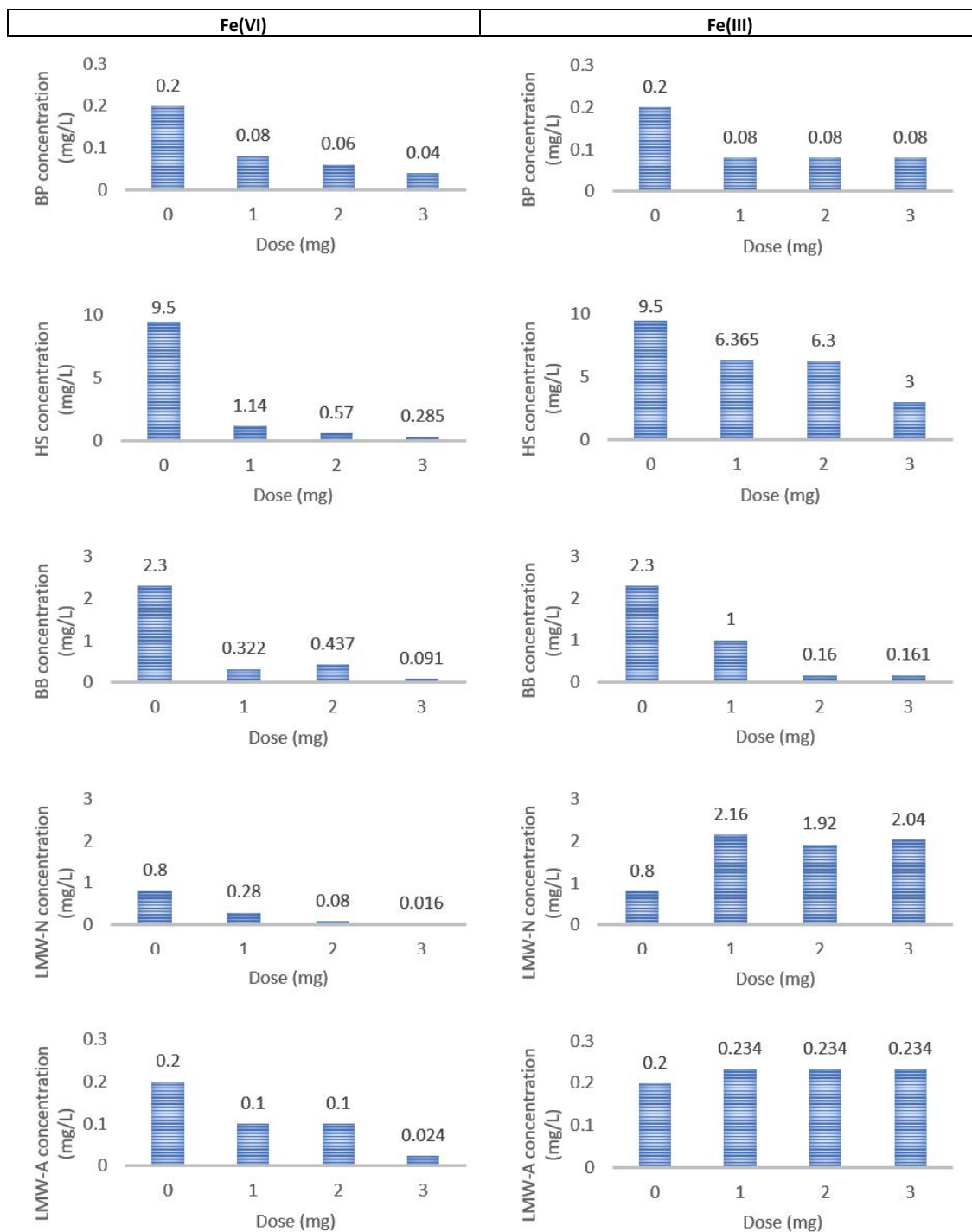


Fig. 3. Impact of Fe(VI) vs. Fe(III) coagulants on natural organic matter of seawater contains humic acids.

acid (LMW-A) while Fe(III) increased the concentration of (LMW-A) (Fig. 3).

The reduction of these compounds is primarily attributed to the coagulation effect of both compounds. Using the same Fe dose, the Fe(VI) coagulant showed better performance than Fe(III) coagulant. This is due to the double impact of coagulation and oxidation of the Fe(VI) coagulant. While Fe(VI) acts as strong oxidant, the ferric hydroxide(III) produced from the decomposition of Fe(VI) improves the coagulation condition for the removal of metals, non-metals, radionuclides and humic acids [29]. The mechanism of the ferrate oxidation would provide a shift in the distribution of NOM toward smaller more oxygenated compounds, also Fe(VI) has a better adsorption capabilities compared to Fe(III) [30,31].

In this study, Fe(VI) was found to be substantially more effective at turbidity, DOC, BP, HS, BB, LMW-N, and LMW-A removal as compared to Fe(III) in seawater contains high HA concentrations.

Liquid ferrate coagulant helps in reducing NOM, which contributes to membrane biofouling. In addition, ferrate produces only very minimal free-chlorine and iron residuals which were well below the limit recommended by membrane manufacturers [17]. Furthermore, CFS-Fe(VI) improves the efficiency of HA removal at a reduced coagulant dosage compared to the conventional coagulant (CFS- Fe(III)). So, the amount of the produced sludge and treatment cost would be lower [17]. It is therefore suggested that Fe(VI) can be a potential alternative for traditional coagulation treatment of seawater with high humic substances concentration.

#### 4. Conclusions

The study investigated the performance of Fe(VI) vs. Fe(III) coagulants on removal of humic acids in raw feed water pretreatment for SWRO desalination plants. The results revealed that Fe(III) has a slightly lower HA removal efficiency compared to Fe(VI). Fe(VI) showed superior performance in the pretreatment of seawater containing high HA concentrations. The LMW compounds were removed at substantially higher percentages, which is very important in reducing membrane biofouling rates. This is due to the triple role of Fe(VI) in seawater treatment, which acts as a powerful oxidant, disinfectant and coagulant. The results of this study have shown that liquid ferrate achieved better removal of turbidity, total organic carbon and DOC and NOM than ferric chloride in seawater containing HA. Indeed, this study showed that use of Fe(VI) in SWRO pretreatment is a promising coagulant to enhance the performance of pretreatment through the reduction of humic acid concentrations, and would contribute to membrane biofouling reduction in SWRO desalination plants.

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