Desalination Pretreatment—Assessment of Ferrate to Treat Algae Impacted Seawater

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ABSTRACT: This study evaluates an electrolytically generated ferrate reagent (sodium ferrate(VI)) as an alternative oxidant, disinfectant, and coagulant for treating algae-impacted seawater, comparing it to traditional bulk ferric chloride treatment.

INTRODUCTION

Harmful algal blooms (HABs) increase organic and solid loads in desalination plant seawater feeds, risking damage to pretreatment and reverse osmosis (RO) membrane performance [1,2]. Effective multi-step pretreatment is required to prevent both physical fouling by particulate materials and biofouling on the membrane surface.

Conventional methods combine oxidation and filtration to reduce the concentration of particles and organic substances that cause membrane biofouling [3]. The type of chemicals used to treat algal organic matter (AOM) significantly affects both process efficacy and cost [2,3]. Effective AOM oxidation and removal reduces membrane biofouling [4].

This study evaluates an electrolytically generated ferrate reagent (sodium ferrate(VI)) as an alternative oxidant, disinfectant, and coagulant for treating algae-impacted seawater, comparing it to traditional bulk ferric chloride treatment.

BACKGROUND

Historically, a ferrate solution has not been commercially available or widely used in treatment processes because it decomposes rapidly and cannot be manufactured, transported, or stored. As a result, hazardous bulk ferric chloride has been commonly used as a treatment chemical in applications requiring oxidation, disinfection and coagulation.

However, a proprietary new technology—an in-situ electrolytic ferrate reagent generation system—has now made the commercial use of a non-toxic ferrate reagent a reality. In seawater desalination facilities reliant on bulk ferric chloride, the electrolytically generated ferrate reagent offers a non-toxic, environmentally friendly alternative for treating algae-impacted seawater, removing AOMs and reducing membrane biofouling.

A comparative study of the ferrate reagent and bulk ferric chloride was undertaken in a water research laboratory in College Station, Texas.

OBJECTIVES

The comparative study included two phases. Phase one assessed and quantified the effect of ferrate reagent dose on key seawater parameters such as Total Organic Carbon (TOC) and BQ (Bacteria); and evaluated the effectiveness of algae oxidation/coagulation and separation. Phase two assessed the disinfecting effect of the ferrate reagent on Total Active Solids (TAS) biofilm growth under flow conditions. A ferrate solution (7,000 ppm) and a commercially available ferric chloride solution (35%) were used for Fe(III) coagulant addition.

PHASE ONE

A seawater sample (five gallons) was collected from Galveston Bay Seaside Park for use in the study. The samples were collected from approximately 4.0ft. out and had the following characteristics:

- TOC 41.5 ppm
- pH 8.31 S.U
- BQ (Bacteria) 1,443

Preliminary dosage rates of ferrate and ferric chloride were conducted in the range of 0.60 – 2.0 ppm.

A sample volume of 200 mL was transferred to three beakers and stirred rapidly. The first set of beakers was dosed with the selected ferric chloride dose. After two minutes, the mixing rate was reduced to a slow stir for two minutes; stir bars were removed, and samples were allowed to settle for up to two hours. The process was repeated for the ferrate. It was found that a 0.80 ppm dose was most effective (Figure 1).

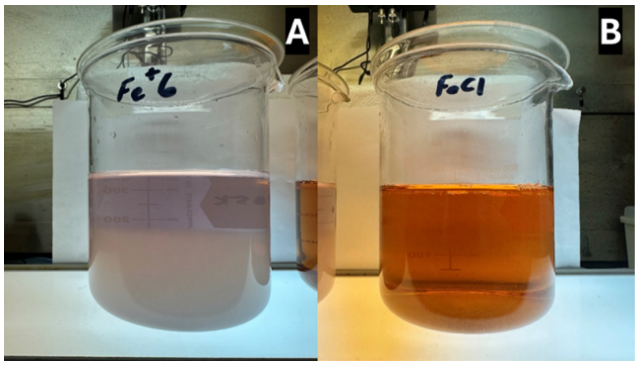

Figure 1- Floc Formation of 0.80 ppm Dose of Ferrate (A) and Ferric Chloride (B) at Two Hours

The supernatant of each seawater sample spiked with 0.80 ppm of the corresponding treatment reagent was analyzed for TOC, pH, and BQ. Results are presented in the following table:

Parameter	Original Seawater Sample	Electrolytic Sodium Ferrate	Bulk Ferric Chloride
pH	8.30	9.44	9.00
TOC	41.5 ppm	7.12 ppm 82.9% reduction	38.9 ppm 6.26% reduction
BQ Bacteria	1,443	110 92.3% reduction	1,000 30.69% reduction

Observations from the analysis include:

- Both ferrate and ferric chloride reagents produced comparable increases in the treated sample's pH. The ferrate reagent, due to its higher alkalinity, raised the pH by 1.4 units, whereas the ferric chloride reagent increased pH by 0.7 units.
- The ferrate reagent achieved a substantial reduction in TOC levels compared to ferric chloride: 83.9% for ferrate versus 6.25% for ferric chloride. This is attributed to ferrate's strong oxidation capability, which leads to significant organic oxidation and partial coagulation due to the resulting ferric hydroxide. In contrast, bulk ferric chloride is a much weaker oxidizer, achieving only marginal TOC removal through organic adsorption and coagulation.
- The ferrate reagent was significantly more effective at reducing BQ than ferric chloride, achieving over 92% reduction compared to just 31% for ferric chloride.

Bulk Algae and Bacteria Culturing—A 1.5-liter culture stir bottle was filled with 1,000 mL of seawater to which 50 mL of algae nutrient broth was added. Aeration was provided by a fishtank pump device, and an ultraviolet (UV) light was set six inches from the bottle. Moderate mixing occurred. At 96 hours, the algae growth had increased greatly and was viable for additional ferrate and ferric chloride dose studies (Figure 2). Bacteria were cultured from seawater in soy agar broth culture flasks to allow for slime-bacterial growth (Figure 3). These cultures were maintained to establish flow-through analyses of biofilm tendencies on RO filter flat sheets.

Figure 2- Algae Culture at Three Days

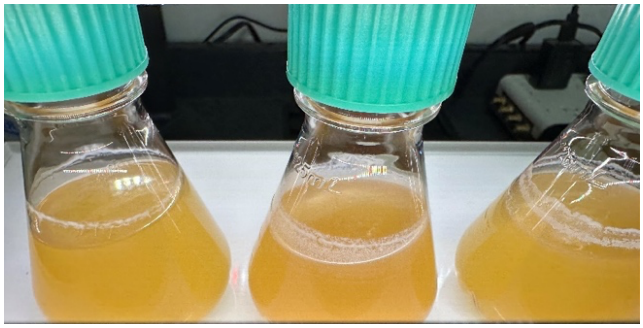

Figure 3- Slim Bacteria at Four Days, Note Biofilm Ring at Top

Algae Cell Disruption via Ferrate Reagent Oxidation— Two 600.0 mL beakers were filled with 450.0 mL of sterile saline water. Each beaker was "spiked" with 50.0mL of the cultured algae. The beaker was rapidly mixed for two minutes. A dose of 0.80 ppm of ferrate was added to Beaker #1 (Figure 4-A) and a dose of 0.80 ppm of ferric chloride was added to Beaker #2 (Figure 4-B). Then, the beakers were rapidly mixed for two minutes and allowed to settle for one hour.

As seen in Figure 4-A, the algae cells in ferrate-dosed sample underwent significant disruption of the algae cell walls and oxidation of the organism, as noted by the *browning/white* of the chlorophyllin. Disrupted cell material settled rapidly (within 15 minutes), creating a clear liquid, as shown in Figure 4-A. On the contrary, the sample treated with ferric chloride (Figure 4-B) showed very little settling and no evidence of algae cellular disruption.

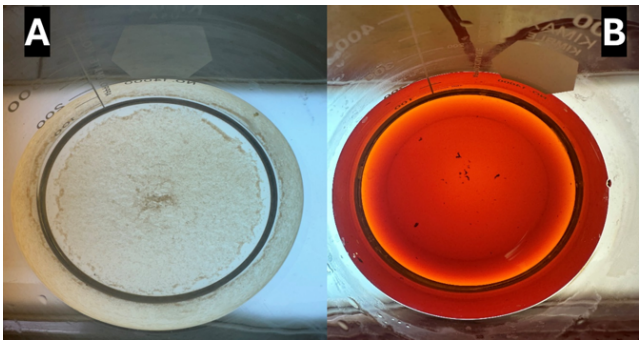

Figure 4- Effect of 0.80 ppm Doses of Ferrate (A) and Ferric Chloride (B) on Algae Cells

Phase One Summary—The electrolytic sodium ferrate reagent (dose of 0.80 ppm) demonstrated high effectiveness in reducing TOC (82.9%) and BQ (92.3%), high algae cell-disrupting capability, and fast-settling floc, resulting in effective liquid/solid separation by decanting. Whereas the bulk ferric chloride reagent (dose of 0.80 ppm) had little effect on seawater constituents or on algae removal.

PHASE TWO

Two TSA broth growth flasks were inoculated with the stock seawater bacteria culture and incubated at room temperature for 5 days with gentle mixing on the rotating table. The incubation time allowed for the bacteria levels to increase and begin to propagate a biofilm layer around the inside liquid layer area and the bottom of the flask. Two acrylic flow cells were autoclaved before use. Flow tubing was boiled for 20 minutes. Two ASTM Certified 316 stainless steel coupons were cleaned and autoclaved before insertion in the flow cell and acted as a biofilm growing substrates (~ 1 cm^2 area). The flow apparatus assembly is detailed in Figure 5.

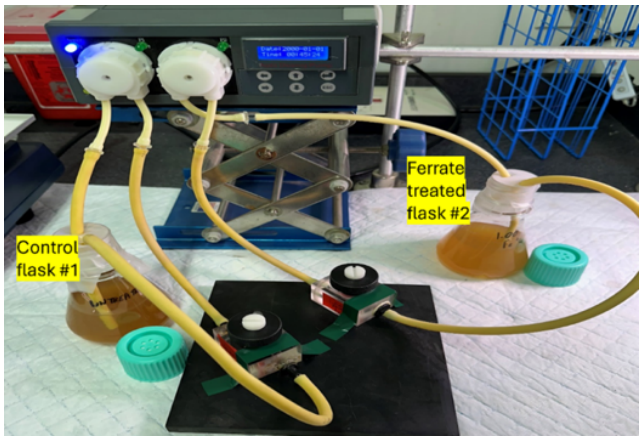

Figure 5- Flow Through Cell Assembly to Access Biofilm

A fresh ferrate reagent solution (7,000 ppm) was generated and used for treating culture Flask #2 at a 1.0 ppm dose. The flask was agitated for 30 minutes and allowed to settle for one hour. A volume of 100 mL of the settled supernatant was transferred to sterile Flask #2 (Figure 6) before being set up in the flow cell apparatus. The pH of the treated flask was 8.88. Flask #1 was untreated. The TOC levels in Flask #1 were 325.0 ppm and 23.05 ppm in Flask #2, representing a 93.0% reduction with the 1.0 ppm ferrate dose.

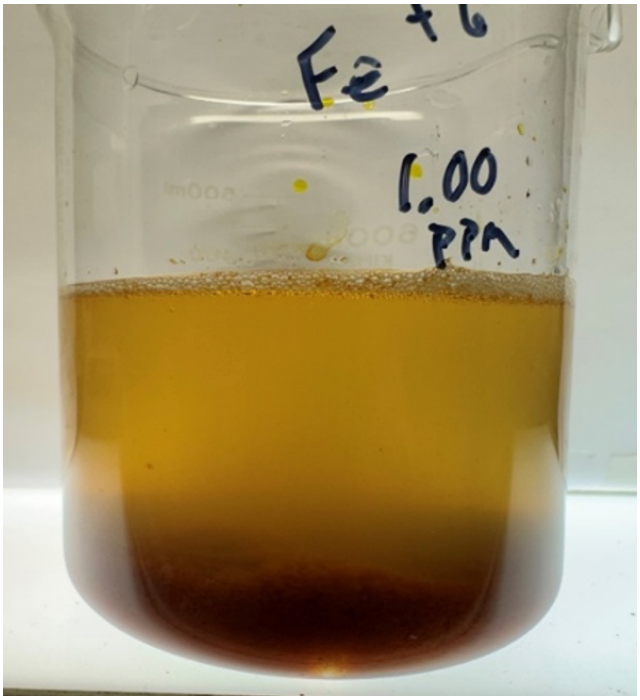

Figure 6- Algae Culture Treated with 1.0 ppm Ferrate at One Hour

Biofilm Assessment—Flow-through tests were conducted for 14 days by maintaining the sample flow rate at 5.0 mL/minute. To maintain a nutrient level in the test flasks, every three days, each culture flask was dosed with 2.00 mL of sterile TSA broth to stimulate bacterial growth. After the 14-day test period, the system was turned off, disassembled, and drained. Each culture flask was assayed via BQ. The BQ levels in Flask #1 were 2,340 BQ, and in Flask #2, 203 BQ, representing a 91.0% reduction. The coupons installed in the cells are shown in Figures 7 and 8.

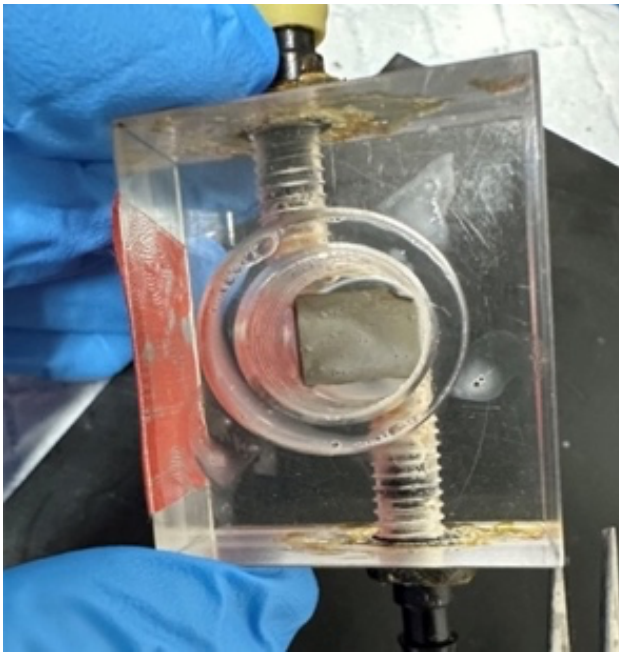

Figure 7- Untreated Flask, Note the Biofilm Adhering to the Coupon Surface

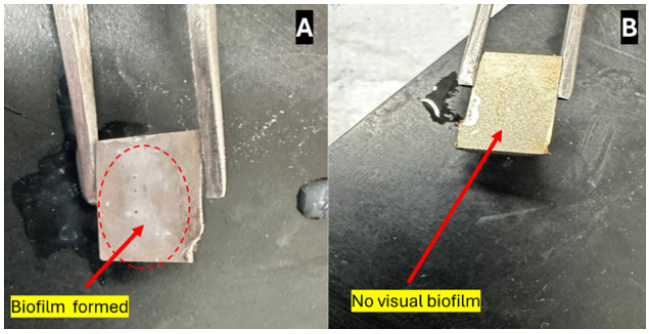

Figure 8- Biofouling Details of Control Coupon (A) and Ferrate Treated Coupon (B)

Phase Two Summary—A ferrate dose rate of 1.00 ppm maintained a disinfectant environment and deterred further bacteria growth over a 14-day period.

The flow-through study showed that untreated seawater bacteria allowed biofilm formation on the stainless-steel coupon, whereas the 1.00 ppm ferrate-treated culture inhibited bacterial growth and prevented biofilm formation. The enhanced oxidative reaction of the ferrate reagent had disrupted the cellular walls of the bacteria, thus reducing further mitosis. Additionally, the residual effects over the 14 days prevented further algal blooms. Microscopic examination of an algae culture flask treated with 1.00 ppm ferrate indicated disrupted cellular walls. After five days, all greening of the algae broth had turned brown, indicating no chlorophyll cycles occurring even under optimal light exposure.

CONCLUSION

Electrolytic ferrate reagent combining oxidizing, disinfecting and coagulating properties demonstrates significant advantages over traditional ferric chloride for treating algae-impacted seawater in desalination plants. It effectively reduces organic and bacterial loads, disrupts algal and bacterial cells, and prevents biofilm formation, all while offering an environmentally friendly and non-toxic alternative. This makes ferrate a promising solution for improving pretreatment processes and protecting RO membranes from biofouling and damage.

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