UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE PERFORMANCE AND COST-BENEFIT ANALYSIS OF IRON COAGULANTS AND POLYMER ADDITIVE IN ENHANCING SEAWATER TREATMENT DURING HARMFUL ALGAL BLOOMS

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE

By

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Norman, Oklahoma
2023

THE PERFORMANCE AND COST-BENEFIT ANALYSIS OF IRON COAGULANTS AND POLYMER ADDITIVE IN ENHANCING SEAWATER TREATMENT DURING HARMFUL ALGAL BLOOMS

A THESIS APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

BY THE COMMITTEE CONSISTING OF

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DEDICATION:

This thesis is dedicated to my parents Fahad and Majedah who have always encouraged and motivated me to achieve my goals. Also, I dedicated this thesis to all my brothers and sisters who were always by my side.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Dr. Keith Strevett for his expert advice and encouragement. Also, I would like to express my deepest appreciation to Dr. Elizabeth Butler, and Dr. Tohren Kibbey for their time and effort.

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ABSTRACT

Water usage is growing at more than twice the rate of the population, and an increasing number of regions are reaching the limit at which water services can be sustainably delivered, specifically in arid regions (United Nations Water, 2007). Building large infrastructures such as water transfer systems and seawater desalination plants has gained support to alleviate water scarcity. Seawater reverse osmosis (SWRO) is one of the preferred technologies used in the treatment process of seawater desalination. The quality of the source water plays an important role in extending the membrane life in this system, where it can prevent membrane fouling which occurs because of pore-clogging or adsorption of solute on the membrane surface, which could be a result of the presence of harmful algal blooms. The objectives of this research are to determine the optimum coagulant dose of ferric chloride, ferric sulfate, and ferrous sulfate and the impact of pH on the coagulant dose for removing algae. Also, determining the impact of cationic organic polymer additive, which is polyDADMAC (e.g., Polydiallydimethylammounium Chloride), on floc stability and the minimum economic cost of the coagulants with and without polymer additive. The experiment was done on artificial seawater (33 g/L) containing 1 g/L of bentonite clay and 10 mg/L of sodium alginate to mimic the harmful algal blooms. It was observed that 40 mg/L $FeCl_3$, 20 mg/L $FeSO_4$, or 30 mg/L $Fe_2(SO_4)_3$ at a pH of 8.25 has the highest turbidity removal, which highly improved the quality of seawater. Moreover, the addition of polyDADMAC to the iron coagulants increased the removal of water turbidity. Furthermore, the coagulation process using iron coagulants led to an increase of more than 90% of total organic carbon, and dissolved organic carbon removal in seawater contains sodium alginate and cultivated algae. When 5.45 mg/L polyDADMAC was added to the coagulants, the removal of total organic carbon and dissolved organic carbon reached more than 75% due to the presence of carbon in polyDADMAC. The iron coagulants and polyDADMAC addition to them have the same performance when tested on artificial seawater containing 10 mg/L cultivated algae instead of sodium alginate where the water turbidity decreases to less than 2 NTU. After the cost analysis was completed, it was found that ferric sulfate without the 5.45 mg/L polyDADMAC has the lowest cost of $\$0.421/\mathrm{m}^3$ for plant capacity of 1,000 m^3/day.

CHAPTER 1. INTRODUCTION

Water scarcity affects every continent and has increased globally in the last century. Water usage is growing at more than twice the rate of the population, and an increasing number of regions are reaching the limit at which water services can be sustainably delivered, specifically in arid regions (United Nations Water, 2007). The Middle East is a region significantly impacted by increased heat, aridity, and population growth, which are essential factors affecting the increases in water scarcity (Prochazka et al., 2018). Building large infrastructure such as water transfer systems and seawater desalination plants has gained support to alleviate the water scarcity issues in this region (European Commission, 2015). Seawater desalination would work best for countries surrounded by seawater regarding the amount of water, construction, and cost. That would prevent the danger to humans, animals, and other organisms' life caused by water scarcity.

Seawater reverse osmosis (SWRO) is one of the preferred technologies used in the treatment process of seawater desalination. Reverse osmosis is an important technology used in water treatment that involves a pressure-driven process where a semipermeable membrane removes the dissolved constituents in the feed water (Malaeb et al., 2011). The feed water quality plays a vital role in extending the membrane life in this system, where it can prevent membrane fouling. Membrane fouling occurs because of pore-clogging or adsorption of solutes on the membrane surface, which could result from harmful algal blooms because the passage of algae through the membrane will clog the membrane pores. When membrane fouling occurs, it will reduce water quality, increase system downtime, and increase membrane maintenance and operation costs.

Seawater treatment during periods of algal blooms is considered one of the challenging treatment issues facing desalination plants. Harmful algal blooms (HABs) are blooms of toxic, microscopic algae that cause illness and death in humans, fish, seabirds, and other ocean life (Villacote et al., 2015). Almost every coastal country can be affected by HABs since marine algae are ubiquitous in the world's oceans. Red tide is an example of HABs that can severely impact human health, aquatic ecosystems, and the economy (United States Environmental Protection Agency). It is a marine environmental event where protists, including algae and dinoflagellates, undergo a tremendous growth period called an algal bloom (Guy, 2014).

These issues caused by HABs pose a severe threat to countries that largely depend on SWRO plants for their water supply. Thus, efficient pretreatment is often considered the only strategy to reduce the fouling potential by decreasing the amount of organic matter and inactivating the microorganisms in the feed water (Alshahri et al., 2019).

Coagulation, followed by granular media filtration, is the most common technology used in most treatment plants in the Middle East (Villacote et al., 2015). This study will focus on implementing coagulation process pretreatment before SWRO treatment and investigate how the coagulation process and polymer additive have cost advantages on SWRO plants compared to previous study. There are two main types of coagulants, aluminum coagulants, such as aluminum sulfate, aluminum chloride, and sodium aluminate, and iron coagulants, such as ferric chloride, ferric sulfate, and ferrous sulfate. Iron coagulants are preferred for seawater over aluminum because of the relatively high solubility of aluminum in seawater. Also, ferric chloride is the most common coagulant used for seawater coagulation. However, there has been some consideration of using other iron salts, such as ferric sulfate and ferric chloride (James & Johannes, 2011). That leads to the main question of this research, which is can different types of iron coagulants still be effective in producing excellent water quality that can support the increase of the lifetime of the pretreatment system and seawater reverse osmosis membrane during HABs.

This research hypothesizes that pretreatment with ferric chloride economically decreases water turbidity resulting from algae greater than other iron-related coagulants. Also, polydiallyldimethylammonium chloride (polyDADMAC) addition significantly (95% Cl) increases solids removal because of its high charge density which promotes the agglomeration of suspended particles and provides operational and maintenance cost advantages due to floc stability. This research aims to determine the optimum coagulant dose of ferric chloride, ferric sulfate, or ferrous sulfate and the impact of pH on the coagulant dose removing algae since the pH can change the surface charge. Furthermore, it focuses on determining the impact of polyDADMAC on floc stability and the minimum economic cost of the coagulants with and without polymer additives.

CHAPTER 2. LITERATURE REVIEW

2.1 Water Scarcity

Kuwait, located in the Middle East, specifically in an arid region, has one limited natural water resource, groundwater, while most of the country's demands are met by seawater desalination (Fadlelmawala & Alotaibi, 2004). As of 2004, there was no clear plan to avoid this scarcity (Fadlelmawala & Alotaibi, 2004) which is a considerable threat to the country, especially during the increases in population growth, which leads to an increase in the water demand. The water resources in Kuwait are brackish groundwater, fresh groundwater, and non-conventional water resources. Brackish groundwater exists in the Kuwait Group aquifer and the Damam limestone aquifer, stretching east of the Arabian Peninsula and slightly sloping towards the Arabian Gulf (Alruwaih, 2000). In 1960 a large-scale project started to provide the consumer with brackish water through a separate pipe network utilized for blending with distilled water, irrigation, landscaping, and household purposes.

Regarding fresh groundwater, the mean average annual rainfall value in Kuwait is about 110 mm, while the annual variability ranges from a low of 31 mm to a high of 242 mm, and the evaporation potential and actual consistently exceed available precipitation (Fadlelmawala & Alotaibi, 2004). The amount of precipitation is insufficient to produce excessive rainfall for direct infiltration or overland runoff except in a few areas where actual runoff and accumulation of surface water are possible. Fresh groundwater is uniquely present in the northern parts of Kuwait at the Al-Roudhatain and Umm Al-Aish depressions, where it occurs in the form of lenses floating on top of Kuwait Group's brackish water (Fadlelmawala, 2008). The non-conventional water resources, specifically desalination, provide about 90% of the country's domestic water needs (Fadlelmawala & Alotaibi, 2004). Moreover, Kuwait applied the reuse of treated wastewater for the landscape, irrigation, and highways, which is considered a non-conventional water resource.

Because of the scarcity of water resources in Kuwait, integrated water resources management is required for sustainable development. Over the years, the increase in water demand in Kuwait called for building new seawater desalination plants using multi-stage flash (MSF) processes that are energy-intensive and require much time and money (Hamoda, 2001). Kuwait was interested in employing the less costly reverse osmosis process for desalinating seawater brackish water, expecting declined reverse osmosis capital and operation and maintenance costs. Another cost-effective solution proceeded in Kuwait is the reuse of treated wastewater which has the advantage of improving the environmental aspects of water resources management.

2.2 Water Treatment

Seawater desalination by reverse osmosis to produce potable water has been widely used in the Arabian Gulf region, including Kuwait, Saudi Arabia, United Arab Emirates, Oman, and Bahrain (Al-Shammiri & Al-Dawas, 1997). Reverse Osmosis (RO) is a physical process that uses the osmotic pressure difference between saltwater and pure water to remove salt from water. In this process, a pressure more significant than the osmotic pressure is applied to the feedwater to reverse the flow, which results in pure water passing through the synthetic membrane pores separated from the salt, as shown in Figure 1 (Younos & Tulou, 2005). Osmotic pressure is the pressure that must be applied to the solution side to stop fluid movement when a semipermeable membrane separates a solution from water (Feher, 2012). High pressure from 100 to 800 psi is used in RO filtration to force the water through the semipermeable membrane (Backer, 2013).

Moreover, RO effectively removes total dissolved solids concentrations of up to 45,000 mg/L, which can be applied to desalinate brackish water and seawater (Younos & Tulou, 2005). Furthermore, no heating or phase separation change is necessary for this process; the major energy required for desalting is for pressurizing the seawater feed (Khawaji et al., 2008). The typical seawater RO plant consists of four major components, which are feed water pretreatment, high-pressure pumping, membrane separation, and permeate post-treatment. Pretreatment is needed to eliminate the undesirable constituent in the seawater, which would lead to membrane fouling. A typical pretreatment contains chlorination, coagulation, acid addition, multi-media filtration, micron cartridge filtration, and dechlorination (Khawaji et al., 2008). The feedwater characteristics, membrane type and configuration, recovery ratio, and product water quality are factors that determine the type of pretreatment used.

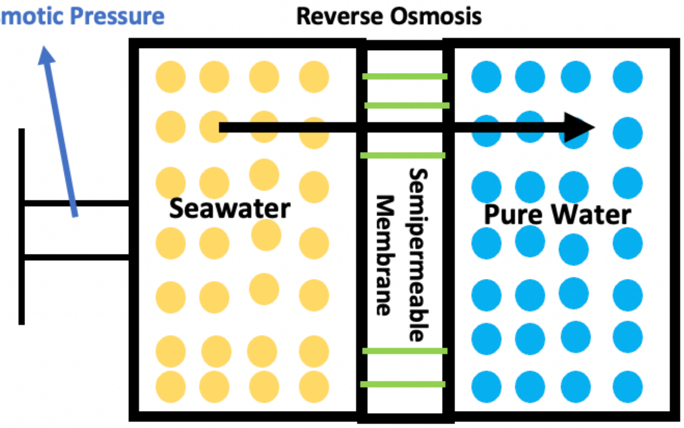

Figure 1: Reverse Osmosis process inspired from Younos and Tulou, 2005.

2.3 Seawater Reverse Osmosis During Harmful Algal Blooms

The presence of harmful algal blooms in the raw feed water can cause an increase in chemical consumption within the desalination plant, increase the membrane fouling rate, and might lead to plant shutdown. Effective pretreatment is considered the only strategy to reduce the fouling potential by decreasing the amount of organic matter and inactivating the microorganisms in the feed (Alshahri et al., 2019). Coagulation is commonly applied in conventional pretreatment systems to improve process performance regarding turbidity removal and surface loading rate (Villacorte et al., 2015). Iron coagulants work excellent for seawater coagulation, while aluminum coagulants are not because of the high solubility of aluminum, which could be carried over to RO membranes leading to precipitative scaling.

Alshahri et al. (2019) evaluated the using in-situ liquid ferrate for seawater pretreatment. Comparing the liquid ferrate to ferric chloride in a pretreatment system of seawater treatment, Alshahri et al. (2019) demonstrated the benefit of coagulation pretreatment. The efficiency of seawater reverse osmosis (SWRO) pretreatment is commonly assessed by measuring the turbidity and organic removal in the feedwater. The comparison between Fe (VI) and Fe (III) in turbidity and DOC removal shows that liquid ferrate (Fe (VI)) has better performance than Fe (III). Moreover, comparing the two coagulants with the same dosage amount regarding the natural organic matter (NOM) and algal organic matter (AOM), particularly biopolymers removal, shows that liquid ferrate still performs better than ferric chloride in the feedwater. Organic matter is a mixture of different organic compounds, including aquatic humic and fulvic acids and products generated from bacterial and algal activity (Alshahri et al., 2019). The NOM is removed through a combination of charge neutralization, entrapment, adsorption, and complexation with coagulant metal ions into insoluble particulate aggregates (Parson, 2014). The AOM contains the same compounds that are present in the biopolymer fraction, which are acids, proteins, simple sugars, anionic polymers, and negatively charged and neutral polysaccharides, which consider a major concern for the biofouling of RO membranes. Therefore, the liquid ferrate removes the biopolymer through adsorption and enmeshment in ferric hydroxide, forming large Fe-biopolymer aggregates (Alshahri et al., 2019).

The results show that the removal performance of liquid ferrate increases with the increase in pH because of the increase in ferrate stability in alkaline conditions. Overall, the results from this study found that liquid ferrate has better performance than ferric chloride as a coagulant. However, this study did not include an economic comparison between the two coagulants. An extensive literature survey did not discover a comprehensive evaluation of coagulation or additives as RO pretreatment for HABs.

2.4 Cost

Building a desalination plant requires a high amount of energy, impacting the economic cost. The cost of a desalination plant differs depending on many factors, including the type of feed water, amount of the feed water, quality of the feed water, type of energy, and desalination method. The two main types of water are seawater and brackish water, and the type of energy can be divided into two categories which are conventional energy, such as gas, oil, and electricity, and renewable energy, such as solar and wind. Moreover, the two major desalination methods are the thermal method, including multi-effect distillation (MED), MSF, and vapor compression (VC), and the membrane method, including RO. Regarding feed water type, seawater treatment will cost much more than brackish water since it contains more contaminants. According to Karagiannis and Soldatos (2008), the cost of seawater produced from <1000 to >60,000 m^3/day capacity of desalination unit is ranged from 0.35-9.00 EUR/m^3. Furthermore, the cost of seawater produced from conventional energy supply systems ranged from 0.35-2.70 EUR/m^3, wind energy supply systems ranged from 1.00-5.00 EUR/m^3, photovoltaics energy supply systems ranged from 3.14-9.00 EUR/m^3 and solar collectors energy supply system ranged from 3.50-8.00 EUR/m^3. Therefore, using conventional energy will positively impact the economy, but it has a more negative impact on the environment. Regarding the thermal method, the cost of seawater produced from desalination plant sized from 12,000-55,000 m^3/day using the MED method ranged from 0.76-1.56 EUR/m^3, desalination plant sized from 23,000-528,000 m^3/day using MESF method ranged from 0.42-1.40 EUR/m^3 and desalination plant sized from 1,000-1,200 m^3/day using the VC method ranged from 1.61-2.13 EUR/m^3 (Karagiannis & Soldatos. 2009). While in the membrane method, the cost of seawater produced from desalination plants sized from 15,000-60,000 m^3/day using the RO method ranged from 0.38-1.30 EUR/m^3. Thermal methods are more expensive than membrane methods due to the large quantities of fuel needed to vaporize salt water (Karagiannis & Soldatos, 2008).

The total cost of water produced from desalination plants is divided into capital and operation costs. The capital cost includes the costs that have been expended during the construction period and before the commercial use of the plant, while the operation cost is the cost expended after the construction period and during the plant's life cycle and consists of repeated costs (Marshad, 2014). The operation cost is divided into direct cost, which includes spare parts, fuel, electricity, labor, and chemical and indirect costs, which include utilities, plant administration, general expenses, and insurance. Marshad's (2014) study used the method of fragments to determine the monthly operating cost of the Shuqiq plant. This plant uses RO seawater desalination. In the fragment method, for a given set of historical data, a new monthly time series is formed by dividing each monthly cost by the corresponding annual value, and each year is referred to as one set of fragments (Marshad, 2014).

However, the cost of chemicals used in SWRO plants constitutes 6% of the total operating cost (Water Reuse Association, 2011). The Neka power plants' reverse osmosis desalination of seawater was designed to produce 6,000 m^3/day of desalinated water (Sadeghi et al., 2022). According to Sadeghi et al. (2022), the Neka plant spends $2,838,557 as of 2023 exchange rate as the total annual chemical cost for reverse osmosis. The chemicals cost include acid, NaOH, NaOCl, antiscalant, antioxidant, coagulator, and coagulation aid. The coagulator cost constitutes 1.625% of the total annual chemical cost, while the coagulation aid cost constitutes 15.8%. The monthly usage of coagulators in the Neka plant is 0.5 m^3, and the monthly usage of coagulation aid is 0.54 m^3. The two major factors that impact the cost of coagulator and coagulation aid are the amount of usage and increases and decrease in the cost of chemical (Sadeghi et al., 2022).

CHAPTER 3. MATERIALS AND METHOD

3.1 Materials

The three different iron coagulants used in this study are ferric chloride (Fisher Scientific CAS-NO: 10025-77-1), ferrous sulfate (J.T. Baker Chemical Co. CAS-NO: 7782-63-0), and ferric sulfate (Acros Organics CAS-NO: 142906-29-4). polyDADMAC (MiliporeSigma Aldrich CAS-NO: 26062-79-3) was used as a coagulant aid. The chemicals used to prepare the artificial seawater are sea salt (Fisher Scientific-Instant Ocean), calcium chloride (Acros Organic CAS-NO: 10043-52-4), and sodium bicarbonate (Fisher Scientific CAS-NO: 144-55-8). Sodium Alginate (MiliporeSigma CAS-NO: 9005-38-3) was used to mimic the HABs. Sodium carbonate (Fisher Scientific CAS-NO: 497-19-8), sodium phosphate monobasic (Fisher Scientific CAS-NO: 10049-21-5), and vitamin stock solution includes biotin (MiliporeSigma EC-NO: 200-399-3), and vitamin B_{12} (MiliporeSigma EC-NO: 200680-0) were used for the enriched seawater medium for algae growth. Along with trace metal solution that includes copper sulfate (Fisher Scientific CAS-NO: 7758-99-8), zinc sulfate (MiliporeSigma CAS-NO: 7446-20-0), cobalt chloride (MiliporeSigma CAS-NO: 7647-79-9), manganese chloride (Fisher Scientific CAS-NO: 13446-34-9), and sodium molybdate dihydrate (MiliporeSigma CAS-NO: 10102-40-6). Hydrochloric acid (Fisher Scientific CAS-NO: 7647-01-0) and sodium carbonate (Fisher Scientific CAS-NO:497-19-8) were used to adjust the pH level of the solutions.

3.2 Artificial Seawater

The procedure of preparing artificial seawater is adapted from (Kaladharan, 2000). Artificial seawater of 33 g/L salinity was prepared by dissolving 280g of sea salt crystals in 8L of deionized water along with 8 g of calcium chloride and 0.8g of sodium bicarbonate. After one day, the pH of the artificial seawater was adjusted to 8.25 to meet the seawater's properties. Furthermore, the turbidity of the artificial seawater was less than 2 NTU. Therefore, 1 g/L of bentonite clay was added to increase the turbidity of the artificial seawater. The artificial seawater characteristics used in the study before applying the treatment process are summarized in Table 1. The total alkalinity increases after the addition sea salt used in the experiment (Table 1).

Table 1. Feed Water Characteristics.

Parameter	Artificial Seawater with Bentonite Clay	Artificial Seawater with Bentonite and Sodium Alginate	Artificial Seawater with Bentonite and Cultivated Algae
pH	8.25	8.25	8.25
Average Turbidity	130 NTU	180 NTU	227 NTU
Average Total Alkalinity	380 mg/L as $CaCO_3$	380 mg/L as $CaCO_3$	380 mg/L as $CaCO_3$
TOC	NA	8 mgC/L	9.3 mgC/L
DOC	NA	6 mgC/L	7.2 mgC/L

3.3 Preparing Sodium Alginate Solution & Enriched Seawater Medium for Algae Growth

Sodium alginate is a cell wall component of marine brown algae that contains about 30 to 60% alginic acid (Loureiro dos Santos, 2017). Sodium alginate is used as an alternative for algal blooms in seawater. The sodium alginate stock solution adapted from (Alshahari et al., 2019) was achieved by 1g of sodium alginate in 1L of artificial seawater. However, algae growth uses the F/2 (enriched seawater medium) recipe from the University of California Santa Barbara (UCSB), where 2 mL of 15% $NaNO_3$, 1% NaH_2PO_4, trace metal stock, and vitamin stock was added to 4L of artificial seawater separated into two Erlenmeyer flasks along with 5mL of soil extract solution into each flask. After having the recipe done, 100mL of fresh algae culture was added to each flask, and they were exposed to light for three weeks. The original culture was obtained for an active saltwater aquarium.

Table 2: Vitamins Stock Solution.

Vitamin	Add to 500mL of Deionized Water
Biotin	0.5 mg
Vitamin B_{12}	0.5 mg

Table 3: Trace Metal Stock Solution.

Metal	Add to 1L of Deionized Water
$CuSO_4\ 5H_2O$	1.86 mg
$ZnSO_4\ 7H_2O$	4.4 mg
$CoCl_2\ 6H_2O$	2 mg
$MnCl_2\ 4H_2O$	36 mg
$Na_2MoO_4\ 2H_2O$	1.26 mg

Table 4: Chemical Buffer Solution.

Compound	Added in 100ml Deionized Water
15% $NaNO_3$	15.0 g
1% NaH_2PO_4	1.0 g

3.3.1 Soil Extract Solution:

Macronutrients required for algal growth were extracted from nutrient-rich soil according to the UCSB recipe. The soil extract solution started with sieving four handfuls of Espoma organic potting soil mix through a 0.85mm sieve diameter. Then, the dirt was added to 1 L of deionized water in a large Erlenmeyer flask, autoclaved for 20 minutes, and set for 24 hours.

3.4 Jar Test

The jar test was done to explore the performance of each coagulant used in treating the seawater following the method D2035 provided by the American Society for Testing and Materials (ASTM), as shown in Figure 2. It started with preparing the sample that needed to be treated by adding 8 g of bentonite clay to 8 L of artificial seawater to increase the turbidity of the sample. In six 1L beakers, 600ml of the sample was added in each beaker with 10 mg/L sodium alginate stock solution, which was prepared by dissolving 0.5g in 500ml of seawater or 10 mg/L cultivated algae. Then, the beakers were located at the center of the Jar Test Flocculator (Velp Scientifica, NY, USA), ensuring that the paddles were precisely at the center of each beaker. After that, the flocculator rapid mixing was initiated at 120 rpm speed for 1 minute after the coagulant dosage was added to disperse coagulant species into the sample. Then, the speed of mixing was reduced to 30rpm for 20 minutes. This slower mixing encourages floc formation while minimizing floc shear. After the flocculation process, the mixing paddles were removed to promote settling. After a settling time of 5 minutes for ferric coagulants and 15 minutes for ferrous coagulant with and without polymer additives, samples were withdrawal at a depth of 2.5 inches from the water surface. Samplers were analyzed for color, turbidity, pH, and organic carbon (dissolved and total). The coagulant stock solutions were prepared by dissolving 10 g of the type of coagulant needed into 1 L of deionized water, which will give 10 mg/L coagulant concentration when 1 ml is added to the 1 L sample. However, the polymer stock solution 1% was prepared by mixing 2.9 ml of polyDADMAC 35% weight percent in 100 ml of deionized water, which would give a 5.45 mg/L concentration when 0.5 ml is added to the 1 L sample (1% wt = 10.9 g/L).

Figure 2. Jar Test Experimental Setup.

3.5 Analytical Method

The pH was measured five times before adding the coagulants for each sample using an Accumet AB150 pH Benchtop Meter to determine the impact of pH on coagulant dosage for removing algae. The pH was adjusted to 7, 7.5, 8, 8.25, 8.5, 9, and 9.25 using 0.5 M HCl and Na_2CO_3. The turbidity was observed using HACH-DR/890 Portable Colorimeter using program number 95 to indicate the number of suspended sediments and particles in the water. The turbidity was measured five times for each sample. Alkalinity was carried out five times for each sample using HACH-Digital Titrator Kit. TOC analysis was determined once for each sample following method 10129 by HACH Company for low TOC concertation measurement. The analysis of DOC is practically identical to that of TOC; however, a 0.45-micron pore size was used to filter the sample. LISST-Portable │XR, which uses the same laser light scattering method, was used to measure the flocs particles size three times for each sample.

3.6 Cost Benefit

A net benefit value (NBV) model adapted from Chen et al. (2009) was used to determine the cost-benefit value using Equation 1.

$$NBV = \sum B_i - \sum C_i \qquad (1)$$

Where B_i represents the value of benefit item *i,* and C_i represents the value of cost item *i,* all with the same monetary unit. If the calculated result of NBV > 0, the project will be economically viable, while if the calculated result of NBV < 0, the project will not be economically viable. The highest NBV, the more profitable the project will be.

Figure 3 shows the cost and benefits variables in the calculations to represent the cost-benefit value. Cost variables are divided into eight factors which are capital, membrane, chemical, electric, manpower, maintenance, pretreatment, and interest, while the benefit variable is the water sale. The method and data used in this study were adapted from Sarica A. (2018). Sarica A. (2018) determined system cost and profits to establish an SWRO plant with 1,000 m^3/day capacity expressed in units of \$/m^3. Figure 3 shows the variables of cost and benefit that Sarica A. (2018) used to calculate the cost and profit. In this study, this data will be used with changing the chemical's price according to the determined iron coagulants and polyDADMAC prices observed in this study to calculate the total cost of the system and apply it in Equation 1.

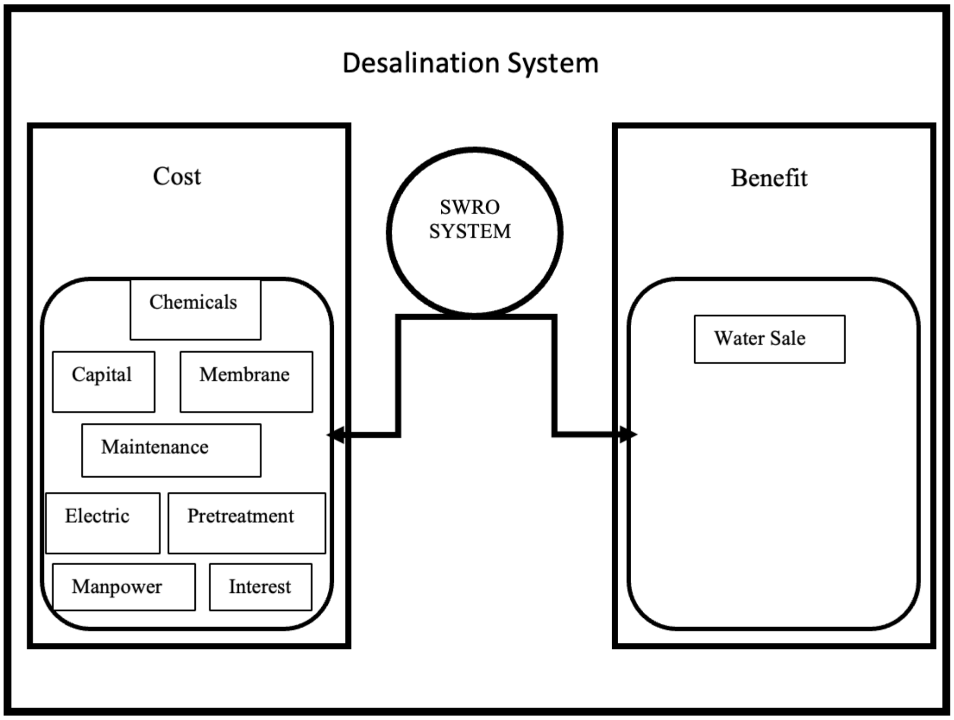

Figure 3: Factors Related to Costs and Benefits of Desalination System Adapted form Chen et al. (2009).

3.7 Statistical Analysis

The statistical analysis of this study was found by applying the t-test, which is a type of statistical test used to compare the means of two groups (Kim T., 2015). The t-test in this study was used to investigate the statistical difference between the iron coagulants with and without adding polymer and pH levels in lowering the water turbidity and increasing the floc's size. The probability value (p-value) resulting from the t-test is what determines whether there is a statistical difference or not. If the p-value is less than 0.05, there is a statistical difference, while if it is higher than 0.05, there is no statistical difference.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Coagulation Process on Sodium Alginate

Ferric chloride is the first primary coagulant used to cause particles to become destabilized and begin to clump together by neutralizing the charge in this study. Ferric chloride reacts with the water to form precipitated Iron (III) hydroxide (Equation 2). $Fe(OH)_3$ is the clumped particle that is formed during the reaction of ferric chloride with water, which leads to lower turbidity.

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_{3\,(s)} + 3HCl \qquad (2)$$

Five different dosages of ferric chloride were studied to determine the optimum coagulant dosage. The optimum dosage occurs at the lowest turbidity measurement. Figure 4 shows the optimum dosage of ferric chloride to lower the turbidity of 600 ml seawater that contains 10 mg/L sodium alginate stock and 1 g/L bentonite clay with constant pH of 8.25.

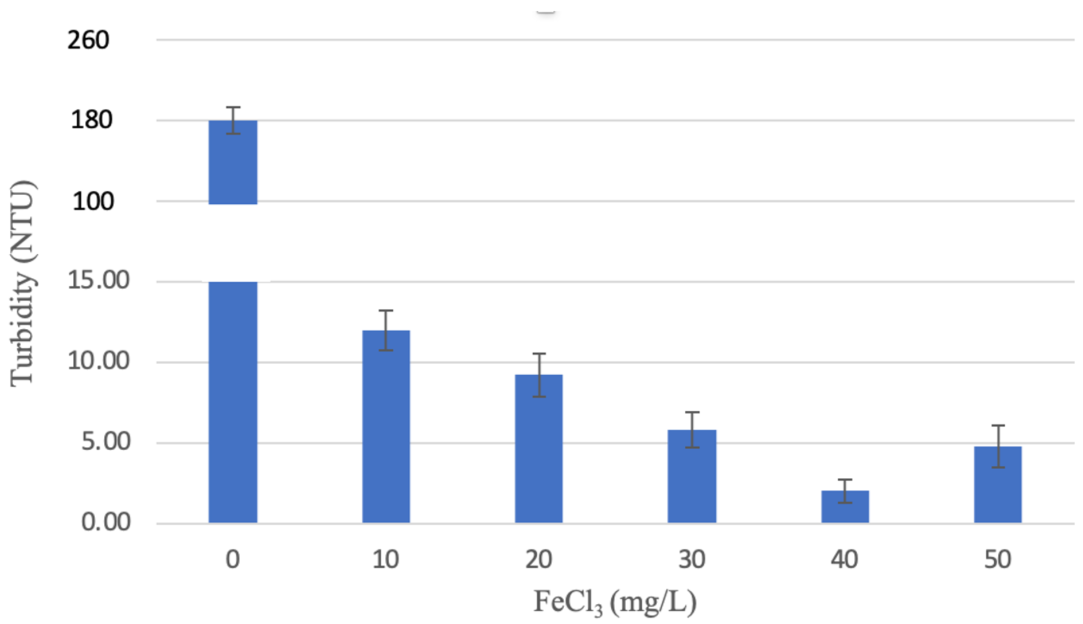

Figure 4. The Impact of Ferric Chloride Dosage on Water Turbidity with Standard Deviation Error Bars.

As shown in Figure 4, the turbidity started to decrease from a dosage of 0mg/L to 40mg/L, and this drop indicates that the stable particles in the water are destabilized due to introducing small, highly charged molecules into the water to destabilize the charges on particles (Bradley, 2022). A significant change in the turbidity did occur between each ferric chloride concentration (95% CI). In this study, a t-test with one-tailed distribution and paired type were used as a statistical test to compare the mean of two groups in to investigate any statistical difference between the group being tested. The p-value of turbidity measurement determined using a t-test for ferric chloride coagulant dosage in coagulation treatment on sodium alginate shows a statistical difference between all the dosages of ferric chloride shown in Figure 4 since the p-value is less than 0.05 (Table 1 in Appendix B). However, at a dose of 50 mg/L, the turbidity increased due to the charge reversal caused by the additional ferric chloride dose (overdosing) that led to restabilizing the suspended solids (Malik, 2018).

However, Figure 4 shows that the lower amount of turbidity occurs at a dose of 40 mg/L, which makes it the optimum dose to lower the turbidity of 600 ml of seawater that contains 10 mg/L sodium alginate stock and 1 g/L bentonite clay since the turbidity raised after adding more than 40mg/L of ferric chloride. These results support the hypothesis, as it has been proven that ferric chloride decreases water turbidity resulting from algae. These results are also consistent with the previous research by Alshahri et al. (2019), where ferric chloride, used as a primary coagulant to treat seawater, contains sodium alginate. Alshahri et al. (2019) observed that ferric chloride effectively increases turbidity removal in seawater containing sodium alginate.

A cationic liquid polymer, polyDADMAC works as a coagulant aid to produce large, strong, quickly settled floc when added to the primary coagulant. It has a high charge density and promotes the agglomeration of suspended particles making it very effective in flocculating, decoloring, killing algae, and removing organics such as humus (Mwangi et al., 2013). In this study, the concentration of 5.45 mg/L of polyDADMAC was used for ferric chloride coagulant to explore its impact on coagulant dose and floc stability. The impact of 5.45 mg/L of polyDADMAC on the coagulation process using ferric chloride significantly (95%CI) reduced the turbidity compared to using ferric chloride without polymer addition (Figure 5). Furthermore, the p-value of turbidity measurement determined using a t-test for ferric chloride coagulant dosage with the addition of 5.45 mg/L polyDADMAC in coagulation treatment on sodium alginate shows that there is a statistical difference between the dosage except for 30-40 mg/L, and 30-50 mg/L where p-value exceeds 0.05 (Table 4 in appendix B). As shown in Figure 5, 5.45 mg/L of plo振DADMAC addition to the ferric chloride increase the turbidity removal because of the large, strong, quickly settled floc created by the addition of polyDADMAC compared to Figure 4.

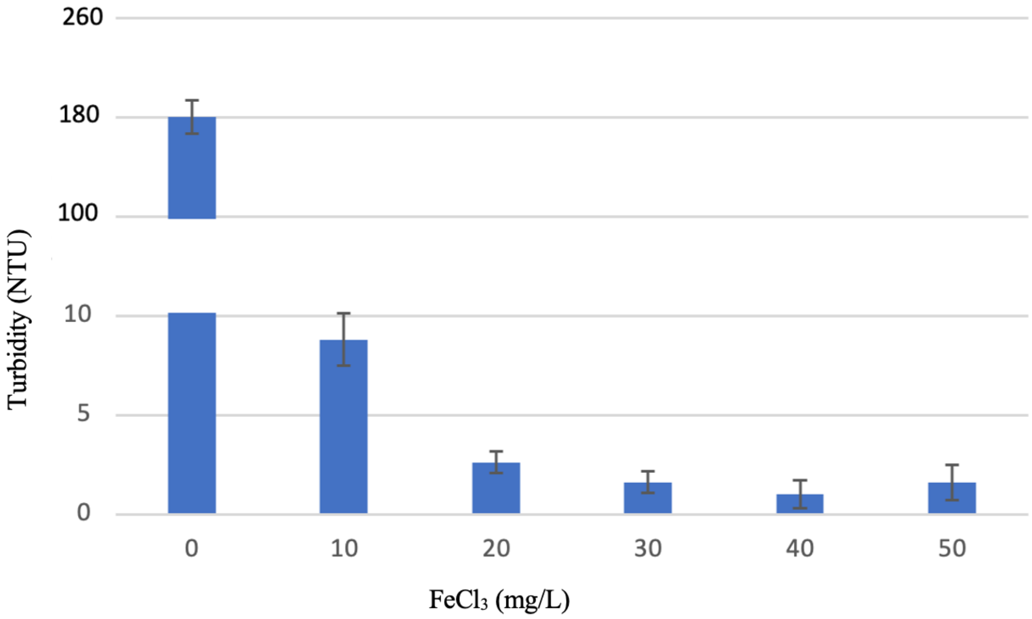

Figure 5. The Impact of Ferric Chloride Dosage with The Addition of 5.45 mg/L polyDADMAC with Standard Deviation Error Bars.

These results correspond with a study by Lee et al. (2006), where the group presented results of dissolved organic nitrogen (DON) removal using aluminum salt and polyDADMAC during coagulation. Their study revealed that the turbidity of water was reduced with the presence of polyDADMAC (Lee et al., 2006).

In order to explore the impact of polyDADMAC on floc stability, floc size was measured before and after adding 5.45 mg/L of polyDADMAC to the three primary coagulants used in this study. Figure 6 explains the impact of 5.45 mg/L polyDADMAC on flocs size when ferric chloride is used as a primary coagulant significantly (95% CI).

Furthermore, there is no statistically significant floc size increase when ferric chloride is used as a coagulant without 5.45 mg/L polyDADMAC for sodium alginate except between 0 mg/L and all other ferric chloride dosages (Table 3 Appendix B). While in the presence of 5.45 mg/L polyDADMAC when ferric chloride is used as a coagulant, there is a statistical increase in floc size except between 20-30 mg/L and 20-50 mg/L (Table 5 in Appendix B). It is clearly shown in Figure 6 that the size of the flocs highly increased after the addition of polyDADMAC to the ferric chloride, which enhanced the floc stability (Li et al., 2006).

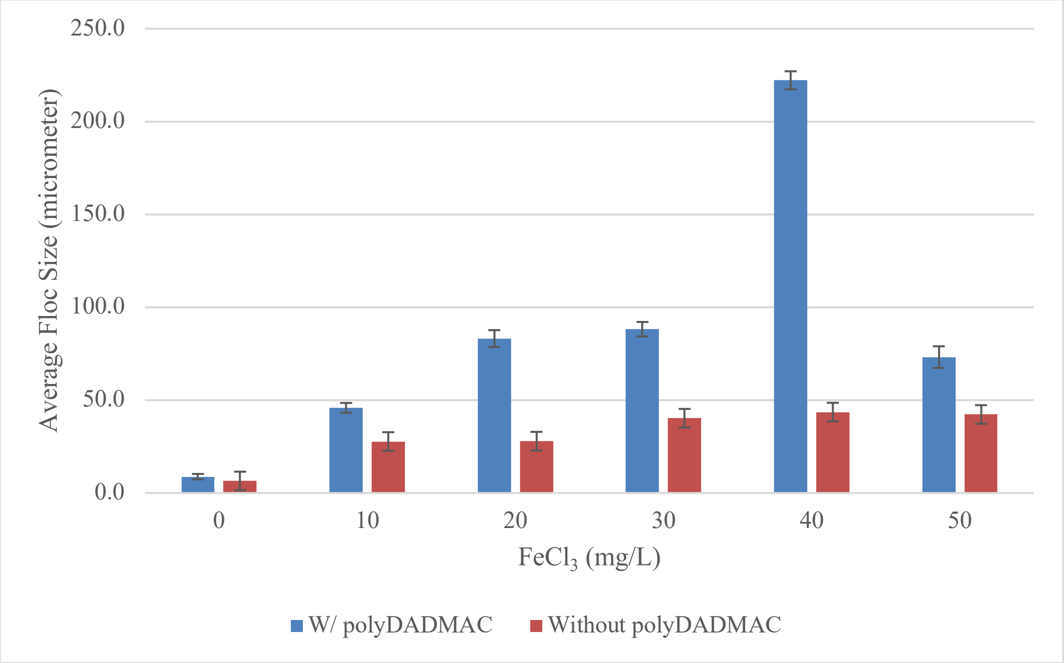

Figure 6. Floc Size Before and After the Addition of 5.45 mg/L polyDADMAC to Ferric Chloride with Standard Deviation Error Bars.

Moreover, the largest floc size occurs at 40 mg/L ferric chloride dose, which supports the observation of the optimum ferric chloride dosage where the lowest water turbidity removal occurs at the point where the largest floc size occurs. These results correspond with Wang et al. (2013). The Wang et al. (2013) study investigated the effect of three types of polymers, including polyDADMAC flocculants, on floc properties after applying coagulation/flocculation pretreatment. Wang et al. (2013) observed that all three types of polymers, including polyDADMAC, increase floc size, enhancing the floc's stability.

Ferrous sulfate ($FeSO_4$) was the second primary coagulant tested in this study. Its reaction in the water is shown in Equation 3, where the clumped particles are composed of $Fe(OH)_3$ that are settled during the jar test.

$$FeSO_4 + 3H_2O \leftrightarrow Fe(OH)_{3\,(S)} + 3H^+ + SO_4^{-2} + e^- \qquad (3)$$

Figure 7 shows the behavior of five different ferrous sulfate dosages to lower the turbidity in 600 ml seawater containing 10 mg/L sodium alginate stock and 1 g/L bentonite clay. As Shown in Figure 7, the optimum ferrous sulfate is equal to 20 mg/L because this is where the lowest turbidity occurs.

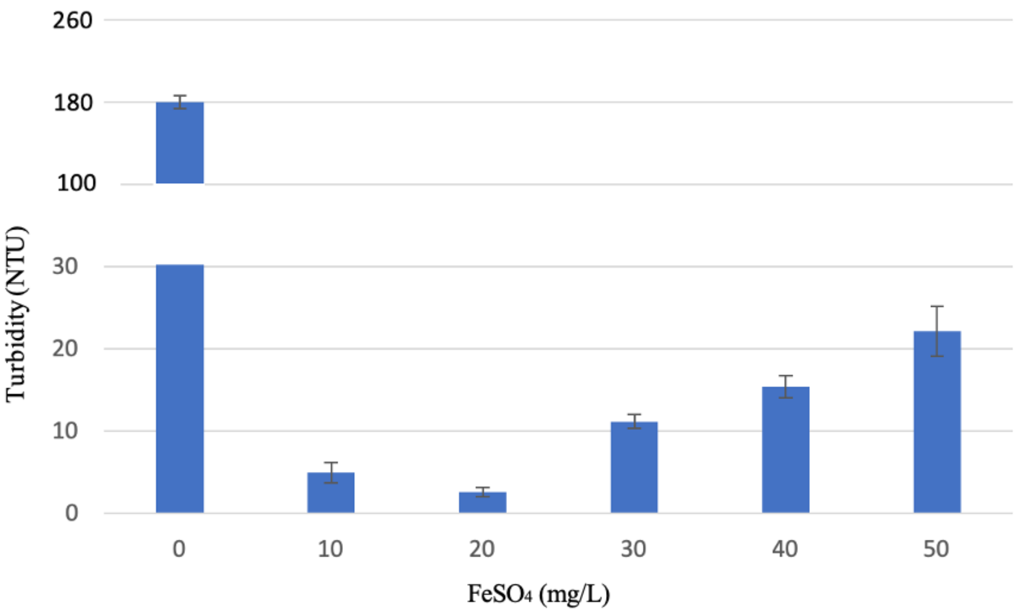

Figure 7. The Impact of Ferrous Sulfate Dosage on Water Turbidity with Standard Deviation Error Bars.

The turbidity decreases from a dosage of 0 mg/L to 20 mg/L, and this drop demonstrates that the particles are destabilized and settled. A significant change in the turbidity did occur between each ferrous sulfate concentration (95% CI). The turbidity increases in dose from 30 mg/L to 50 mg/L is the overdoing of ferrous sulfate coagulant. The p-value of turbidity measurement determined using a t-test for ferrous sulfate coagulant dosage in coagulation treatment on sodium alginate shows a statistical difference between all coagulant's dosage since the p-values are less than 0.05 (Table 1 in Appendix B). Moreover, their complete settling occurs when turbidity measurements become constant. Ferric chloride as a coagulant decreases water turbidity more than ferrous sulfate coagulants, which supports the hypothesis in this study that ferric chloride decreases water turbidity more than other related iron coagulants.

In Parmar et al. (2011) study, ferrous sulfate is used as a coagulant to treat dairy industry wastewater. It was observed that ferrous sulfate increases the turbidity removal of the wastewater, which matches the observation of the current study with different water types and characteristics.

Figure 8 shows the impact of 5.45 mg/L polyDADMAC as a coagulant aid when added to ferrous sulfate in decreasing the water turbidity. As shown in Figure 8, the addition of 5.45 mg/L polyDADMAC decreases the water turbidity more than when only ferrous sulfate was used as a coagulant due to the increase of the larger floc creation results from adding 5.45 mg/L polyDADMAC compared to Figure 7.

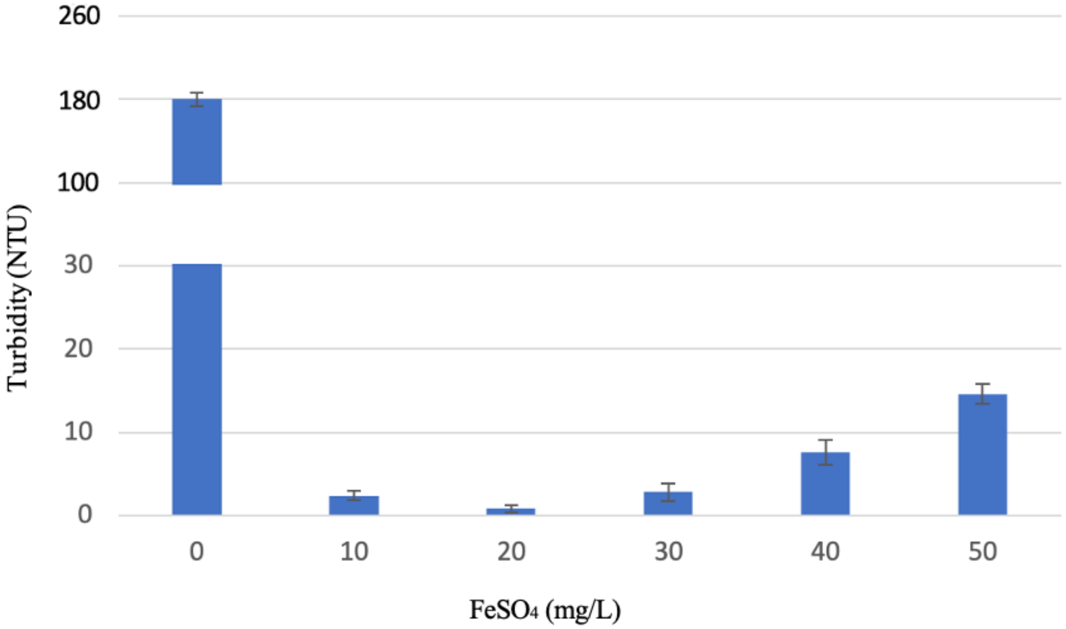

Figure 8. The Impact of Ferrous Sulfate Dosage with 5.45 mg/L polyDADMAC on Water Turbidity with Standard Deviation Error Bars.

Statistically, adding 5.45 mg/L polyDADMAC resulted in significantly reduced turbidity measurement when ferrous sulfate coagulant was used to treat seawater with sodium alginate except between 10-30 mg/L (Table 4 in Appendix B). These results collaborate with Ayol et al. (2004). In Ayol et al. (2004) study, cationic and nonionic polymers singly and in combination were used to explore whether dual polymer conditioning of water treatment residuals offers any advantages by measuring the turbidity of the water. Ayol et al. (2004) observed that cationic polymer could decrease water turbidity.

The impact of the addition of 5.45 mg/L polyDADMAC to ferrous sulfate on floc size was explored in this study. Figure 9 illustrates the impact of 5.45 mg/L polyDADMAC on flocs size when ferrous sulfate is used as a primary coagulant.

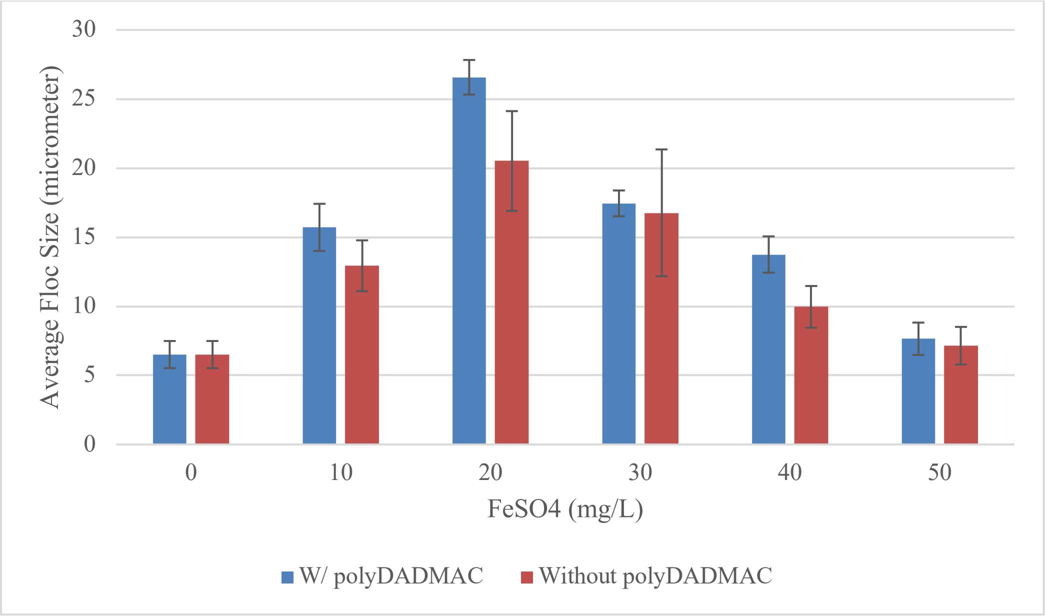

Figure 9. Floc Size Before and After the Addition of 5.45 mg/L polyDADMAC to Ferrous Sulfate with Standard Deviation Error Bars.

It is clearly shown that the size of the flocs highly increased after the addition of 5.45 mg/L polyDADMAC significantly (95%CI). Furthermore, the largest floc size occurs at 20 mg/L ferrous sulfate dose, which is the optimum dose of ferrous sulfate. PolyDADMAC is effective with ferric chloride instead of ferrous sulfate since the maximum floc size when polyDADMAC was added to ferric chloride reached 222 micrometers, while in ferrous sulfate, it reached 26.5 micrometers. Moreover, there is a statistically significant increase in floc size when ferrous sulfate is used as a coagulant for sodium alginate expect between 0-50 mg/L, 10-30 mg/L, 10-50 mg/L, and 30-40 mg/L (Table 3 Appendix B). While in the presence of 5.45 mg/L polyDADMAC when ferrous sulfate is used as a coagulant, there is a statistical increase in floc size except between 0-40 mg/L and 40-50 mg/L (Table 5 in Appendix B). These results are consistent with Ayol et al. (2004) because they also explored the impact of cationic polymer on floc size to achieve their objective, and it was observed that as the cationic polymer increased, the floc size increased as well, which proved that cationic polymer increases floc size.

Ferric sulfate is the third primary coagulant tested in this study. Its reaction in coagulation is similar to the ferric chloride reaction, as shown in Equation 4, where $Fe(OH)_3$ is the clumped particles that are settled after the coagulation process.

$$Fe_2(SO_4)_3 + 3H_2O \leftarrow\rightarrow 2Fe(OH)_{3\,(S)} + 3H^+ + 3SO_4^{2-} \qquad (4)$$

Figure 10 explains the efficacy of five different doses of ferric sulfate in lowering the turbidity in 600 ml seawater containing 10 mg/L sodium alginate stock and 1 g/L bentonite clay. As shown in Figure 10, 30 mg/L is the optimum dose of ferric sulfate where the lowest turbidity measurement occurs.

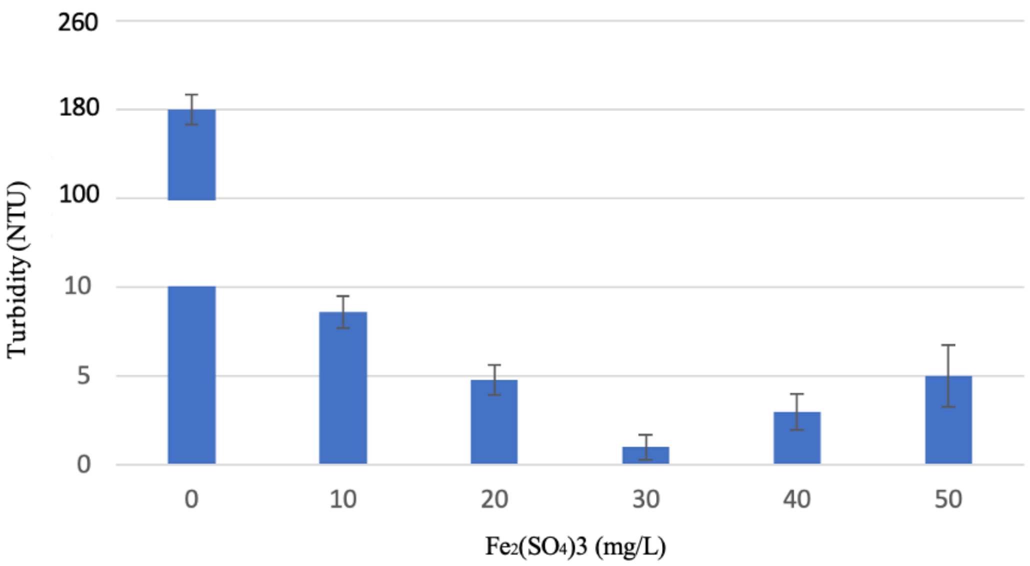

Figure 10. The Impact of Ferric Sulfate Dosage on Water Turbidity with Standard Deviation Error Bars.

The turbidity decreases from 0 mg/L to 30 mg/L ferric sulfate dose, indicating that the particles are destabilized. A significant change in the turbidity did occur between each ferric sulfate concentration (95% CI). The rise of turbidity after 30 mg/L ferric sulfate dosage is the overdoing of ferric sulfate coagulant. Furthermore, there is a statistically significant decrease in turbidity when ferric sulfate is used as a coagulant in the treatment of sodium alginate except between 20-50 mg/L (Table 1 in Appendix B). It is clearly shown in the observation that ferric sulfate decreases the turbidity more than ferric chloride and ferrous sulfate. These results correlate with the Prakash et al. (2014) study. Prakash et al.'s (2014) study aimed to treat a seawater sample to remove impurities by various coagulants, which are alum, ferric chloride, and ferric sulfate. Prakash et al. (2014) observed that the optimum dose of ferric sulfate removed %96.6 of water turbidity, which matches the observation of the current study since ferric sulfate reached more than 95% percent water turbidity removal (Figure 10).

Adding 5.45 mg/L polyDADMAC to the ferric sulfate during the treatment decreased water turbidity, as shown in Figure 11.

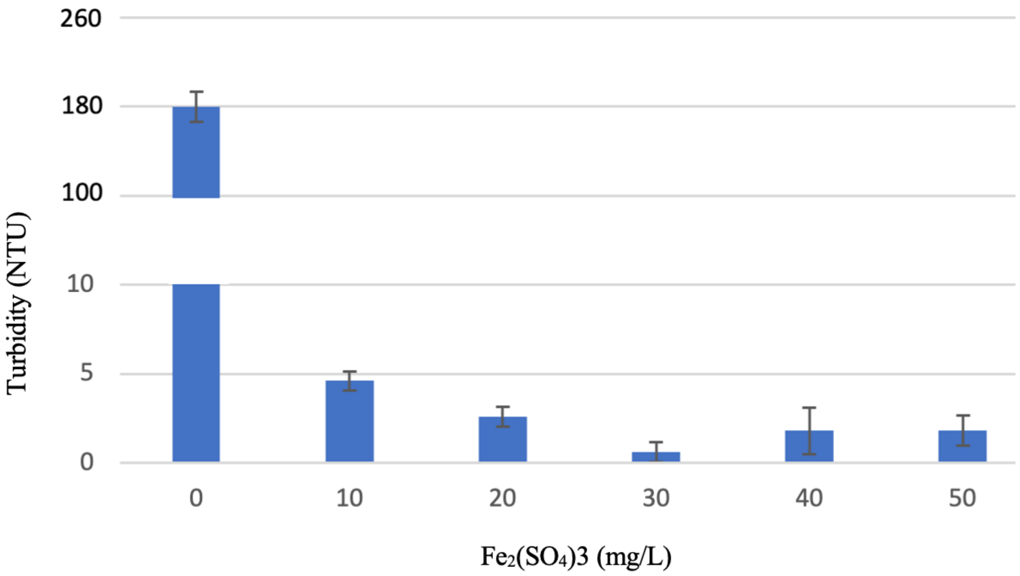

Figure 11. The Impact of Ferric Sulfate Dosage with 5.45 mg/L polyDADMAC on Water Turbidity with Standard Deviation Error Bars.

Adding 5.45 mg/L polyDADMAC increased the floc size, which made the water turbidity highly decrease compared to Figure 10. Statistically, 5.45 mg/L polyDADMAC significantly reduced the turbidity when ferric sulfate was used as a coagulant except between 20-40 mg/L, 30-40 mg/L, and 40-50 mg/L (Table 4 in Appendix B). These results collaborate with Graham et al. (2008) study. In Graham et al. (2008), a commercial tannin-based cationic polymer (TBP) was explored to establish its chemical properties and coagulation performance in preliminary trials using water containing a kaolin suspension. During the investigation of TBP coagulation performance on decreasing water turbidity, the results were compared to polyDADMAC, and Graham et al. (2008) observed that polyDADMAC could decrease water turbidity, which matches the results of the current study.

Figure 12 illustrates the impact of 5.45 mg/L polyDADMAC on flocs size when ferric sulfate is used as a primary coagulant.

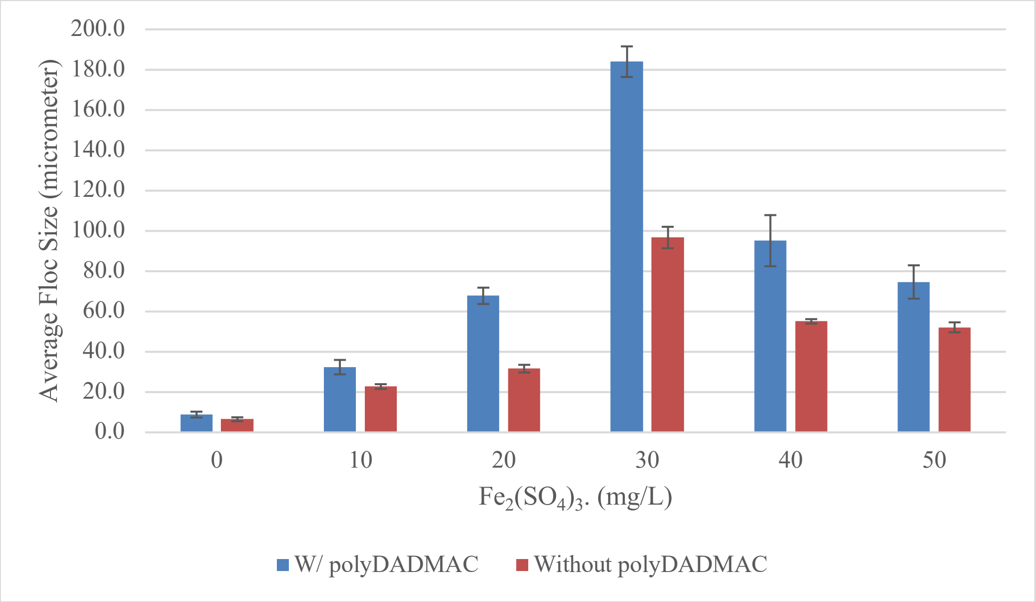

Figure 12. Floc Size Before and After the Addition of 5.45 mg/L polyDADMAC to Ferric Sulfate with Standard Deviation Error Bars.

It is clearly shown that the size of the flocs increased after the addition of 5.45 mg/L polyDADMAC significantly (95%). Furthermore, the largest floc size occurs at 30 mg/L ferric sulfate dose, which supports the observation of the optimum ferric sulfate dosage where the lowest water turbidity occurs at the point of forming the largest floc size. Moreover, there is a statistically significant increase in floc size when ferric sulfate is used as a coagulant for sodium alginate except between 40-50 mg/L

(Table 3 Appendix B). While in the presence of 5.45 mg/L polyDADMAC when ferric sulfate is used as a coagulant, there is a statistical increase in floc size except between 20-50 mg/L (Table 5 in Appendix B). These results are consistent with Yu et al. (2010). In Yu et al. (2010) study, floc's formation, breakage, and regrowth were investigated using alum and polyDADMAC to explore the reversibility of floc breakage on deionized water containing kaolin clay. Yu et al. (2010) observed that polyDADMAC increases the floc size, which matches the results of the current study.

4.2 The Impact of pH on Coagulant Optimum Dosage

pH is one of the main factors that can impact the coagulation process. Most of the colloids in water are negatively charged, and due to electrical repulsion, they may remain stable, so the addition of iron coagulants will interact with the negative colloids to neutralize their charge (Malik, 2018). Therefore, the efficiency of the optimum dose of coagulant could be impacted at varying pH values due to the formation of less than the optimum ions in the solution, where a low pH value may not allow the coagulation process to proceed, while is high pH value may cause coagulated particles to redisperse (Emerson Process Management, 2009). The impact of pH levels can only be determined experimentally. In this study, the optimum coagulant dosage efficiency was examined at seven different pH levels for ferric chloride coagulant and six pH levels for ferrous sulfate and ferric sulfate before adding the coagulants. The pH levels were adjusted before adding the coagulants. Solution pH does influence turbidity removal (Figure 13).

As shown in Figure 13 pH level of 8.25 is the preferred pH level that achieves the highest removal of turbidity using the iron coagulant. However, the range of pH levels that remove 90% percent of turbidity differs depending on each coagulant type. The 90% percent of turbidity removal of 40mg/L ferric chloride occurs at a pH range of 8 to 9, as shown in Figure 12. However, 90% of turbidity removal of 20mg/L ferrous sulfate occurs at a pH range of 8 to 9.00, which matches the same range of 40mg/L ferric chloride. At the same time, 90% of turbidity removal of 30mg/L ferric sulfate occurs at a pH range of 7 to 9, much wider than 40mg/L ferric chloride and 20mg/L of ferrous sulfate.

Furthermore, Table 2 in Appendix B illustrate the p-value of turbidity removal of the three iron coagulants' optimum dose during sodium alginate treatment at different pH level where the results are statistically different since all the p-values are less than 0.05. The observations of the pH impact on ferric chloride and ferric sulfate collaborate with Liu et al. (2012) study. In Liu et al. (2012) study, ferric chloride and ferric sulfate were used to remove water turbidity from landfill leachate. During the test of the coagulant on different pH levels, Liu et al. (2012) observed that the optimum pH level of ferric chloride to be effective in turbidity removal is 8, and for ferric sulfate is 7.5 which matched the pH range of removing %90 of turbidity using the optimum dose of these two coagulants in the current study.

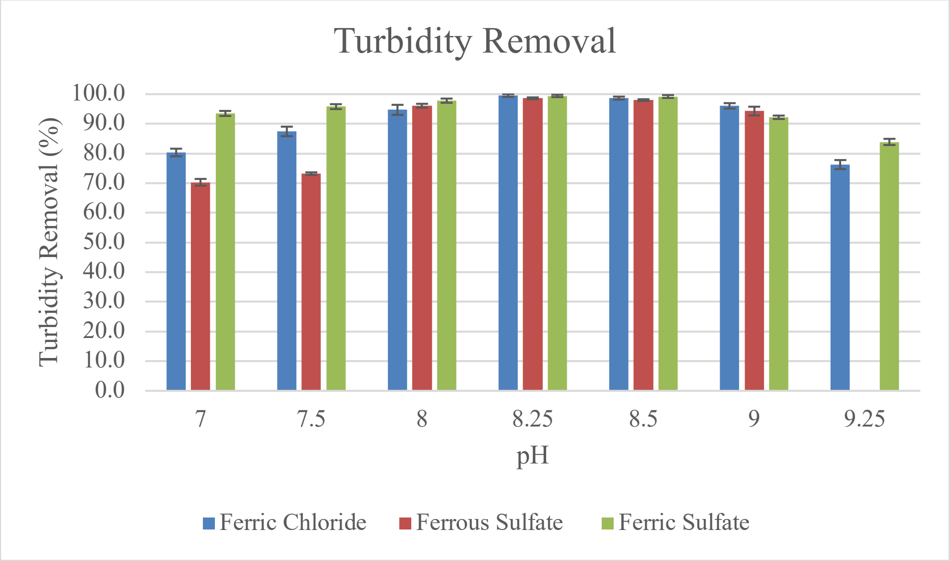

Figure 13. The Impact of pH level on the optimum Dose of The Iron Coagulants with Standard Deviation Error Bars.

4.3 Coagulation Process on Cultivated Algae

After investigating the performance of iron coagulants on lowering the turbidity of a solution containing sodium alginate, cultivated algae was used to explore the performance of iron coagulants and support the observations. This study added 10 mg/L of cultivated algae solution to 600 ml of seawater containing 1g/L bentonite clay. The optimum dosage of each coagulant with and without 5.45 mg/L polyDADMAC addition was used to investigate, in triplicate, their performance on cultivated algae. Figure 14 shows the performance of each coagulant using its optimum dosage to lower the turbidity. As shown in Figure 14, the turbidity measurement in all three coagulants proved that the optimum dosage is effective when the solution contains either sodium alginate or cultivated algae.

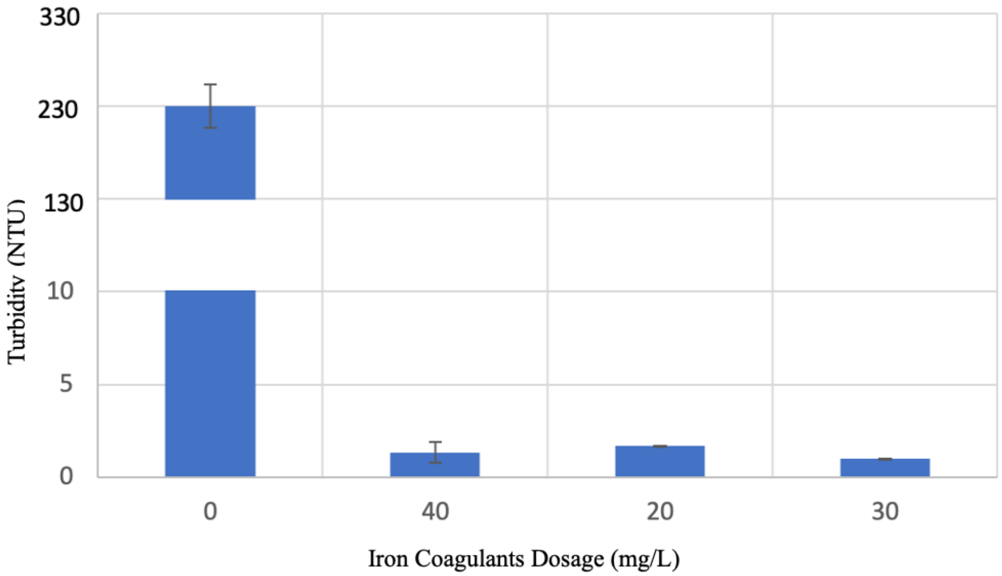

Figure 14. The Performance of the Optimum Iron Coagulants Dosage (40 mg/L Ferric Chloride, 20 mg/L Ferrous Sulfate, and 30 mg/L Ferric Sulfate) on Lowering Water Turbidity for Cultivated Algae with Standard Deviation Error Bars.

Figure 15 shows the performance of each coagulant using its optimum dosage with the addition of 5.45 mg/L polyDADMAC to lower the turbidity. The optimum dosage of all three coagulants with 5.45 mg/L polyDADMAC addition effectively lowers the turbidity when the solution contains sodium alginate or cultivated algae (Figure 15).

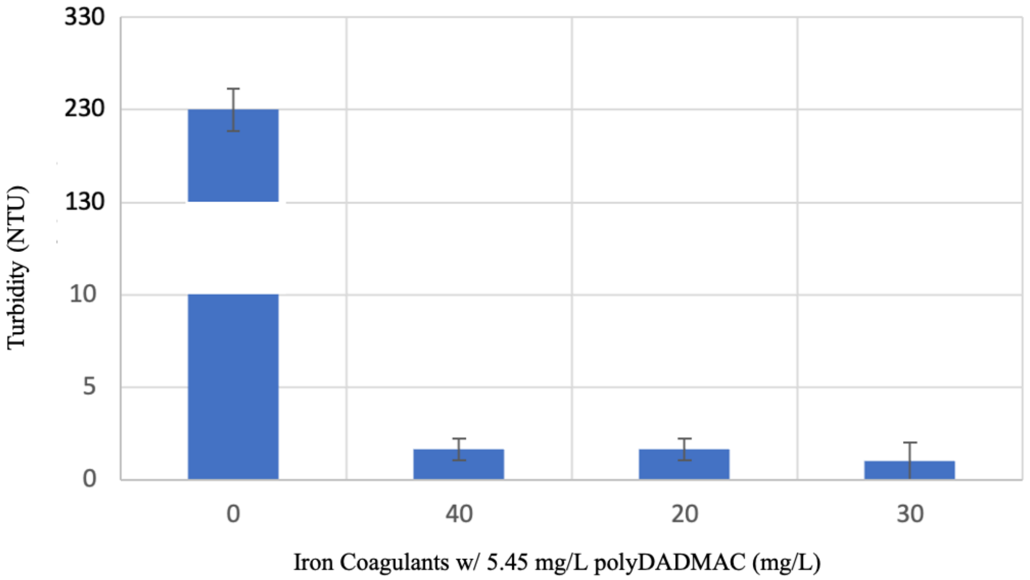

Figure 15. The Performance of the Optimum Iron Coagulants Dosage (40 mg/L Ferric Chloride, 20 mg/L Ferrous Sulfate, and 30 mg/L Ferric Sulfate) with 5.45 mg/L polyDADMAC Addition on Lowering Water Turbidity for Cultivated Algae with Standard Deviation Error Bars.

The difference between using sodium alginate and cultivated algae during the coagulation process is increased seawater turbidity in the feed water, as shown in Table 1. Table 6 in Appendix B illustrates the p-value of turbidity measurement at optimum iron coagulant dosage with and without 5.45 mg/L polyDADMAC on cultivated algae. The results are not statistically different since all the p-values exceed 0.05 except between 0-40 mg/L, 0-20 mg/L, and 0-30 mg/L iron coagulants dosage with and without polyDADMAC addition (Table 6 in Appendix B). These results are consistent with Alshahri et al. (2019) study. In Alshahri et al. (2019) study, ferric was used to treat seawater containing algae, and it was observed that ferric could lower less than 90% of seawater turbidity, which matches the observation of the current study, but in the current study, the turbidity removal reached more than 90%.

4.4 Removal of Total Organic Carbon & Dissolved Organic Carbon

TOC is one of the most widely used measures for quantifying the amount of natural organic matter (NOM) in water, while DOC is considered a collective parameter used to quantify the concentration of organic matter in the water that passed through a filter has a 0.45-micron pore size (Alshahri et al. 2019 and Priya et al. 2020). According to Alshahri et al. (2019), the performance of RO membranes has been correlated to DOC content in the feedwater, where concentrations higher than 2 mgC/L have been shown to impact membrane fouling and likely lead to biofouling; this is the main reason for increasing the amount of TOC and DOC to more than 2 mgC/l in the feed water in this study. The impact of optimum iron coagulants dosage and 5.45 mg/L polyDADMAC on DOC and TOC removal in artificial seawater containing sodium alginate and artificial seawater containing cultivated algae was investigated in this study to explore that these coagulants can decrease the TOC and DOC to less than 2 mgC/L to protect and extend the lifetime of membranes. Figures 16 show the optimum dosage of iron coagulant on removing more than 90% of existing TOC in seawater containing sodium alginate and cultivated algae. These results correspond with Qasim et al. (1992). In Qasim et al. (1992) study, the removal of TOC was investigated using ferric coagulant on raw water containing 4.8 mgC/L TOC. Qasim et al. (1992) observed that coagulation by using ferric coagulants able to increase TOC removal, which matched the observation explored in the current study.

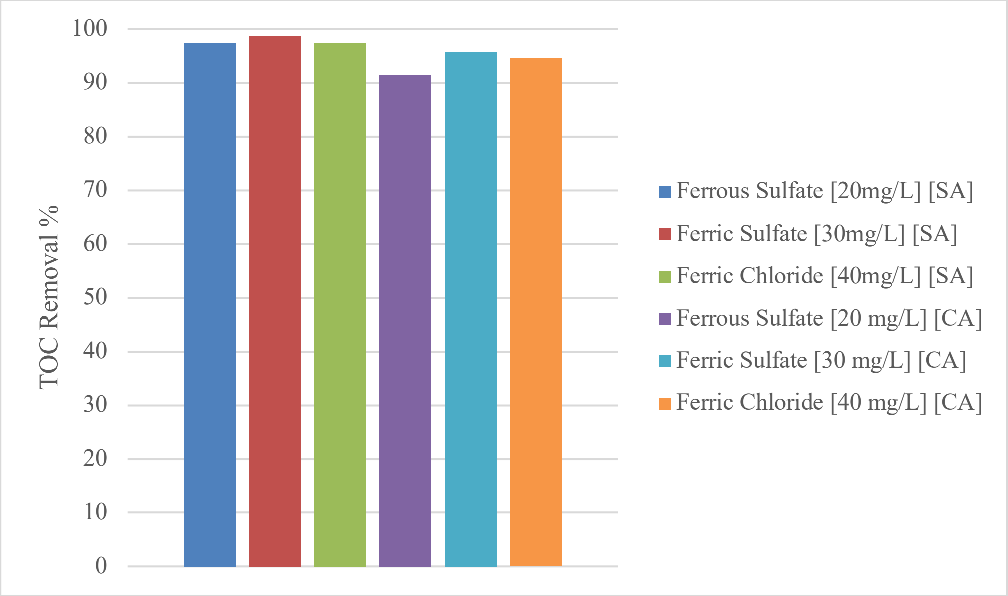

Figure 16. The Performance of Optimum Dosage of Iron Coagulants on TOC Removal in Sodium Alginate [SA] and Cultivated Algae [CA].

Figure 17 illustrates the performance of the optimum dosage of iron coagulant on removing existing DOC in seawater containing sodium alginate and cultivated algae. It is clearly shown that the optimum dosage of iron coagulant can remove more than 90% of existing DOC in seawater containing sodium alginate and cultivated algae. The results correspond with the Alshahri et al. (2019) study. In the Alshahri et al. (2019) study, the removal of DOC on seawater contains sodium alginate, and seawater contains cultivated algae. Alshahri et al. (2019) observed that ferric coagulant increased the DOC removal to about %70 for seawater containing sodium alginate and seawater containing cultivated algae which matched the results of the current study with different DOC percent removal.

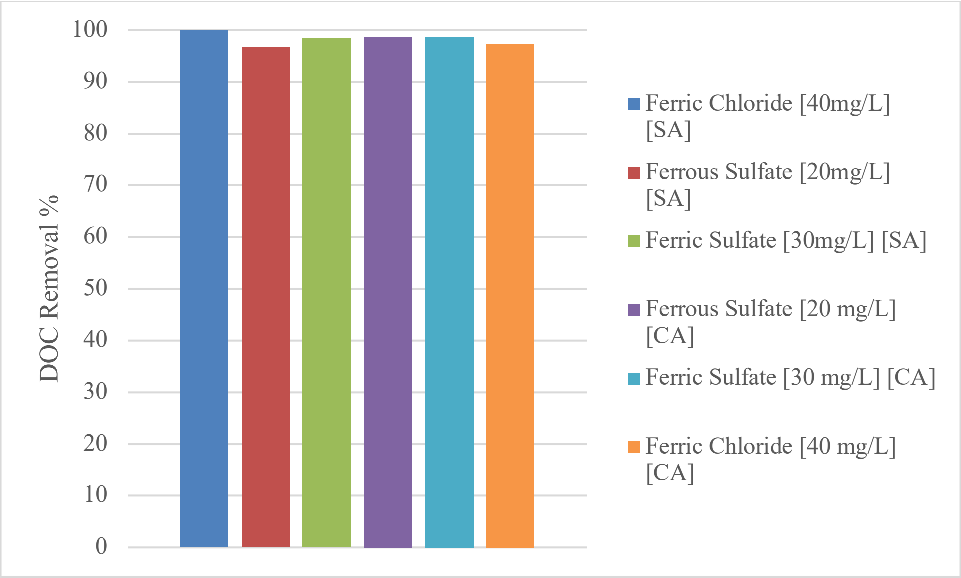

Figure 17. The Performance of Optimum Dosage of Iron Coagulants on DOC Removal in Sodium Alginate [SA] and Cultivated Algae [CA].

Figure 18 explains the performance of the optimum dosage of iron coagulants with 5.45 mg/L polyDADMAC addition on seawater containing sodium alginate and cultivated algae. It is clearly shown that 5.45 mg/L polyDADMAC additive can remove more than 75% of DOC in seawater containing sodium alginate and cultivated algae, which is still considered adequate to prevent membrane fouling since the DOC after the treatment is less than 2 mgC/L. These results corresponded with Sun et al. (2016) study. In Sun et al. (2016) study, the performance of epichlorohydrin-dimethylamine was compared to two other cationic polymers, which are poly dimethyl diallyl ammonium (PDMDAAC) and polyacrylamide (PAM) as coagulant aids to polyferric chloride (PFC) in removing turbidity and DOC through coagulation process was investigated. Sun et al. (2016) observed that the cationic polymer as a coagulant aid could increase the DOC removal in contaminated deionized water, which matched the observation of the current study with a difference in the type of water and coagulants used.

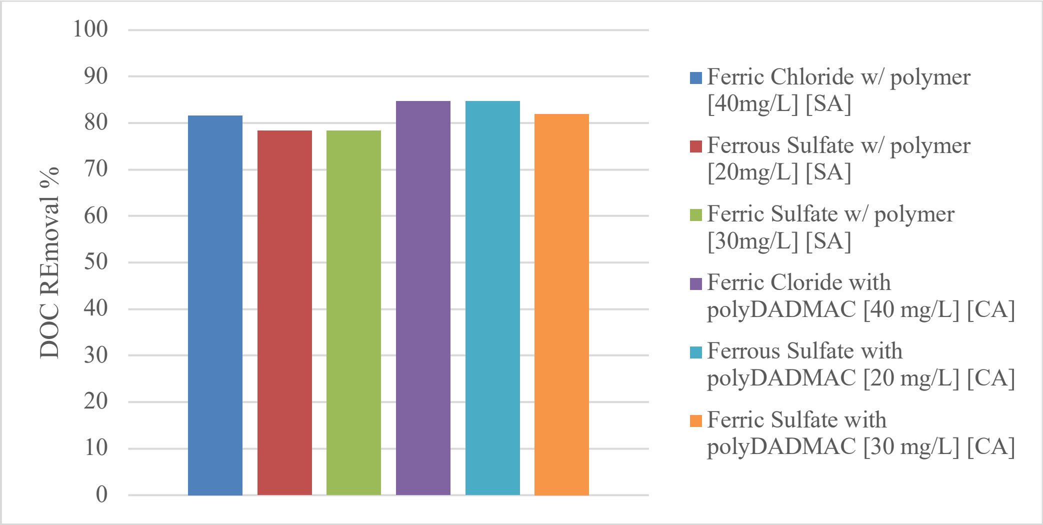

Figure 18. The Performance of Optimum Dosage of Iron Coagulants with 5.45 mg/L polyDADMAC on DOC Removal in Sodium Alginate [SA] and Cultivated Algae [CA].

Figure 19 shows the performance of the optimum dosage of iron coagulant with 5.45 mg/L polyDADMAC addition on removing TOC in seawater containing sodium alginate. Using iron coagulants, along with the addition of 5.45 mg/L polyDADMAC addition in the treatment of seawater containing sodium alginate, removes more than 75% of existing TOC. Moreover, the observations exploring the impact of polyDADMAC on TOC removal in the current study are consistent with Edzwald et al. (1987) study. Edzwald et al. (1987) investigated the cationic polymer’s performance in removing TOC through indirect filtration. Edzwald et al. (1987) observed that the cationic polymer removes approximately %40 of TOC from water through indirect filtration, which matches the results in the current study with different TOC percent removal.

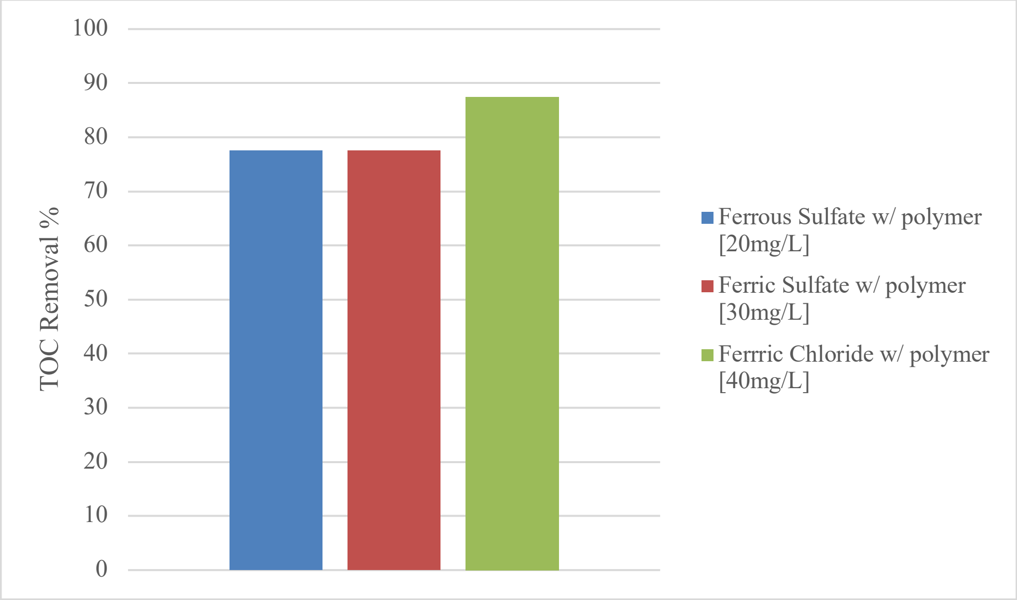

Figure 19. The Performance of Optimum Dosage of Iron Coagulants with 5.45 mg/L polyDADMAC on TOC Removal in Sodium Alginate.

4.5 Cost Benefit

The price of each iron coagulant and polyDADMAC was calculated depending on the mass needed to treat 1,000 m^3/day of artificial seawater containing sodium alginate or cultivated algae to investigate which iron coagulant will provide the lowest cost using cost-benefit analysis in this study. The mass of coagulants and polyDADMAC was calculated according to the optimum concentration used in the treatment. The price of each iron coagulant and polyDADMAC, according to Gan et al. (2021) recorded in Table 5.

Table 5: Coagulants and polymer prices (obtained from Gan et al., (2021), and https://www.Alibaba.com on April 8, 2023).

Chemical	Price ($/ton)
Ferric Chloride	1,000
Ferrous Sulfate	1,200
Ferric Sulfate	350
polyDADMAC	1,350

This study's cost and benefit factors were determined using the data from Sarica's (2018) study. The cost of all factors and the total cost, when the optimum dosage of the three iron coagulants used for the SWRO system has a capacity of 1,000 m^3/day, is recorded in Table 6. The total cost of chemicals includes only the coagulant without any additional chemicals. The addition of polyDADMAC increased the total cost by $0.007 (Table 7). When ferric sulfate is used as the primary coagulant, the total project cost will be $0.421/$m^3$ which is lower than the other related iron coagulants (Table 6). The addition of ployDADMAC increased the total project's total cost by $0.007 (Table 7). Since the dose of polyDADMAC is constant, the total cost of the project when the addition of polyDADMAC to ferric sulfate appeared to be $0.428/$m^3$ which is the lowest cost when polyDADMAC is added to the treatment (Table 7).

Table 6. Total cost of iron coagulant for plant capacity of 1,000 m^3/day.

Unit Cost of Factors			Price (\$/m^3)		
A_{Capital}			0.067		
$A_{\text{Maintenance}}$			0.013		
A_{Membrane}			0.035		
A_{Electric}			0.15		
$FeCl_3$ $A_{\text{Chemicals}}$	$FeSO_4$ $A_{\text{Chemicals}}$	$Fe_2(SO_4)_3$ $A_{\text{Chemicals}}$	0.04	0.024	0.011
$A_{\text{Pretreatment}}$			0.008		
A_{Manpower}			0.007		
A_{Interest}			0.13		
A_{Total}			0.450	0.434	0.421

Table 7. Total cost when 5.45 mg/L polyDADMAC is added to the iron coagulants for plant capacity of 1,000 m^3/day.

Chemicals	Total Cost (\$/m^3)
Ferric Chloride w/ polyDADMAC	0.457
Ferrous Sulfate w/ polyDADMAC	0.441
Ferric Sulfate w/ polyDADMAC	0.428

The benefit-cost of water sale to the ships and facilities, according to Sarica's (2018) study, is recorded in Table 8. These water sale prices were included in Equation 1 to determine the NBV. The NBV of using different iron coagulants with and without the addition of polyDADMAC is recorded in Table 9. Using ferric sulfate as a primary coagulant without the addition of polyDADMAC will provide the most economically viable price, where the earnings will be $5.58 when water is sold to the ships and $0.87 when water is sold to the facilities. Moreover, in Sarica's (2018) study, the earnings when water is sold to ships is $5.51, and when water is sold to facilities is $0.8, which is less than the earnings provided in this study. These results contradict the hypothesis of the current study, where it turns out that pretreatment with ferric sulfate economically decreases water turbidity resulting from algae greater than other iron-related coagulants.

Table 8. Benefit cost of water sale according to Sarica A. (2018) study.

Water Sale Price to	($/m^3)
Ships	6
Facilities	1.29

Table 9. Net Benefit Value (NBV) for usage of each iron coagulant with and without polyDADMAC.

Net Benefits Value of	Ships ($/m^3)	Facilities ($/m^3)
Ferric Chloride	5.55	0.84
Ferrous Sulfate	5.57	0.86
Ferric Sulfate	5.58	0.87
Ferric chloride w/ polyDADMAC	5.54	0.83
Ferrous Sulfate w/ ployDADMAC	5.56	0.85
Ferric Sulfate w/ polyDADMAC	5.57	0.86

CHAPTER 5. CONCULSION AND RECOMMENDATION

This study focused on testing the performance and cost-benefit of three types of iron coagulant with and without polymer additive to provide acceptable water quality that can protect RO membrane from fouling at a low economic cost. Measuring turbidity and organic removal are the two parameters defining the pretreatment quality. The method started with testing the iron coagulants on 600 ml of 33 g/L artificial seawater contains 1g/L bentonite clay to increase the turbidity and 10 mg/L of sodium alginate to mimic the HABs in the artificial seawater sample. Determining the optimum dose of iron coagulants with and without polyDADMAC additive that lowers the turbidity as much as possible was achieved by dosing 5 different coagulant doses and recording the lowest turbidity reading along with its dose. The optimum dosage of each coagulant was different, 40 mg/L for ferric chloride, 20 mg/L of ferrous sulfate, and 30 mg/L for ferric sulfate. Then, the turbidity removal at the optimum coagulant dosage was tested under several pH levels to explore the impact of pH levels. It was observed that high and low pH levels decrease turbidity removal, which impacts the water quality.

Moreover, the impact of 5.45 mg/L polyDADMAC on floc stability and turbidity was explored by running the coagulation process through a jar test and measuring the floc size before and after polyDADMAC addition. It was observed that 5.45 mg/L ployDADMAC enhanced the turbidity removal and produced large and easily settled coagulants. Furthermore, during the measurement of the TOC and DOC removal when the optimum coagulant dosage was used with and without 5.45 mg/L polyDADMAC, it was demonstrated that they are effective in reducing the amount of

TOC and DOC for less than 2 mgC/L, which can increase the RO membrane lifetime. After that, the performance of the coagulants was tested on cultivated algae, and it had the same performance as on the sodium alginate. The cost of each coagulant with and without 5.45 mg/L polyDADMAC for the SWRO project has a capacity of 1,000 m^3/day, was calculated along with the uses of previous study cost analysis data to explore the cost-benefit of each coagulant with and without polyDADMAC additive. It was found that ferric sulfate without the 5.45 mg/L polyDADMAC has the highest benefit cost to achieve water quality that enhances the protection of the RO membrane.

It is recommended to use actual seawater during the period of HABs to get a better understanding of the behavior of iron-coagulants with and without polyDADMAC additive. As well as more research about the impact of HABs on treatment methods other than RO, such as MSF, and explore if the coagulation pretreatment able to protect it or not.

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APPENDIX A:

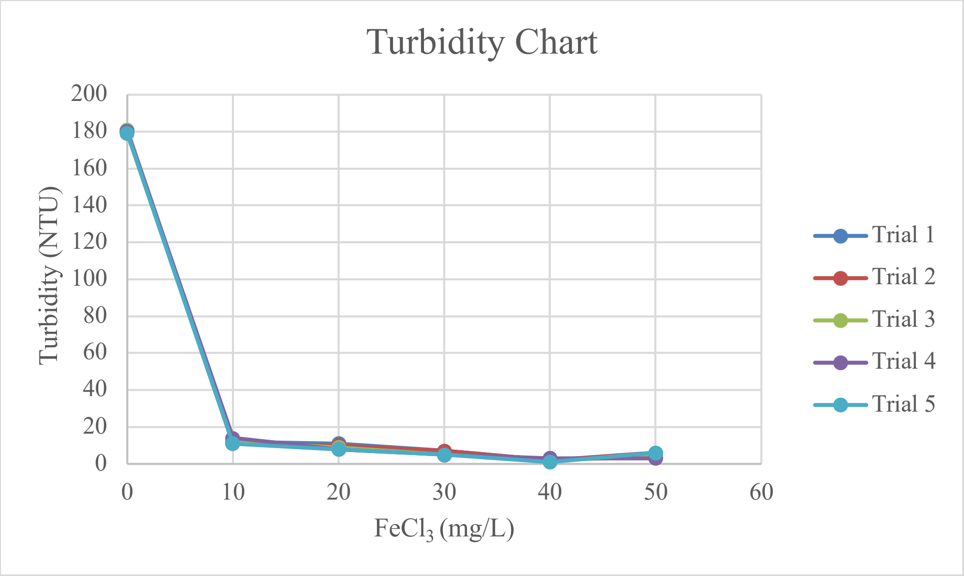

Figure 1. Turbidity at Ferric Chloride Different Dosage.

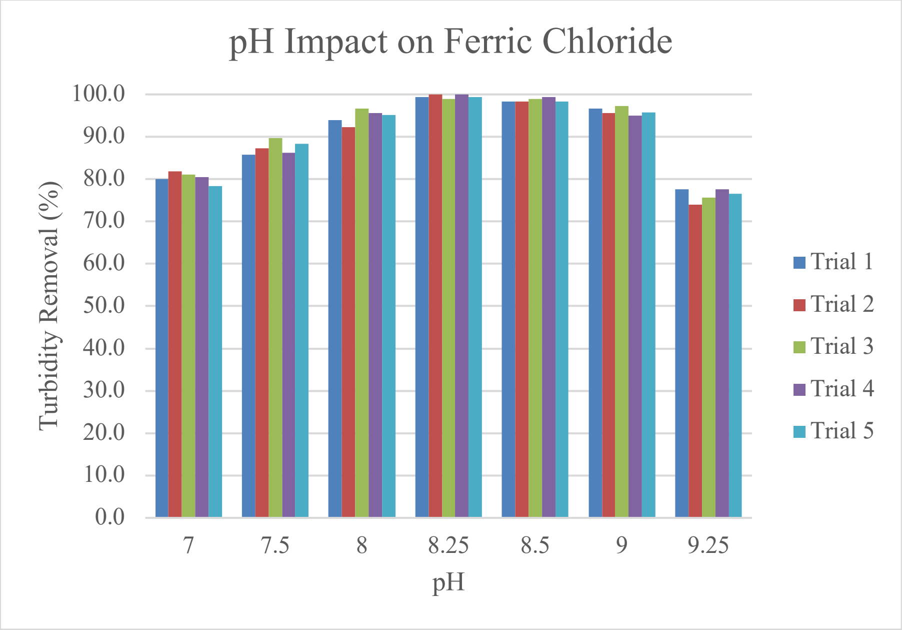

Figure 2. Mean Turbidity Removal at Ferric Chloride Optimum Dosage on Different pH levels.

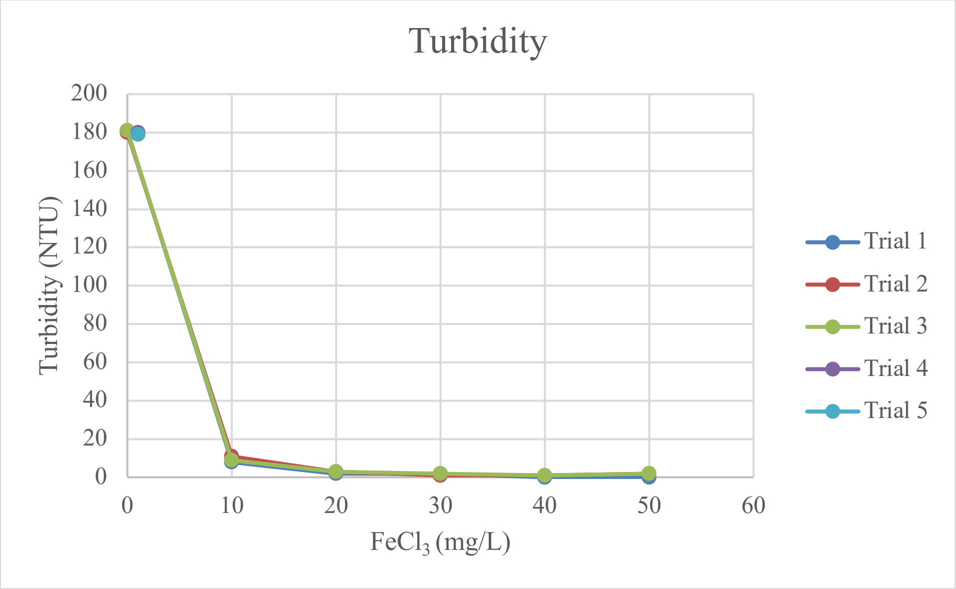

Figure 3. Mean Turbidity at Ferric Chloride Different Dosage with 5 mg/L polyDADMAC.

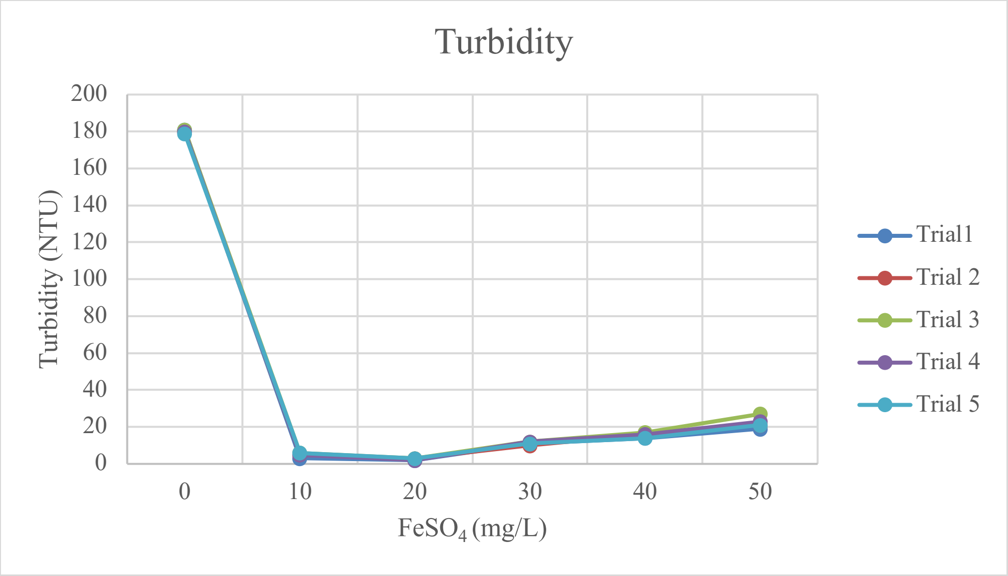

Figure 4. Mean Turbidity at Ferrous Sulfate Different Dosage.

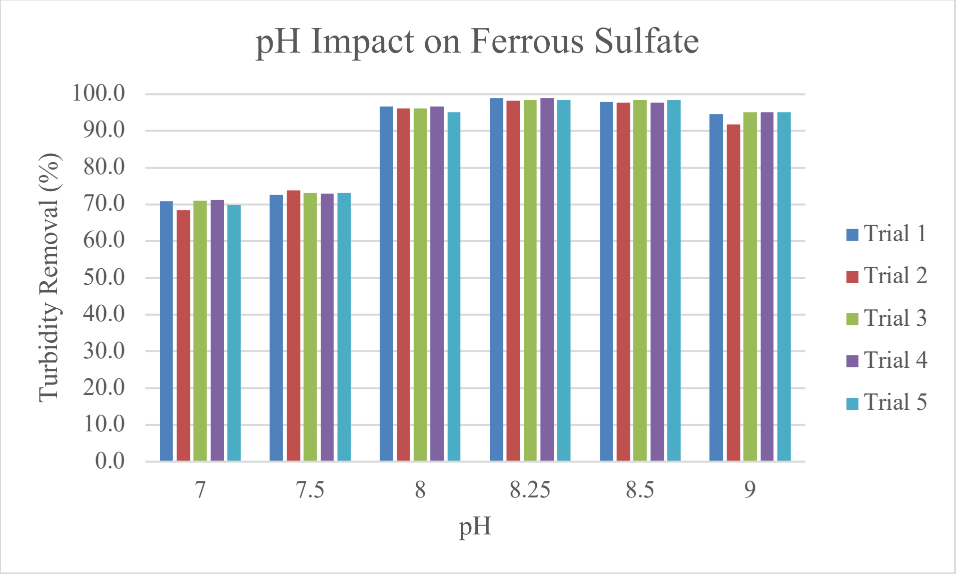

Figure 5. Mean Turbidity Removal at Ferrous Sulfate Optimum Dosage on Different pH levels.

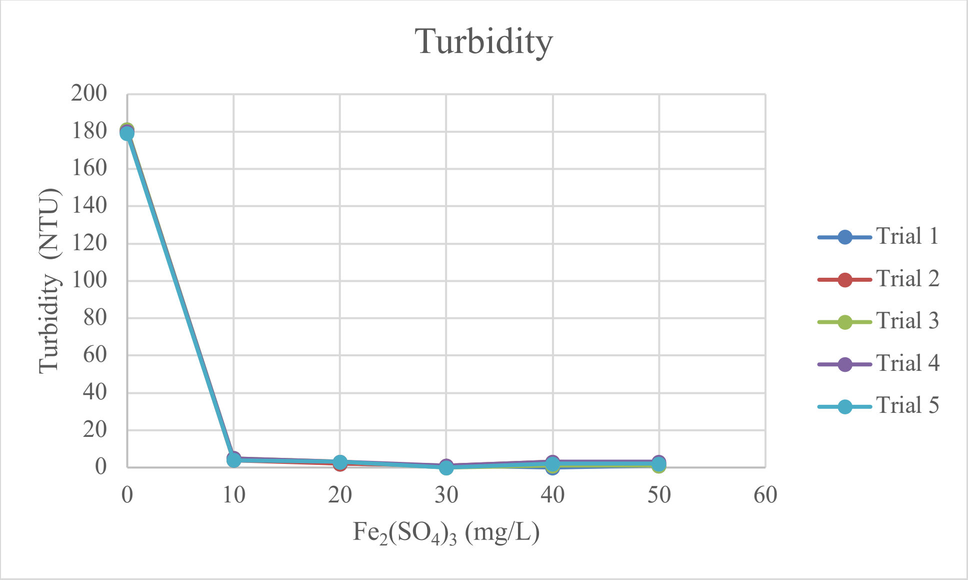

Figure 6. Mean Turbidity at Ferrous Sulfate Different Dosage with 5 mg/L polyDADMAC.

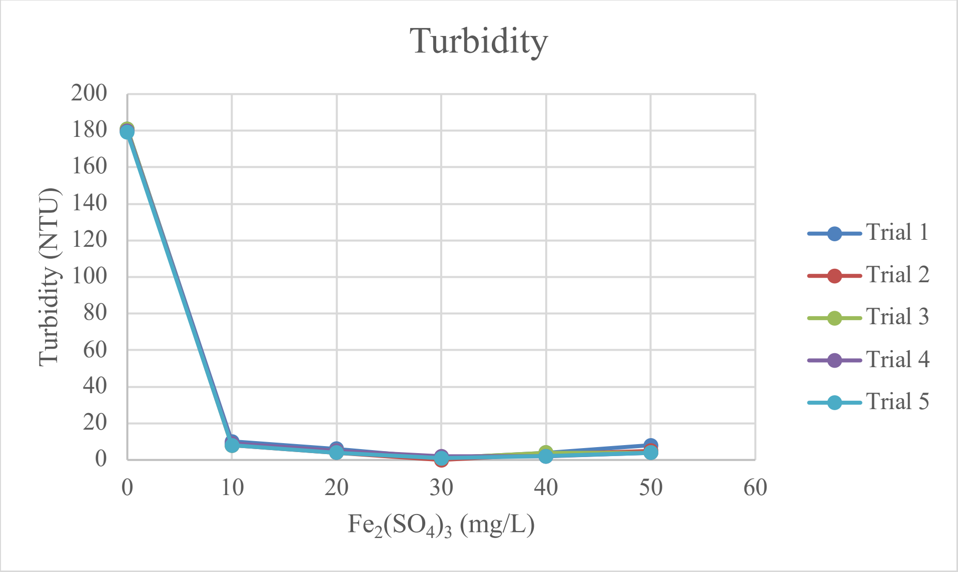

Figure 7. Mean Turbidity at Ferric Sulfate Different Dosage.

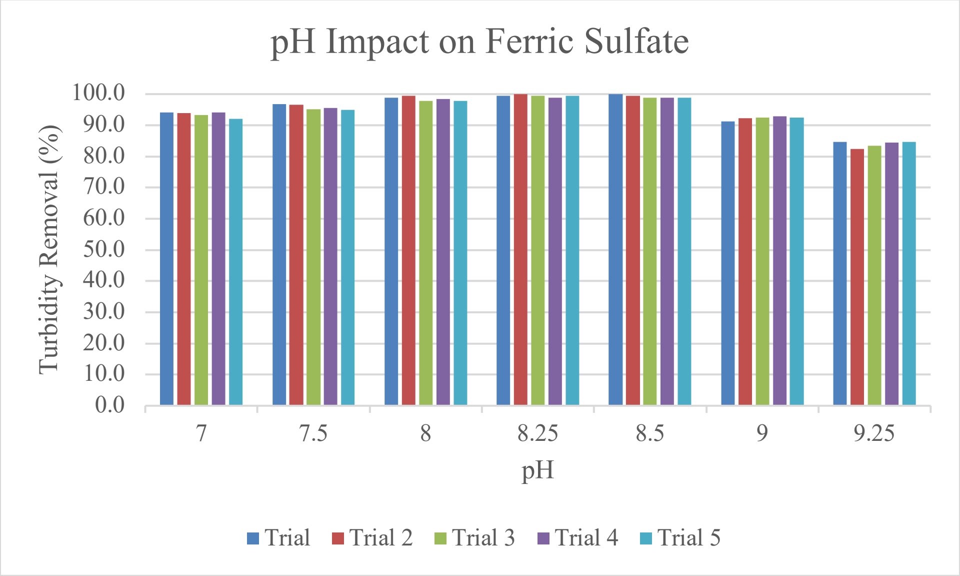

Figure 8. Mean Turbidity Removal at Ferric Sulfate Optimum Dosage on Different pH levels.

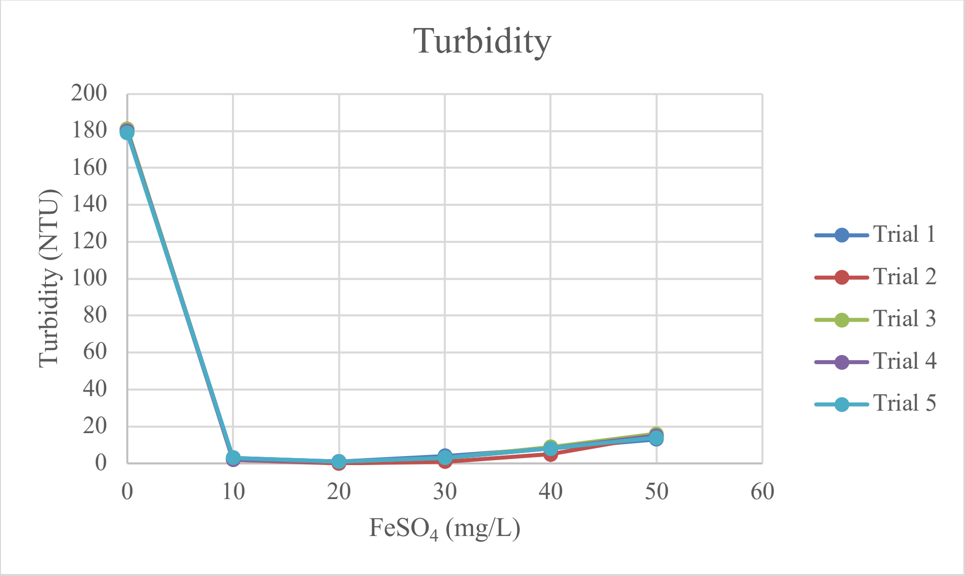

Figure 9. Mean Turbidity at Ferrous Sulfate Different Dosage with 5 mg/L polyDADMAC.

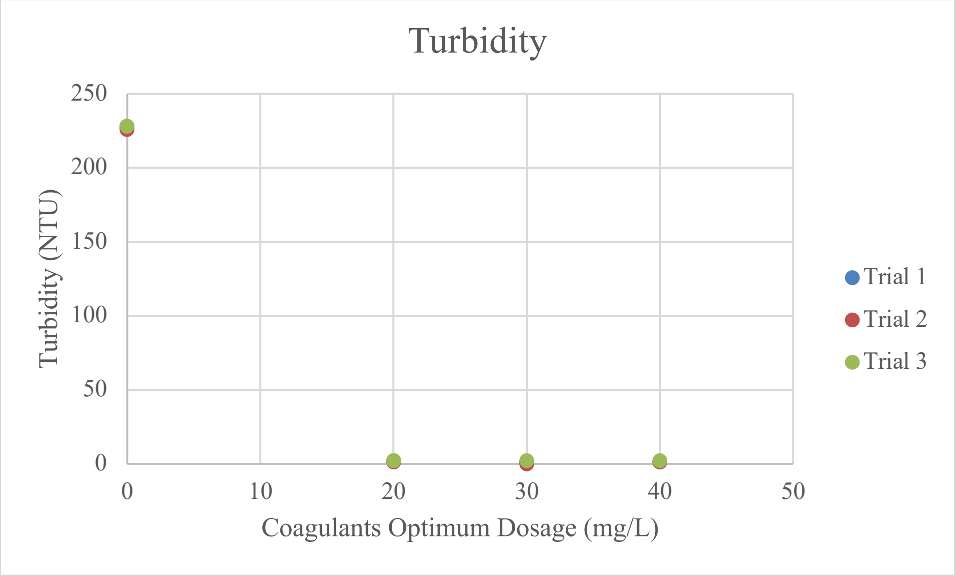

Figure 10. Mean Turbidity at iron coagulants optimum Different Dosage.

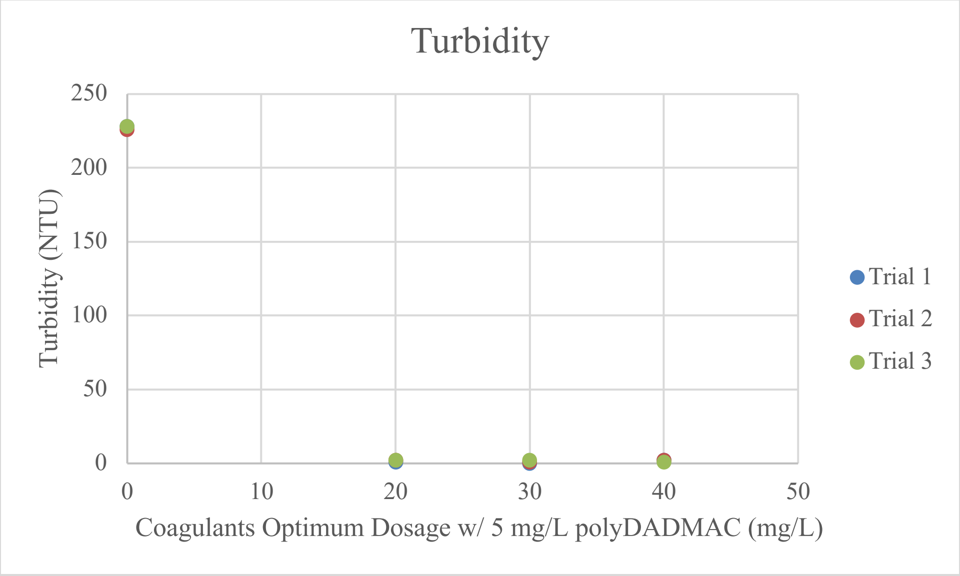

Figure 11. Mean Turbidity at iron coagulants optimum Different Dosage with 5 mg/L polyDADMAC.

APPENDIX B:

Table 1. T-test for Turbidity at Different Iron Coagulants Dosage on Sodium Alginate.

Ferric chloride Dosage (mg/L)	P-Value of Turbidity	Ferrous Sulfate Dosage (mg/L)	P-Value of Turbidity	Ferric Sulfate Dosage (mg/L)	P-Value of Turbidity
0 & 10	4.3E-10	0 & 10	1.3E-09	0 & 10	8.9E-11
0 & 20	1.4E-10	0 & 20	2.0E-10	0 & 20	1.1E-11
0 & 30	2.2E-10	0 & 30	1.5E-10	0 & 30	1.7E-10
0 & 40	5.8E-11	0 & 40	4.7E-10	0 & 40	4.9E-12
0 & 50	1.4E-09	0 & 50	1.4E-08	0 & 50	6.2E-10
10 & 20	1.9E-02	10 & 20	1.9E-03	10 & 20	2.3E-05
10 & 30	9.8E-04	10 & 30	2.2E-04	10 & 30	2.3E-05
10 &40	3.0E-06	10 &40	3.3E-05	10 &40	2.0E-04
10 & 50	1.5E-03	10 & 50	4.3E-05	10 & 50	1.1E-03
20 & 30	7.8E-05	20 & 30	3.6E-05	20 & 30	2.6E-04
20 & 40	2.0E-04	20 & 40	1.3E-05	20 & 40	4.3E-03
20 & 50	1.5E-03	20 & 50	5.4E-05	20 & 50	3.7E-01
30 & 40	1.4E-03	30 & 40	9.8E-04	30 & 40	1.7E-02
30 & 50	1.4E-03	30 & 50	9.8E-04	30 & 50	5.5E-03
40 & 50	1.6E-02	40 & 50	8.8E-04	40 & 50	1.7E-02

Table 2. T-test for % Turbidity Removal (%TR) at Different pH levels and at Iron Coagulant Optimum Dosage.

pH (40 mg/L $FeCl_3$)	P-Value of (%TR)	pH (20 mg/L $FeSO_4$)	P-Value of (%TR)	pH (30 mg/L $Fe_2(SO_4)_3$	P-Value of (%TR)
7 & 7.5	0.0006958	7 & 7.5	0.00680765	7 & 7.5	0.00052516
7 & 8	0.0000867	7 & 8	0.00000032	7 & 8	3.17326E-05
7 & 8.25	0.0000023	7 & 8.25	0.00000017	7 & 8.25	7.27976E-05
7 & 8.5	0.0000028	7 & 8.5	0.00000038	7 & 8.5	3.0507E-05
7 & 9	0.0000086	7 & 9	0.00000012	7 & 9	0.037296583
7 & 9.25	0.0107509	7.5 & 8	0.00000031	7 & 9.25	7.42823E-05
7.5 & 8	0.0002773	7.5 & 8.25	0.00000008	7.5 & 8	1.30307E-05
7.5 & 8.25	0.0000790	7.5 & 8.5	0.00000020	7.5 & 8.25	0.000189427
7.5 & 8.5	0.0000606	7.5 & 9	0.00000694	7.5 & 8.5	3.70662E-05
7.5 & 9	0.0000847	8 & 8.25	0.00016478	7.5 & 9	0.001702986
7.5 & 9.25	0.0003815	8 & 8.5	0.00102475	7.5 & 9.25	3.00557E-05
8 & 8.25	0.0029085	8 & 9	0.03388474	8 & 8.25	0.009986233
8 & 8.5	0.0017356	8.25 & 8.5	0.02420096	8 & 8.5	0.012867488
8 & 9	0.0701297	8.25 & 9	0.02420096	8 & 9	0.000106307
8 & 9.25	0.0000094	8.5 & 9	0.00686465	8 & 9.25	1.37009E-05
8.25 & 8.5	0.0182093	NA	NA	8.25 & 8.5	0.180750631
8.25 & 9	0.0021728	NA	NA	8.25 & 9	1.7434E-05
8.25 & 9.25	0.0000027	NA	NA	8.25 & 9.25	6.42917E-06

8.5 & 9	0.0034324	NA	NA	8.5 & 9	6.04715E-05
8.5 & 9.25	0.0000018	NA	NA	8.5 & 9.25	3.57886E-06
9 & 9.25	0.0000089	NA	NA	9 & 9.25	6.85379E-05

Table 3. T-test of Floc Size without polyDADMAC at Different Iron Coagulant Dosage.

Ferric chloride Dosage (mg/L)	P-Value of Floc Size	Ferrous Sulfate Dosage (mg/L)	P-Value of Floc Size	Ferric Sulfate Dosage (mg/L)	P-Value of Floc Size
0 & 10	0.01	0 & 10	0.00945	0 & 10	5.34589E-05
0 & 20	0.00	0 & 20	0.01674	0 & 20	0.001917124
0 & 30	0.01	0 & 30	0.01527	0 & 30	0.000531434
0 & 40	0.01	0 & 40	0.04066	0 & 40	9.85966E-05
0 & 50	0.01	0 & 50	0.30915	0 & 50	0.000181408
10 & 20	0.48	10 & 20	0.04911	10 & 20	0.017634142
10 & 30	0.05	10 & 30	0.34425	10 & 30	0.000850157
10 &40	0.09	10 & 40	0.14997	10 &40	0.000342357
10 & 50	0.06	10 & 50	0.30915	10 & 50	0.000325742
20 & 30	0.05	20 & 30	0.02629	20 & 30	0.000940103
20 & 40	0.05	20 & 40	0.03203	20 & 40	0.000992937
20 & 50	0.05	20 & 50	0.01330	20 & 50	0.006690413
30 & 40	0.27	30 & 40	0.16849	30 & 40	0.001714492
30 & 50	0.16	30 & 50	0.00424	30 & 50	0.002338161

40 & 50	0.37	40 & 50	0.04284	40 & 50	0.08323035

Table 4. T-test for Turbidity at Different Iron Coagulants Dosage with 5 mg/L polyDADMAC Addition on Sodium Alginate.

Ferric chloride Dosage (mg/L)	P-Value of Turbidity	Ferrous Sulfate Dosage (mg/L)	P-Value of Turbidity	Ferric Sulfate Dosage	P-Value of Turbidity
0 & 10	7.4E-10	0 & 10	1.7E-10	0 & 10	1.13585E-11
0 & 20	7.7E-11	0 & 20	7.4E-11	0 & 20	2.03832E-10
0 & 30	7.5E-11	0 & 30	2.0E-10	0 & 30	7.38111E-11
0 & 40	3.4E-10	0 & 40	7.2E-10	0 & 40	1.71041E-09
0 & 50	6.2E-10	0 & 50	5.2E-10	0 & 50	6.26636E-10
10 & 20	1.1E-04	10 & 20	1.4E-03	10 & 20	0.001599101
10 & 30	3.0E-04	10 & 30	1.9E-01	10 & 30	0.00011246
10 &40	1.5E-04	10 &40	7.2E-04	10 &40	0.009467489
10 & 50	1.2E-04	10 & 50	3.9E-05	10 & 50	0.00231792
20 & 30	4.5E-02	20 & 30	1.6E-03	20 & 30	0.005528247
20 & 40	1.4E-03	20 & 40	7.8E-05	20 & 40	0.120990765
20 & 50	1.7E-02	20 & 50	9.4E-06	20 & 50	0.049650342
30 & 40	1.5E-01	30 & 40	1.1E-04	30 & 40	0.054350476

30 & 50	5.0E-01	30 & 50	8.2E-05	30 & 50	0.016338962
40 & 50	3.5E-02	40 & 50	5.6E-04	40 & 50	0.5

Table 5. T-test of Floc Size without polyDADMAC at Different Iron Coagulant Dosage with 5 mg/L polyDADMAC Addition.

Ferric chloride Dosage (mg/L)	P-Value of Floc Size	Ferrous Sulfate Dosage (mg/L)	P-Value of Floc Size	Ferric Sulfate Dosage (mg/L)	P-Value of Floc Size
0 & 10	0.00195	0 & 10	0.0089531	0 & 10	0.00733825
0 & 20	0.00107	0 & 20	0.00155575	0 & 20	0.00034605
0 & 30	0.00058	0 & 30	0.00407812	0 & 30	0.00039987
0 & 40	0.00012	0 & 40	0.05396541	0 & 40	0.0042804
0 & 50	0.00079	0 & 50	0.0309215	0 & 50	0.00360129
10 & 20	0.00046	10 & 20	0.01033203	10 & 20	0.00760353
10 & 30	0.00197	10 & 30	0.04224472	10 & 30	0.00035935
10 &40	0.00016	10 & 40	0.0009009	10 &40	0.00482055
10 & 50	0.01413	10 & 50	0.01666704	10 & 50	0.00213176
20 & 30	0.12605	20 & 30	0.00649062	20 & 30	0.0012165
20 & 40	0.00032	20 & 40	0.0035091	20 & 40	0.04692212
20 & 50	0.11427	20 & 50	0.00146703	20 & 50	0.21766381
30 & 40	0.00001	30 & 40	0.00112306	30 & 40	0.00072923

30 & 50	0.04864	30 & 50	0.00714749	30 & 50	0.00080639
40 & 50	0.00069	40 & 50	0.12816087	40 & 50	0.02508397

Table 6. T-test for Turbidity at Different Iron Coagulants Dosage with and without 5 mg/L polyDADMAC on Cultivated Algae.

Type of Coagulants with Concentration	P-Value
0 mg/L & 40 mg/L Ferric Chloride	3.26308E-06
0 mg/L & 20 mg/ Ferrous Sulfate	1.09092E-06
0 mg/L & 30 mg/L Ferric Sulfate	1.0845E-06
0 mg/L & 40 mg/L Ferric Chloride w/ polymer	7.63626E-06
0 mg/L & 20 mg/L Ferrous Sulfate w/ polymer	7.63626E-06
0 mg/L & 30 Ferric Sulfate w/ polymer	7.59134E-06
40 mg/L Ferric Chloride & 20 mg/L Ferrous Sulfate	0.211324865
40 mg/L Ferric Chloride & 30 mg/L Ferric Sulfate	0.211324865
40 mg/L Ferric Chloride & 40 mg/L Ferric Chloride w/ polymer	0.333333333
40 mg/L Ferric Chloride & 20 mg/L Ferrous Sulfate w/ polymer	0.211324865
40 mg/L Ferric Chloride & 30 mg/L Ferric Sulfate w/ polymer	0.211324865
20 mg/L Ferrous Sulfate & 30 mg/L Ferric Sulfate	0.09175171
20 mg/L Ferrous Sulfate & 40 mg/L Ferric Chloride w/ polymer	0.5
20 mg/L Ferrous Sulfate & 20 mg/L Ferrous Sulfate w/ polymer	0.5
20 mg/L Ferrous Sulfate & 30 mg/L Ferric Sulfate w/ polymer	0.211324865
30 mg/L Ferric Sulfate & 40 mg/L Ferric Chloride w/ polymer	0.26429774
30 mg/L Ferric Sulfate & 20 mg/L Ferrous Sulfate w/ polymer	0.211324865

30 mg/L Ferric Sulfate & 30 mg/L Ferric Sulfate w/ polymer	0.5
40 mg/L Ferric Chloride w/ polymer & 20 mg/L Ferrous Sulfate w/ polymer	0.5
40 mg/L Ferric Chloride w/ polymer & 30 mg/L Ferric Sulfate w/ polymer	0.26429774
20 mg/L Ferrous Sulfate w/ polymer & 30 mg/L Ferric Sulfate w/ polymer	0.09175171