

# **Biofouling control of industrial seawater cooling towers**

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## **ABSTRACT**

Biofouling control of industrial seawater cooling towers

Mohammed Albloushi

The use of seawater in cooling towers for industrial applications has much merit in the Gulf Cooperation Council countries due to the scarcity and availability of fresh water. Seawater make-up in cooling towers is deemed the most feasible because of its unlimited supply in coastal areas. Such latent-heat removal with seawater in cooling towers is several folds more efficient than sensible heat extraction via heat exchangers. Operational challenges such as scaling, corrosion, and biofouling are a major challenge in conventional cooling towers, where the latter is also a major issue in seawater cooling towers. Biofouling can significantly hamper the efficiency of cooling towers. The most popular methods used in cooling treatment to control biofouling are disinfection by chlorination. However, the disadvantages of chlorination are formation of harmful disinfection byproducts in the presence of high organic loading and safety concerns in the storage of chlorine gas.

In this study, the research focuses on biofouling control in seawater cooling towers by investigating two different approaches. The first strategy addresses the use of alternative oxidants (i.e. ozone micro-bubbles and chlorine dioxide) in treatment of cooling towers. The second strategy investigates removing nutrients in seawater using granular activated carbon filter column and ultrafiltration to prevent the growth of microorganisms.

Laboratory bench-scale tests in terms of temperature, cycle of concentration, dosage, etc. indicated that, at lower oxidant dosages (total residual oxidant (TRO) equivalent = 0.1 mg/l Cl<sub>2</sub>), chlorine dioxide had a better disinfection effect than chlorine and ozone. The performance of oxidizing biocides at pilot scale, operating at assorted conditions, showed that for the disinfectants tested, ozone could remove 95 % bioactivity of total number of bacteria and algae followed by chlorine dioxide at 85%, while conventional chlorine dosing only gave 60% reduction in bioactivities. Test results of GAC bio-filter showed that around 70 % removal of total organic carbon in the seawater feed was achieved and was effective in keeping the microbial growth to a minimum. The measured results from this study enable designers of seawater cooling towers to manage the biofouling problems when such cooling towers are extrapolated to a pilot scale.

Keywords: Cooling tower; Oxidants; Biofouling; organic carbon; GAC

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**LIST OF ABBREVIATIONS**

DO	Dissolved Oxygen
ORP	<i>Oxidation Reduction Potential</i>
TRO	Total Residual Oxidant
RH	<i>Relative humidity</i>
TOC	Total Organic Carbon
DOC	Dissolved Organic carbon
UV 254	Ultraviolet at 254 wavelength
IC	Ion Chromatography
DBP	Disinfection By Product
ICP-MS	Inductively coupled plasma mass spectrometry
GC	Gas Chromatography
L	Liter
mg	Milligram
CT	Cooling tower

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## PUBLICATIONS

The following publications have been generated from this research work:

- 1- Paper No1: Performance assessment of oxidants as a biocide for biofouling control in industrial seawater cooling towers.

Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Sari. Al-Sayegh, Kim Choon NG, Gary.L. Amy, and TorOve.

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- 2- Paper No 2: Effect of organic on chemical oxidation for biofouling control in pilot-scale seawater cooling towers.

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- 3- Paper No 3: Investigation the efficiency of biocides in controlling algal biofouling in seawater industrial cooling towers.

Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Kim Choon NG, Gary.L. Amy, and TorOve.

Reference: Journal of Process Safety and Environmental Protection

Status: in review

- 4- Paper No 4: Nutrient removal to minimizing biofouling in seawater cooling towers.

Mohammed. Al-Bloushi, Sanghyun. Jeong, Kim Choon NG, and TorOve.

Status: in editing

- 5- Paper No 5 title: Effect of (GAC/UF) Hybrid process pretreatment of industrial seawater cooling towers to minimizing biofouling.

Mohammed. Al-Bloushi, Sanghyun. Jeong, Kim Choon NG, and TorOve.

Status: in review

## **Chapter 1**

### **1 Introduction**

A large of waste heat energy is generated from industrial processes. This heat needs to be disposed of frequently to control the industrial processes and protect equipment from overheating. The most common media used to remove the heat is water because water has a higher specific heat than most other media. The cooling operations using water typically apply three different techniques: once through systems, closed recirculating systems, and water-cooling tower. The most common systems used for seawater cooling are once-through cooling systems, where seawater removes the heat from process loads via heat exchangers before being returned back to the sea. Once-through cooling systems generally require a large amount of seawater. An alternative approach for seawater cooling is using cooling towers, where heat is released to the atmosphere rather than into the sea, and requires a significantly lower amount of seawater. Cooling tower systems are well suited to remove the excess heat through evaporation.

Because of the shortage of fresh water in many regions of the world, the demand for seawater as an alternative make-up water in cooling tower systems has rapidly increased over the past decades. In Saudi Arabia where there is a lack of fresh water and groundwater resources, a huge amount of seawater is used in operation of cooling towers. Oil refineries, petrochemical and power plants are the highest users of cooling water, which demand large amounts of cooling water to remove the heat. For example, a power

plant generating 1000 megawatt (MW) needs around 1500 m<sup>3</sup>/minute of cooling water. Subsequently, seawater is mainly used as a cooling medium in heavy industries, oil refineries, petrochemical plants and thermal power stations. Seawater is the most feasible (low-cost and unlimited) process-cooling medium in the Middle East arid region. For example, Marafiq at Saudi Arabia (Marafiq: water desalination plant company) supplies seawater to industrial city facilities. Operation of seawater cooling towers can be a challenge as they are prone to corrosion, scaling and biofouling phenomenon, due to organic and inorganic loadings in seawater. Cause of the larger dissolved inorganic content (e.g. Na, Mg, Ca, K, Cl, S etc.) in service water, it has been expected that the performance of seawater cooling towers declines by 1% for each 1% increase in salt content in the water cooling tower [1]. Increase in dissolved minerals due to evaporation combined with the higher operating temperatures in the cooling tower will lead to greater calcium and magnesium precipitations. The large open surface areas of cooling towers, packing and filler materials are often directly exposed to ambient air temperatures and sunlight. This combined with increasing concentration of nutrients in the water due to evaporation, can promote biofilm formation and algal growth in seawater cooling towers. The effect of biofilm and algal growth under such conditions, if not controlled, can cause heavy biofouling which severely affects heat transfer efficiency and the performance of the cooling tower [2]. This study aims to focus on the challenges of biofouling in seawater cooling towers.

### 1.1 Scope of the Research:

The aim of this research project is to focus on biofouling control strategies in seawater cooling towers by using two approaches. The first strategy is use of alternative oxidants in treatment of seawater cooling towers. The second strategy is to remove specific nutrients from the seawater thereby preventing the growth of microorganisms. The overall goal of this research is to determine the most suitable method to control biofouling in seawater cooling towers.

### 1.2 Research goals

The overall research goals of this study are to investigate the efficiency of alternative biofouling control strategies in seawater cooling towers. By investigating two alternative strategies (*i.e.* disinfection and nutrient removal), the research activities were conducted in two phases.

1. First goal: to study and evaluate ozone and chlorine dioxide as an alternative to sodium hypochlorite (*i.e.*, chlorine). Both of these oxidants could be introduced by more commonly practiced side-stream injection in minimizing biofouling in cooling tower operation.
2. Second goal: to study the effect of removing key nutrients from the seawater to minimize algae and bacteria growth in seawater cooling tower system thus preventing biofouling.

The first phase investigated the efficiency of alternative treatment oxidants of seawater cooling tower using ozone micro-bubbles and chlorine dioxide at pilot scale. The second

phase investigated the efficiency of nutrient removal in seawater cooling systems to prevent biofouling. The aim is to determine the key nutrient removal and test alternative pretreatment options and efficiency in removal. Two systems are applying to the seawater cooling tower pretreatment: GAC bio-filter and membrane (Ultrafiltration). However, the objective of this phase is to define a suitable method of nutrient removal in seawater to prevent the growth of biofouling by using two approach of bio-filter at pilot scale.

### 1.3 Background

#### 1.3.1 Problem statement.

Bio-fouling is a critical issue in seawater industrial cooling tower processes. It reduce the live time of equipment within bio-corrosion, causes blockages, and demand for high energy consumption and affecting the heat transfer efficiency. Biofouling also decreases energy efficiency due to increased hydraulic pressure in the piping and pumping system. These effects result in increased energy demands (e.g. pumping costs), reduced cooling efficiencies and overall increase costs.

#### 1.3.2 Current practice.

One of the most common methods used in cooling tower process to control biofouling is disinfection by chlorination. Chlorination has a long history of use in water cooling system treatment. Primary advantages of chlorination in seawater treatment in general are: effective in inactivation of microorganisms, long periods of positive disinfection

residual are maintained. However, the disadvantage of chlorination is the formation of harmful disinfection byproducts (DBPs) in the presence of high organic loading.

#### 1.4 Research questions.

The main research questions underlying this study are:

Are ozone and chlorine dioxide more efficient oxidants to control biofouling and biofilm growth than chlorination?

Is TRO maintaining the regulation at blowdown of the ozone and chlorine dioxide oxidants? Can nutrient removal from makeup seawater of the cooling tower control biofouling?

Is the removal of AOC sufficient to prevent biofouling?

How efficiently is AOC removed in a GAC bio-filter?

Can the performance of CTs be enhanced by ultrafiltration?

Can cooling tower equipment be protected by removing the nutrients from seawater cooling tower by using hybrid filter (GAC and UF)?

#### 1.5 Hypotheses.

Biofouling in seawater cooling systems depends on water quality. To control the biofouling in cooling tower process, chlorination disinfection is used commonly around the world. Nutrients removal can be used to control biofouling in seawater cooling

towers. The concentration limitation of the nutrients in seawater is one of the key strategies to growth biofouling in the system. Fast growing algae suffer more from nutrient limitation than slow growing algae at low nutrient availability. So, nutrient limitation may be able to be control and minimize biofouling in seawater cooling system.

My hypotheses are:

1. The alternative treatment of seawater cooling towers by ozone micro-bubbles and chlorine dioxide is more efficient to prevent biofouling growth than chlorination at 0.2 ppm of TRO in blowdown.
2. Nutrient removal can contribute to biofouling control by using a GAC bio-filter column to reduce AOC bellow limiting growth conditions.
3. A hybrid filter (GAC and UF) will increase the removal of nutrients compared to a GAC bio-filter to prevent the biofouling growth.
4. This new approach can assist to control biofouling in seawater cooling towers and increase the lifetime of the equipment.

The objective of this study is to test alternative oxidants in treating seawater by using ozone micro-bubbles and chlorine dioxide at pilot scale. There will be evaluation of both ozone and chlorine dioxide as an

alternative to

Another objective will be to determine the relationship between specific algal growth rate and the limiting nutrient concentration in the seawater. The removal of nutrients from seawater through biofiltration treatment can be an effective method. Also, filtration can alternatively be used as a biological pretreatment of feed water. The effectiveness of nutrient removal on the seawater-cooling tower will be studied at both bench-scale and

pilot-scale, and verified by measuring parameters such as biodegradable DOC; LC-OCD (biopolymers and LMW acids); F-EEM (protein-like organic matters) etc. The seawater cooling tower performance will be evaluated after removing nutrients.

## 1.6 Thesis structure

This thesis reports the theoretical and experimental work conducted in this study and is presented in seven chapters:

**Chapter 1.** Introduction.

**Chapter 2.** Literature review of cooling water systems relevant to cooling tower types, cooling water concerns and chemical and physical treatment.

**Chapter 3.** Materials and methods used at bench-scale and pilot-scale during the cooling tower experiments.

**Chapter 4.** Performance assessment of alternative oxidants (*i.e.* chlorination, chlorine dioxide, ozone) in seawater industrial cooling towers for biofouling control.

**Chapter 5.** Effect of organics on chemical oxidation for biofouling control in pilot-scale seawater cooling towers.

**Chapter 6.** Investigation of the efficiency of biocides in controlling algal biofouling in seawater industrial cooling towers.

**Chapter 7.** Nutrient removal to minimize biofouling growth in seawater cooling towers.

**Chapter 8.** Nutrient removal by using a hybrid bio-filter (GAC and UF) to prevent biofilm growth and biofouling in seawater cooling towers

**Chapter 9.** Conclusions and future work: thesis theoretical and experimental work is summarized in this chapter along with some recommendations for future research work.

## Chapter 2

### 2 Literature review

#### 2.1 Cooling water systems

Heat energy is generated in a wide variety of industrial applications and activities. Cooling systems, engines, and different industrial applications can all generate a large amount of excess heat. Extra heat generated should be spread away, and the best medium to remove the heat is water. To control various industrial processes applications and prevent process equipment from damage by overheating, cooling water systems are commonly used to transfer and remove the excess heat from the process [3]. Cooling water systems control the temperature by transferring heat from a hot process line into the cooling water line, where the cooling water is either replaced with fresh makeup water or cooled before it being used again. A basic principle for a cooling tower is illustrated in Figure 2-1 [4]. Typically, 80 to 90 % of the heat energy is removed from the cooling water by evaporation [5]. In large systems water is the medium used due to low-cost, has a high a specific heat, and can be discharged to the sea. The cooling tower can be operated with a variety of water sources such as seawater, ground water, river water, recycled water and potable water [3]. Table 2-1 demonstrates the percentage of overall water used in a water cooling system in most common industries. For instance, the biggest plant required a huge amount of water like a power plant of 1000 megawatt (MW) needs around  $1500 \text{ m}^3$  /minute cooling water.

Decreasing availability of fresh water is a challenge in many regions of the world, the demand for seawater as an alternative make-up water in cooling tower systems has rapidly increased over the past decades. In The Middle East, a huge amount of seawater is used in operation of cooling towers due to a lack of freshwater and groundwater resources. For example, in Saudi Arabia, operating cooling towers with seawater are deemed most suitable as there is a scarcity of freshwater and groundwater resources. Currently, seawater is used as a cooling medium in systems up to thousands of MW capacity, particularly in heavy industries, oil refineries, petrochemical plants, and thermal power stations. In the Gulf Cooperating Council (GCC) countries, seawater is readily available as a process-cooling medium.

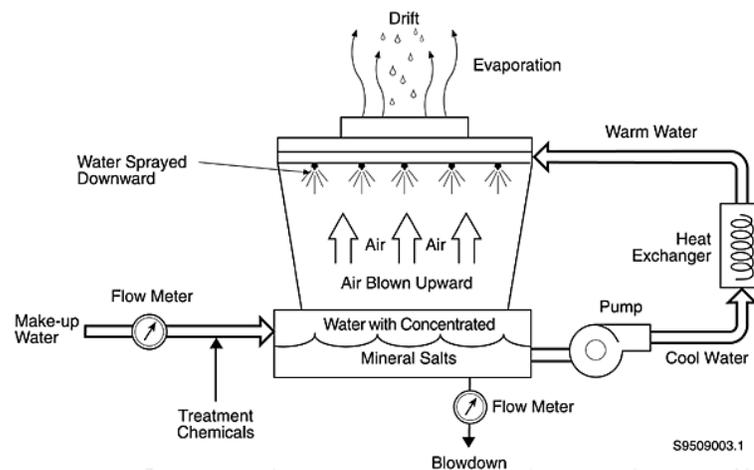


Figure 2-1: Diagram of a cooling water system (U.N.E. *Electrical Energy Equipment*,2006)

Table 2-1: Percentage of overall water used in cooling system

Industry	Water used in cooling systems
Work office building	30 %
Food factory - refrigeration	10 – 30 %
Oil refinery and chemical plants	60 – 85 %
Power plants stations	90 – 95 %

## 2.2 Cooling tower basic components

The water cooling tower process principle is evaporative condensation and exchange of applied heat. The cooling tower system is simple equipment, compared to most of other industrial device. Most of the new cooling towers were built with treated wood, cedar, plastic or redwood. These materials have a good resistant to the negative effect of water [6]. The high quality materials for cooling tower components are permanently required, improved systems for integrating them into a long-term unit, stable, and reliable. The basic components of the cooling tower are:

1. Frame and casing: most towers have structural frames that support the exterior enclosures (casings), motors, fans, and other components.
2. Film fill: plastic surfaces over which the water spreads
3. Cold-water basin: is located near the bottom of the tower and has a low point for the cold-water discharge connection.
4. Drift eliminators: water droplets entrapped in the air stream.
5. Air inlet: the point of entry for the air entering a tower.
6. Louvers: cross-flow towers.

7. Nozzles: Uniform water distribution at the top of the fill.
8. Fans: Both axial (propeller type) and centrifugal fans are used in towers as demonstrated in Figure 2-2 [4].

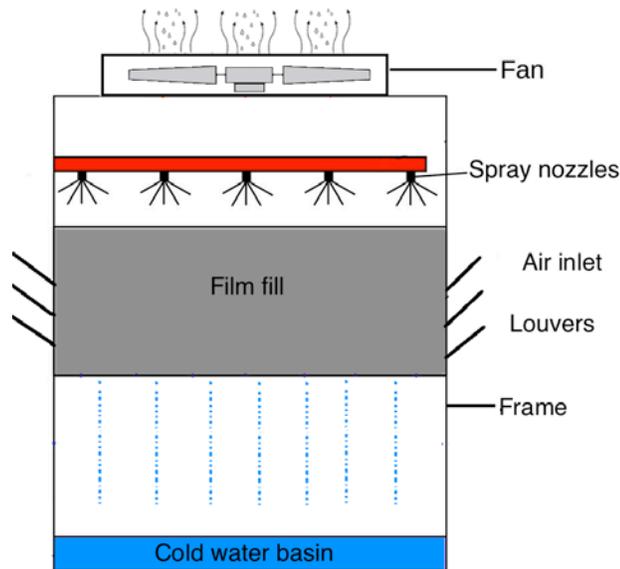


Figure 2-2: Cooling tower components.

### 2.3 Types of cooling towers

Cooling towers are generally classified as two types; natural draught and mechanical draught cooling towers.

#### 2.3.1 Natural draught cooling towers

The process of a natural draft cooling tower is the hot air moves upwards through the tower, while the fresh cool air is drawn into the tower through air inlets at the bottom, as

illustrated in Figure 2-3. Natural draught systems are most commonly found used for large heat duties such as electric power plants processes [7, 8].

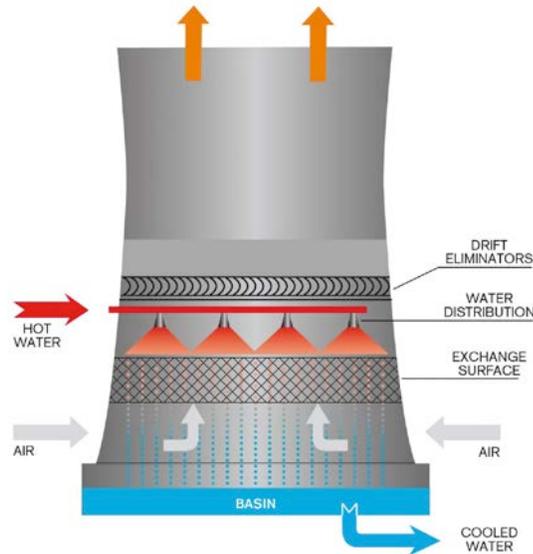


Figure 2-3: Natural draught cooling towers (Adapted from Hamon, April 2010).

### 2.3.2 Mechanical draught cooling towers

The process of mechanical draught cooling tower is air is forced through the circulation water by using a large fan. The hot water falls from the top of the cooling tower over the fill surface, helping to increase the contact time between the water and the air, which helps to cool the water. Mechanical draught cooling tower are commonly found used in industrial processes and buildings [9, 10]. Moreover, mechanical draught cooling towers are characterized based on the location of the fan in the towers as follows:

- Induced draught: where fans are located at the top of the tower and suck the air in at the bottom, as illustrated in Figure 2-4.
- Forced draught: where fans are located in the inlet of the tower to push the air through, as illustrated in Figure 2-5.

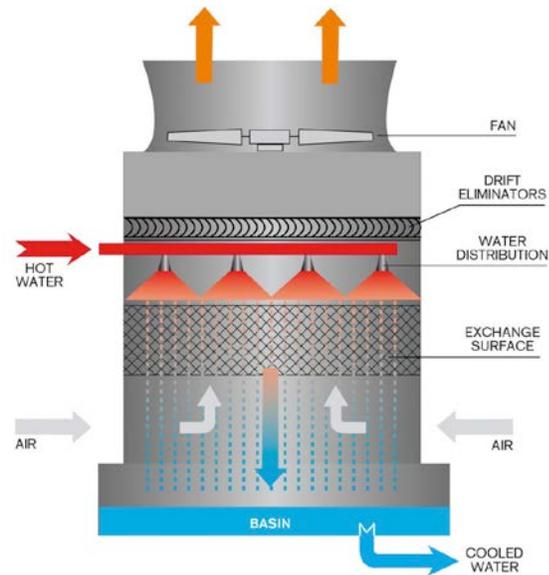


Figure 2-4: Mechanical Induced draught cooling towers (Adapted from Hamon, April 2010).

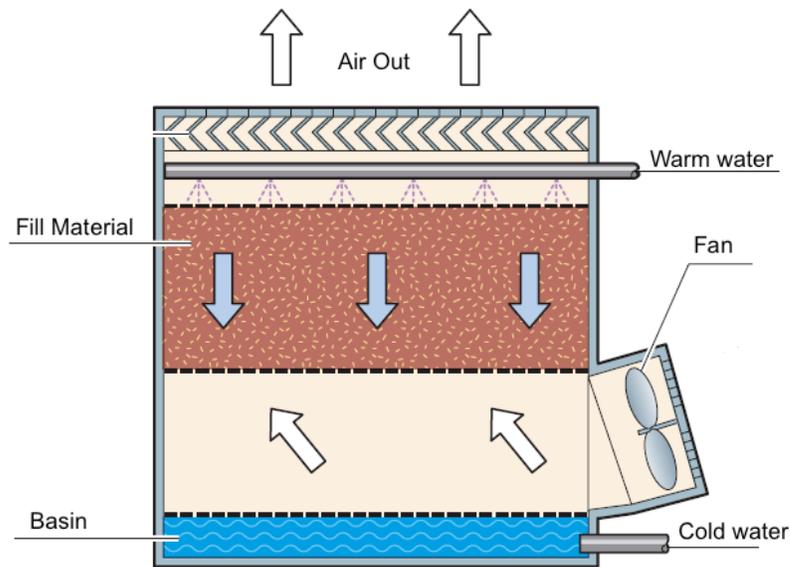


Figure 2-5 : Forced draught cooling towers (Adapted from Hamon, April 2010).

In general, the cooling water system design efficiency depends on the process cooled, the characteristics of the water and environmental considerations, capacity, and [11].

#### 2.4 Cooling water challenges

It is important to evaluate the performance of cooling towers during the operation and it is difficult to significantly improve the energy performance of cooling towers. The factors, which should be considered in a cooling tower performances assessment, are capacity, approach, heat load, wet bulb temperature, and the relationship between these factors [4]. Depending on the quality of seawater supply the key issues in seawater cooling systems are:

➤ Scaling

Scaling is a inorganic precipitation and crystal growth at a surface in contact with water. The high scaling formatting salts deposit on heat transfer surfaces de to the high temperature.

➤ Corrosion

Corrosion is a destruction of a metal by chemical or electrochemical reaction. This corrosion causes failure of equipment and reduced cooling efficiency.

➤ Biofouling

Fouling is suspended insoluble particulates in recirculating water form deposits on a surface that lead to the formation of accumulation.

These issues will reduce the life-time of cooling tower systems, and also cause a reduction in capacity, increase operation and maintenance costs, increase in expensive parts replacements and also increased water usage. Biofouling is one of the critical issues in industrial cooling tower systems. It damages equipment, can induce bio-corrosion impacts, can cause clogging of the systems and thus increased energy consumption due to decreased heat transfer [12-14]. It also has been reported (Carlton 2001) that biofouling in cooling tower intake resulted in \$1 billion in damages and control costs annually [15]. Microbiological fouling in cooling tower systems is caused by the growth of algae and bacteria in the process. Open recirculating water systems support microbial growth more quickly than closed systems and are more extensive. The availability of organic and inorganic nutrients, sunlight, and continuous aeration of the cooling tower contribute to

an environment that is ideal for microbial growth [12]. A number of microorganisms (algae, protozoa, and bacteria) can grow in a cooling tower system under certain conditions, as outlined in Table 2-2 [16] .

Table 2-2. Types of biofouling that exist in cooling towers [17]

Micro-organisms	Impact on cooling tower system
Algae	<ul style="list-style-type: none"> <li>● Provide a nutrient source for bacterial growth.</li> <li>● Deposit on surface contributes to localized corrosion process.</li> <li>● Loosened deposits can block and foul pipe work and other heat exchange surfaces.</li> </ul>
Fungi	<ul style="list-style-type: none"> <li>● Proliferate to high number and foul heat exchanger surfaces.</li> </ul>
Bacteria	<ul style="list-style-type: none"> <li>● Some types of pathogenic bacteria such as Legionella may cause health hazards.</li> <li>● Sulfate reducing bacteria can reduce sulfate to corrosive hydrogen sulfide.</li> <li>● Cathodic depolarization by removal of hydrogen from the cathodic portion of corrosion cell.</li> </ul>

## 2.5 Biofouling control in cooling tower

The number of articles published on seawater disinfection has been growing steadily as shown in figure 2-6. Over the years where most of the publications were related to environmental science, agricultural and biological science and chemical engineering as shown in Figure 2-7. The need for disinfection in cooling systems has been described in many articles.

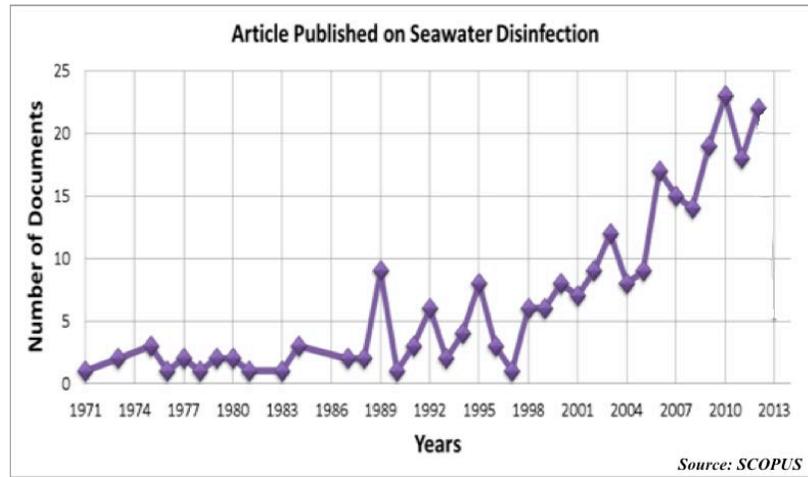


Figure 2-6. Number of articles published on seawater disinfection (SCOPUS).

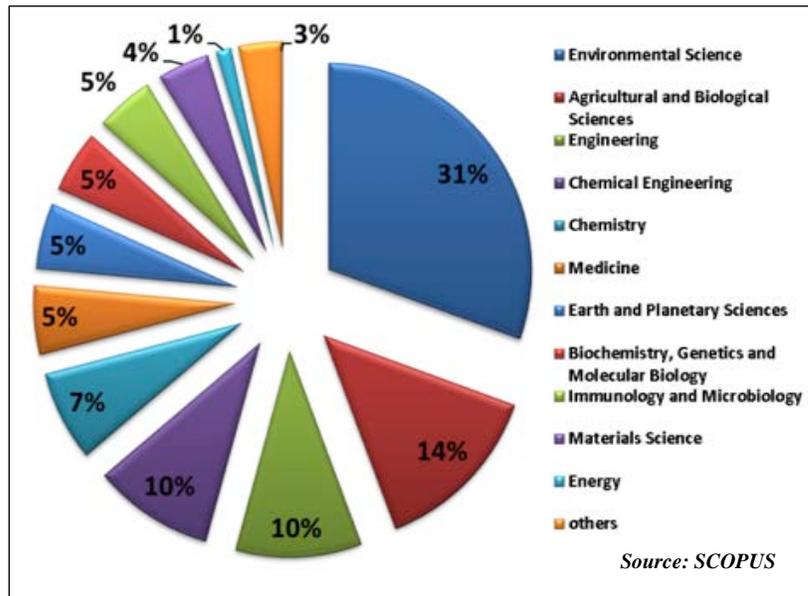


Figure 2-7. Articles published on different fields (SCOPUS).

The cooling towers were usually taking water from natural sources such as rivers, ground water, potable water, and seawater. These waters will contain microorganisms, which will settle on the heat transfer surface. This will affect the cooling tower efficiency. The issue is that the temperature of the waterside surface in heat exchangers is usually close to the temperature for microbial growth. To control biofouling in cooling towers, two methods are basically applied, chemical and physical treatment. This treatment might be used separately or in some cases in a combination [18].

#### 2.5.1 Chemical control

The most widely practiced approach to minimize biofilms in cooling water processes is using chemical treatment, focusing on the reduction or removal of the microorganisms. Chemical control commonly used in cooling tower treatment is the application of biocides to kill the microorganisms or to reduce the activity. Oxidizing and non-oxidizing biocides are used to control the biofouling [19]. A wide range of chemical disinfectants is used such as chlorine, chloramines, ozone and chlorine dioxide classified as oxidizing agents. Many of these compounds are also commonly used in drinking water treatment to inactivate microorganisms and inhibit biofilm formation. The aim of chemical control is to inhibit or remove biofilms as it forms. The efficacy of chemical biocide treatment for biofouling control in recirculating water systems is based on the inactivation range and the concentration of the biocide. Dosing of the biocides has to be carefully designe in order of be economical and effective [20]. The common practice of chemical dosing in cooling tower water is done using three approaches:

- a) Continuous – dosing of a fixed concentration depending on the amount of microorganisms present.
- b) Shock – an intermittent dose of high concentration.
- c) Pulse – dosing a preset concentration on a fixed schedule.

Chemical disinfection of seawater and product water is required to prevent the biofouling growth in the industrial cooling towers. Chemical oxidants react with natural organic matter (NOM) in seawater and produce halogenated disinfection byproducts (DBPs). DBPs concentrations depend on several factors such as the type and amount of oxidants treatment used, organic and inorganic matters, and the contact time. The most frequent DBPs formed during chlorination of natural water are Trihalomethanes (THMs) and haloacetic acids (HAAs) [21]. Because of the possible health risks, the maximum contamination limit (MCL) standard for Trihalomethanes (THMs) in Table 2-3 [22].

Table 2-3: Maximum contamination limit standard for Trihalomethanes (THMs) in drinking water and surface water (Agus, E 2009).

<b>Contaminant</b>	<b>MCL , <math>\mu\text{g/l}</math></b>	<b>EU standard, <math>\mu\text{g/l}</math></b>
<b>Total THM</b>	80	100
	<b>MCL, <math>\mu\text{g/l}</math></b>	<b>WHO, <math>\mu\text{g/l}</math></b>
<b>Chloroform</b>	70	300
<b>Bromodichloromethane</b>	0	60
<b>Dibromochloromethane</b>	60	100
<b>Bromoform</b>	0	100

MCL Maximum contaminant limit

### 2.5.1.1 Chlorination

Among the various available oxidants for disinfection, chlorine has remained one of the most popular biocides and method used around the world [23]. A primary advantage of chlorination is that it is effective in inactivating a wide range of pathogens and microorganisms, and can be dosed to maintain a positive disinfection residual over a longer period. This property has been typically exploited in drinking water pipelines and distribution networks. The preference for using chlorination is often based on the fact that it has been used for many decades, is viewed as economical, there is high degree of familiarity, and it seen as a mature and proven technology. On the other hand, in recent years chlorination has become less favored in drinking water treatment due to:

- Formation of harmful by products (DBPs) in the presence of high organic content (e.g. NOMs)
- Safety concerns when using chlorine gas (e.g. storage issues)
- Taste and odor are resulting from high-levels of chlorination.
- Emergence of chlorination resistant microorganisms, e.g. inefficiency in inactivating protozoan oocyst such as *Cryptosporidium*.

Some of these may also have relevance to cooling tower operation. Trihalomethanes (THMs) were classified as a volatile organic group produced when chlorine reacts with the organics in the water. Total THMs are a compound that includes chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. THM is used as an indicator of the total disinfection byproducts formed in the water [24]. The total concentration of THMs is limited to 100 µg/l at Europe regulation standards. This

regulation has now also been applied to the discharge of cooling tower waters to the sea where chlorination is used in the process. Chlorine was reported to have controlled biofilm at continuous chlorination dose of 0.2 mg/l [25]. Rajagopal et al. (1996) reported that, intermittent chlorination is ineffective in controlling biofilm and suggested continuous high chlorination for intake pipes [26].

Free chlorine is effective in inactivating microbes, degradation of humic acid and organic matters during the chlorination can enhance regrowth [27]. Low-level intermittent chlorination (0.4–0.8 mg/l of residual-free chlorine for 0.5–1 hr a day) on Cu/Ni 70/30 copper nickel alloy help to promote the formation of protective oxides in the alloys, reduce biofilm growth and to promote slime removal after the influx of mud and debris [28]. Sriyutha et al. (2005) reported intermittent chlorine dosing of 1.2 mg/l of 2 hr on/2 hr off would be as effective as 1.2 mg/l of 0.5 hr on/1 hr off [29]. Targeted chlorination (low dose at required area in short time) significantly reduced the total Trihalomethanes (TTHM) formation. Bromoform was found to be the dominant THM in seawater chlorination [30]. Parinet et. al (2012) confirmed that bromoform and dibromo acetic acid were measured at levels up to 18-fold greater than the maximum contaminant levels of 60 and 80 µg/L in a chlorinated seawater [31]. Some of the chlorination reactions formation:-

- Chlorine gas:  $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$
- Sodium Hypochlorite:  $\text{NaOCl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NaOH}$
- Calcium Hypo chlorite:  $\text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HOCl} + \text{Ca}(\text{OH})_2$

(Nebot et al. 2006) focused on fouling control in seawater cooling systems using chlorination. The study reports that five types of fouling usually occur in the cooling system, namely (i) biological (ii) corrosion (iii) particulate (iv) chemical reaction and (v) precipitation. One of the possible strategies for fouling monitoring and detection is by using a side-stream system that is parallel to the actual full-scale plant. Although the construction cost for the side stream pilot system is usually higher, however, this system offers various benefits by studying on the real time fouling phenomenon at a smaller scale without affecting actual operation. 0.2 mg/l of residual chlorine was found sufficient to reduce the fouling accumulation by over 85%. For all the chlorine residuals (both low and high), seasonal fouling variation was not observed. This indicates even low chlorine residual (0.05mg/l) dose would play a great role in minimizing fouling. Inorganic analyses on the deposits collected from the chlorinated tubes revealed that iron level increased with residual chlorine concentration. This could be due to precipitation of iron resulting from chlorine oxidation of  $\text{Fe}^{2+}$  in seawater [32].

Severn Trent DeNora (2009) reported on the disinfection of ballast seawater using electro-chlorination. The results indicated that a residual chlorine concentration of 2.95 mg/L-3.71 mg/L with ballast seawater containing <2 mg/L TOC was sufficient to inactivate 98%–100% mesozooplankton, 99%–99.9% phytoplankton and 99%–100% bacteria in 5 hours [33]. 14 mg/L-16 mg/L treating ballast seawater containing 10 mg/L TOC effectively inactivated >99% zooplankton, phytoplankton and bacteria after a 24-

hour treatment period [34]. Testing of the treated water was shown to be non-toxic to aquatic organisms following a sodium bisulfite neutralization step [32].

Liu, Y. et al. (2011) reported that nutrients for biofilm and biological growth in cooling towers can be contributed by many sources. In Both the air and water represent a carbon source. Chemicals used to treat cooling water such as antiscalants and corrosion inhibitors can also provide additional nutrients that help biological growth. Evaporation processes taking place in the cooling tower can further concentrate nutrient levels in the cooling water making them more accessible. Additionally, a huge surface area of the evaporative fill materials, large water sumps/basins, and long cooling water loops promote an extensive growth of biofilms. Most studies focused only on the total planktonic bacterial count in the recirculating water as an indicator for biocide effectiveness. This could be misleading due to the large surface areas in cooling systems where a majority of the biofilm and its associated bacteria community can be found. It also has to be noted that biofilms are difficult to remove due to excretion of extracellular polymeric substances during the formation. Thus, a good inactivation rate of plankton bacteria by biocides does not guarantee removal of biofilms. The primary objective of the study presented was to evaluate the impact of an oxidizing biocide (chlorine) and non-oxidizing biocide (glutaraldehyde) on the biofilm [35].

Biofilms need to be controlled and inactivated in the seawater cooling systems due to their massive potential of fouling [36]. It has been reported mussels have the capability to tolerate intermittent chlorination [37]. Bivalve mussels close their shell during chlorination and remain isolated for an extended time, thus making the intermittent

chlorination ineffective. The study of control mussels in cooling water was aimed to optimize chlorination to achieve cost-effective dosing and acceptable environmental discharge. The findings of this study have been shown that each species requires different exposure time to achieve 100% mortality rate. Some species are more resistant to chlorine than the others [37].

#### 2.5.1.2 Ozonation

Ozone is a rapid and powerful oxidant with disinfection properties and has been used in the drinking water treatment applications. The effectiveness of ozone is around 100 to 300 times that of chlorine and can be used successfully at low concentrations. Ozone disinfection in drinking water was introduced in the late 19th century, however, it was not widely used in the beginning and gained popularity in water treatment industry in the late 20th century due to its high oxidation and disinfection capability. Many studies have shown that ozone has lower contact time (CT) (product of the concentration of a disinfectant and the contact time with the water being disinfected) and effective in inactivating bacteria, viruses, and protozoan cysts under certain conditions [38]. Ozone has several applications in the treatment of water such as oxidation of reduced metals, oxidation of synthetic organic compounds and removal of odor and taste causing compounds.

Ozone has also been reported used to control fouling in seawater intake pipes. Recently, ozone has been utilized in many public water treatment plants for chemical disinfection [39]. More than 300 large-scale facilities in the United States currently use ozone to treat both water and wastewater [39]. Different ozone disinfection equipment is commercially

available, and is more widely used in Europe in drinking water treatment than the US [40]. For biofouling control in seawater, a high ozonation dosage of 5 mg/l for 5 minutes a day was reported to be sufficient to keep titanium, aluminum, brass and epoxy coated PVC cooling tubes clean [41]. Ikegami et al. (2006) reported that low ozone concentration between 0.2 to 0.5 mg/l could control fouling at an acceptable level [42]. Ozone residual equivalent of 1.0 mg/l of total residual oxidants was sufficient to disinfect seawater for mariculture efficiently [43]. High Ozonation dosage, 5 mg/l for five minutes a day in seawater was sufficient to keep titanium, aluminum brass and epoxy coated PVC cooling tubes clean [41]. Jones et al. (2006) stated that ozonation with a TRO of less than 1 mg/l as  $\text{Br}_2$  could inactivate several marine invertebrates and fish species [44]. The ozonation in seawater led to brominated HAAs (halo acetic acids), and HNMs (halo nitromethane) were produced in both natural and synthetic higher bromide saltwater [45]. It is also reported (Perrins et.al 2006) that at seawater pH, bromate is less likely to form due to the domination of hypobromous acid. Similar to chlorination in seawater, hypobromous acid produced by the ozone-bromide reaction will react with natural organic matters in seawater to form brominated THMs such as bromoform [46]. Due to the presence of higher bromide (65 mg/l) in seawater, ozone reacts rapidly (half-life of 5.7 seconds) with bromide to form the hypobromous acid (HOBr) and hypobromite (OBr<sup>-</sup>). At seawater pH of approximately 8.1, the hypobromous acid will be the dominant free bromine source since the pKa of HOBr/Obr<sup>-</sup> is 9.0. Figure 2-8 shows the reaction pathway for decomposition of ozone in seawater. Since the HOBr is more dominant in seawater, it is anticipated that brominated organic (e.g., bromoform) formation will be more than bromate [33].

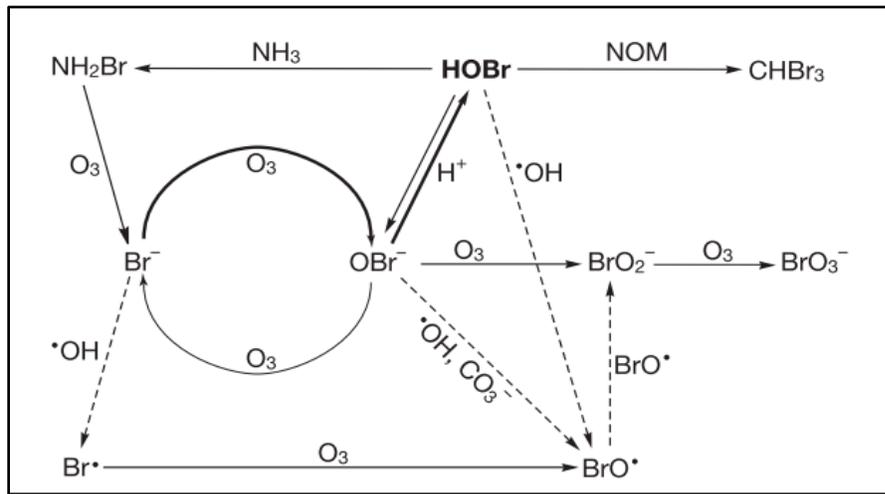


Figure 2-8: Ozone reaction pathway in seawater (adapted from Herwig et al. 2006)

It has been reported (Earth Tech, 2005) that formation of ozone DBPs (mainly bromate and brominated THMs) can be controlled by:

- i. By lowering the pH, more HOBr is produced thus leading to lower bromate.
- ii. Ammonia addition with short contact time can decrease both the DBPs.
- iii. Hydrogen peroxide addition will decrease the brominated THMs but may increase or lower bromate formation.
- iv. Low Ozone/TOC ratio leads to low DBPs [47].

The chemistry of ozone in seawater is considerably different than that in freshwater. The most important difference with ozone chemistry in seawater compared to freshwater is the presence of bromide in seawater. [40]

Herwig et al. (2006) studied ozone treatment of ballasted seawater. Ozonation experiments were carried out by bubbling ozone directly into the ballast tanks of a oil tanker. The ballast capacity of the oil tanker is 41,6000 tons of seawater. A corona discharge ozonation system used in this study was housed in a 20-foot standard container. The results demonstrated a two to three fold of increase in DO (max of 20 mg/l) after ozonation. The elevated oxygen levels could accelerate the corrosion in the ballast tanks. TRO level more than 5mg/l Br<sub>2</sub> was recorded during the longer ozonation period. Bromate formation was not detected for all the experiments [44].

Perrin et al. (2006) discussed the effect of ozonation on seawater collected from different locations, studying the factors that governed the formation and decay of residual oxidants that were produced during ozonation. The formation of total residual oxidant (TRO) in the seawater during ozonation was mainly comprised of free bromines (HOBr and OBr<sup>-</sup>). These results indicate that TRO increased linearly with time for the synthetic seawater. This study might not be applied to in-line ozonation study using venturi. TRO decay during rapid mixing could be much faster. Bacteria cell counts reduced after ozonation, but the concentration rebounded over time to near the control levels. For instance, at initial TRO of 0.27 mg/l, cell counts dropped by ten fold after 5 hours. However, significant regrowth was recorded within the couple of hours where the cell counts were comparable to controls by 24 hours [40].

### 2.5.1.3 Chlorine dioxide

Chlorine dioxide ( $\text{ClO}_2$ ) is a popular disinfectant used in water treatment.  $\text{ClO}_2$  has a green-yellowish appearance and irritating odor, and behaves very differently from chlorine ( $\text{Cl}_2$ ). Chlorine dioxide is also an alternative oxidant that has been reported used for seawater. The effectiveness of chlorine dioxide is at least as high as that of chlorine as in at lower dosage concentrations, and has been extensively applied in drinking water disinfection [48]. The major differences between the  $\text{ClO}_2$  and other common biocides are as follows:

- a)  $\text{ClO}_2$  is more soluble in water than  $\text{Cl}_2$  (approximately 10 times more)
- b) It is effective over a wide range of pH (e.g. the pKa for the chlorite ion, chlorous acid equilibrium, is extremely low at pH 1.8)
- c)  $\text{ClO}_2$  has lower oxidation strength than  $\text{Cl}_2$  (0.96 vs. 1.49) but higher oxidation capacity than  $\text{ClO}_2$  (5 electron vs. 2 electron)
- d)  $\text{ClO}_2$  does not react with water (*i.e.* does not hydrolyze like  $\text{Cl}_2$ ) but dissolves as a true gas and can be removed from solution by aeration
- e)  $\text{ClO}_2$  disinfects by oxidation and not by halogenation. Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Halogenation (chlorination) in NOM laden water could lead to the formation of THMs.
- f)  $\text{ClO}_2$  does not react (or very slow reaction rate) with bromide. Thus, bromine related disinfection by-products (DBPs) are not of a concern.
- g)  $\text{ClO}_2$  does not react with ammonia-nitrogen.

- h)  $\text{ClO}_2$  is more effective than chlorine in reduce the number of living organisms as demonstrate in Figure 2-9 [48].

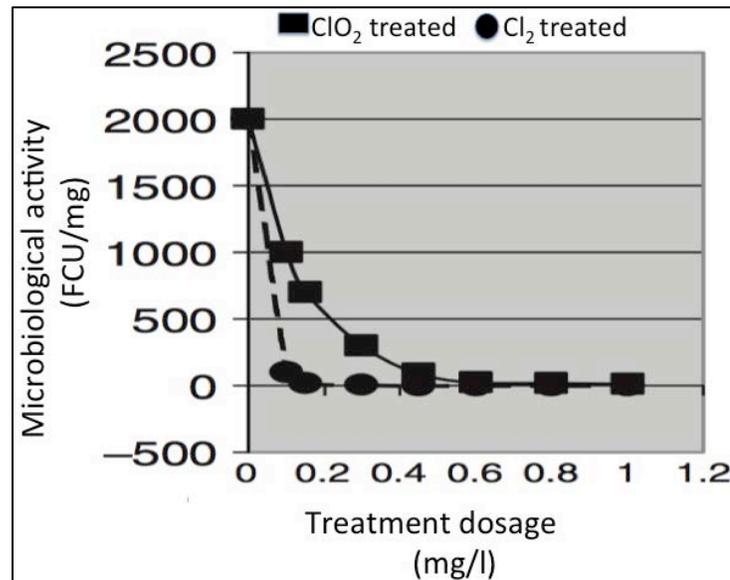


Figure 2-9: Comparing microbiological activity after treatment with  $\text{ClO}_2$  vs.  $\text{Cl}_2$  (Adapted from Agus, E.2009).

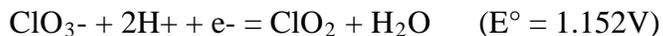
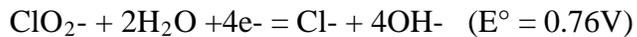
The disadvantages of chlorine dioxides are as follows:

- a) The primary DBP arising from  $\text{ClO}_2$  treatment is formation of chlorite. In drinking water, maximum contaminant level for chlorite is 1 ppm, thus higher  $\text{ClO}_2$  dosage is not possible since the usual conversion rate of  $\text{ClO}_2$  to chlorite in drinking water is around 50% to 70%. The remaining percentages are chlorate and chloride.

- b) On-site chemical storage for ClO<sub>2</sub> generation.
- c) Explosive at higher concentrations if exposed or leak to the atmosphere.
- d) Degenerate if exposed to sunlight and UV.
- e) Disinfection effectiveness decreases with decreasing temperature.

Chlorine dioxide has been used as a oxidant in several industrial application such as potable water treatment, dairy, fruit and vegetable processing, and industrial waste treatment. The use of chlorine dioxide has increased as disinfectant in distillation plants in the Gulf region [22]. Chlorine dioxide disinfected oysters appeared to have an extended shell life up to 12 days. Many sources have reported that THM formation is lower in chlorine dioxide treatment due its lower reactivity with organic matter [22].

Some of reactions of ClO<sub>2</sub> are as follows:



ClO<sub>2</sub> can be generated via several ways:

- 1) Acid chlorite system
- 2) Aqueous chlorine-chlorite
- 3) Recycled aqueous chlorine
- 4) Gaseous chlorine-chlorite

- 5) Gaseous chlorine-solids chlorite matrix
- 6) Electrochemical
- 7) Acid/peroxide/chloride

$\text{ClO}_2$  disinfects by reacting with organic nature in the bacteria cells. It reacts directly with the amino acids and RNA in the cell, thus inhibiting the protein production. Petrucci et al. (2005) have summarized that chlorine dioxide can be effectively used as an ideal biocide for the following reasons:-

- i.  $\text{ClO}_2$  does not react with bromide that could lead to the formation of organo-bromine compounds
- ii.  $\text{ClO}_2$  does not react with ammonia in the seawater
- iii. It has high reactivity with regard to a number of structures including secondary and tertiary amines, organo-sulfur compounds and activated aromatic rings.
- iv. It does not halogenate
- v. Effective wide range of pH
- vi.  $\text{ClO}_2$  oxidation can help to weaken and loosen the EPS of the bio-fouling, thus retarding the growth of denser and thicker films [49].

Ecochlor (2010) shows clearly that chlorine dioxide treatment is very effective in disinfecting microbes in seawater and can fulfill the ballast water discharge regulation. Results also indicated that chlorine dioxide would reduce to chlorite, chlorate, and chloride during the oxidation process. The reported test result also clearly showed that chlorine dioxide treatment in seawater did not lead to the formation of bromate. Table 2-4

shows the formation of DBPs in seawater due to chlorine and chlorine dioxide treatment. The amount of DBP formed during the chlorine dioxide treatment is significantly lower than chlorination [50].

Table 2-4: DBP Formation in ballast seawater due to chlorine and chlorine dioxide treatment. [Ecochlor,2010]

Parameter	Chlorine ug/L	Chlorine Dioxide ug/L
BDCM		<1
Bromoform		<1
Chloroform		<1
DBC		<1
THM (Total)	260 - 410	<1
HAA (Total)	48.5 - 100	12 - 36

Belluati et al. (2007) reported that, chlorine dioxide as an alternative disinfectant can maintain good disinfection while minimizing DBP formation, especially bromate. Their study performed tests to obtain the conversion of chlorine dioxide to chlorite. The results revealed that the chlorine dioxide-chlorite conversion decreased over the time. As for the formation of chlorate, the purity of chlorine dioxide generation played significantly in chlorate formation. Chlorate could be generated as a by-product during the generation of chlorine dioxide [51].

### 2.5.2 Physical treatment

The definition of physical–chemical treatment can be refined to refer to pure chemical treatment using specific compounds while physical treatment is a process applied to water without changing the chemistry. Physical treatment strategies can be applied to cooling water tower process to reduce biofouling and growth of biofilms. For example, sponge rubber balls have been used in heat exchangers in cooling water systems by cleaning the tubes of the units. The size of the balls is slightly higher than the internal diameter of the tubes, thus physically removing any biofilm formed. Also, ultrasound has been reported to remove the hard mineral deposits in the heat exchanger surfaces caused by rusting at high temperatures [52]. Furthermore, ultrasounds can reduce the biofilm accumulation in the cooling water device up to 90 %.

The dose of 100 mg/l of polymer fibers in the water can be used to control biofouling in cooling water, and this technology could be useful to stop the biofilm to form [53]. There are several of other physical treatment may be applied to cooling water process to reduce the growth of biofouling. In next section will explore the use of activated carbon and ultrafiltration for cooling water treatment.

#### 2.5.2.1 Nutrient removal

Nutrient removal is another approach to control biofouling and biofilm growth and to prevent algae growing. Nutrient removal is a common practice in wastewater treatment, particularly in tertiary treatment for potential reuse of the treated water. Several research

studies have shown that wastewater treatment processes can remove the major quantities of natural organic matter, suspended solids, nitrogen, phosphorus and microorganisms contained in wastewater [54].

Removing the growth substrates from the water treatment process will reduce the biofouling potential, which will ideally offer an environmentally attractive alternative to the use of biocides [55]. Sand filters have been used for biofouling control in cooling tower processes and with good effect. 70–80% reduction of oxidizing biocides usage can be achieved by using bio-filter, which reduce the nutrient levels and microbial growth in cooling towers system [56]. The most important nutrients limiting growth of algae are nitrogen and phosphorus in natural water. S. Kunikane (1984) studied the relationship between specific algal growth rate and the limiting nutrient concentration in the medium. The relationship between total nitrogen and total phosphorus versus algal concentration is shown in Figure 2-10, with algal biomass concentration within the range of total nitrogen and total phosphorus ratio of 5-20 mg nitrogen mg<sup>-1</sup> phosphorus [57].

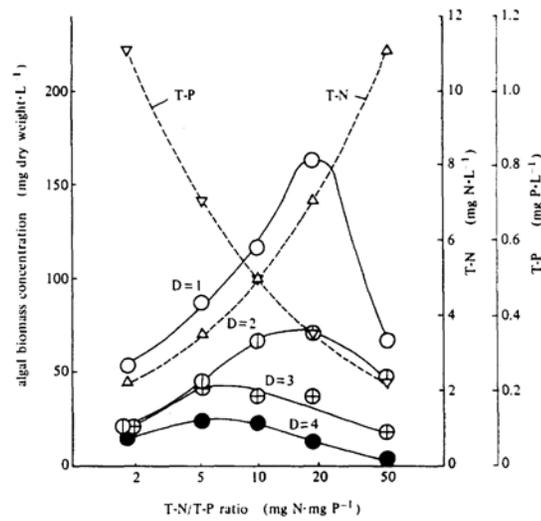


Figure 2-10: Biomass concentration of nutrients (total nitrogen and total phosphorus ratio). [Adapted from Kunikane, S., 1984]

Luederitz, V (2001) reported that 90% of organic load and total N and P were removed by wastewater treatment (reed-bed systems) in Germany and the USA [58]. A sequencing batch reactor (SBR) process was used to accomplish a wide range of treatment, including nutrient removal. The technique succeeded in removal efficiencies of 91 to 98% for total nitrogen and phosphate and chemical oxygen demand [59]. All referenced research to date was done mostly with fresh water and some with wastewater, but not in seawater. There is a very little literature related to seawater conditions. So a research question is whether these methods can be applied in a seawater-cooling tower.

Seawater cooling towers are prone to biofouling due to organic and inorganic loadings in the seawater feed. The availability of organic and inorganic nutrients, along with sunlight and continuous aeration of the cooling tower contributes to an environment that is ideal for microbial growth [12]. Some microorganisms (algae, protozoa, and bacteria) can also

grow in a cooling tower system under certain environmental conditions [2]. Evaporation will also concentrate the nutrient levels (e.g. organic carbon, nitrate, nitrite, phosphates etc.) in the seawater, hence promoting the formation of biofouling. In this study, the organic nutrient removal was targeting for the seawater cooling towers treatment. The concentration of the P and TN are less in the seawater (less than 100 ug/l) while the total organic carbon around 1.3 mg/l). However, the contamination in the petrochemical cooling tower are from the organic carbon which are the product.

#### 2.5.2.2 Granular activated carbon (GAC):

Granular activated carbon (GAC) operated as a biological filter is becoming more commonly used in the removal of organic carbon in water treatment. Natural organic matter (NOM) removal was positively correlated with contact time increases. Naidu et al. (2013) have reported that a granular activated carbon (GAC) bio-filter has a capability to reduce biofouling by maintaining a stable microbial activity in the bio-filter [60]. GAC has a several advantages such as has a large and unequal surface which will increase the adsorption of the organic and microorganisms [61]. Many research reports investigated GAC and anthracite used as a bio-filter media to remove particulate matter and organic matter from seawater [62]. Assailable organic carbon (AOC) is one of the parameters linked directly to biofouling in the feed water [63]. AOC is dissolved organic carbon (DOC) that is bioavailable and utilized by microorganisms with subsequent biomass

increase. AOC can be measured for seawater based on bio-luminescence using *V. fischeri* [64].

#### 2.5.2.3 Ultrafiltration (UF):

Is a variety of membrane filtration and define as the separation of two or more components through a medium, which allows small molecules (like water) to pass but suspended solids and solutes of high molecule holds back larger. Membranes are used for various applications such as:

- Produce filtered water.
- Clean industrial eluent and recover valuable constituents,
- Purify subtle solutions for (food, the drug industry and biotechnology).

Also, the membrane has a capacity to remove the biological and non-biological matters of the water pretreatment. There are many research papers showing that membranes can remove microorganisms from wastewater and reuse water significantly [65]. The advantages of membrane technology for water treatment are clarification and disinfecting, high quality of treated water, compact system, easy to operate, less maintenance, less chemical use [66, 67]. There are several membrane separations such as microfiltration (MF) and ultrafiltration (UF) and reverse osmosis (RO) that are efficient removing particles [68]. Ultrafiltration can remove viruses and algae from wastewater, which are particles larger than the largest pore size, as demonstrate in Figure 2-11 [69]. Recently the use of

ultrafiltration (UF) in treatment of drinking water has become a more significant technology as alternative to the conventional clarification [65].

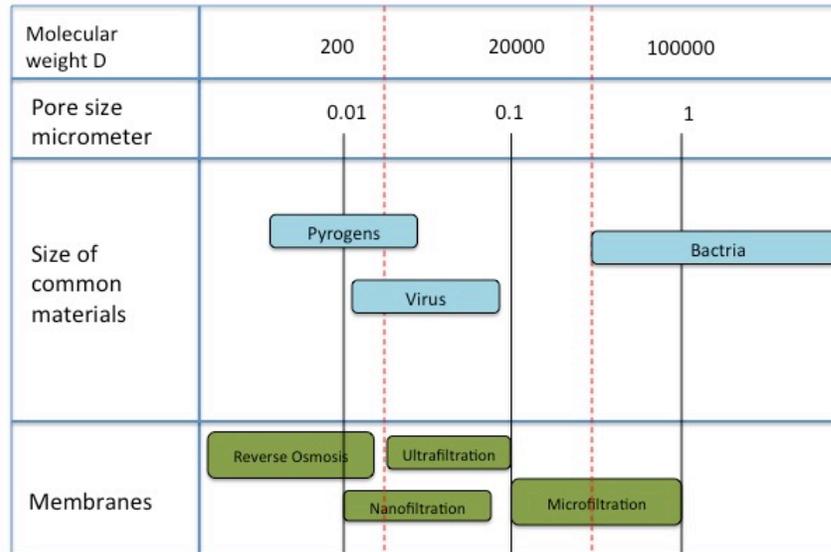


Figure 2-11: Membranes data.

Also, UF has been applied as pretreatment in Reverse Osmosis (RO) systems for fouling removal [70, 71].

Furthermore, studies have been conducted to improve the ultrafiltration process performance by adding a bio-filter such as activated carbon (AC) in the pretreatment process [72]. The hybrid AC/UF process is very effective in removing organic matter from seawater. UF can achieve a complete removal of *Microcystis aeruginosa* cells, but less removal of algogenic organic matter (AOM) in water. By adding activated carbon to a UF process treatment the removal of DOC can be significantly improved [73]. The removal of dissolved organic carbon (DOC) by UF was around 7%, while when adding the activated carbon the removal increased to 70% [72]. Studies also have reported more

than 95% of algae removal, expressed as chlorophyll [74]. Results showing that GAC/UF can improve the NOM removal rate have been reported [75].

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## **Chapter 3**

### **3 Materials and Methods**

This chapter describes the materials and methods used in the experimental plan and tests related to this study. Two approaches were used to control of biofouling the in seawater cooling towers: First phase studied ozone micro-bubbles and chlorine dioxide at bench-scale and pilot-scale for treatment of cooling towers. Second phase studied nutrients removal form seawater feed supply to cooling tower basins by using a bio-filter and ultrafiltration of microorganism removal at pilot-scale.

#### **3.1 Bench scale:**

True batch reactor (TBR) was used to conduct bench-scale assessment. The aim of the TBR is to represent comparative oxidants decay under well-defined conditions and to perform various experimental conditions that can quickly identify the key factors important to oxidant performance and decay. The bench-scale testing was done under more controllable (while being flexible) condition in providing insights.

### 3.1.1 Bench-scale setup

A laboratory bench-scale study was carried out to assess various key factors of seawater cooling tower operation. The customized true batch reactor (TBR), as shown in Figure 3-1 is mainly made of borosilicate glass with one inlet and outlet of hot water, temperature probe, and oxidant injection. The borosilicate glass reactor is encapsulated with an outer water jacket to simulate various operating temperatures. The reactor is designed and can be operate at wider operating ranges, ranging between 4°C to 80°C. Homogenous mixing in the reactor is achieved using magnetic stirrer. Oxidant, such chlorine ( $\text{Cl}_2$ ), chlorine dioxide ( $\text{ClO}_2$ ) and ozone ( $\text{O}_3$ ) are injected at the lowest point via septum located at the lower end of the reactor using a syringe. The bench-scale studies are based on theoretical steady-state conditions for a full-scale plant as shown in Figure 3-2.

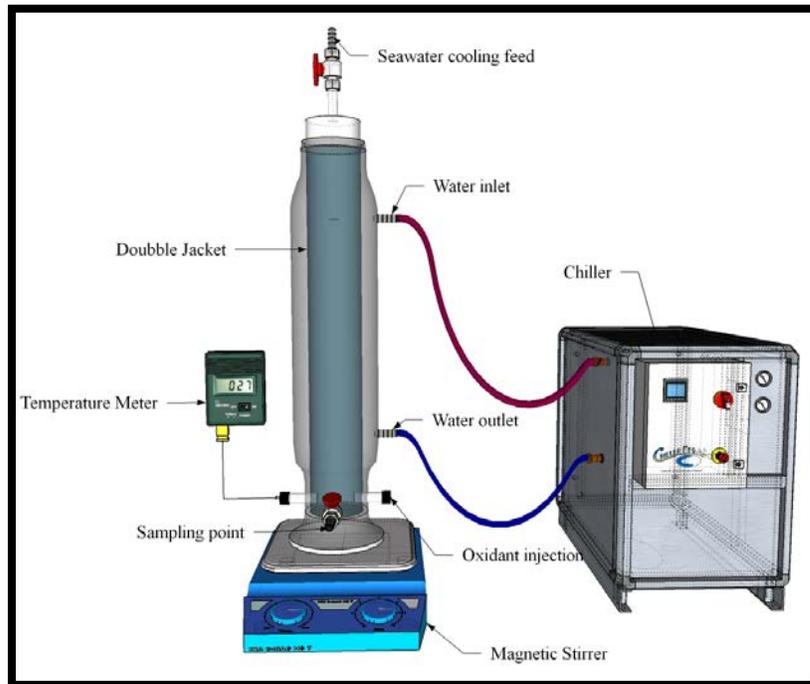


Figure 3-1: Double jacket bench reactor for decay analyses.

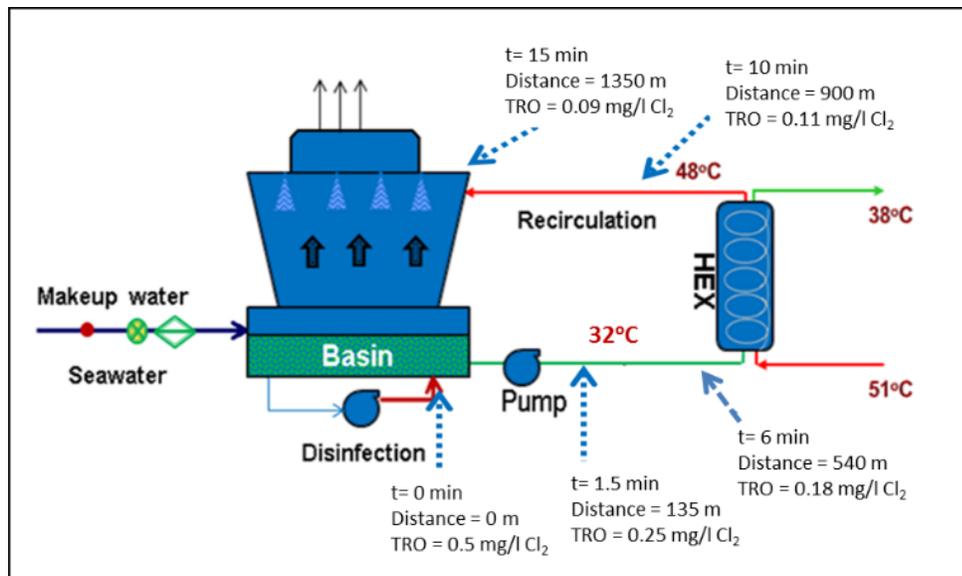


Figure 3-2: Equivalent TRO decay kinetics in cooling tower pipe network.

Values are extrapolated to an equivalent industrial-scale cooling tower system with a pipe flow velocity of 1.5 m/s and a pipe network length of approximately 0.5 km from the cooling tower. Tests were conducted at two temperatures (e.g. 32°C for inlet seawater, 48°C for outlet seawater) to emulate the cooling tower return water temperatures by using thermal baths.

### 3.1.2 Methods

The study investigated the effect of the cycle of concentrations (COC) of seawater cooling towers (defined as the ratio of the concentration of chlorides in make-up water to the concentration of chlorides in recirculating water) at varied levels of seawater temperature and oxidant dosages, and the impact on residual disinfectant decay (TRO). TRO readings were measured using disinfection by-product (DPD) powder pillows (spectrophotometric; DPD Method 8167). For ease of comparison, dosage and residual measurements for all the oxidants are expressed in chlorine equivalents (mg/l Cl<sub>2</sub>) using suitable conversion factors for ozone and chlorine dioxide respectively (e.g. 1 mg/l Cl<sub>2</sub> = 0.67 mg/l O<sub>3</sub> = 1.9 mg/l ClO<sub>2</sub>). Different cycles of concentration (COC) of Red Sea water samples (e.g. COC = 1.25 and COC = 1.50; measured by seawater electrical conductivity) were prepared using a rotary evaporator. A set of oxidant dosages ranging from 0.1 - 0.5 mg/l Cl<sub>2</sub> for chlorination, 0.067 - 0.335 mg/l O<sub>3</sub> for ozonation and 0.19 - 0.95 mg/l ClO<sub>2</sub> for chlorine dioxide were injected into the seawater feed. To maintain the dosage rate for these oxidants, a standard method (USEPA DPD Method 8021) was targeted to

control sodium hypochlorite (chlorination) by using the free chlorine powder pillows test while the indigo method (Hach's AccuVac Ampules; Method 8311) was implemented to measure the ozonation. Furthermore, chlorine dioxide stock solution was prepared by adding sulfuric acid to sodium chlorite solution (Standard Method 4500-ClO<sub>2</sub>) and then verifying the dosing rate by using DPD powder pillows (Method 10126).

Table 3-1 shows the test matrix used for monitoring the TRO decay. For each test, TRO residuals were measured at time intervals 1.5, 3.0, 6.0, 10.0 and 15.0 minutes after biocide injection. Over 80 different combinations were performed during TRO decay studies.

Table 3-1: TRO decay test matrix for each oxidant at different COC, temperature and dosage.

Test	Cycle of Concentration (COC)	Temperature (°C)	Dosage (eqv. mg/l Cl <sub>2</sub> )
1	1.00	32.0	0.30
2	1.00	32.0	0.50
3	1.00	48.0	0.30
4	1.00	48.0	0.50
5	1.25	32.0	0.30
6	1.25	32.0	0.50
7	1.25	48.0	0.30
8	1.25	48.0	0.50
9	1.50	32.0	0.30
10	1.50	32.0	0.50
11	1.50	48.0	0.30

12	1.50	48.0	0.50
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### 3.1.3 Laboratory Analysis

The efficiency of oxidants was determined by analyzing the total live/dead cell (algae and bacteria) counts in seawater using a BD Accuri™ C6 Flow Cytometer (FCM). The concentration required in seawater sample is 1X of SYBR® Green I + 10 µg/ml of Propidium Iodide (PI) were used to stain live and dead cells respectively. Transfer 495 µl of seawater sample to a sterile Eppendorf tube incubate and add 5 µl of the 100X of SYBR® Green + 1000 µg/ml Propidium Iodide to the seawater sample (at room temperature) for 15 minutes. Prior to staining, Sodium Thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) was added to each seawater sample to quench residual oxidants. Then, transfer 200 µl of the incubate sample to a 96-well plate, set the pump speed to medium, sample volume to be analyzed to 100 µl and FL1 threshold to 600. Furthermore, the raw of seawater was characterized for this study and water quality parameters are summarized in Table 3-2.

Table 3-2: Characterization of Red Sea water.

Parameter	Raw Red Sea water	Parameter	Raw Red Sea water
pH (SU)	8.13	UVA254 (1/cm)	0.016
Temperature (C°)	26.4	SUVA (L/mg-m)	1.4
TDS (mg/l)	38,000	Bromide (mg/l)	71.0
Conductivity (mS/cm)	60.0	Chloride (mg/l)	23,624
Turbidity (NTU)	5.34	Fluoride (mg/l)	1.3
ORP (mV)	147	Nitrite as NO <sub>2</sub> <sup>-</sup> (mg/l)	0.0047
Total Alkalinity (mg/l as CaCO <sub>3</sub> )	120	Ortho-P as PO <sub>4</sub> <sup>-3</sup> (mg/l)	0.1
Total Hardness (mg/l as CaCO <sub>3</sub> )	7,500	Sulfate (mg/l)	2,650
Mg Hardness (mg/l as CaCO <sub>3</sub> )	6,300	silica (mg/l)	0.13
Ca Hardness (mg/l as CaCO <sub>3</sub> )	1,200	Sodium (mg/l)	12,000
DOC (mg/l)	1.101	Potassium (mg/l)	560
Total Iron (mg/l)	0.02	Chromium (mg/l)	0.1749E-2
Boron (mg/l)	4.6	Copper (mg/l)	0.5235E-4
Aluminum (mg/l)	0.1214E-1	Lead (mg/l)	0.1902E-4
Antimony (mg/l)	0.2232E-4	Lithium (mg/l)	0.03207
Arsenic (mg/l)	0.6108E-3	Manganese (mg/l)	0.1541E-2
Barium (mg/l)	0.522E-2	Molybdenum (mg/l)	0.0001625
Cadmium (mg/l)	0.1295E04	Nickel (mg/l)	0.01628
Chromium (mg/l)	0.1749E-2	Selenium (mg/l)	0.03042
Copper (mg/l)	0.5235E-4	Silver (mg/l)	ND
Lead (mg/l)	0.1902E-4		
Total Iron (mg/l)	0.02		

### 3.1.4 : Appendix

#### 3.1.4.1 Flow Cytometer (FCM).

##### FCM Cleaning and Calibration Check Protocol:

- 1) Open the “Cleaning and Calibration FILE”.
- 2) Transfer 200  $\mu$ L of liquid in the following order to individual wells.
  - Detergent (yellow)
  - Soap (green)
  - MQ water
  - Beads (1  $\mu$ m, brown bottle, shake before use)
  - MQ water
- 3) Run all four samples and assess the “MQ Water” sample and the “beads” samples
- 4) Save the results (including name and date)
- 5) The bead count result should be approximately 4000 and close to zero for MQ water. If inconsistent count is obtained, repeat the procedure. Proceed with advance cleaning step if the results are still inconsistent after several repetitions.
- 6) SYBR Green I and Propidium Stain preparation protocol

100 times concentrate stock need to be prepared prior to staining in seawater. The final dye concentrations required in our seawater sample is 1X SG I + 10 $\mu$ g/ml PI. Therefore, 100  $\mu$ l concentrate stock can be prepared by adding 1  $\mu$ l of 10,000X SGI into 99  $\mu$ l of 1000 $\mu$ g/ml PI in MQ water.

#### Seawater Staining Protocol

1. Transfer 495  $\mu$ l of seawater sample to a sterile Eppendorf tube.
2. Incubate in dark environment and room temperature for 15 minutes. Note that samples need to be stored at 4°C if samples need to be analyzed at a later time.
3. Add 5  $\mu$ l of the 100XS GI+1000  $\mu$ g/ml PI to the seawater sample (at room temperature). Note that after this addition, the final dye concentration is now 1X SGI+10  $\mu$ g/ml PI
4. Vortex the sample and incubate in dark environment for 15 minutes at room temperature
5. After 15 minutes, vortex the sample and transfer 200  $\mu$ l of the sample to a 96-well plate
6. Open the pre-determined template and set the pump speed to medium, sample volume to be analyzed to 50  $\mu$ l and FL1 threshold to 600.

### 3.2 Pilot-scale studies

The efficiency of alternative treatment oxidants for seawater cooling towers using ozone micro-bubbles and chlorine dioxide were investigated at the pilot-scale. All three cooling towers were fully functioning with seawater and different dosing systems. Using sodium hypochlorite as baseline, chlorine dioxide, and ozone were employed for the disinfection operation as per the required conditions pilot-scale model recirculating cooling seawater systems.

The pilot-scale cooling tower setup is designed to reject 15 kW heat load from the condenser. The condenser load is simulated using a 15 kW inline heater where the process temperature can be fixed and controlled using PID. The maximum temperature at the heater outlet is fixed at 60°C. The heat exchanger inlet and outlet temperatures can be adjusted by regulating the cooling recirculating flow.

Comparative assessment of these disinfectants was carried out under various conditions. Water quality parameters were monitored by on-line (or field) measurements with lab analyzes. The impact of water quality and disinfection practices and their effects toward biofouling, microbial activities, scaling and corrosion, etc. were also monitored and assessed during this pilot-scale study. In addition, all of the key factors related to the cooling tower operation and its performance were investigated.

#### 3.2.1 Pilot plant model recirculating cooling water systems

The pilot plant cooling towers were constructed at KAUST's Central Utility Plant (CUP)

where can supply fresh seawater from intake plant. The pilot-scale facility was set outside (Figure 3-3), such that it could be exposed to all types of environmental conditions, e.g., pollutants, including dust, mold, humidity, temperature and other types of contaminants that are commonly present or similarly experienced at a full-scale facility due to its operations.



Figure 3-3: View of the Cooling Tower Pilot Plant

The pilot plant cooling towers are mechanical demonstrating types and its diagram is depicted in Figure 3-4. The pilot test program is summarized the condition of the experiment in Table 3-3. The automated pilot operation runs was maintained by the

LabView system allowing the control of all three cooling tower systems (pump on/off, power on/off, dosing rate, water quality monitoring, etc.) with remote access. The cooling system has open loop supplies by seawater and close loop supplies by freshwater. The makeup seawater was operated using HTT 2000 GemmeCotti all plastic (PVDF) pump while heater, oxidant, and recirculate flow were made using HTT 5000 GemmeCotti (PVDF) pumps.

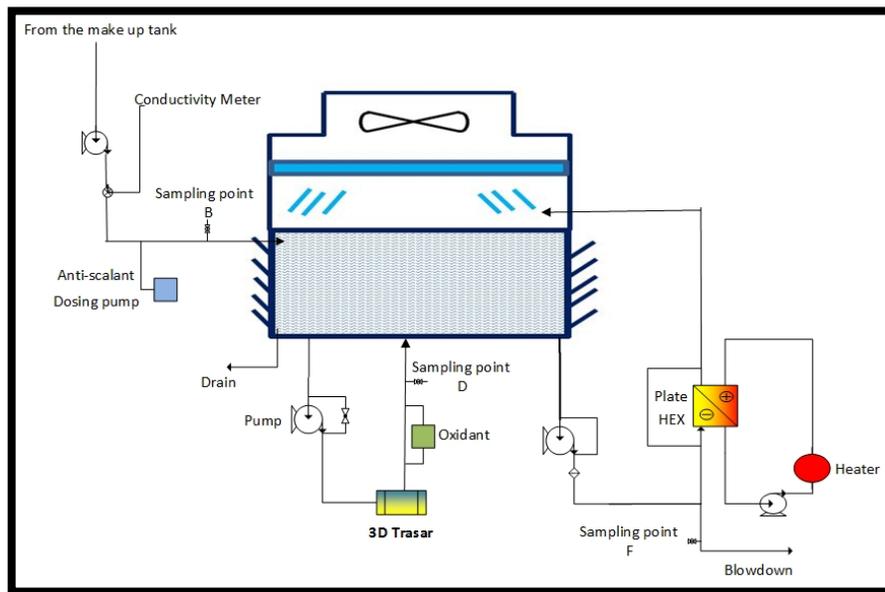


Figure 3-4: Diagram of a pilot plant cooling seawater system.

Table 3-3: Pilot plant test program.

<b>Test No</b>	<b>Test Program</b>	<b>Duration (days)</b>	<b>Remarks</b>
1	Cooling Tower (CT) operation without treatment (No oxidation)	40	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Disinfectant switched off.</li> <li>- Anti-scalant dosing on.</li> <li>- Organics spike (Me OH).</li> </ul>
2	CT operation with Oxidant Treatment (Oxidation)	30	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Disinfectant switched on.</li> <li>- Anti-scalant dosing on.</li> <li>- TRO = 0.2 ppm at blowdown (as Cl<sub>2</sub>).</li> <li>- Organics spike (Me OH).</li> </ul>
1	Cooling Tower (CT) operation without treatment (No oxidation)	30	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Disinfectant switched off.</li> <li>- Anti-scalant dosing on.</li> <li>- Organics spike (Algae).</li> </ul>
2	CT operation with Oxidant Treatment (Oxidation)	30	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Disinfectant switched on.</li> <li>- Anti-scalant dosing on.</li> <li>- TRO = 0.2 ppm at blowdown (as Cl<sub>2</sub>).</li> </ul>

Based on the mass and salt balance of the cooling tower and using the following parameter shown in Table 3-4, the make-up water, blow down and COC time can be calculated. These calculated values are shown in Figure 3-5.

Table 3-4: Design Parameter for the Cooling Tower

Heat Load	4.27	Rton
Total Water Volume of CT	65	kg
Heat Rejection	15.01759	kW
Hfg	2417.8	kJ/kg
Evaporation Loss	0.006211	kg/s
Water Circulation rate	0.357562	kg/s
Windage losses	0.000358	kg/s
Wind loss	0.1	% of total cooling flow
X feed	32000	ppm
A constant	3.233883	
B constant	5.5E-06	
Integral Constant	-171892	

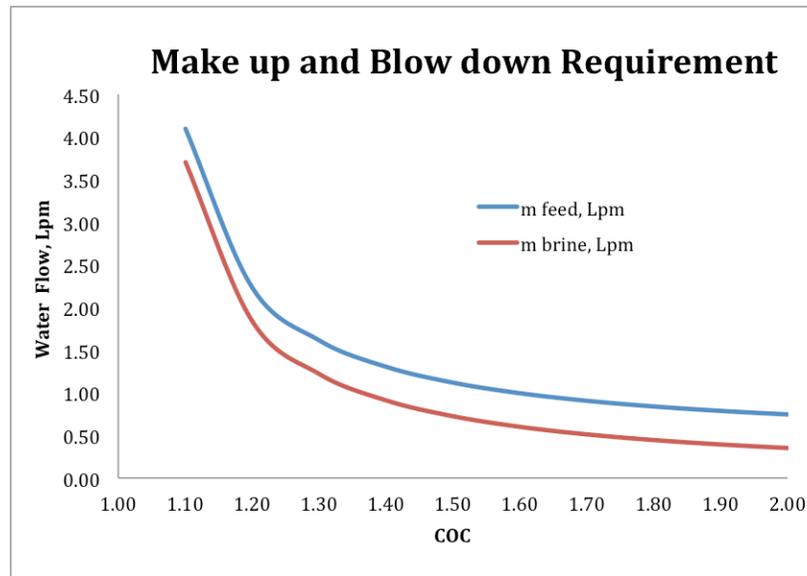


Figure 3-5: Make and Blow down Requirement at specific COC

The basic components of cooling tower are frame and casing made of fiber-reinforced plastic (FRP) with (height of 1550 cm and diameter of 750 cm), film filled with packing material made of PVC (height of 525 cm), cold-water basin with 52 L capacity that is located near the bottom of the tower and fans. The cooling towers specification and materials can be found in supplementary information (Table 3-4). In the experimental system, the cooling tower basin supplied by seawater at 2 liters per minute (LPM, L/min) through make-up cooling tower. The recirculating seawater was pumped at 24 LPM from the cooling tower basin passing the heater exchanger and sprayed into to cooling tower, while the oxidant was pumped at 21 LPM from the basin passing the chemical disinfection and back to the cooling tower basin.

### 3.2.2 Heat exchanger

Certikin titanium plate heat exchangers (Figure 3-6) were constructed with electro seawater resistant heater (15 KW) (diameter length of 592 mm) as in Figure 3-7, worked by transferring the heat water from close loop to seawater open loop in cooling tower. The seawater flew across the heat exchanger in opposite directions of freshwater to maintain a constant heat transfer. The heat exchanger fitted into a five plates (length of 200 mm and height of 460 mm) and the surface of each plate was manufactured with a pattern of channels allowing the water to flow across each one in turn. The temperature difference between inlet and outlet of heat exchanger remained at targeted temperature difference of  $10^{\circ}\text{C} \pm 2$ .



Figure 3-6: Titanium Plate Heat Exchangers



Figure 3-7: 15 kW Inline Titanium Heater- to simulate heat load

### 3.2.3 Chemical disinfection (Oxidant)

The cooling towers for three different chemical disinfection systems were: cooling tower no. 1 (CT1, sodium hypochlorite as baseline): 2,000 mg/l Cl<sub>2</sub> stock of sodium hypochlorite (5.65–6 %). The chlorine gas is dissolved in water tank (Figure 3-8) and produce to hypochlorous acid as the following equation:



When sodium hypochlorite (NaOCl) is used as source of chlorine [76]:





Figure 3-8: Sodium Hypochlorite Dosing System

Cooling tower no. 2 (**CT2, chlorine dioxide**): 20 L of HCl @ 9%w/w (prepared by adding 4.86 L of HCl 37%w/w into 15.14L of MQ water) and 20 L of sodium chlorite @ 7.5%w/w (prepared by dissolving 2,006 g of NaOCl<sub>2</sub> into 20 L of MQ water) ClO<sub>2</sub> mainly generated “on site” as in Figure 3-9 and the following equation used [49]:

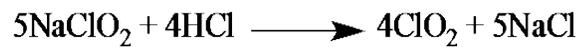




Figure 3-9: Chlorine Dioxide Generator (HCl-NaClO<sub>2</sub>)

Cooling tower no. 3 (**CT3, ozone**): ozone of 1.5 g/Nm<sup>3</sup> (normal temperature and pressure were 20°C and 1 bar, respectively) was generated in-situ (as in Figure 3-10) at 1L/min of O<sub>2</sub> by passing concentrated oxygen into a corona-discharged ozone-producing cell. The generated ozone was then injected in the form of micro-bubbles into the seawater line. The concentration of the produced ozone was regulated by the lab-view. The disinfection residuals also remained within the targeted levels after addition (TRO = 0.2 at ORP level of +600 mV).



Figure 3-10: Ozone Generator

#### 3.2.4 Anti-scalant system

The Phosphonate based anti-scalant 1393T (supplied by NALCO) was used in the experiment to control the scaling of the heat exchanger. The dosing of 1393T can be achieved by conventional (automated) dosing pump (Figure 3-11) by diluting the anti-scalant using MQ water by a factor 10,000 X. 80 ml of anti-scalant in 100 L of MQ water is required per week to operate the cooling tower at COC=1.2 and anti-scalant dosage of 1mg/l. The concentration of 1393T can be measured by using 3D Trassar (flow cell), which calibrated with SO 940 standard solution



Figure 3-11: Anti-scalant Dosing Systems (NALCO-1393T)

### 3.2.5 Data Acquisition System-Labview Software Development

One of the key significant equipment of this pilot plant scale is the Data Acquisition (LabVIEW software) and Control System. National Instrument hardware and software used to fully automate the pilot and measuring devices (sensors) of process monitoring systems. The measured values are delivered to the computer program through the data acquisition system. Table 3-5 demonstrate the descriptions of the hardware that have been configured for pilot setting.

Table 3-5: National Instrument Data Acquisition and Control Hardware

No	Item	Qty	Remarks
1	NI PXI-8108 Core 2 Duo 2.53 GHz controller, 2Gb RAM	1	Processor for Real time monitoring
2	SCXI-1503 16-Channel RTD Input Module	3	48 channels for RTD 4-wire Class A measurement
3	SCXI-1100 32-Channel Multiplexer	4	128 channels of 4-20 mA to received input current signal from various sensors (flow meter, pressure, TRO analyzers and etc
4	NI PXI-6704 high resolution analog output	1	16 analog voltage outputs and 16 analog current outputs to control the dosing pumps and oxidant generators
5	NI PXI-6221	1	16 Analog inputs, 24 Digital I/O, 2 Analog Outputs: multipurpose
6	NI PXI-6514 Industrial	1	32 Source/Sink DI, 32 Source DO: to switch off the pumps or receives digital signals from sensor

Using Labview as the programming software, we would be able to operate the pilot plant 24/7 with ease. PID algorithm can be used to control the oxidant dosage while safety features such as auto-shut down and alarm can be easily programmed. Seawater make up tank was designed to feed the cooling tower basin and monitor the chlorination level of the feed. Figure 3-12 and Figure 3-13 are the graphical user interface (GUI) specifically developed for pilot experimental.



Figure 3-12: Make-up tank GUI (Intake line is closed by motorized valve when the inlet chlorine level increased more than 0.1 mg/l  $\text{Cl}_2$ )



Figure 3-13: Graphical User interface with Real Time Data Acquisition and Logic Control

### 3.2.6 Field measurement

The online parameters such as conductivity, pH and oxidation-reduction potential (ORP) were analyzed by using 3D TRASAR technology as in Figure 3-14. This was designed for measuring the key system parameters for the cooling tower operation. In parallel, hand field test was conducted at pilot plant site to double-check the in-situ data at different sampling points, which were not covered by online analyzers. Hand held parameters measured were pH, conductivity, dissolved oxygen (DO), ORP, turbidity and TRO.



Figure 3-14: NALCO 3D TRASAR (In situ analyzer)

### 3.2.7 Lab analysis

Total organic carbon (TOC) was measured by using a Shimadzu analyzer after filtering through a Whatman filter (pore size = 0.45  $\mu\text{m}$ ).

Flow cytometer (FCM) was used to measure live/dead cell counts in the seawater. The mix stain of SYBR Green I (SGI) and Propidium Iodide (PI) was used to quantify the live cells in all samples points of all pilot-cooling towers.

The  $\text{UV}_{254}$  utilizing a 254 nm ultraviolet light source and the amount of light absorbed provides an ongoing indication of natural organic matter (NOM) in the seawater samples. More specifically,  $\text{UV}_{254}$  is the best detector of aromatic or reactive organics, which can form disinfection by-products (DBPs) when combined with chlorine.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) used for the detection of trace metals. Ion chromatography (IC) (Dionex IC 3000 model) allowed the separation of ions and polar molecules based on their affinity to the ion exchanger. A small volume of sample typically 2 to 3 mL was introduced into an ion chromatograph.

Disinfection by-products (DBPs) can result from reaction between organic and inorganic matter in water by chemical treatment agents during the water disinfection process. The DBPs were included; namely chlorite, chlorate and bromate trihalomethanes (THMs) and were analyzed using gas chromatography-mass spectrometer (GC-MS) with purge and trap (EPA 524.2) [77].

### 3.2.8 Liquid Chromatography - Organic Carbon Detection

To characterize the natural organic matter (NOM), Liquid chromatography-organic carbon detection (LC-OCD) was developed to identify quantitative information and qualitative results regarding organic compounds in natural water. LC-OCD model 8 system has UV detector (UVD), online organic carbon detector (OCD), and organic nitrogen detector (OND). In this study, the characteristics of different constituents of NOM identified are summarized in Table 3-6.

Table 3-6: Characteristics of different constituents of NOM.

NOM	Size (Da)
Biopolymers (BP)	> 20,000
Humics (HS)	≈1000
Building Blocks (BB)	300 - 450
LMW	<350

Biopolymer fraction is an important organic fouling. The low molecular weight (LMW) acids fraction consists of simple acids (e.g., acetic acid) and can be considered as a surrogate for AOC. Seawater samples were filtered Whatman filter (pore size = 0.45 μm). in 20-mL glass vials. Then, Compounds were separated using two-column size (250 × 20 mm, Toyopearl TSK HW-50S).

### 3.3 GAC column:

The bio-filter was tested in a pilot-scale seawater cooling towers, this experiments were conducted to evaluate AOC and DOC removal efficiencies using GAC as fillers. Characteristics of GAC filter filling materials were presented on Table 3-6. The GAC column biofiltration experimental set-up is demonstrated in Figure 3-15. Two transparent acrylic cylinder filter columns, which had a diameter of 12 cm and a height of 150 cm were connected together and operated in parallel for makeup feed of the basin. The columns were filled up to a depth of 10 cm from the bottom with stone size 5 mm and following granular activated carbon (GAC) as the media, which was filled up to 100 cm in height (6 kg) respectively, were used in the column test. The empty bed contact time (EBCT) of the bio-filter was about 7.5 min. The nominal size (d50) of GAC (1.03 mm) whereas surface area of GAC ( $1000 \pm 50$  m<sup>2</sup>/g). These specifications of media were provided from the supplier (Galgon Carbon). The filters were operated at flow rate 1.5 l/min to maintain a stable bacterial activity. The bio-filters were backwashed infrequently at flow rate 3 l/m for 15 min. The influent seawater used in the column test was from the intake system of the RO desalination unit and the filtration rate was 8 m/ h. The GAC column filter was referred in this research to as a bio-filter.

Table 3-7: Characteristics of GAC filter.

Specification	Values
Nominal size (d50, mm)	1.03
Bulk density (kg/m <sup>3</sup> )	540
Surface area (m <sup>2</sup> /g)	1000 ± 50
Nominal size (d10, mm)	0.54
Colour	Black

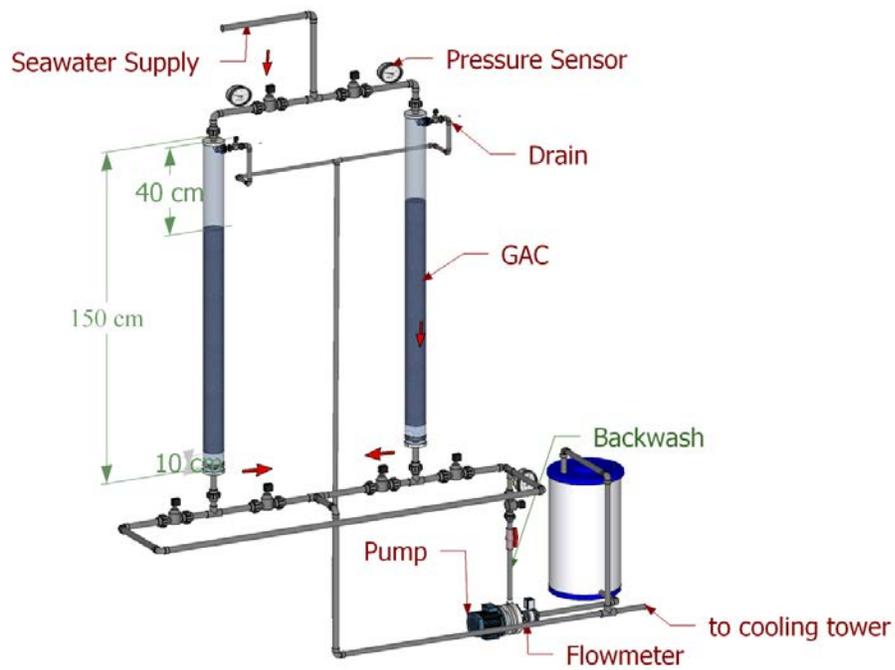


Figure 3-15: GAC bio-filter unit diagram.

### 3.4 Ultrafiltration:

The UF membrane module unit (WMZ-12521A-216) as well as the control system was supplied by Applied Membrane INC, is a kind of hollow-fiber membrane module in a PVC membrane vessel was used in the experiment. Characteristics of the membranes are shown in Table 3-8. The unit consists of one membrane vessel 10.2 cm diameter by 51.5 cm length UF membrane module and control system. The flow of the feed water was from inside of the fiber to the outside of the fiber. Figure 3-16 illustrates a schematic diagram of the UF membrane unit experimental facility. The seawater was pumped to the UF membranes for direct UF, because of high turbidity of feed seawater the pretreatment by cartage filter (size 5  $\mu\text{m}$  and 1  $\mu\text{m}$ ) respectively were applied before the UF unit. In the backwash phase, a controller equipped on the unit, controlled the Backwash of the UF membrane unit module. The washing water was sent to be pressurized from the outside to the inside of the UF (duration of 60 s) was made during a 48 h interval.

Table 3-8: Characteristics of the membrane.

Item	Value
Nominal Capacity GPD	1600
System Capacity m <sup>3</sup> /day	6.06
Material	PVDF
Minimum, dynamic psig	40
Maximum, dynamic psig	100
System diameter cm	L 71, D 30, H 66
Membran Element size, (Dia.*L)	2.5 * 21
UF size	0.02 micron

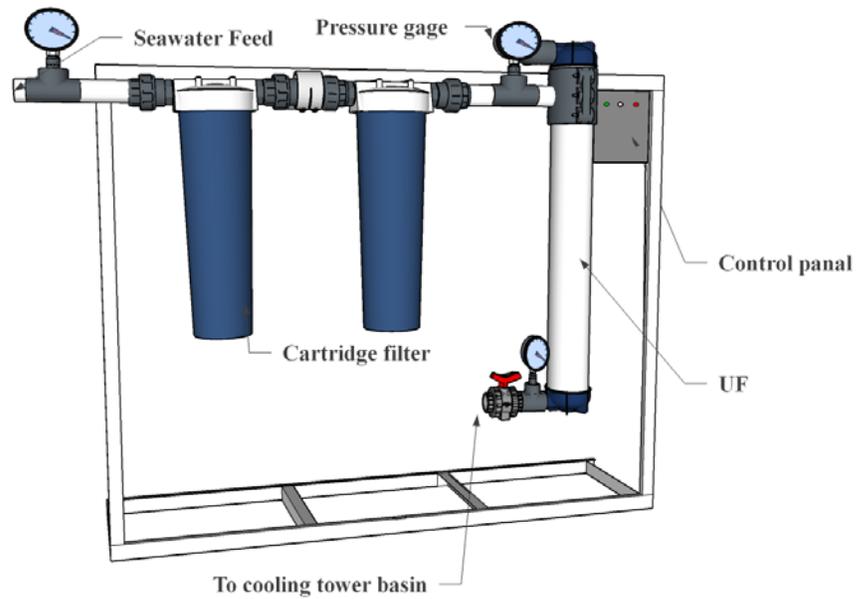


Figure 3-16: Ultrafiltration diagram.

### 3.5 Hybrid (GAC/UF) system:

The bio-filter was tested in a pilot-scale seawater cooling towers, and experiments were conducted to improve AOC and DOC removal efficiencies using a hybrid (GAC/UF) system as a bio-filter. Characteristics of the hybrid (GAC/UF) system bio-filter filling materials were presented in Table 3-9. The hybrid system biofiltration experimental set-up is demonstrated in Figure 3-17. Two transparent acrylic cylinder filter columns, which had a diameter of 12 cm and a height of 150 cm were connected together in parallel for makeup feed. The columns were filled up 100 cm in height (6 kg) respectively, and following UF membrane module unit (WMZ-12521A-216) supplied by Applied Membrane INC, is a kind of hollow-fiber membrane module in a PVC membrane vessel.

Table 3-9: Characteristics of the hybrid (GAC/UF) system.

Specification (GAC)	Values	Specification (UF)	Values
Nominal size (d50, mm)	1.03	Nominal Capacity GPD	1600
Bulk density (kg/m <sup>3</sup> )	540	System Capacity m <sup>3</sup> /day	6.06
Surface area (m <sup>2</sup> /g)	1000 ± 50	Minimum/Maximum, dynamic psig	40/ 100
		System diameter cm	L 71, D 30, H 66
		Membrane Element size, (Dia.*L)	2.5 * 21

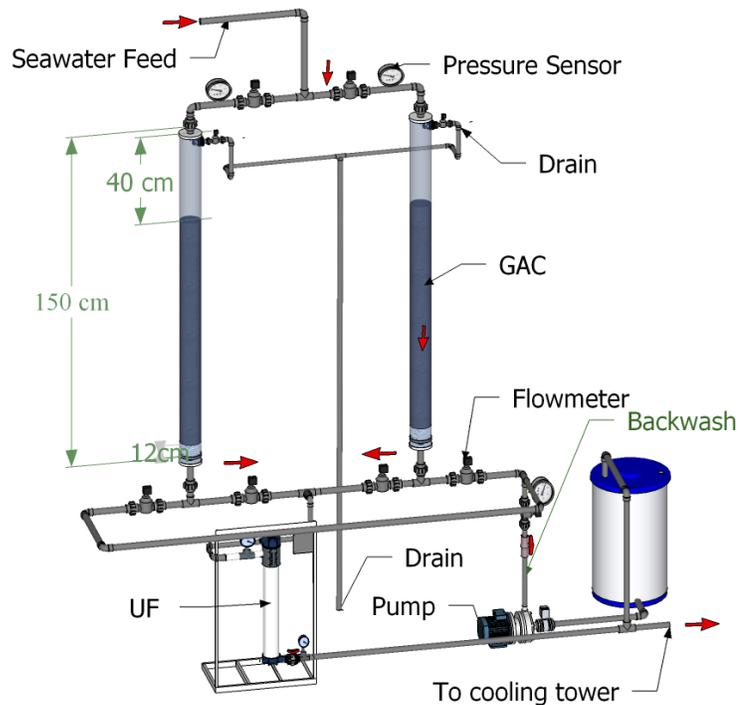


Figure 3-17: Hybrid (GAC/UF) system pretreatment diagram.

The empty bed contact time (EBCT) of the GAC bio-filter was about 7.5 min. The nominal size ( $d_{50}$ ) of GAC (1.03 mm) whereas surface area of GAC ( $1000 \pm 50 \text{ m}^2/\text{g}$ ). The GAC bio-filter was backwash infrequently at flow rate 3 l/m for 15 min. The UF unit consists of one membrane vessel 10.2 cm diameter by 51.5 cm length UF membrane module and control system. The Backwash of the UF membrane unit module (duration of 60 s) was made during a 48 h interval. The hybrid (GAC/UF) systems were operated at flow rate  $1.5 \text{ l/min} \pm 0.3$  and the filtration rate was 8 m/ h.

## **Chapter 4**

### **4 Publication # 1**

The following publication, “Performance assessment of oxidants as a biocide for biofouling control in industrial seawater cooling towers”, written by Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Sari. Alsayegh, Kim Choon NG, Gary.L. Amy, and TorOve. Leiknes, was published in 2017 in Journal of Industrial and Engineering Chemistry.

## **Performance assessment of oxidants as a biocide for biofouling control in industrial seawater cooling towers**

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### 4.1 Abstract

The use of seawater in cooling towers for industrial installations has rapidly increased, particularly in the acute-water-stressed Middle East countries where annual water availability per capita is less than 300 m<sup>3</sup>. Compared to the commonly used once-through cooling systems, cooling towers have several advantages; (i) lower pumping cost, (ii) lower temperature in the water supplied (close to the dew point of ambient air), and (iii) no thermal pollution discharged to the sea. However, operating challenges include

scaling, corrosion, and biofouling depending on the quality of the seawater feed. Among them, biofouling is a critical issue and can significantly hamper the efficiency of seawater cooling towers. The aim of this study was to investigate the effectiveness of alternative oxidants (e.g. ozone and chlorine dioxide) compared to the more common use of chlorine to control biofouling in seawater cooling towers. Effects of seawater temperature, cycle of concentration (COC) and oxidant dosage along with residual decay and kinetics were studied as these parameters are important for cooling tower operation. At lower oxidant dosage (total residual oxidant equivalent = 0.1 mg/L Cl<sub>2</sub>), chlorine dioxide showed a better disinfection effect compared to chlorine and ozone. However, at higher dosages all tested oxidants had a similar disinfection capability. Results derived from the bench-scale study were relevant in cooling tower operation, the selection of appropriate disinfectant and its types, and developing design criteria for full-scale implementation from pilot and/or demonstration-scale.

**Keywords:** Biofouling; Biocide; Cooling tower; Disinfection; Oxidants; Seawater.

## 4.2 Introduction

The use of seawater as an alternative make-up water in cooling tower systems has rapidly increased over last decades. In the Gulf Cooperating Council (GCC) countries, seawater is readily available as a process-cooling medium. In particular, operating cooling towers with seawater is deemed most suitable in Saudi Arabia as there is a scarcity of freshwater and groundwater resources. Currently seawater is being used as a cooling medium in systems up to thousands m<sup>3</sup> of make-up water

capacity, particularly in heavy industries, oil refineries, petrochemical plants, and thermal power stations. Conventional seawater cooling has been achieved using a once through cooling system in process industries, removing process heat via heat exchangers and discharging back into the sea [1]. However, such systems have suffered from high pumping costs and ambient-dependent seawater temperature. Recycling cooling systems offer better solutions because of much lower flow rates required, primarily higher potential effect from evaporation, as well as minimizing thermal pollution of coastal waters [2-5]. Seawater cooling towers have faced more challenges compared to systems using freshwater, particularly due to high scaling and fouling potentials caused by higher dissolved cations and anions present in seawater (e.g.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.), as well as a small reduction in the evaporation rate as a function of high salt content [6]. Moreover, organic and inorganic contents in seawater fed to cooling towers make them prone to corrosion and biofouling [7]. Key factors promoting biofilm formation and algal growth within the cooling towers are; (i) open and large surface areas of packing and filler materials, (ii) direct exposure to ambient air and sunlight, and (iii) concentration of nutrients as water evaporates. Biofouling (i.e. biofilm formation/growth) and scaling in cooling tower pipes, basin and heat exchangers can also lead to significant reduction in heat transfer efficiencies [8, 9]. A previous report shows that annual maintenance costs of undesired scaling and fouling of cooling towers can be up to billions of dollars [4]. In addition, disinfection is needed to inactivate and control the potential growth of pathogenic organisms, *Legionella pneumophila* in particular [10], as microbial communities thrive in

cooling towers due to the warmer water temperatures and excessive nutrients in the tower basins [11].

Chlorination is one of the well-known biofouling control methods and commonly being applied in many places. An advantage of chlorination is inactivation of a wide range of pathogens and microorganisms while maintaining a period of positive disinfection residual within pipelines and the systems. However, an excessive chlorination may cause the formation of harmful disinfection byproducts (DBPs), where 1 % dosage of chlorine in the cooling tower systems can react to form trihalomethanes, haloacetate- trails, halocarbons, halophenols and haloacetic acids [12]. Moreover, DBPs are readily formed in the presence of high organic loading, which is common in cooling tower operations. Although a continuous chlorine dosage of 0.2 mg/L suppresses mussels growth in seawater [13], it also results in DBPs formation which is a major environmental concern. Even with these concerns, continuous high chlorination for mussel infested intake pipes is recommended and intermittent chlorination is not sufficient in controlling mold [14]. Free chlorine is effective in inactivating microbes, however, it has reported that degradation of humic acid and organic matter during chlorination can enhance bacterial regrowth [15]. Trihalomethanes (THM) formation can be reduced in the cooling tower by targeting appropriate dose of chlorination at certain times [16].

Ozone has been used as an oxidant for drinking water disinfectant since the late 1800s [17]. Ozone is known to be a highly efficient disinfectant in drinking water, with a reactivity level up to 300 times greater than chlorine at the same dosage

concentration [18]. However, there is limited information in the literature concerning fouling control with ozone in seawater intake pipes. Sugita et al. (1992) claimed that a residual ozone equivalent of 1.0 mg/L of total residual oxidant (TRO) was sufficient to disinfect seawater for marine culture [19]. Ikegami et al (2006) reported that a lower ozone concentration range of 0.2 to 0.5 mg/L could be adequate to control fouling phenomena [18]. A study indicated that a high ozone dosage of 5 mg/L, applied less than 5 min per day, was a sufficient disinfection interval to keep the surfaces of titanium, aluminum, brass and epoxy coated PVC cooling tubes clean [20]. The ozone chemistry in seawater is significantly different than that in freshwater because of the presence of bromide [21]. Chlorine dioxide ( $\text{ClO}_2$ ) is an alternative oxidant that has been used for microbial control in seawater and drinking water disinfection [22, 23]. Agus et al. (2009) reported an increasing use of  $\text{ClO}_2$  as disinfectant in distillation plants in the Gulf region, particularly in the UAE [24]. The effectiveness of  $\text{ClO}_2$  can be similar to chlorine but applied at lower dosage concentrations. Key advantages compared to chlorine are; (i) less contact time, (ii) lower dosages needed for biofouling control, and (iii) good solubility in water. In addition,  $\text{ClO}_2$  does not react with bromides to form hypobromites and is more efficient at higher temperatures and pH [25, 26]. For these reasons,  $\text{ClO}_2$  is currently used as a disinfectant in many applications; dairy, fruit and vegetable, poultry, food, potable water treatment and industrial waste treatment [15]. Disinfection of oysters with  $\text{ClO}_2$  can extend the shelf life up to 12 days. Due to its lower reactivity with organic matter [27], it has been reported that THM formation in  $\text{ClO}_2$  treatment is lower compared to chlorine, however, it is

less favored in drinking water treatment due to the potential of harmful DBPs formation, as well as problems with taste and odor. Furthermore, it is known that  $\text{ClO}_2$  is less efficient against protozoa like *Cryptosporidium*.

As mentioned earlier, the research was initiated in addressing several industrial seawater cooling tower facilities' issues in Middle East countries (i.e. Saudi Arabia) where are using sodium hypochlorite (i.e., chlorine) generation systems in controlling the biofouling and microbial fouling. Recently, the environmental regulation of TRO at seawater cooling tower discharge has been lowered to 0.2 mg/L. This change affects the performance of the chlorination in the biofouling control in the cooling towers. The goal of this research, therefore, is to find alternative chemical disinfect to meet the environmental regulation (0.2 mg/L of TRO at discharge) with high performance of biofouling control.

In this regard, the study was started with two alternative oxidants;  $\text{O}_3$  and  $\text{ClO}_2$  comparing with an existing disinfectant type, sodium hypochlorite and to assess their performances in seawater cooling towers for biofouling mitigation and control. The results shows the comparison between the three oxidants revealed that chlorine dioxide performed the best (in terms of TRO) compared to chlorine and ozone, which is one of key important findings.

### 4.3 Methodology

#### 4.3.1 Bench-scale setup

A laboratory bench-scale study was carried out to assess various key factors in seawater cooling tower operation. The customized batch reactor is mainly made of glass with inlet and outlet of hot water, temperature probe, oxidant injection, and operated by using real seawater, same as the cooling tower feed. (Figure 4-1). The batch reactor was placed on a magnetic stirrer to ensure completely mixed conditions. The bench-scale studies were conducted in theoretical steady-state conditions for a full-scale plant as shown in Figure 4-2. The customized batch reactor was designed to investigate three parameters; effects of cycle of concentration, temperature and oxidant dosage along with residual decay and kinetics that might improve the feed seawater quality. This lab scale design is not to simulate the pilot cooling tower design, rather to study the above parameters that affecting the operational conditions of the cooling tower to improve the pretreatment efficacy.

Tests were conducted at two temperatures (e.g. 32°C for inlet seawater, 48°C for outlet seawater) to emulate the cooling tower return water temperatures by using thermal baths and heat exchanger (HEX).

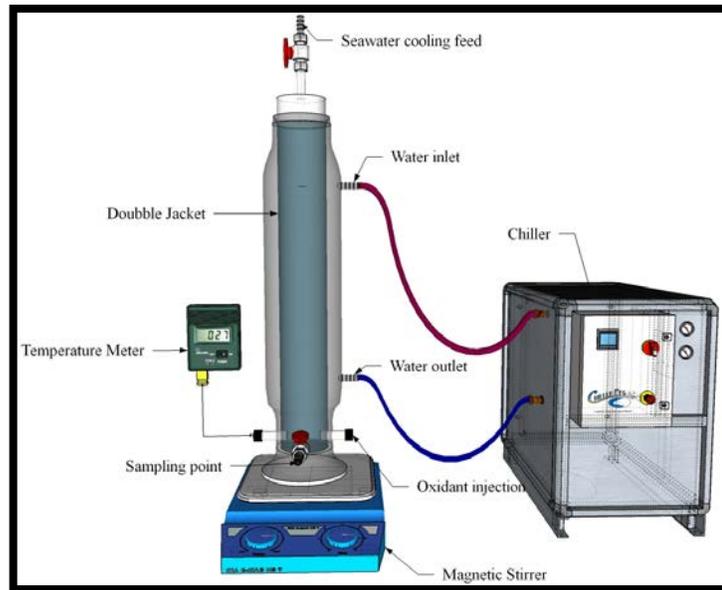


Figure 4-1: Double jacket bench reactor for decay tests.

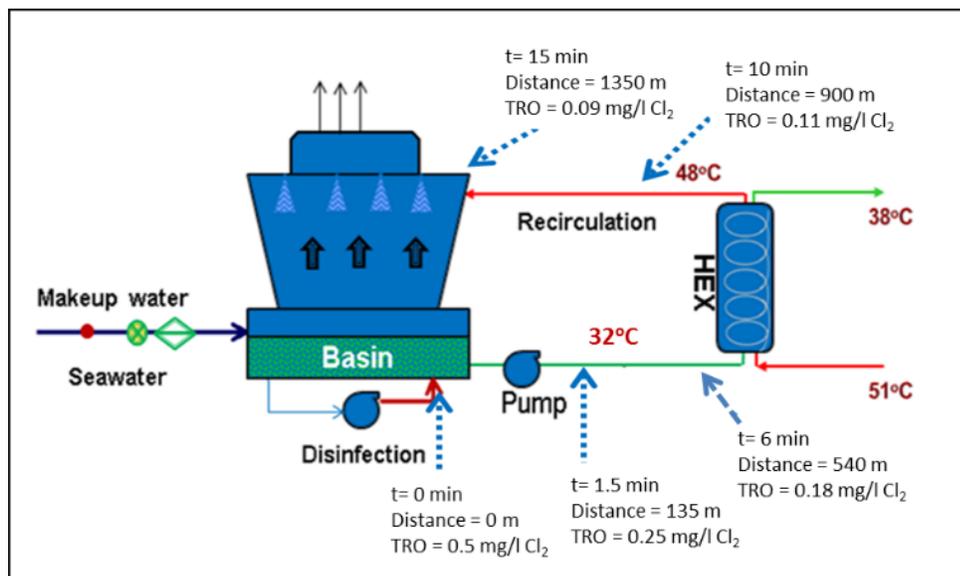


Figure 4-2: Equivalent TRO decay kinetics in cooling tower pipe network.

#### 4.3.2 Methods

The study investigated i) the effect of the cycle of concentrations (COC) of seawater cooling towers (defined as the ratio of the concentration of chlorides in make-up water to the concentration of chlorides in recirculating water) at varied levels of seawater temperature and oxidant dosages, and ii) the impact on residual disinfectant decay (TRO). TRO readings were measured using disinfection by-product (DPD) powder pillows (spectrophotometric; DPD Method 8167). For ease of comparison, dosage and residual measurements for all the oxidants are expressed in chlorine equivalents ( $\text{mg/L Cl}_2$ ) using suitable conversion factors for ozone and chlorine dioxide respectively (e.g.  $1 \text{ mg/L Cl}_2 = 0.67 \text{ mg/L O}_3 = 1.9 \text{ mg/L ClO}_2$ ). Different COCs of Red Seawater samples (e.g.  $\text{COC} = 1.25$  and  $\text{COC} = 1.50$ ; measured by seawater electrical conductivity) were prepared using a rotary evaporator. A set of oxidant dosages ranging from  $0.1 - 0.5 \text{ mg/L Cl}_2$  for chlorination,  $0.067 - 0.335 \text{ mg/L O}_3$  for ozonation and  $0.19 - 0.95 \text{ mg/L ClO}_2$  for chlorine dioxide were injected into the seawater feed. To maintain the dosage rate for these oxidants, a standard method (USEPA DPD Method 8021) was targeted to control sodium hypochlorite (chlorination) by using the free chlorine powder pillows test, while the indigo method (Hach's AccuVac Ampules; Method 8311) was implemented to measure the ozonation. Chlorine dioxide stock solution was prepared by adding sulfuric acid to sodium chlorite solution (Standard Method 4500-ClO<sub>2</sub>) and then verifying the dosing rate by using DPD powder pillows (Method 10126).

Table 4-1 shows the test matrix used for monitoring the TRO decay. For each test, TRO residuals were measured at different time intervals 1.5, 3.0, 6.0, 10.0 and 15.0 min after oxidant injection. Over 80 different combinations were performed during TRO decay studies.

Table 4-1 TRO decay test matrix for each oxidant at different COCs, temperatures and oxidant dosages.

Tests	COC	Temperature (°C)	Dosage (eqv. mg/L Cl <sub>2</sub> )
1	1.00	32	0.30
2			0.50
3			0.30
4			0.50
5	1.25	32	0.30
6			0.50
7			0.30
8			0.50
9	1.50	32	0.30
10			0.50
11			0.30
12			0.50

In addition, the P value of T-test was used to assess whether the experimental results are equal or not with what is observed. A small p-value ( $\leq 0.05$ ) indicates strong evidence and large p-value ( $> 0.05$ ) indicates weak evidence.

### 4.3.3 Laboratory Analysis

The efficiency of oxidants was determined by analyzing the cell viability, *i.e.* total live/dead cell counts of algae and bacteria in seawater, using a BD Accuri™ C6 Flow Cytometer (FCM). 1X of SYBR® Green I + 10 µg/ml of Propidium Iodide (PI) were used to stain live and dead cells, respectively. A 495 µl of water sample was transferred to a sterile Eppendorf tube and 5 µl of the 100X of SYBR® Green + 1000 µg/ml Propidium Iodide (PI) was added to the water sample. Then it was incubated at room temperature for 15 min. Prior to staining, sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) was added to each seawater sample to quench residual oxidants. Finally, 200 µl of the incubate sample was transferred to a 96-well plate for measurement (pump speed = medium, and FL1 threshold = 600).

Detailed characteristics of seawater used in this study can be found in supplementary information (Table S1).

## 4.4 Results and Discussion

Bench-scale studies was evaluated based on the following key factors; (i) the impact of cycle of concentration (COC) on overall oxidant demand, (ii) temperature impact on decay kinetics, (iii) residuals expectations with operational time during decay, and (iv) comparison of oxidant types and their performances.

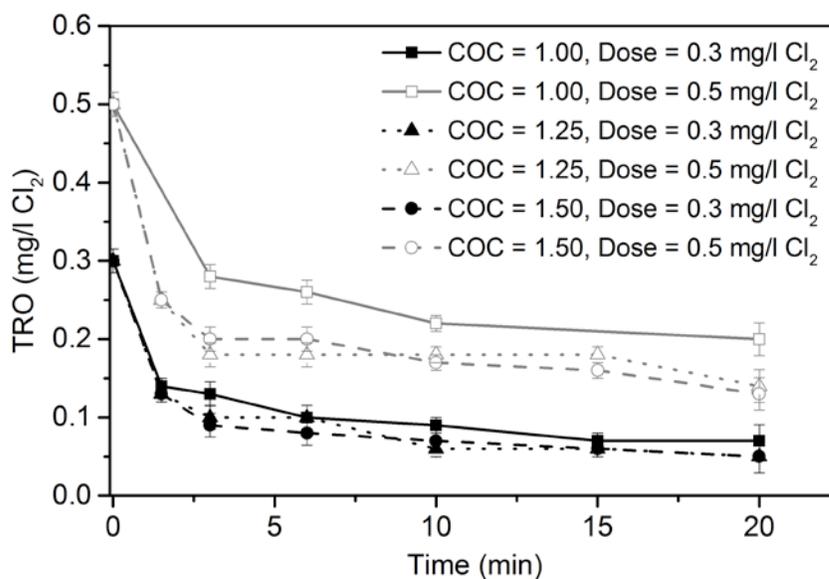
#### 4.4.1 Effect of COC on oxidant demands

Oxidants (e.g. chlorine) are usually dosed directly into the cooling towers basins. As evaporation of seawater in the basin increases the concentration of salt, the effect of COC on oxidant demand for elevated concentrations needs to be examined. Three COC levels were tested, initially on raw seawater with value 1.00 and then for values 1.25 and 1.50. Two temperatures of seawater were tested, 32°C and 48°C, emulating the basin feed water and the return water to the cooling tower basin after the heat exchanger. Figure 4-3a and Figure 4-3b demonstrate the TRO profiles for the conditions tested at 32°C and 48°C, respectively. It can be seen that conventional, a typical decay demand trends can be observed at all the conditions where suggested to follow first order kinetics. Moreover, the decay curves appear to follow a two-phase behavior, an initial rapid decay with a later slower decay. In fact, one could model such behavior as an initial zero-order decay over the first sampling interval, followed by first order decay.

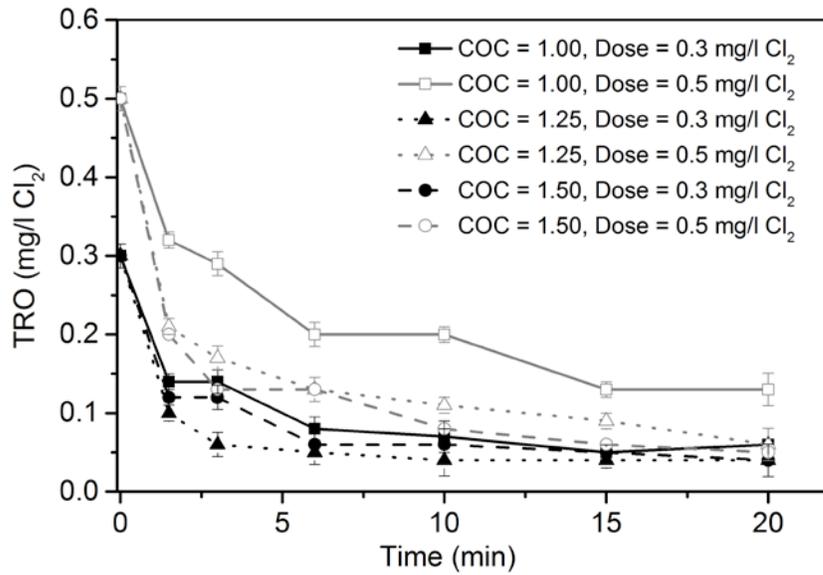
The rapid decline represents the reaction of the oxidant meeting the oxidant demand in seawater (0.2 ppm TRO at blowdown). Once the demand is met, the decay rate is found to drop gradually, maintaining a positive residual for a longer period than 15 min. Under these conditions positive residuals availability is maintained within the piping network.

As can be seen from Figures 3a and b, positive TRO values (around 0.09 mg/l Cl<sub>2</sub>) was maintained throughout the cooling tower system, which is a significant

implication on operations regarding biological growth, regrowth, and biofouling. At both temperatures, higher TRO values are observed in COC = 1.00 (raw seawater) compared to the other COCs. The lower TRO values obtained at COC = 1.25 and COC = 1.50 is attributed to the increase of organics and inorganics in the seawater due to the evaporation, leading to additional oxidant demand. Paired t-test statistical analyses were also performed on the data sets using Sigma Plot, where p values less than 0.05 indicates 95% confidence level of statistical significance. Table 4-2 shows the calculated p values for each case study. In all cases, a significant change in TRO was observed in raw seawater (COC = 1.00) and COC = 1.25. However, no significant TRO or chlorine demand was found in COC = 1.25 to COC=1.50, with an exception of 0.5 mg/L Cl<sub>2</sub> at 32 °C.



(a)



(b)

Figure 4-3: TRO decay after seawater chlorination at (a) 32°C and (b) 48°C at different COCs and oxidant dosages.

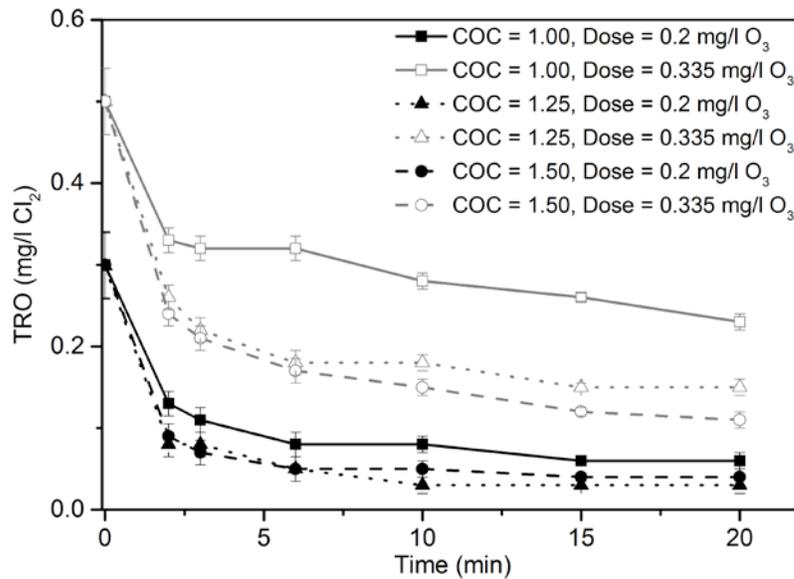
Table 4-2: Effect of chlorination at different COCs.

Dosage (mg/l Cl <sub>2</sub> )	Temperature (°C)	COC*	
		1.00 to 1.25	1.25 to 1.50
0.3	32	<b>p = 0.025</b>	p = 0.457
0.3	48	<b>p = 0.022</b>	p = 0.063
0.5	32	<b>p = 0.005</b>	p = 1.000
0.5	48	<b>p = 0.004</b>	<b>p = 0.030</b>

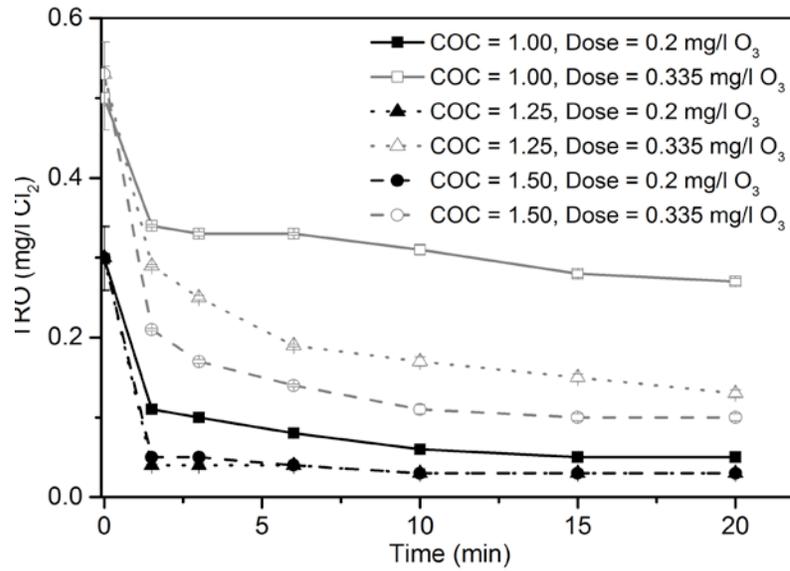
\* p indicates statistically significant difference between cases.

All of these results show that as seawater concentration increases due to higher COC levels (COC=1.25 and COC=1.50), there is no significant differences in chlorine demand or variation in temperature for the two conditions tested, however, this difference is more significant at higher levels of COC.

The same set of experiments was conducted using ozone as the oxidant. The TRO decay trends were expected to be similar to seawater chlorination as both oxidants produce free bromines (hypobromous acid and hypobromite ion) in high bromide-containing water [13]. Figure 4-4a and Figure 4-4b show the TRO decay profiles for seawater ozonation at 32oC and 48oC at ozone dosages of 0.200 mg/l O<sub>3</sub> (0.3 mg/l Cl<sub>2</sub>) and 0.335 mg/l O<sub>3</sub> (0.5 mg/l Cl<sub>2</sub>), respectively. The statistical p values obtained from the paired t-test of this ozonation study are shown in Table 4-3.



(a)



(b)

Figure 4-4: TRO decay after seawater ozonation at (a) 32°C and (b) 48°C at different COCs and dosages.

Table 4-3: Effect of ozonation at different COCs.

Dosage (mg/l Cl <sub>2</sub> )	Temperature (°C)	Cycle of Concentration*	
		1.00 vs 1.25	1.25 vs 1.50
0.2	32	<b>p = 0.002</b>	p = 0.154
0.2	48	<b>p = 0.011</b>	p = 0.500
0.335	32	<b>p = 0.002</b>	<b>p = 0.010</b>
0.335	48	<b>p = 0.031</b>	<b>p = 0.003</b>

p indicates statistically significant difference between cases.

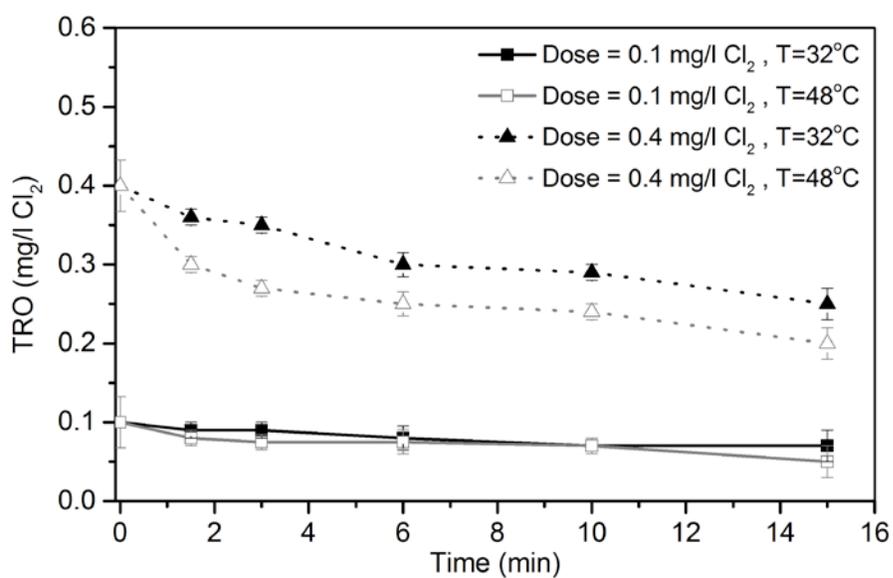
From the p values reported in Table 4-3 and TRO decay curves in Figure 4-4a and Figure 4-4b, the TRO values observed between the COC 1.00 (raw seawater) and

COC = 1.25 were found to be as expected. For comparison between COC = 1.25 and COC = 1.50, TRO values appear to differ at higher ozone dosage 0.335 mg/l O<sub>3</sub> (0.5 mg/l Cl<sub>2</sub>). This could be due to more rapid reaction of ozone in seawater during the initial few seconds after injection (ozone half-life in seawater is 5.7 s).

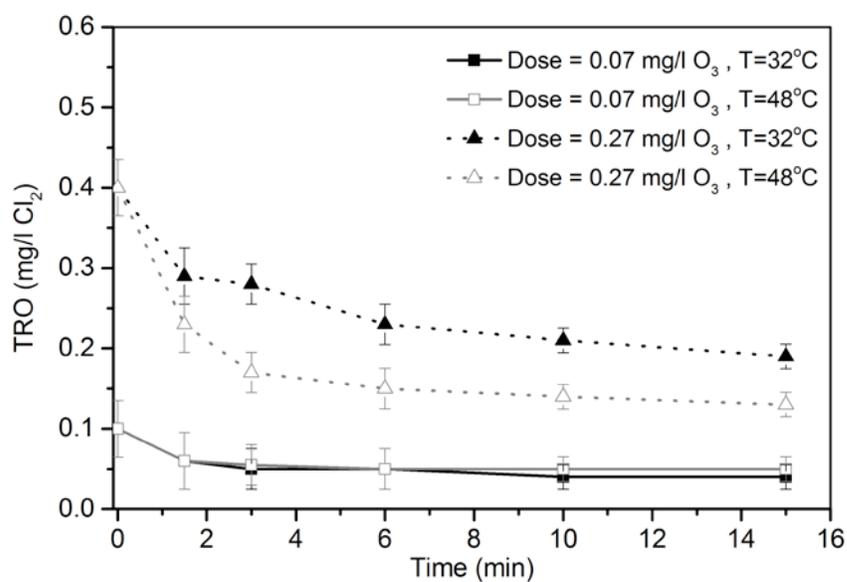
#### 4.4.2 Effect of temperature on oxidant demands

As cooling towers operate at various temperature conditions (e.g. due to process load variation, day and night variation, summer and winter variation), it is also important to study the effect of temperature on TRO decay. In addition to chlorine and ozone, chlorine dioxide was included in an assessment of temperature effects. The oxidants were injected at two different dosages (equivalent 0.1 mg/l Cl<sub>2</sub> and 0.4 mg/l Cl<sub>2</sub>) and temperatures (32°C, 48°C) at constant COC of 1.20 ±0.05. Decay curves for the three oxidants are presented in Figure 4-5. Comparative statistics using p values at 95% confidence level are given in Table 4-4. At higher oxidant dosages, all the oxidants exhibited lower TRO values at the higher temperature (48°C). Hence, higher positive residuals could be maintained at lower temperature due to the lower first-order reaction kinetics. This is confirmed from the slopes of the TRO decays during the first 2 min after injection. A similar trend was observed for the lower oxidant dosages even though too small to observe a clear TRO decay trend. The results show that there was an effect on oxidant decay, which can affect residual levels under low temperature operation. For example, above findings suggest that a lower decay or

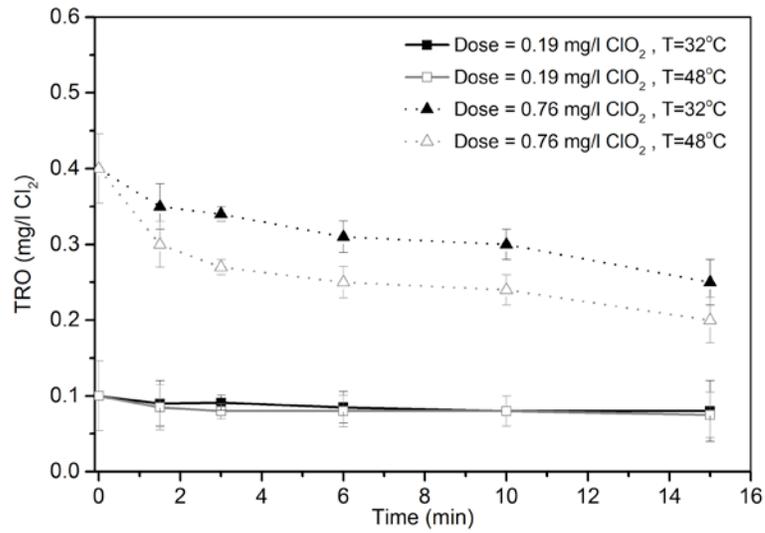
higher residuals are expected if the oxidant is applied in the basin rather than after the heat exchanger for an equivalent dose.



(a)



(b)



(c)

Figure 4-5: TRO decay profile for (a) chlorine, (b) ozone and (c) chlorine dioxide in seawater at different oxidant dosages and temperatures.

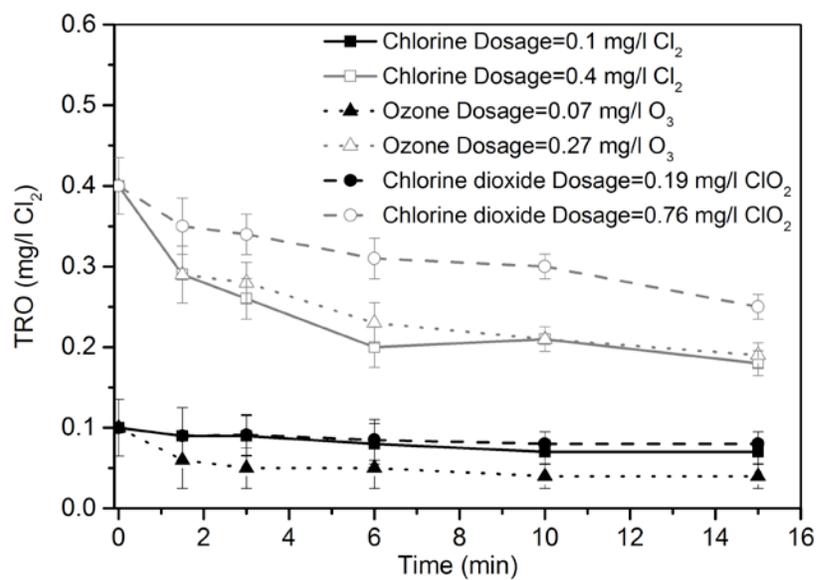
Table 4-4: Effect of temperature at different oxidant dosages.

Oxidants	Eqv. Dosage (mg/l Cl <sub>2</sub> )	Temperature* 32°C vs. 48°C
Chlorine	0.1	<b>p = 0.041</b>
	0.4	<b>p = 0.006</b>
Ozone	0.1 (0.07 mg/l O <sub>3</sub> )	p = 0.346
	0.4 (0.27 mg/l O <sub>3</sub> )	<b>p = 0.007</b>
Chlorine Dioxide	0.1 (0.19 mg/l ClO <sub>2</sub> )	<b>p = 0.041</b>
	0.4 (0.76 mg/l ClO <sub>2</sub> )	<b>p = 0.006</b>

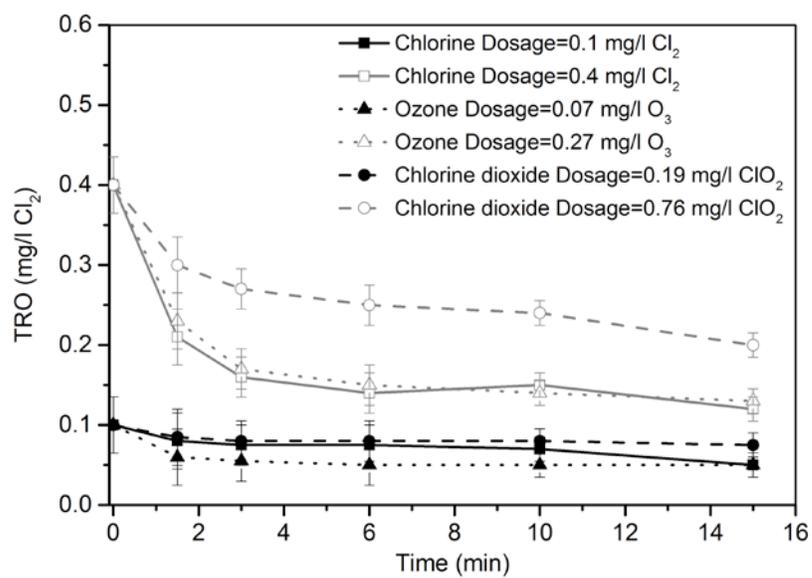
p indicates statistically significant difference between cases.

#### 4.4.3 Comparison of total residual oxidants (TRO) between oxidants

Figure 4-6 demonstrates the decay profiles at two temperatures (32°C and 48°C) and dosages (eqv. 0.1 mg/l Cl<sub>2</sub> and 0.4 mg/l Cl<sub>2</sub>) at constant COC of 1.20 ±0.05. A paired t-test analysis presented in Table 4-5 clearly indicates there are no significant difference between the chlorine (TRO 0.12 mg/l Cl<sub>2</sub> at 42 °C) and ozone (TRO 0.13 mg/l Cl<sub>2</sub> at 42 °C) at all the conditions tested. This is probably due to ozone and chlorine reacting with bromide in seawater and forming bromine, which is a secondary disinfectant. At lower dosage (eqv. 0.1 mg/l Cl<sub>2</sub>), the TRO decay for all the oxidants was almost the same. This is attributed to the oxidant dosages being too low and barely satisfying the seawater demand. However, at the higher dosage (eqv. 0.4 mg/l Cl<sub>2</sub>) the TRO value for chlorine dioxide was higher (e.g., lower decay rate) than for chlorine and ozone for both temperature conditions (32°C and 48°C). As chlorine dioxide is a very selective oxidant, a more positive residual available for disinfection was expected. This is due to that chlorine dioxide has different reaction mechanisms compared to chlorine and ozone, resulting in residuals lasting for a longer time due to its selectivity [28, 29]. All the above results are significant in choosing the appropriate oxidant for the cooling tower operation.



(a)



(b)

Figure 4-6: TRO decay comparison for chlorine, ozone and chlorine dioxide at (a) 32°C and (b) 48°C.

Table 4-5: Comparison of oxidant residuals in seawater.

Dosage (mg/l Cl <sub>2</sub> )	Temperature (°C)	Oxidant*	
		Chlorine vs. Ozone	Chlorine vs. Chlorine Dioxide
0.1	32.0	p = 0.063	p = 1.000
	48.0	p = 0.063	p = 0.346
0.4	32.0	p = 0.250	<b>p = 0.006</b>
	48.0	p = 0.438	<b>p = 0.006</b>

\* p indicates statistically significant difference between cases.

#### 4.4.4 Microbial analyses – Cell viability

Effectiveness of oxidant as a biocide was evaluated in terms of cell viability (*i.e.* viable cell counts), quantified by using a flow cytometer. Analysis was conducted for the operating condition COC = 1.20 ±0.05, and T = 32°C and 48°C, and equivalent dosages 0.1 and 0.4 mg/l Cl<sub>2</sub>. A rapid decrease in bacterial cell counts was observed after injection of each oxidant at the lower temperature (32°C) and higher oxidant dose (Figure 4-7). Despite the difference in mortality rates, all three oxidants achieved viable cell counts lower than 3 cells/μL within 10 min. A summary of viable cell counts for all test conditions is presented in Table 4-6. At higher dosages (eqv. 0.4 mg/l Cl<sub>2</sub>), all three oxidants achieved similar mortality rates. Higher mortality rates were observed at the higher temperature of 48°C for all the dosages. Values for the low dosage (eqv. 0.1 mg/l Cl<sub>2</sub>) indicate insufficient disinfection efficiency of all oxidants, however, chlorine dioxide was found to be more effective

than ozone and chlorine. The findings in this study show the effect of residual oxidant concentrations on the biofouling control and its dependence on the temperature.

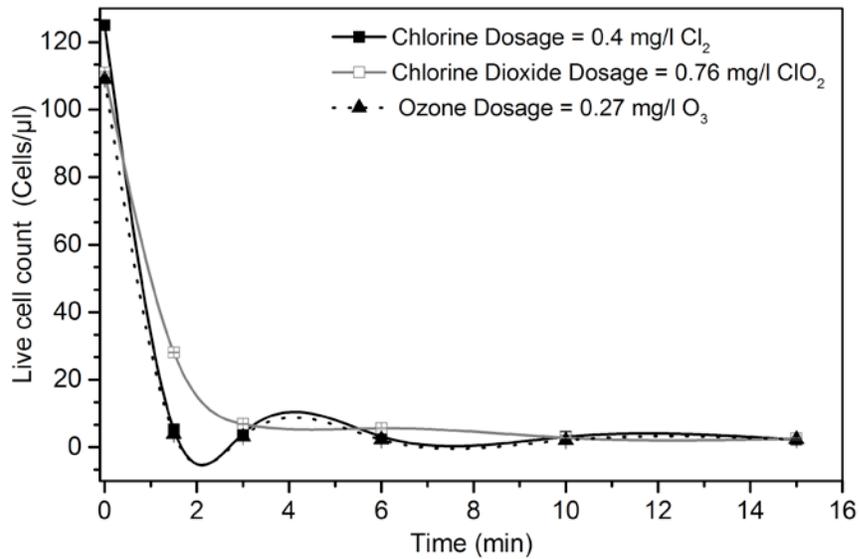


Figure 4-7: Live cell counts after injection of chlorine, ozone and chlorine dioxide into the seawater as function of time.

Table 4-6: Viable cell counts after 10 min of oxidant dosing (unit: cells/μL).

Oxidant	Dosage (mg/l Cl <sub>2</sub> )	Temperature	
		32°C	48°C
Chlorine	0.1	34.3	25.2
Ozone	0.1 (0.07 mg/l O <sub>3</sub> )	56.0	24.5
Chlorine Dioxide	0.1 (0.19 mg/l ClO <sub>2</sub> )	19.2	8.1
Chlorine	0.4	2.8	2.5

Ozone	0.4 (0.27 mg/l O <sub>3</sub> )	2.1	1.5
Chlorine Dioxide	0.4 (0.76 mg/l ClO <sub>2</sub> )	2.8	1.8

#### 4.5 Conclusions

This research work analyzes and evaluates O<sub>3</sub> and ClO<sub>2</sub> as alternative disinfectants to chlorine in the treatment of seawater cooling towers at bench scale. The bench-scale study was conducted in assessing various key factors that are important to the cooling tower operation under laboratory condition. A customized and simulated batch reactor was assembled and utilized in assessing comparative oxidant behaviors and decay behavior under well-defined controlled experimental conditions. The bench-scale testing was conducted for identifying some of parameters and factors that are critical to provide greater insights into the cooling tower operations. The impact of COC on overall oxidant demand, temperature on decay kinetics, and residuals expectations with operational time during decay and, comparison of oxidant types and their performances were studied.

Followings are some of the key findings from the bench-scale assessment.

- It was found that additional oxidant was demanded when the seawater is concentrated (due to cooling tower operation, i.e., at higher COC).
- Higher temperature also led to the dissipation of TRO (implication of oxidant addition at various stages of cooling tower operation).

Comparing three oxidants revealed that ClO<sub>2</sub> has a higher TRO values than chlorine and O<sub>3</sub> at higher dosages

In terms of viable cell counts, ClO<sub>2</sub> also yielded higher disinfection rate at very low oxidant dosage. However, at higher dosages (eqv. 0.4 mg/L Cl<sub>2</sub>) all the oxidants have comparable mortality rates

All of these above findings and assessment of these oxidants obtained from bench-scale study. However, further study is needed under a more realistic condition for the full-scale implementation.

#### 4.6 Acknowledgements

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## 4.8 Supplementary

Table S1: Characteristics of Red Sea water.

Parameter	Value	Parameter	Value
pH (SU)	8.13	UVA254 (1/cm)	0.016
Temperature (°C)	26.4	SUVA (L/mg-m)	1.4
TDS (mg/l)	38,000	Bromide (mg/l)	71.0
Conductivity (mS/cm)	60.0	Chloride (mg/l)	23,624
Turbidity (NTU)	5.34	Fluoride (mg/l)	1.3
ORP (mV)	147	Nitrite as NO <sub>2</sub> - (mg/l)	0.0047
Total Alkalinity (mg/l as CaCO <sub>3</sub> )	120	Ortho-P as PO <sub>4</sub> -3 (mg/l)	0.1
Total Hardness (mg/l as CaCO <sub>3</sub> )	7,500	Sulfate (mg/l)	2,650
Mg Hardness (mg/l as CaCO <sub>3</sub> )	6,300	Silica (mg/l)	0.13
Ca Hardness (mg/l as CaCO <sub>3</sub> )	1,200	Sodium (mg/l)	12,000
DOC (mg/l)	1.101	Potassium (mg/l)	560
Total Iron (mg/l)	0.02	Chromium (mg/l)	0.1749E-2
Boron (mg/l)	4.6	Copper (mg/l)	0.5235E-4
Aluminum (mg/l)	0.1214E-1	Lead (mg/l)	0.1902E-4
Antimony (mg/l)	0.2232E-4	Lithium (mg/l)	0.03207
Arsenic (mg/l)	0.6108E-3	Manganese (mg/l)	0.1541E-2
Barium (mg/l)	0.522E-2	Molybdenum (mg/l)	0.0001625
Cadmium (mg/l)	0.1295E04	Nickel (mg/l)	0.01628
Chromium (mg/l)	0.1749E-2	Selenium (mg/l)	0.03042
Copper (mg/l)	0.5235E-4	Silver (mg/l)	ND
Lead (mg/l)	0.1902E-4		
Total Iron (mg/l)	0.02		

## **Chapter 5**

### **5 Publication No # 2**

The following publication, “Effect of organic on chemical oxidation for biofouling control in pilot-scale seawater cooling towers”, written by Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Gary.L. Amy, and TorOve. Leiknes, was published in 2017 in Journal of Journal of Water Process Engineering, Article reference: DOI information: 10.1016/j.jwpe.2017.09.002.

**Effect of organic on chemical oxidation for biofouling control in pilot-scale seawater cooling towers**

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## 5.1 Abstract

Due to the scarcity of potable water in many regions of the world, the demand for seawater as an alternative evaporative cooling medium in cooling towers (CTs) has increased significantly in recent years. Seawater make-up in CTs is deemed the most feasible because of its unlimited supply in the coastal areas of Gulf and Red Sea. However, the seawater CTs have higher challenges greatly mitigating their performances because it is an open system where biofouling and bio-corrosion occurring within the fillers and piping of recirculation systems. Their pilot-scale CTs were constructed to assess the performance of three types of oxidizing biocides or oxidants, namely chlorine, chlorine dioxide (ClO<sub>2</sub>) and ozone, for biofouling control. The test results showed that

the addition of organic (5 mg/L of methanol MeOH) increased the bacterial growth in CT basin. All oxidants were effective in keeping the microbial growth to the minimum. Oxidation increased the ORP level from 270 to 600 mV. Total residual oxidant was increased with oxidation but it was slightly increased with organic addition. Other parameters including pH, DO, conductivity levels were not changed. However, higher formation of disinfection by-products (DBPs) was detected with chlorination and ozonation. This indicates the organic level should be limited in the oxidation for biofouling control in seawater CTs.

**Keywords:** Biofouling; Disinfection; Organic; Oxidants; Seawater cooling tower

## 5.2 Introduction

Cooling water systems control temperatures by transferring heat from a hot line process into cooling water to remove the heat. Thus, the cooling water is heated up and it must be either cooled down before it is reused or replaced with fresh makeup water ( Figure 5-1) [1]. Typically, 80 to 90% of heat energy is removed from the cooling water by evaporation [2]. The efficiency of cooling water systems depends on the types of process applied, the water characteristics and environmental aspects [3]. Most industrial production processes, such as refineries, steel mills, petrochemical plants, chemical processing plants, and electric utilities, need cooling water for their efficient and proper operation. [4]. The two main types of cooling towers (CTs) are natural draft and mechanical draft. In mechanical draft CT the air is forced through circulation water by using large fans. Hot water is dropped from the top of a CT over a fill surface, helping to

increase the contact time between the water and the air, which helps to cool the water [5]. It is important to evaluate the performance of CTs, to assess the levels against their design values, and to identify areas of energy wastage for system improvements [1, 5].

Seawater CTs have proven to offer numerous advantages over conventional once-through systems. Due to the greater dissolved mineral content (e.g. sodium, magnesium, calcium, potassium, chlorite, sulfate, etc.) contained in seawater, it has been estimated that the performance of seawater CTs will drop by 1% per every 1% increase in salt content in the cooling water [6]. In addition, the evaporation concentrates nutrient levels (e.g. organic carbon, nitrate, nitrite, phosphates, etc.) in seawater, hence promoting the biofilm formation. Biofilm and microbial growth (commonly referred to as biofouling) in cooling water systems can be quite severe and decreases heat transfer efficiencies [7].

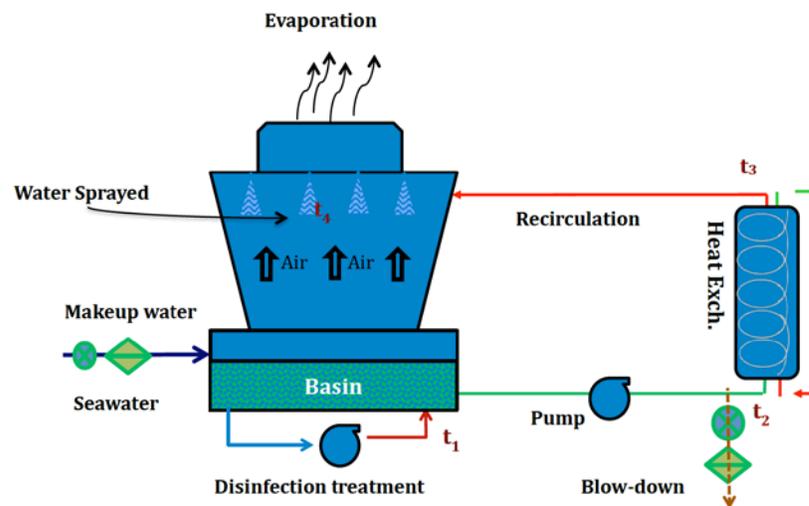


Figure 5-1: Schematic diagram of a cooling water system.

Subsequently, biofouling can reduce the lifetime of CTs systems, result in reduced

capacity, increased operation and maintenance costs, cause expensive parts replacements, and increase water usage [8-10]. It has also been reported that invasion of zebra mussels in CT intake systems requires \$1 billion in damages and control costs annually in the United States [11]. Biofouling in CT systems is mainly caused by the growth of algae and bacteria in the process. This is accelerated in open recirculating water systems compared to closed systems [8]. A number of microorganisms (algae, protozoa, and bacteria) can grow and exist in a CT system under certain conditions [12, 13].

Chemical oxidants (e.g. chlorine, chloramines, ozone, chlorine dioxide) are often employed in water treatment to inactivate microorganisms and inhibit biofilm formation [14]. One of the most popular methods to control biofouling in CT processes is chlorination. Chlorine has also been reported to control growth of mussels with a continuous chlorination dose of 0.2 mg/L [15]. Rajagopal *et al.* (put in date) reported that intermittent chlorination is ineffective in controlling mussels and recommended a continuous high chlorination for mussel infested intake pipes [16]. However, disinfection by-products (DBPs) formation needs to be carefully considered when chlorinated water is used in CT operation. In addition, chlorination is not favored in drinking water due to safety concerns about the storage of chlorine gas, taste and odor problems resulting from high-level chlorination, and ineffectiveness against protozoa like *Cryptosporidium*.

Ozone has been used as a disinfectant in drinking water since the late 1800s [17]. The effectiveness of ozone is around 100 to 300 times greater than that of chlorine. Ozonation in drinking water treatment is more widely used in Europe and the disinfection efficiencies is well understood for fresh water [18, 19]. Ozone is also effective even at

low concentration and has been reported to successfully control fouling of seawater intake pipes if adequate contact time between ozone and the water is guaranteed [20]. High ozone dosage (5 mg/L) for 5 min daily in seawater was sufficient to keep titanium, aluminum brass and epoxy coated PVC cooling tubes clean [21]. However, reports show that the chemistry of ozone in seawater is considerably different than that in freshwater due to the presence of bromide in seawater [18, 22].

Chlorine dioxide ( $\text{ClO}_2$ ) has been used as a disinfectant in many industries such as dairy, fruit and vegetable processing, poultry, food processing, potable water treatment and industrial waste treatment. [19], [23]. The use of  $\text{ClO}_2$  as disinfectant has increased in distillation plants in the Gulf region [24]. Wang *et al.* (2010) reported that  $\text{ClO}_2$  disinfected oysters can extended shell life up to 12 d [25]. The effectiveness of  $\text{ClO}_2$  is at least as high as that of chlorine, even at lower concentrations, and the contact time required is shorter than chlorine [26-29]. Moreover, many literature reports show that trihalomethanes (THM) formation is low in  $\text{ClO}_2$  treatment due to lower reactivity with organic matter [14, 30].

In this study, the research was focused on biofouling control in seawater CTs using alternative treatment by ozone microbubbles and  $\text{ClO}_2$  and comparing these with classical chlorination in a pilot-scale CTs, and particularly the affect of organic load of the water. The effectiveness as a biocide was evaluated by determining the viable cell count using a flow cytometer (FCM). Water quality parameters such as pH, conductivity, dissolved organic carbon (DOC) and oxidation-reduction potential (ORP) were measured. Total residual oxidant (TRO) was also measured on-site for all three CTs to maintain the

regulation requirement (0.2 mg/L) for discharge to the sea.

### 5.3 Material and methods

The efficiency of alternative oxidant treatment for seawater CT using ozone microbubbles and  $\text{ClO}_2$  were investigated at pilot-scale in parallel, with three CTs fully functioning with seawater and different dosing systems. Chlorine (dosed as sodium hypochlorite) as a control,  $\text{ClO}_2$ , and ozone were all tested for disinfectant as per the required conditions for recirculating cooling seawater systems. A comparative assessment of these disinfectants was carried out under various conditions. Water quality parameters were monitored by both on-line (or field) and laboratory measurements. The disinfection performance was assessed with and without organic loads by adding methanol (MeOH) during the pilot study.

#### 5.3.1 Pilot plant cooling water systems with recirculating

The CTs were constructed at KAUST's Central Utility Plant (CUP) and supplied fresh Red Sea seawater using an intake pump. The pilot-scale facility was installed outside, such that it could be exposed to all types of environmental conditions (e.g., pollutants, dust, mold, humidity, temperature, etc.) and various types of contaminants that are commonly present or similarly experienced at a full-scale facility during operations. The CTs are designed as mechanical draft systems, as illustrated in Figure 5-2. The pilot test program and conditions for the experiments conducted are summarized in Table 5-1.

Table 5-1: Pilot-plant CT test program.

Test No	Test Program	Duration (days)	Remarks
1	CT operation without any other treatment (No oxidation)	40	<ul style="list-style-type: none"> <li>- COC* =1.2.</li> <li>- Disinfectant switched off.</li> <li>- Anti-scalant dosing on.</li> <li>- Organic spike (MeOH**)</li> </ul>
2	CT operation with oxidation	30	<ul style="list-style-type: none"> <li>- COC* =1.2.</li> <li>- Disinfectant switched on.</li> <li>- Anti-scalant dosing on.</li> <li>- TRO = 0.2 ppm at blowdown (as Cl<sub>2</sub>).</li> <li>- Organic spike (MeOH**).</li> </ul>

\*COC: Cycle of concentration. \*\*MeOH: Methanol.

The automated pilot operation was maintained by the LabView system, allowing the control of all three CT systems with remote access (e.g. pump on/off, power on/off, dosing and water quality monitoring systems, etc.). The makeup seawater was fed to the pilots using a HTT 2000 GemmeCotti all plastic (PVDF) pump, while heater, oxidant, and recirculate flow supplied using HTT 5000 GemmeCotti (PVDF) pumps.

The basic components of the CTs are frame and casing made of fiber-reinforced plastic (FRP) with height of 1550 cm and diameter of 750 cm, filled with packing material made of PVC (height of 525 cm), and a cold-water basin (52 L capacity) located near the bottom of the tower and fans. The CTs specification and materials can be found in the supplementary information (Table 5-4S). In the experimental system, the CT basin

was supplied by seawater at 2 L/min for make-up water. The seawater was recirculated at a rate of 24 L/min from the CT basin, passing through the heater exchanger and then sprayed into the CT, and the seawater treated by chemical disinfection through the oxidant as demonstrated in Figure 5-2.

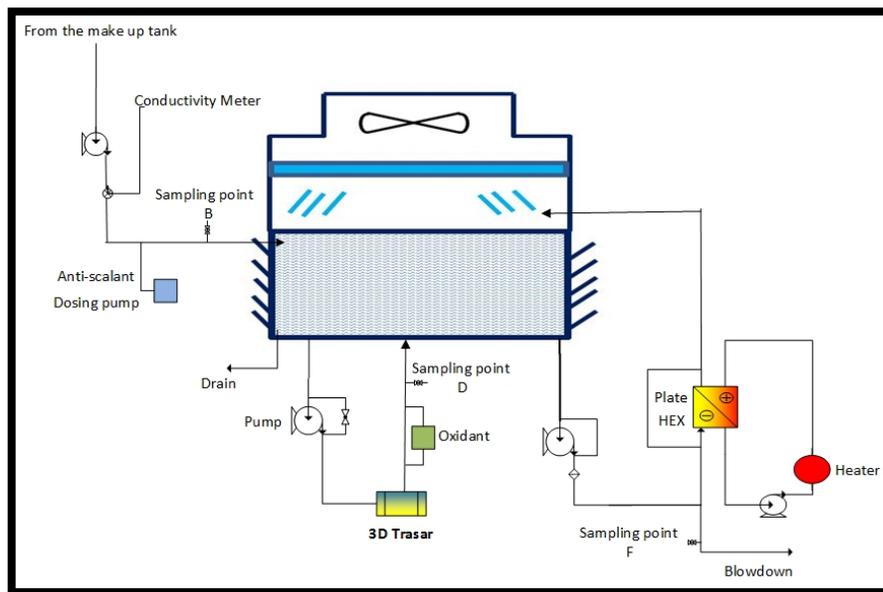


Figure 5-2. A flow diagram of a pilot plant CT seawater system.

### 5.3.2 Heat exchanger

Certikin titanium plate heat exchangers were constructed with electro seawater resistant heater (15 KW) (diameter length of 592 mm), and used for transferring the heat from a hot water closed loop to the open seawater open loop in the CT. The heat exchanger was designed with a counter-current flow configuration of the seawater vs. the heated freshwater to maintain a constant heat transfer. The heat exchanger consisted of five

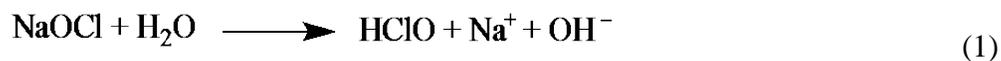
plates (length 200 mm, height 460 mm) and the surface of each plate was manufactured with a pattern of channels allowing the water to flow across each one in turn. The temperature difference between inlet and outlet of the heat exchanger remained at the targeted temperature difference of  $10 \pm 2^\circ\text{C}$ .

### 5.3.3 Organic spiking

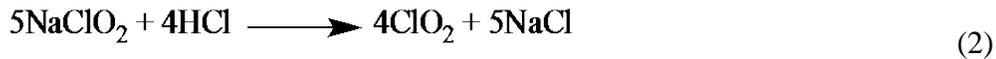
This study was divided into two phases; no.1 - without oxidant dosing, and no.2 - with oxidant dosing. For the second phase a small dose of organic substrate (MeOH, 5 mg-C/L) was added to the CT basin as a nutrient in order to promote biological growth and to see the effect of organic loading in the oxidation performance in the seawater CTs, range of MeOH concentrations (2-5 mg-C/L) were tested in the preliminary test showed that a concentration of 5 mg-C/L was more efficient to microbial growth. The MeOH was used as organic carbon nutrient source for the PCT to simulate the industrial cooling towers.

### 5.3.4 Chemical disinfection (Oxidation)

Three different chemical disinfection systems were applied in the CTs. Cooling tower no. 1 was used as a control with 2,000 mg/l  $\text{Cl}_2$  stock of sodium hypochlorite (5.65–6 %)(**CT1, sodium hypochlorite**). When sodium hypochlorite ( $\text{NaOCl}$ ) is used as source of chlorine [31]:



In cooling tower no. 2 (**CT2, chlorine dioxide**),  $\text{ClO}_2$  was generated “on site” by mixing 20 L of hydrochloric acid (HCl) at 9% w/w (prepared by adding 4.86 L of HCl 37% w/w into 15.14L of Milli-Q water) and 20 L of sodium chlorite ( $\text{NaClO}_2$ ) at 7.5% w/w (prepared by dissolving 2,006 g of  $\text{NaOCl}_2$  into 20 L of Milli-Q water), giving the following equation [32]:



In cooling tower no. 3 (**CT3, ozone**), an ozone concentration of  $1.5 \text{ g/Nm}^3$  (normal temperature  $20^\circ\text{C}$ , pressure 1 bar) was generated in-situ by passing concentrated oxygen at 1L/min of  $\text{O}_2$  into a corona-discharged ozone-producing cell. The generated ozone was then injected in the form of micro-bubbles into the seawater line. The disinfection residuals remained within the targeted levels after addition (TRO = 0.2 at ORP level of +600 mV).

### 5.3.5 Analyzes

#### 5.3.5.1 Field measurements

The online parameters such as conductivity, pH and ORP were measured using 3D TRASAR technology. This was designed for measuring the key system parameters for the CT operation. Online monitoring of ORP is a practical and useful technique for cooling towers operation because it can evaluate the performance of the chemical disinfection and oxidant dose of the treatment system; the pH data can also be used as an indicator. In parallel, field tests with a hand-held unit were conducted at the pilot plant

site, which were not covered by online analyzers. Hand-held parameters measured included pH, conductivity, dissolved oxygen, ORP and turbidity. TRO readings were measured by using Disinfection By-product (DPD) powder pillows (spectrophotometric; DPD Method 8167). For ease of comparison, dosage and residual measurements for all the oxidants are expressed as mg/L. TRO is a significant method to effectively evaluate the residual disinfectant of the chemical oxidant used in the control of biological growth.

Dissolved oxygen (DO) levels can be affected by biofouling growth in the CTs, low DO concentration caused by biofouling. The effect of the COC of seawater cooling towers (defined as the ratio of the concentration of chloride in make-up water to the concentration of chloride in recirculating water) at varied levels of seawater temperatures, oxidant dosages, and the impacts on residual disinfectant decay (TRO). The COC increase resulted in an increasing the amount of dissolved ions and organic present in seawater, which can cause biofouling problems.

#### 5.3.5.2 Lab analysis

Total organic carbon (TOC) was measured using a Shimadzu analyzer after filtering through a Whatman filter (pore size = 0.45  $\mu\text{m}$ ). Flow cytometer (FCM) was used to measure live/dead cell counts in the seawater, based on a mixed stain of SYBR Green I (SGI) and Propidium Iodide (PI). The  $\text{UV}_{254}$  utilizing a 254 nm ultraviolet light source and the amount of light absorbed provided a measure of the natural organic matter (NOM) in the seawater samples. More specifically,  $\text{UV}_{254}$  is the best detector of aromatic

or reactive organics, which can form disinfection by-products (DBPs) when combined with chlorine. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used for the detection of trace metals. Ion chromatography (IC) (Dionex IC 3000 model) allowed the separation of ions and polar molecules based on their affinity to the ion exchanger. A small volume of sample, typically 2 to 3 mL, was introduced into the ion chromatograph. DBPs can result from the reaction between organic and inorganic matter in water by chemical disinfectants. The DBPs including chlorite, chlorate and bromate trihalomethanes (THMs) were analyzed using gas chromatography-mass spectrometer (GC-MS) with purge and trap (EPA 524.2) [33].

#### 5.4 Results and discussion

All three CT trains were able to successfully mimic actual full-scale plant conditions, which is critical for the pilot testing. The targeted COC=1.2 was also maintained as well as the inlet to outlet temperature difference of  $10 \pm 2^\circ\text{C}$  across the heat exchanger. The CTs were operated for 70 d continuously under two different conditions (Table 5-1); no oxidation for 40 d and with oxidation for 30 d. Continuous antiscalant dosing was applied throughout the experiment to avoid scaling formation for both conditions.

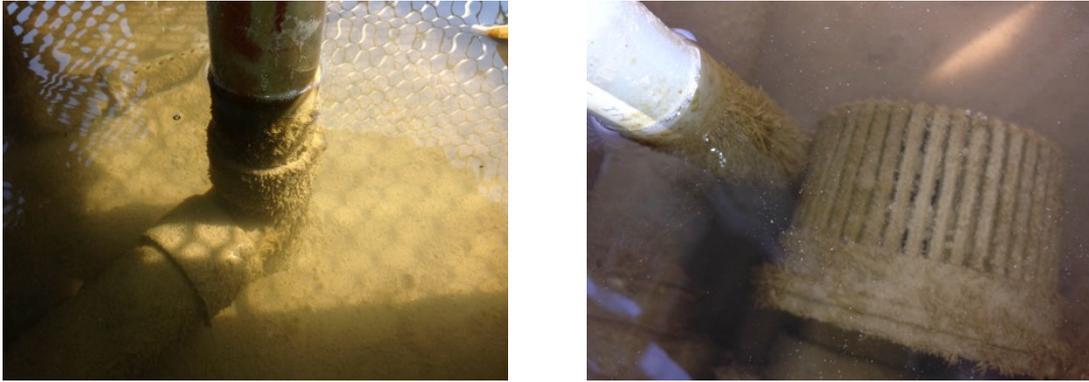


Figure 5-3. Photos of the biofouling growth in the CT basin.

#### 5.4.1 Biological growth

Biological growth was monitored under varying conditions the different disinfection practices tested. No disinfection was used for the first 10 d, resulting in very little biological growth. An additional carbon source was then applied for the next 30 d by adding MeOH. As shown in Figure 5-3, biological growth was observed within a few days after MeOH addition. A slight higher cell growth was detected in the CT1 (chlorination) compared to CT2 and CT3.

A relatively high biological growth was observed for all three CTs (in terms of cell counts measured by FCM) when adding 5 mg-C/L of MeOH as organic substrate (Figure 5-4). In addition, a continuous increase in the live cell count and the number of total cells was observed with continuous MeOH dosing.

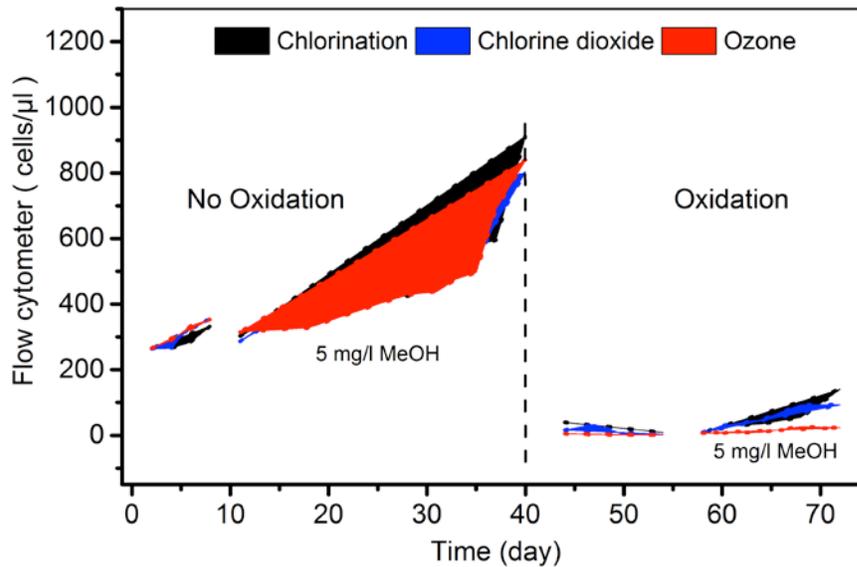


Figure 5-4. Cell counts with and without organic substrate (MeOH) addition for all CTs.

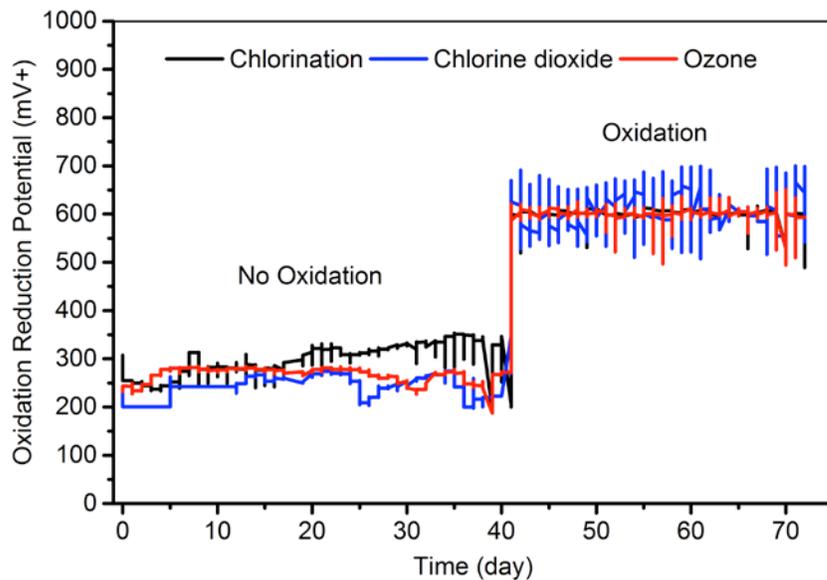
However, immediately after 40 d, when oxidant was added all the three disinfectants were effective in keeping the active cell counts to a minimum in the CTs basins. Even with 5 mg-C/L MeOH dosing a minimal level of cells was maintained. Ozone was the most effective disinfectant in keeping the microbial count to a lower value, which was nearly zero, compared to chlorine and  $\text{ClO}_2$  at the same TRO value.

## 5.4.2 Effect of oxidation

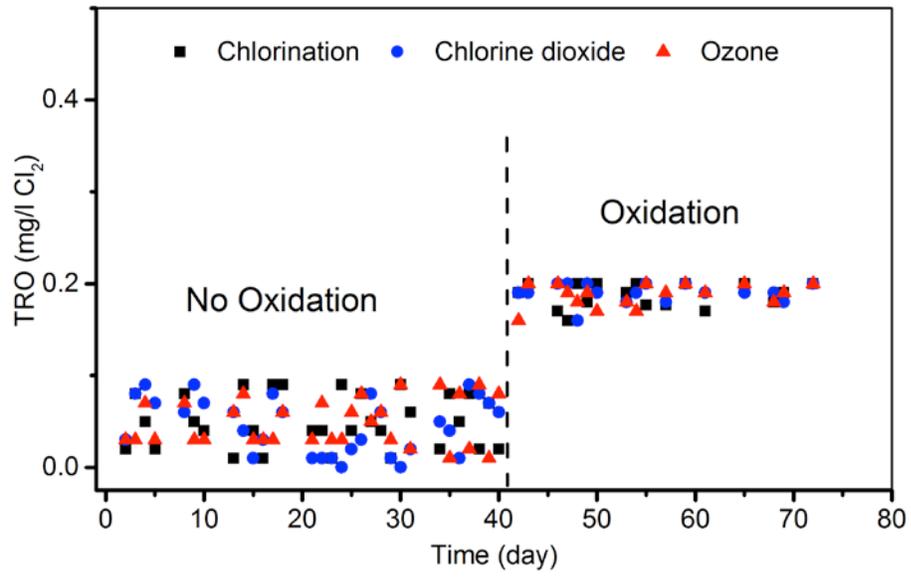
### 5.4.2.1 Oxidation reduction potential

The ORP results show an average value around +270 mV when the disinfection is not applied (**Figure 5a**). However, the ORP value increased up to +600 mV when the disinfection was switched on. The targeted ORP level at sampling point F (blowdown, as shown in **Figure 2**) was reached by adjusting the chemical dosing, which was controlled

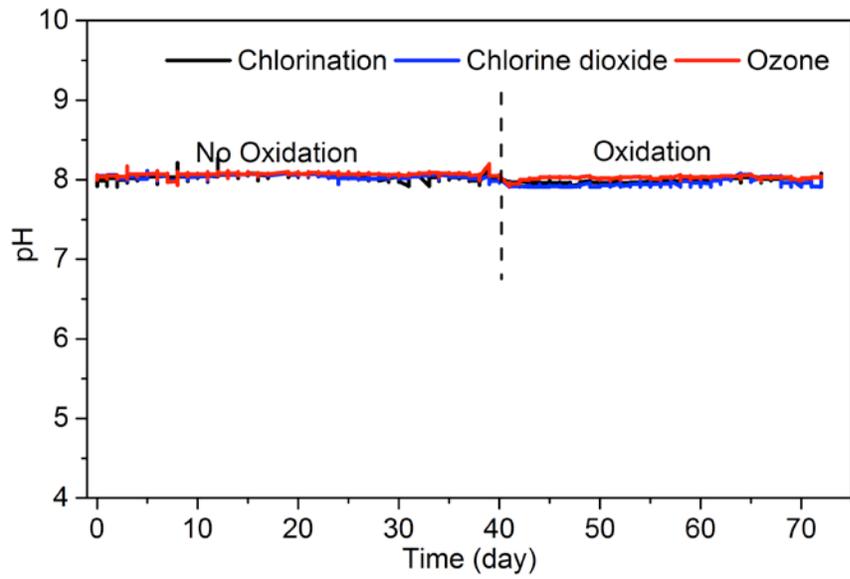
using Lab-view (set point = +600 mV; equivalent to TRO of 0.2 ppm). The ORP values for all three CTs were mostly stable around +600 mV with oxidation, while for CT2 (using chlorine dioxide) they fluctuated slightly. In CT 1 (chlorination), when MeOH was added, ORP level increased (from  $261 \pm 22$  to  $309 \pm 25$  mV) without oxidation. On the other hand, this effect was lowered with oxidation (no MeOH =  $601 \pm 11$  mV and MeOH addition =  $605 \pm 12$  mV). However, this effect was minimal in CT2 ( $\text{ClO}_2$ ) and CT3 (ozone), which were less than 0.5%.



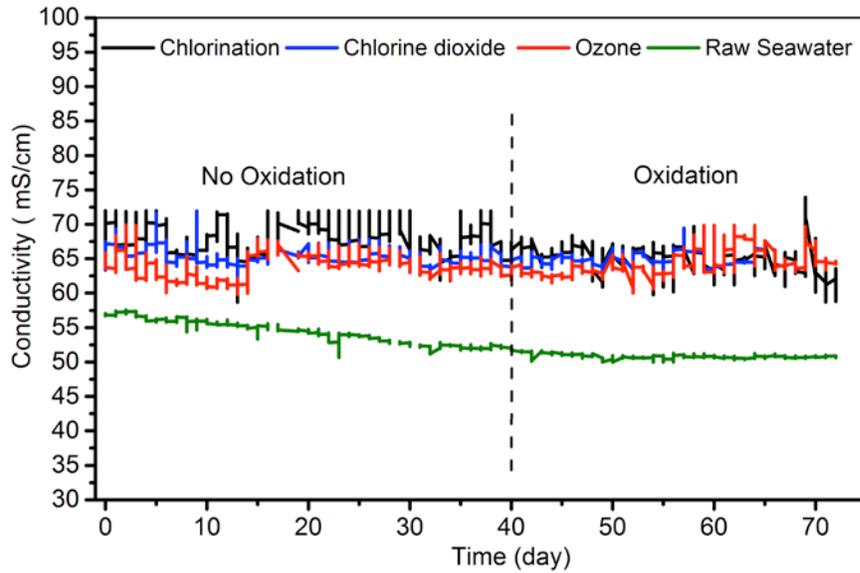
(a)



(b)



(c)



(d)

**Figure 5-5.** In-site measurement data of (a) ORP, (b) TRO, (c) pH and (d) conductivity for CTs.

#### 5.4.2.2 Total residual oxidant

The TRO values measured for all three CTs were below 0.07 mg/L of  $\text{Cl}_2$  in the first 40 d, operation without the addition of any disinfection. After the period promoting higher level of biological growth, the disinfection practice was reinstated for 30 d. The disinfection residuals were targeted to maintain a TRO of around 0.2 mg/L of  $\text{Cl}_2$  at ORP level of +600 mV after disinfection addition, as shown in **Figure 5-5b**. This value complies with the regulation requirement (0.2 mg/L of  $\text{Cl}_2$ ). Without oxidation, there was no change of TRO. On the other hand, when oxidation is switched on, TRO increased and even became higher with 5 mg/L of MeOH; without oxidation = around 0.05, with oxidation and no MeOH = around 0.18, and with oxidation and MeOH = 0.20 mg/L  $\text{Cl}_2$ .

Among three oxidants tested, ozone and  $\text{ClO}_2$  tend to be effective in keeping the microbial count to lower value compared to the chlorine for the same TRO value. However, the ozone was injected by using ozone micro-bubble injection method to improve the mixing efficiency in the seawater and to increase the contact service area of seawater, thus it showed a higher disinfection rate. Table 5-5S (Supplementary Information) shows the overview of average values of TRO and ORP during the experiment.

#### 5.4.2.3 pH, conductivity and **dissolved oxygen**

On-site pH measurements for all three CTs showed that there was no change in pH over the 70 d of operation, and maintained at around 8.0 (**Figure 5-5c**). This indicates that disinfectant and/or chemical addition did not affect the seawater pH. The conductivity values measured fluctuated at the beginning of operation (without oxidation), and become more stable towards the end (**Figure 5-5d**). The plots of all three CTs show a similar average value for conductivity around 65 mS/cm in the CT basins. The conductivity values were also measured onsite on grab samples using handheld probes on several locations within the three CT lines. The conductivity measurements on the sampling points B (makeup line) was around 54 mS/cm, while the conductivity of the CT basin sampling points D was close to 65 mS/cm, thus approximating the targeted COC of 1.2 for all three CTs. In addition, DO was measured for all CTs and it was observed that DO increased slightly during the period of  $\text{MeOH}_2$  addition. Table 5-6S (Supplementary Information) shows the overview of the pH, conductivity and DO during the experiment.

### 5.4.3 Disinfection byproducts (DBPs)

The DBPs including TTHMs (chlorinated byproducts), chlorate/chlorite ( $\text{ClO}_2$  byproducts), and bromate (ozone byproducts) were measured throughout the experimental period. Results suggest that DBPs levels (chlorite and chlorate) generated by  $\text{ClO}_2$  were at an acceptable level ( $< 10$  ppb of chlorate), but associated DBPs in for the other two trains were exceeded. The typically acceptable DBPs level (i.e., maximum contamination level, MCLs for drinking water) for TTHMs is not to exceed 80 ppb and bromate not to exceed 10 ppb. For chlorine, the TTHMs formed were about 200 ppb and ozonation resulted in the generation of TTHMs (higher than 300 ppb) and about 114 ppb of bromate (Table 5-2).

Table 5-2: DBPs generated by disinfectant addition in CTs.

DBPs		Uni t	CT1	CT2	CT3
Bromate ( $\text{NaBrO}_3$ )		ppb	2.4	0.8	114.0
Chlorite ( $\text{ClO}_2^-$ )		ppb	5.1	5.9	4.0
Chlorate ( $\text{ClO}_3^-$ )		ppb	57.0	1.9	4.2
TTHMs	Trichloromethane ( $\text{CHCl}_3$ )	ppb	57.0	1.0	58.0
	Tribromomethane ( $\text{CHBr}_3$ )	ppb	48.0	0	50.0
	Dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ )	ppb	106.0	0	48.0
	Bromodichloromethane	ppb	48.0	2.0	211.0

(CHBrCl<sub>2</sub>)

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The results of DBPs can be supported by the UV absorbance at 254 nm (UV<sub>254</sub>). The highest absorbance of around 0.06 cm<sup>-1</sup> was obtained for CT3, which used ozonation. The UV<sub>254</sub> value in CT1 (chlorination) was around 0.04 cm<sup>-1</sup> and the lowest value (around 0.02 cm<sup>-1</sup>) was detected in CT2 (ClO<sub>2</sub>). UV<sub>254</sub> is typically low in raw seawater around 0.01 cm<sup>-1</sup> [34] and commonly used to detect the organic matter with π-bonded molecules of constituents [35]. However, when seawater is affected by the presences of algal and humic substances, the UV<sub>254</sub> becomes higher than 0.02 cm<sup>-1</sup>. The UV<sub>254</sub> of raw seawater feed was around 0.01 cm<sup>-1</sup>. However, DBP formation increased when adding MeOH and the organic level should therefore be limited when using oxidants for biofouling control.

As expected, there was no variation in the content of inorganic compounds. The main inorganic constituents measured by IC and ICP-OES can be found in Table 5-7S.

#### 5.4.4 Economic evaluation

In this study, the economic evaluations of operational costs for all three CTs used different oxidants were demonstrated in Table 5-3. The operating expenses (OPEX) CT2 using ClO<sub>2</sub> is most economical among other CTs. However, it needs to be noted that the capital expenditures (CAPEX) for the CT2 might be higher than CT1.

Table 5-3: Estimated operational cost of three CTs.

Categories	CT1	CT2	CT3
Types of oxidant	Sodium hypochlorite (2000 mg/L)	Hydrochloric acid (9%) + Sodium chlorite (7.5%)	Ozone (1.5 g/Nm <sup>3</sup> )
Consumed oxidants	2.7 L/day	HCl= 0.5 L/day, NaClO <sub>2</sub> = 1.6 L/day	3.1 KWh
Daily operational cost	162 \$/d (60 \$/L)	68 \$/d (HCl 40 \$/L and NaClO <sub>2</sub> 30 \$/L)	372 \$/d (5 \$/KWh)

## 5.5 Conclusions

Biological growth was observed when a MeOH dose was added as additional carbon source to the CT basins in the pilot CT operations. More biological growth was found at higher concentrations of MeOH due to the increase in the organic substrate. However, initiating oxidation with disinfectants immediately reduced cell counts in the CT basins. Two of the oxidants, ozone and ClO<sub>2</sub>, were effective in keeping the microbial growth to a minimum compared to chlorination, even with addition of MeOH. Adding the MeOH did not significantly affect all other chemical parameters. However, the type of disinfectant used varied the amount of DBPs formed and increased with increasing organic content. ClO<sub>2</sub> was found to promote less DPBs formation compared to ozone and chlorination, and to be as effective in minimizing bioactivities for similar TRO levels. However, other parameters such as a cost benefit analysis, corresponding capital and O&M costs, efficacy and efficiency along with ease of operations, treated water quality, environmental impacts, etc., are needed to be carefully considered and evaluated before recommending which disinfectant type to choose over another.

## 5.6 Acknowledgements

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## 5.8 Supplementary Information

Table 5-4 S: Overview of the CT process parameters

<b>DESIGN, OPERATING AND CONSTRUCTION MATERIAL</b>	<b>SPECIFICATION</b>
Tower pump head	1.5 m
Drift loss of water flow rate	0.10 %
Design wind load	200 kg/m <sup>2</sup>
Tower support frame	F.R.P
Casing	F.R.P
Cold water basin	F.R.P
Filling	P.V.C
Filling supporter	P.V.C
Air inlet louver	P.V.C
Blade material / hub material	ABS
Sprinkler head	Nylon
Sprinkler pipe / stand pipe	P.E
Fan diameter / no of blades	500 MM/3 PCS
Fan speed / air volume	945 RPM/60M <sup>3</sup> /MIN
Water inlet / outlet piping	1½ B(40A)
Auto fill/ quick fill	½ B (15 A)
Over flow / drain	1 B(25A)/ ¾ B(20A)
Volume of CT basin	52 L
Volume of water in system	10 L
Make-up water flow	2 L/min
Recirculation water flow	24 L/min
Blow-down water flow	2 L/min
Evaporation	1 L/min
Concentration factor of process water	1.2
Heat water flow	21 L/min
Anti-scalant concentration	3 mg/l
Cycles of concentration	1.2

Table 5-5 S: Summary of average values of ORP and TRO.

Parameters analysis		Without oxidation		With oxidation	
		0 mg/L MeOH	5 mg/L MeOH	0 mg/L MeOH	5 mg/L MeOH
ORP (mv+)	CT 1	261 ± 22	309 ± 25	601 ± 11	605 ± 12
	CT 2	224 ± 21	247 ± 21	607 ± 26	608 ± 30
	CT 3	268 ± 16	270 ± 13	602 ± 6	600 ± 15
TRO (mg/l Cl <sub>2</sub> )	CT 1	0.05 ± 0.03	0.05 ± 0.03	0.18 ± 0.05	0.20 ± 0.02
	CT 2	0.07 ± 0.02	0.04 ± 0.03	0.18 ± 0.04	0.20 ± 0.02
	CT 3	0.04 ± 0.02	0.05 ± 0.03	0.18 ± 0.04	0.20 ± 0.01

Table 5-6 S: Overview of pH, conductivity and DO for all CTs.

Parameters analysis		Without oxidation		With oxidation	
		0 mg/L MeOH	5 mg/L MeOH	0 mg/L MeOH	5 mg/L MeOH
pH	CT 1	8.01 ± 0.03	8.04 ± 0.03	7.97 ± 0.01	8.00 ± 0.02
	CT 2	8.03 ± 0.02	8.04 ± 0.03	7.92 ± 0.02	7.98 ± 0.04
	CT 3	8.05 ± 0.03	8.07 ± 0.01	8.01 ± 0.03	8.03 ± 0.01
Conductivity (mS/cm)	CT 1	68 ± 2	67 ± 2.1	66 ± 1	65 ± 2
	CT 2	64 ± 1	65 ± 1	65 ± 1.1	65 ± 1.1
	CT 3	63 ± 2	64 ± 1.7	63 ± 1	65 ± 2
	RSW	56 ± 1	54 ± 1	51 ± 0.2	51 ± 0.5
DO (mg/L)	CT 1	3.5 ± 0.2	3.5 ± 0.3	3.5 ± 0.2	3.6 ± 0.3
	CT 2	3.6 ± 0.1	3.4 ± 0.2	3.4 ± 0.3	3.6 ± 0.3
	CT 3	3.5 ± 0.2	3.6 ± 0.2	3.5 ± 0.2	3.6 ± 0.3



## **Chapter 6**

### **6 Publication No # 3**

The following publication, “Investigation the efficiency of biocides in controlling algal biofouling in seawater industrial cooling towers”, written by Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun Jeong, Kim Choon NG, Gary. L. Amy, and TorOve. Leiknes.

**Investigation the efficiency of biocides in controlling algal biofouling in seawater  
industrial cooling towers**

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## 6.1 Abstract

Biofouling in the open recirculating cooling water systems may cause biological corrosion, which can reduce the performance, increase the energy consumption and lower heat exchange efficiencies of the cooling tower (CT). Seawater CTs are prone to biofouled due to the presences of organic and inorganic compounds in the seawater. The availability of organic and inorganic nutrients, along with sunlight and continuous aeration of the CT contributes to an environment that is ideal for microbial growth. Various microorganisms (algae, fungi, and bacteria) can grow in a CT system under certain environmental conditions. The most commonly being used method to control the biofouling in the CT is the addition of biocides such as chlorination. In this study, diatom and green algae were added to the CT basin and its viability was monitored in the recirculating cooling seawater loop as well as in the CT basin. Continuous addition of biocides was employed in pilot-scale seawater CTs and it was operated continuously for

60 d. Three different types of oxidizing biocides, namely chlorine, chlorine dioxide ( $\text{ClO}_2$ ) and ozone, were tested. The results showed that all biocides were effective in keeping the biological growth to the minimum regardless of algal addition. Amongst the biocides, ozone could reduce 99% of total live cells of bacteria and algae, followed by  $\text{ClO}_2$  at 97%, while the conventional chlorine showed only 89% reduction in the bioactivities.

**Keywords:** Algae; Biocide; Biofouling; Seawater cooling tower

## 6.2 Introduction

Open recirculating cooling water systems are used to controlling temperatures by transferring heat generated in industrial processes. Generally, cooling water is heated up and then cooled down by evaporation, where is the hot water sprayed over packing material to increase the air stream [1, 2]. The most common used and acceptable type is open recirculating system based on an economic point and water consumption [3]. On the other hand, the open circulating cooling water system suffered some operational risks such as scaling, corrosion and biofouling [4]. Biological fouling (or biofouling) in open circulating cooling water systems causes the equipment damage through biocorrosion, which can increase water circulating costs, reduce heat transfer thus contributing to decrease in energy efficiency of cooling system, and clog the CT systems [5-11]. Geesey and Bryers (2000) have been reported that, 4% of the failures of power stations are caused by fouling at United State. In Europe, the heat exchanger fouling has high costs of

maintenance [12]. Common biofouling types of microorganisms found in a CT system are bacteria, fungi, algae, and larger organisms, mainly barnacles and mussels [10, 13-15]. The microorganisms present in most parts of cooling systems, which are contact with water [16]. The makeup water of the CT is exposed to contaminants including salt, organic nutrients and suspended solids which are responsible for fouling during the cooling water recirculating [16, 17]. Moreover, the water temperature in circulating cooling systems is an ideal environment for biological growth [18].

To control the biofouling in the CT, basically chemical and physical treatments are used and these treatments used to be employed either separately or together [19]. The most widely practiced approach to inhibit the biofilm formation and inactivate the microorganisms or reduce the biological activity in the cooling water process is the chemical treatment using biocides such as chlorine, chloramines, ozone and  $\text{ClO}_2$  classified as oxidant [20-23]. Physical treatment (e.g., membrane filtration) has been recently reported as alternative disinfection methods, but its practical effect has not yet proven [24].

Among the various oxidants, chlorine is one of a popular oxidizing biocides method for controlling biofouling growth in CTs, which is used commonly around the world [10, 25]. A primary advantage of chlorination is effective in inactivating a wide range of pathogens and microorganisms. On the other hand, chlorination is not favored due to formation of harmful by products (DBPs). Chlorination have also been reported an issue in maintaining a residual concentration and appearing corrosion in CT system [24, 26, 27]. Trihalomethanes (THMs) were classified as a volatile organic group produced when

chlorine reacts with the organic in the water and indicator of DBPs formed in the water [28].

Ozone is one of the greatest oxidants and high effectiveness than chlorine at low concentration in the water treatment application [29]. Several studies have shown that ozone has lower contact time CT and effective in inactivating bacteria, viruses, and protozoan cysts under certain conditions [30]. Ozone has several applications of the treatment such as oxidation of reduced metals, treatment of synthetic organic compounds and control fouling in seawater for intake pipes. Recently, Ozone has been utilized in several thousand public water treatment plants as part of chemical disinfection treatment [31, 32]. High ozonation dosage, 5 mg/l for 5 minutes a day in seawater, was sufficient to keep titanium, aluminum brass and epoxy coated PVC cooling tubes clean [33]. Ikegami et al. (2006) reported that low ozone concentration between 0.2 to 0.5 mg/L could control fouling at an acceptable level [29]. Ozone residual equivalent of 1.0 mg/l of TRO was sufficient to disinfect seawater for marine culture efficiently [34]. Due to the presence of higher bromide in seawater, ozone reacts rapidly (half-life of 5.7 seconds) with bromide to form the hypobromous acid (HOBr) and hypobromite (OBr<sup>-</sup>). [32, 35-37].

Chlorine dioxide, ClO<sub>2</sub> is one of the popular disinfectants used in seawater treatment. ClO<sub>2</sub> is more effective than chlorine to reduce the living number of organisms at lower concentrations [38]. ClO<sub>2</sub> has been used as a disinfectant in many industries such as potable water treatment and industrial waste treatment. The use of ClO<sub>2</sub> as disinfectant has increased in distillation plants in the Gulf region [38-40]. Many sources have reported

that THM formation is lower in  $\text{ClO}_2$  treatment due its lower reactivity with organic matter [39].  $\text{ClO}_2$  that can maintain good disinfection while minimizing DBP formation, especially bromate [41]. The major differences between the  $\text{ClO}_2$  and other biocides are:  $\text{ClO}_2$  is more soluble than  $\text{Cl}_2$ . It is effective over a wide range of pH, and  $\text{ClO}_2$  does not react with bromide [38].

In this study, alternative oxidants (ozone and  $\text{ClO}_2$ ) were tested in three different pilot-scale seawater CTs. Their effects as a biocide were evaluated by determining the viable cell count quantified using a flow cytometer (FCM). Total residual oxidant (TRO) was also measured to maintain the sea discharge regulation (0.2 ppm). Algae containing diatom and green algae were added to seawater CT basin to see clearly the effect of biocides on the control the algal fouling.

### 6.3 Materials and methods

The effectiveness of oxidizing biocides in seawater CT was studied at the pilot-scale with addition of algae. CT systems were operated with continuous feeding of seawater and different oxidants (chlorination; sodium hypochlorite as a control,  $\text{ClO}_2$ , and ozone).

Seawater quality parameter analysis was monitored in situ (or field measurements) together with lab analyses. All the key factors related to the CT operations and their performances were investigated. In addition, during this Pilot-scale study the effect of water quality and oxidation practices and their effects toward biofouling and microbial activities were monitored.

### 6.3.1 Pilot-scale model

The pilot-scale CTs were located close to the seawater intake system of seawater reverse osmosis (SWRO) desalination plant where can supply fresh seawater to the CTs. The pilot-scale facility was set in an open atmosphere, which could be exposed to all types of environmental conditions. The design of pilot-scale CTs is a mechanical draughts, where is the fan located at the top of the tower. The pilot test program and the condition of the experiment are given in Table 6-1. The operation of the pilot-scaled controlled by using LabView system with remote access.

Table 6-1 Pilot plant test program.

Tests	Test program	Duration (d)	Remarks
1	CT operation without oxidant treatment (no oxidation)	30	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Biocide switched off.</li> <li>- Anti-scalant dosing on.</li> <li>- Algae addition.</li> </ul>
2	CT operation with oxidant treatment (Oxidation)	30	<ul style="list-style-type: none"> <li>- COC =1.2.</li> <li>- Biocide switched on.</li> <li>- Anti-scalant dosing on.</li> <li>- Algae addition</li> <li>- TRO = 0.2 ppm at blowdown (as Cl<sub>2</sub>).</li> </ul>

In the experimental system, the CT basin supplied by seawater at 2 L/min (LPM) through make-up CT. The recirculating seawater was pumped at 24 LPM from the CT basin passing the heater exchanger and sprayed into to CT, while the oxidant was pumped at 21 LPM from the basin passing the chemical oxidation and back to the CT basin. The

overview of the pilot-scale parameter was summarized in Table 6-2.

Table 6-2 Summary of the CT process parameters.

<b>DESIGN, OPERATING AND CONSTRUCTION MATERIAL</b>	<b>SPECIFICATION</b>
Tower support frame, casing and basin	F.R.P
Filling	P.V.C
Fan diameter / no of blades	500 mm/3 PCS
Volume of CT basin	52 L
Volume of water in system	10 L
Make-up water flow	2 LPM*
Recirculation water flow	24 LPM
Blow-down water flow	1 LPM
Evaporation	1 LPM
Heat water flow	21 LPM
Anti-scalant concentration	3 ppm
Cycles of concentration	1.2

\*LPM: L/min.

### 6.3.2 Chemical disinfection (Oxidant)

Three different oxidants disinfection systems were used in the experiments are:

Cooling tower no. 1 (CT1, sodium hypochlorite as control): 2,000 mg/l  $\text{Cl}_2$  from sodium hypochlorite (5.65–6 %) stock solution.

Cooling tower no. 2 (CT2,  $\text{ClO}_2$ ): 20 L of HCl @ 9% w/w (prepared by adding 4.86 L of HCl 37% w/w into 15.14L of MQ water) and 20 L of sodium chlorite @ 7.5% w/w (prepared by dissolving 2,006 g of  $\text{NaOCl}_2$  into 20 L of MQ water).

Cooling tower no. 3 (CT3, ozone): ozone of  $1.5 \text{ g/Nm}^3$  (normal temperature and pressure were  $20^\circ\text{C}$  and 1 bar, respectively) was generated *in-situ* at 1L/min of  $\text{O}_2$  by passing concentrated oxygen into a corona-discharged ozone-producing cell as demonstrated in Figure 6-1. The generated ozone was then injected in the form of micro-bubbles into the seawater line. The concentration of the produced ozone was regulated by the lab-view.

The disinfection residuals for all CTs also remained within the targeted levels after addition (TRO = 0.2 mg/L at ORP level of + 600 mV).



Figure 6-1: Photo of the pilot plant cooling towers using three different oxidants.

### 6.3.3 Analyses

#### 6.3.3.1 Field measurements

On-site parameters such as conductivity, pH and oxidation-reduction potential (ORP) were measured by using 3D TRASAR technology. This was designed for measuring the key system parameters for the CT operation. In parallel, hand field test was conducted at pilot plant site to double-check the on-site data at different sampling points, which were not covered by on-site analyzers. Hand held parameters measured were pH, conductivity, dissolved oxygen (DO), ORP, turbidity and TRO.

#### 6.3.3.2 Lab analyses

Dissolved organic carbon (DOC) was measured by using a Shimadzu analyzer after filtering the sample through a Whatman filter (pore size = 0.45  $\mu\text{m}$ ). Flow cytometer (FCM) was used to quantify the live/dead cells in all samples points of all pilot-CTs. The mixed stain of SYBR Green I (SGI) and Propidium Iodide (PI) was used. An ultraviolet (UV) light source at 254 nm ( $\text{UV}_{254}$ ) and the amount of light absorbed provides an ongoing indication of natural organic matter (NOM) in the seawater samples. More specifically,  $\text{UV}_{254}$  is the best detector of aromatic or reactive organics, which can form disinfection by-products (DBPs) when combined with chlorine. Inductively coupled plasma optical emission spectroscopy (ICP-OES) used for the detection of trace metals. Ion chromatography (IC) (Dionex IC 3000 model) allowed the separation of ions and polar molecules based on their affinity to the ion exchanger. A small volume of sample (typically 2 to 3 mL) was introduced into the IC analyses. Disinfection by-

products (DBPs) can result from reaction between organic and inorganic matter in water by chemical treatment agents during the water disinfection process. The DBPs were included; namely chlorite, chlorate and bromate trihalomethanes (THMs) and were analyzed using gas chromatography-mass spectrometer (GC-MS) with purge and trap (EPA 524.2) [42].

## 6.4 Results and Discussion

After operating the pilot-scale seawater CTs for 60 d at two conditions: without oxidation and for first 30d, and with oxidation for 30 d with algae addition and continuous antiscalant dosing for both conditions. The results show that, all CTs were able to control the growth of algae successfully in the actual full-scale plant condition. It could also maintain the targeted COC=1.2 and  $\Delta T=10\pm 2^{\circ}\text{C}$  of the inlet and outlet temperature at the heat exchanger. For this study the oxidation treatment of all CTs were firstly suspended for 30 d to promote algae growth after inserting to the CT basin, then introduced the oxidants. This was to assess the efficiency of oxidants biocides in controlling bio-growth including algae after such postponement.

### 6.4.1 CT performance with or without oxidation

This study was divided into Test 1 (no-oxidation), and with algal addition as part of pilot test program, followed by Test 2 (with oxidation). The intention for the first scenario to promote higher level of algal growth by inoculating with actual algae for all three CTs, in

assessing robustness in tackling the higher level of biological growth in CT operations. Addition and inoculation of the algae resulted at elevated algal growth in the pilot-CT as shown in **Figure 6-2a**. At the initial experiment of adding algae to the basin most of the big particles of algae were suspended on the sand filter as shown in **Figure 6-2b**.



**Figure 6-2.** (a) Algal growth in CT basin and (b) suspended algae captured in sand filter.

During the first 30d of the pilot-scale CT operations under a higher level of algal growth was observed as can be seen from Figure 6-3 (measured by FCM). FCM results suggest that all of the three oxidants were effective in keeping the active cell counts to minimal for all CTs after algae addition. Among them, with remained dosing of ozone and  $\text{ClO}_2$  tended to be an effective in keeping the microbial count to lower value compared to the chlorine for the same TRO value.

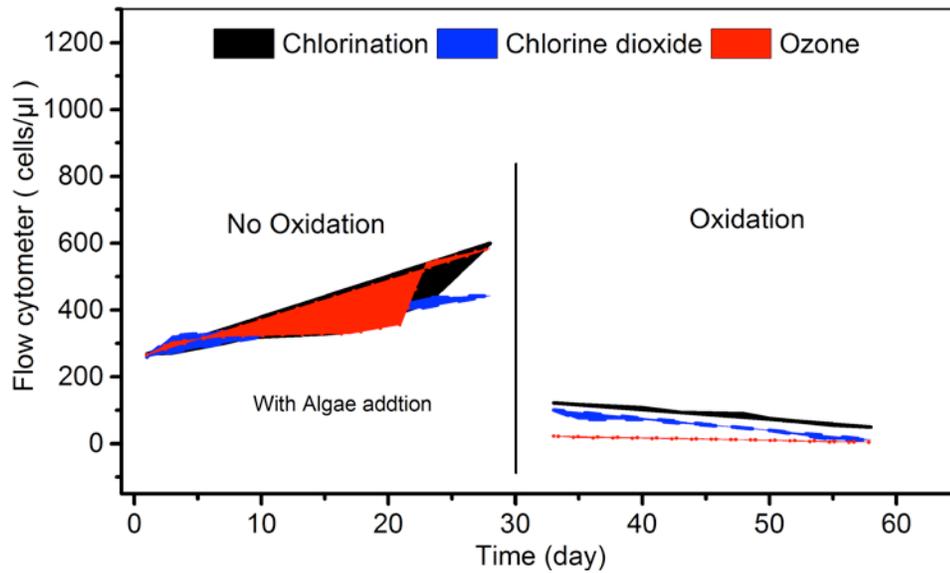


Figure 6-3: FCM data (total cell numbers) of all CTs

#### 6.4.2 Effect of oxidation with algae addition

After a postponement of the oxidation practices for 30 d (Test 1) and with algal inoculation to promote higher level of biological growth, the oxidation practice was then reinstated for additional 30 d. During the first week of the pilot operation after 30 d of suspension resulted in increased biological growth in all CTs. It was also noted with introduction of the oxidation the total microbial count (as FCM) went down significantly (by more than 90%) (Figure 6-3). This shows the robustness of the overall oxidation process, in controlling the biological and algal growth and biofouling. Thus, the remaining weeks continued the oxidation practices, to assess robustness of the overall oxidation process in minimizing the algal growth.

### 6.4.2.1 ORP

During the 30d of this pilot-scale operation (Test 2) with continued oxidation practices, the pilot CTs were able to maintain all of the targeted operational condition, with +600 mV; equivalent to TRO of 0.2 ppm during the operation. The average value of ORP measured during the oxidation suspended was around +300 mV. The ORP value increased up to +600 mV when the oxidation turned on. The targeted ORP level at discharge was reached by adjusting the chemical dosing, which is controlled by using Lab-view (set point = +600 mV). The ORP values for all three CTs during the oxidation were mostly around +600 mV, while the CT2 (using  $\text{ClO}_2$ ) was more fluctuated as indicated in **Figure 6-4**.

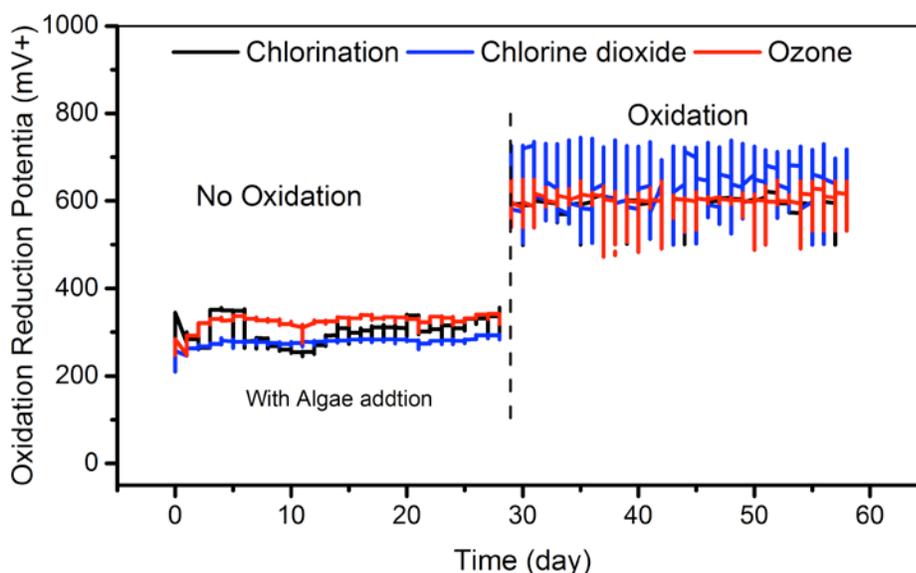


Figure 6-4. *In situ* data analysis of ORP for CT1, CT2 and CT3.

#### 6.4.2.2 TRO

The TRO values measured at field for all three CT's were below 0.07 mg/L Cl<sub>2</sub> in the first 30 d, this is due to the absence of oxidants. After the period promoting higher level of biological growth, the oxidation practice was reinstated and TRO increased to 0.20 mg/L Cl<sub>2</sub> at discharge. This reading was agreed with the regulation requirement 0.20 mg/L Cl<sub>2</sub> due to operating CT with oxidant.

The overview average values of the TRO and ORP during the experiment are given in Table 6-3.

Table 6-3: Average values of ORP and TRO.

Parameters		Without oxidation	With oxidation
ORP (mv+)	CT 1	300 ± 29	598 ± 18
	CT 2	277 ± 11	622 ± 39
	CT 3	321 ± 25	603 ± 16
TRO (mg/l Cl <sub>2</sub> )	CT 1	0.07 ± 0.02	0.18 ± 0.03
	CT 2	0.06 ± 0.03	0.19 ± 0.03
	CT 3	0.07 ± 0.02	0.20 ± 0.03

### 6.4.2.3 pH, conductivity and DO

During tests 1 and 2 all the in situ data of all three CTs behaved consistently. In-situ pH measurements for all CTs showed results around 8.0. It was expected that there was no major pH change over 60 d and slightly fluctuation pH results of CT2 (using  $\text{ClO}_2$ ) with the oxidation were applied at this period.

The plots of all three CTs show a similar conductivity average value of around 65 mS/cm at basin. The conductivity values were also measured at field within the three CT lines. The conductivity measurements on the makeup line is around 54 mS/cm, while the CT basin shows the conductivity close to 65 mS/cm, thus approximating the targeted COC of 1.2 for all three CTs. **Table 6-4** shows overview of the pH and conductivity average value. Dissolved oxygen (DO) was measured for all CTs and observed that, during the organic addition the results increase 70 %. Table 6-5 shows the overview average value of DO. DO concentration was maintained at around 3.6 mg/L at all the cases.

**Table 6-4** Overview of pH and conductivity for all CTs (average values).

Parameters		Without oxidation	With oxidation
pH	CT 1	7.98 ± 0.02	7.96 ± 0.04
	CT 2	8.02 ± 0.02	7.91 ± 0.05
	CT 3	7.98 ± 0.02	8.01 ± 0.03
Conductivity (mS/cm)	CT 1	67 ± 3	66 ± 2
	CT 2	67 ± 1	67 ± 1
	CT 3	65 ± 1	65 ± 1
	RSW	50 ± 0.3	50 ± 0.4

Table 6-5: Average values of DO in all CTs.

Parameters		Without oxidation	With oxidation
DO mg/L	CT 1	3.4 ± 0.2	3.5 ± 0.2
	CT 2	3.5 ± 0.3	3.8 ± 0.1
	CT 3	3.6 ± 0.2	3.5 ± 0.2

### 6.4.3 DBPs

In terms of the DBPs formation, particularly for this period, a significantly lower level of TTHMs was noted for all three trains. The DBPs including TTHMs (chlorinated byproducts), chlorate/chlorite ( $\text{ClO}_2$  byproducts), and bromate (ozone byproducts) were also measured during this operation. The results for TTHMs, chlorite/chlorate and bromate analyses show the chlorite and chlorate level due to  $\text{ClO}_2$  were less than 11 ppb

level. For chlorine, the TTHMs were about 67 ppb. Ozone generated the TTHMs more than 70 ppb and about 30 ppb of bromate as shown in **Table 6-6**. All of the results suggest that DBPs level (chlorite and chlorate) using the  $\text{ClO}_2$  was at acceptable level (< 11 ppb of chlorate), but associated DBPs in other two trains were above.

Table 6-6 Concentrations of DBPs for all CTs.

DBPs	Unit	CT1	CT2	CT3
Trichloromethane ( $\text{CHCl}_3$ )	ppb	35	11	29
Dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ )	ppb	ND	ND	ND
Tribromomethane ( $\text{CHBr}_3$ )	ppb	21	ND	30
Bromodichloromethane ( $\text{CHBrCl}_2$ )	ppb	11	5	12

\*ND: Not detected.

The flow cytometer (FC) results presented in **Figure 3**, suggesting that all of the three oxidants were effective in keeping the active cell counts for all three pilot CTs, even under increase algal growth. Among them ozone tends to be effective in keeping the microbial count to lower value than to the chlorine, while  $\text{ClO}_2$  higher effective than chlorine. However, in terms of the DBPs formation, particularly for this period, a significantly lower level of TTHMs was noted for  $\text{ClO}_2$  (< 10 ppb for TTHMs).

#### 6.4.4 Organics

The algae addition to the CT basin results in a slightly higher level of DOC than raw seawater. Moreover, after 20d a sudden increase of DOC (right after the algae addition)

was observed for all three CTs as shown in **Figure 4**. This is due to that, Algae green and diatom grown in surface water media produced dissolved organic carbon and turbidity [43].

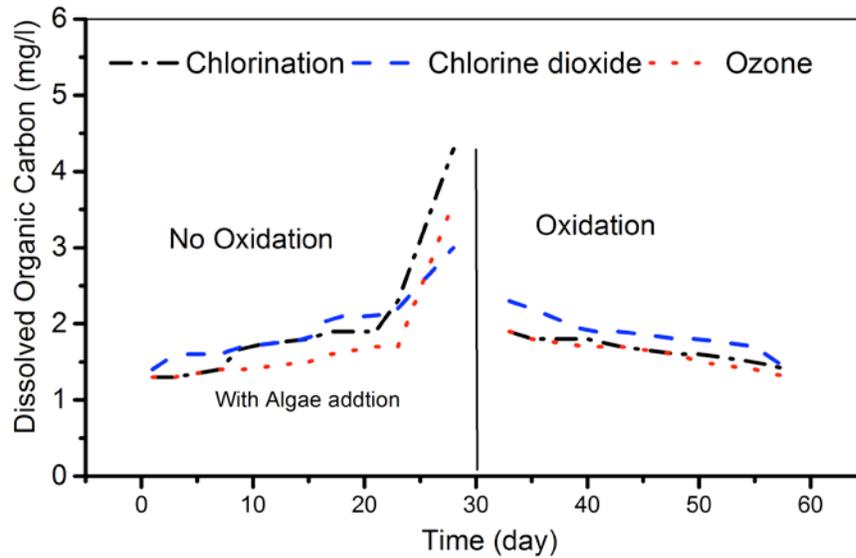


Figure 6-5: Dissolved organic carbon for all CTs.

The UV specific absorbance at 254 nm (UV<sub>254</sub>) has been often used as an indicator of the DBPs concentration of the water oxidants treatment [44, 45]. The highest UV<sub>254</sub> absorbance at high DBPs formation were obtained for CT3 (with ozone) around 0.06 cm<sup>-1</sup>, CT1 (chlorination) around 0.04 cm<sup>-1</sup>, and the lowest for CT2 (ClO<sub>2</sub>) due to less DBPs formation around 0.02 cm<sup>-1</sup> (Figure 6-6).

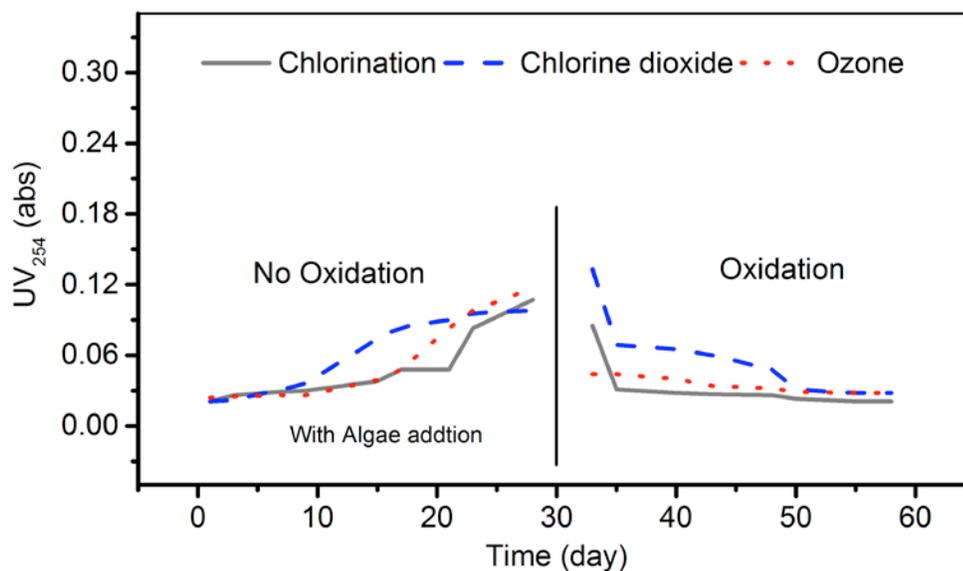


Figure 6-6: UV<sub>254</sub> analysis data for all cooling towers.

#### 6.4.5 Inorganics

Inductively coupled plasma spectroscopy (ICP) and ion chromatography (IC), which are an extremely sensitive detection technique, used to measure the concentration of selected trace constituents of the seawater CTs and their data at both conditions (with oxidation and oxidation) are given in **Table S1** (supplementary information). The efficiency of disinfection and byproduct formation affect the water quality parameters, particularly for surface water where seasonal variation in dissolved organic carbon, temperature, and turbidity [46]. Normally, the chemical oxidation will enhance to the removal of natural organic matter, mineral compounds and suspended solids, this step partially destroys the water quality [47, 48]. For instance, the use of ozone in cooling seawater treatment showed reduction in nitrate and bromide, this is due to the potential to form bromate

compare to cooling towers without oxidation. Other chemical oxidations have similar effect to the water quality as shown in **Table S1**.

## 6.5 Conclusions

Alternative oxidants for treatment of seawater CTs were investigated: Chlorine along with two other oxidants, namely (i)  $\text{ClO}_2$  and (ii) ozone. All the oxidants were evaluated at fixed cycle of concentration (COC) and under ambient temperature conditions. Followings are some of the key findings from the pilot-scale assessment.

- The CT was found to be an effective in replicating the full-scale ones in term of COC and differential (Delta-T) temperature at the heat exchanger with residual chlorine as TRO level.
- Ozone and  $\text{ClO}_2$  oxidants were an effective in keeping the microbial growth to the minimum than chlorine (even after the algae).
- The amount of DBPs formed was note it low when used  $\text{ClO}_2$  of seawater CT treatment.
- Among the oxidants, ozone was found to be effective in minimizing bioactivities for similar TRO level as compared to chlorine and  $\text{ClO}_2$ , however other parameters, in terms of cost benefit analysis, corresponding capital and operation and maintenance costs, efficacy and efficiency along with ease of operations, treated water quality, environmental impacts, etc., are needed to be carefully considered and evaluated, to suggest one oxidant type over another.

## 6.6 Acknowledgements

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## 6.8 Supplementary Information

**Table S1** ICP-MS and IC data for all CTs.

PARAMETAR	unit	No oxidation			Oxidation		
		CT1	CT2	CT3	CT1	CT2	CT3
Fluoride (F <sup>-</sup> )	ppm	0.8	0.8	0.8	1.4	1.2	1.3
Chloride (Cl <sup>-</sup> )	ppm	26476	25427	25612	25773	24522	24967
Nitrite (NO <sub>2</sub> <sup>-</sup> )	ppb	21	17	21	82	37	80
Bromide (Br <sup>-</sup> )	ppm	107	90	101	21	14	7
Sulfate (SO <sub>4</sub> <sup>-2</sup> )	ppm	3824	3688	3695	3815	3555	3629
Sodium (Na <sup>+</sup> )	ppm	14690	13970	14310	1768	1606	1709
Potassium (K <sup>+</sup> )	ppm	697	638	647	517	465	508
Magnesium (Mg <sup>+2</sup> )	ppm	1944	1743	1802	629	573	604
Calcium (Ca <sup>+2</sup> )	ppm	548	519	543	14040	12820	13540
Iron (Fe)	ppb	301	283	297	275	272	279
Nickel (Ni)	ppb	6	5	8	1	1	1
Copper (Cu)	ppb	6	4	3	3	2	1
Zinc (Zn)	ppb	52	35	38	45	25	32
Titanium (Ti)	ppb	BDL	BDL	BDL	BDL	BDL	BDL
Manganese (Mn)	ppb	1	1	1	0.7	BDL	BDL

\*BLD: Below detection limit.

## **Chapter 7**

### **7 Publication No # 4**

The following publication, “Nutrient removal to minimizing biofouling in seawater cooling towers”, written by Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Kim Choon NG, and TorOve Leiknes,

## **Nutrient removal to minimizing biofouling in seawater cooling towers**

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### 7.1 Abstract

In Saudi Arabia a huge amount of seawater is used in operation of cooling towers due to a lack of freshwater and groundwater resources. Seawater is mainly used as a cooling medium in heavy industries, oil refineries, petrochemical plants and thermal power stations and the most feasible (low-cost and unlimited). One of the most popular methods used in the cooling tower process to control the biofouling is disinfection by chlorination, which is used commonly around the world. However, the disadvantages of chlorination are: the formation of harmful disinfection byproducts (DBPs) in the presence of high organic loading and safety concerns in the storage of chlorine gas. Biofouling is a serious problem in industrial cooling tower processes. It damages equipment through bio-

corrosion, causes blockages, and increased energy consumption through decreased heat transfer.

The research strategy is focusing on the control of biofouling in seawater cooling towers by using a new approach is to remove the nutrients from seawater to prevent the growth of biofouling. The concentration limitation of the nutrients in seawater is one of the key strategies to control growth of biofouling in the system. Fast growing algae suffer more from nutrient limitation than slow growing algae at low nutrient availability. So, nutrient limitation may be able to be controlled and minimize biofouling in seawater cooling system. Assimilable organic carbon (AOC) levels are linked with increased growth of biofouling potential in the feed seawater. So, AOC concentration can be used as an indicator of fouling of feed seawater.

Granular activated carbon (GAC) bio-filter has a possibility of reducing biofouling potential in the pretreatment of seawater desalination by removing AOC. GAC is often made from bituminous coal and remove molecular size particles from the water. The test results showed that around 70 % removal was achieved of total organic carbon in seawater feed were effective in keeping the microbial growth to the minimum. The measured results from this study enable designers of seawater cooling towers to manage the biofouling problems when such cooling towers are extrapolated to a pilot scale.

**Keywords:** Nutrient removal, total organic carbon, granulated activated carbon, Biofouling control

## 7.2 Introduction

Seawater is most commonly recycled medium of the heat transfer in cooling tower systems and reject heat from a process into the atmosphere by evaporating. This process can be a chemical, physical or mechanical process [1]. Open recirculating cooling water systems is performed only to cool the warmed water and considered one of alternative technologies to dissipate waste heat [2-6]. Depending on the quality of seawater supply in cooling water systems underwent some operational risks such as scaling, corrosion and biofouling [7]. Any one of these challenges or more mostly a combination of them consequence in reduce the lifetime of cooling towers, reduced capacity, and high operation and maintenance expenses [5, 8-13].

Biofilm and microbial growth in cooling water system are quite severe making heat transfer efficiency worse [11]. Microbiological fouling in cooling tower systems is mainly caused by the growth of algae, fungi and bacteria in the process [14, 15]. This is accelerated in open recirculating water systems compared to the closed system [8, 13, 16-18]. To control the biofouling in the cooling tower, basically chemical and physical treatments are used and these treatments used to be employed either separately or together [19]. The most widely practiced approach to inhibit the biofilm formation and inactivate the microorganisms or reduce the biological activity in the cooling water process is the chemical treatment using biocides such as chlorine, chloramines, ozone and chlorine dioxide classified as oxidant [20-23]. Physical treatment (e.g., bio-filter, membrane filtration) has been recently reported as alternative disinfection methods [24]. Recently, A new technologies such as ultrasound, magnetic field, ultraviolet rays, and

electric field have been applied in the cooling water system [25]. The objective of cooling water treatment is to protect and extend lifetime of the cooling water system equipment.

Granular activated carbon (GAC) is one of the bio-filter becoming more common used in the removal of organic carbon. The high surface contact area of the GAC with a large volume will hence high natural organic removal (NOM). Naidu et al. (2013) have reported that granular activated carbon (GAC) bio-filter has a capability to reduce the biofouling with maintaining a stable microbial activity in the bio-filter [26]. GAC has several advantages such as has a large and unequal surface which will increase the adsorption of the organic and microorganisms [27]. It is found in many types of research that the GAC and anthracite were used as bio-filter media to remove of particulate matter and organic matter from seawater [28]. Assimilable organic carbon (AOC) is one of the parameters linked directly to biofouling in the seawater feed [29, 30].

The membrane filtration is a thin film of organic or inorganic synthetic and used for a separation between a fluid and components by passing the mixture through a porous. The membrane has a capacity to remove the biological and non-biological matters of the water pretreatment. There are many research paper show that membranes can reduce the microorganisms from wastewater and reuse water significantly [31]. The advantages of the membranes technology for the water treatment are clarification and disinfecting, high quality of treated water, compact system, easy to operate, less maintenance, less chemical uses [32, 33]. Ultrafiltration (UF) can remove the viruses and algae from wastewater, that is particles larger than their largest pore size [34]. Recently the use of UF in treatment of the drinking water becomes a more significant technology as alternative to the

conventional clarification [31]. Also, the UF has been applied as pretreatment in the Reverse Osmosis (RO) of fouling removal and this can be apply on the cooling tower treatment [35, 36].

In this study, Nutrient removal is another alternative approach to control biofouling growth in seawater cooling towers at pilot scale. The studies have explained the seawater treatment process can remove the major quantities of natural organic matter, suspended solids, and microorganisms contained in seawater. Water quality parameters such as Dissolved oxygen carbon (DOC), Assimilable Organic carbon (AOC), and LC- OCD were measured.

### 7.3 Material and methods

#### 7.3.1 Seawater

The granular activated carbon (GAC) biofiltration and Ultrafiltration (UF) experiments were conducted at King Abdullah University for Science and Technology (KAUST), Thuwal, Saudi Arabia. The raw seawater supplied from the intake system of RO desalination station and fed into bio-filters and UF continuously. The GAC bio-filter and UF were used as pretreatment for the makeup feed of the seawater cooling towers basin. This experiment was applied into pilot cooling towers PCTs were constructed at KAUST's Central Utility Plant (CUP). The pilot-scale facility was installed outside, such that it could be exposed to all types of environmental conditions. The operation of the pilot-cooling tower (PCT), were lasted for 70 days (d) with no oxidation. For this study

the all three cooling towers operated for different pretreatment systems were: cooling tower no. 1 (**CT1 using UF**), Cooling tower no. 2 (**CT2 using GAC column**) and, cooling tower no. 3 (**CT3 as control**)

### 7.3.2 Experimental set-up

#### 7.3.2.1 GAC column:

The bio-filter was tested in a pilot-scale seawater cooling towers, this experiments were conducted to evaluate AOC and DOC removal efficiencies using GAC as fillers. Characteristics of GAC filter filling materials were presented on Table 7-1. The GAC column biofiltration experimental set-up is demonstrated in Figure 7-1. Two transparent acrylic cylinder filter columns, which had a diameter of 12 cm and a height of 150 cm were connected together and operated in parallel for makeup feed of the basin. The columns were filled up to a depth of 10 cm from the bottom with stone size 5 mm and following granular activated carbon (GAC) as the media, which was filled up to 100 cm in height (6 kg) respectively, were used in the column test. The empty bed contact time (EBCT) of the bio-filter was about 7.5 min. The nominal size (d50) of GAC (1.03 mm) whereas surface area of GAC ( $1000 \pm 50 \text{ m}^2/\text{g}$ ). These specifications of media were provided from the supplier (Galgon Carbon). The filters were operated at flow rate 1.5 l/min to maintain a stable bacterial activity. The bio-filters were backwashed infrequently at flow rate 3 l/m for 15 min. The influent seawater used in the column test was from the intake system of the RO desalination unit and the filtration rate was 8 m/ h.

Table 7-1: Characteristics of granular activated carbon filter.

Specification	Values
Nominal size (d50, mm)	1.03
Bulk density (kg/m <sup>3</sup> )	540
Surface area (m <sup>2</sup> /g)	1000 ± 50
Nominal size (d10, mm)	0.54
Colour	Black

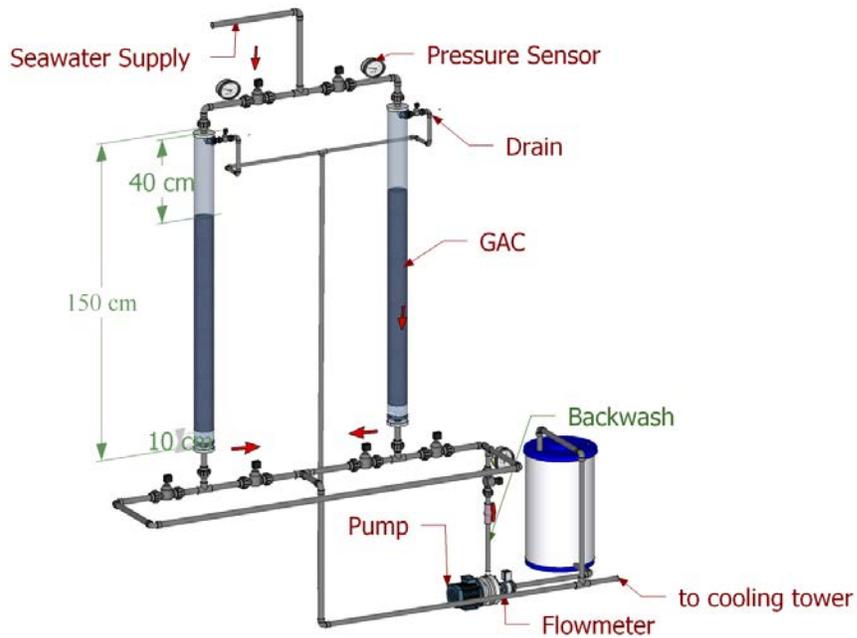


Figure 7-1: granular activated carbon bio-filter unit diagram.

### 7.3.3 Ultrafiltration:

The UF membrane module unit (WMZ-12521A-216) as well as the control system was supplied by Applied Membrane INC, is a kind of hollow-fiber membrane module in a PVC membrane vessel was used in the experiment. Characteristics of the membranes are shown in Table 7-2. The unit consists of one membrane vessel 10.2 cm diameter by 51.5 cm length UF membrane module and control system. The flow of the feed water was from inside of the fiber to the outside of the fiber. Figure 7-2 illustrates a schematic diagram of the UF membrane unit experimental facility. The seawater was pumped to the UF membranes for direct UF, because of high turbidity of feed seawater the pretreatment by cartage filter (size 5  $\mu\text{m}$  and 1  $\mu\text{m}$ ) respectively were applied before the UF unit. In the backwash phase, a controller equipped on the unit, controlled the Backwash of the UF membrane unit module. The washing water was sent to be pressurized from the outside to the inside of the UF (duration of 60 s) was made during a 48 h interval.

Table 7-2: Characteristics of the membrane.

Item	Value
Nominal Capacity GPD	1600
System Capacity $\text{m}^3/\text{day}$	6.06
Material	PVDF
Minimum, dynamic psig	40
Maximum, dynamic psig	100
System diameter cm	L 71, D 30, H 66

Membran Element size, (Dia.\*L)

2.5 \* 21

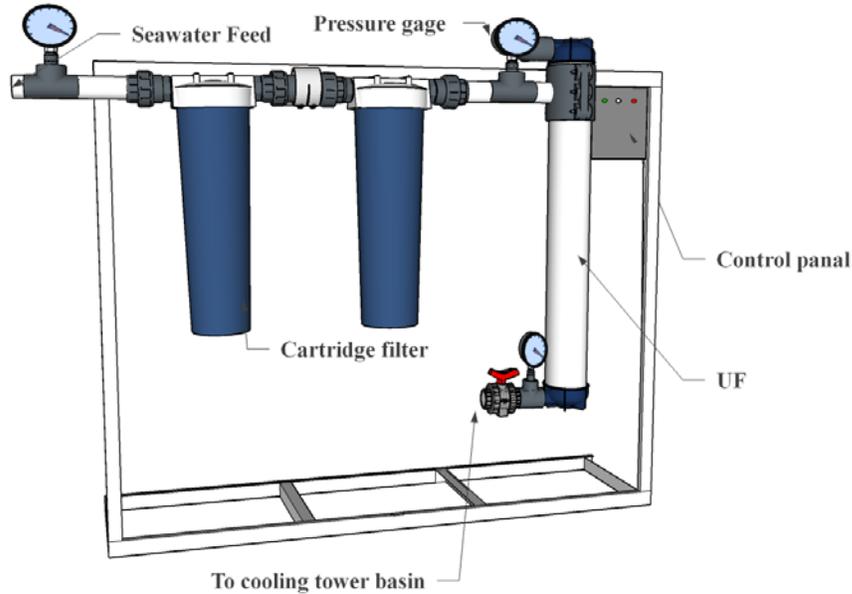


Figure 7-2: Ultrafiltration diagram.

#### 7.3.4 Pilot plant cooling seawater systems with recirculating

The pilot-scale facility was installed outside at KAUST's Central Utility Plant (CUP) where can supply fresh seawater and could be exposed to all types of environmental conditions. The PCTs diagram is depicted in Figure 7-3 and it is automated pilot operation runs were maintained by the LabView system. The basic components of PCTs are frame and casing made of fiber-reinforced plastic (FRP) with (height of 1550 cm and diameter of 750 cm), film filled with packing material made of PVC (height of 525 cm), cold-water basin with 52 L capacity that is located near the bottom of the tower and fans. The cooling towers specification and materials can be found in (Table 7-3).

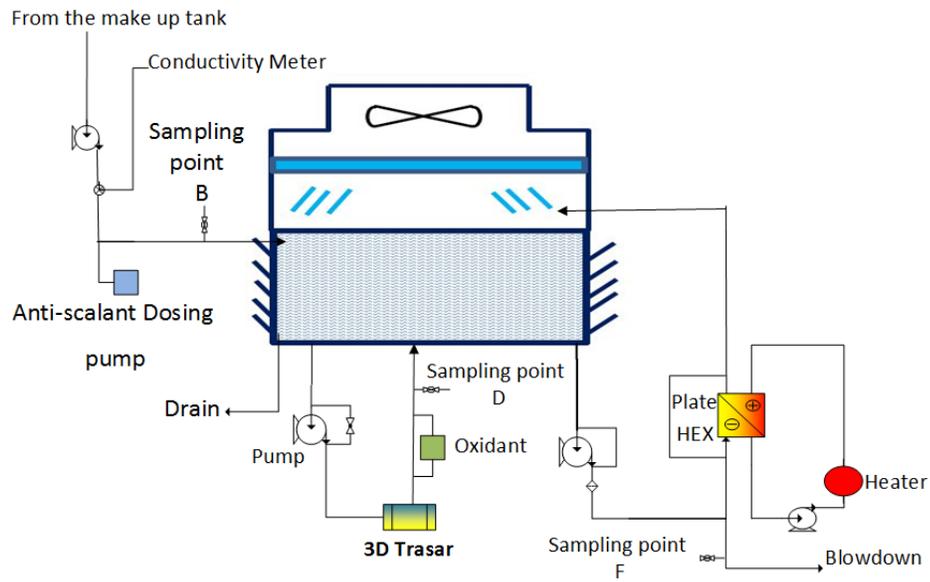


Figure 7-3: Flow diagram of a pilot plant cooling seawater system.

Certikin titanium plate heat exchangers were constructed with electro seawater resistant heater (15 KW) (diameter length of 592 mm), worked by transferring the heat water from close loop to seawater open loop in cooling tower. The temperature difference between inlet and outlet of heat exchanger remained at targeted temperature difference of  $10 \pm 2^\circ\text{C}$ .

Table 7-3: Overview of the cooling Tower process parameters.

DESIGN, OPERATING AND CONSTRUCTION MATERIAL	SPECIFICATION
Tower pump head	1.5 m
Drift loss of water flow rate	0.10 %
Volume of cooling tower basin	52 L/min
Volume of water in system	10 L
Make-up water flow	1.5 L/min
Recirculation water flow	24 L/min
Blow-down water flow	1 L/min
Concentration factor of process water	1.2
Heat water flow	21 L/min
Cycles of concentration	1.2

### 7.3.5 Flow Cytometer

The total live cell counts of algae and bacteria in seawater measured by using a BD Accuri™ C6 Flow Cytometer (FCM). 1X of SYBR® Green I + 10 µg/ml of Propidium Iodide (PI) were used to stain live and dead cells, respectively. A 495 µl of water sample was transferred to a sterile Eppendorf tube and 5 µl of the 100X of SYBR® Green + 1000 µg/ml Propidium Iodide (PI) was added to the water sample. Then it was incubated at room temperature for 15 min. Then, 200 µl of the incubate sample was transferred to a 96-well plate for measurement (pump speed = medium, and FL1 threshold = 600).

### 7.3.6 Liquid Chromatography - Organic Carbon Detection

To characterize the natural organic matter (NOM), Liquid chromatography-organic carbon detection (LC-OCD) was developed to identify quantitative information and qualitative results regarding organic compounds in natural water. LC-OCD model 8 system has UV detector (UVD), online organic carbon detector (OCD), and organic nitrogen detector (OND). In this study, the characteristics of different constituents of NOM identified are summarized in Table 7-4.

Table 7-4: Characteristics of different constituents of natural organic matter.

NOM	Size (Da)
Biopolymers (BP)	> 20,000
Humics (HS)	≈1000
Building Blocks (BB)	300 - 450
LMW	<350

Seawater samples were filtered Whatman filter (pore size = 0.45 μm). in 20-mL glass vials. Then, Compounds were separated using two-column of Toyopearl (dimension: 250 mm x 20 mm, particle size: 20-40μm).

### 7.3.7 Assimilable Organic carbon (AOC)

In this study, the assimilable organic carbon was measured to demonstrate the performance of the GAC removal. Dr. Jeong developed the AOC method for improvement of accuracy and easiness of measurement [30]. The AOC protocol demonstrates in Figure 7-4. The target level AOC 10 ug-C/L and the detection limit is 0.1 ug-C/L.

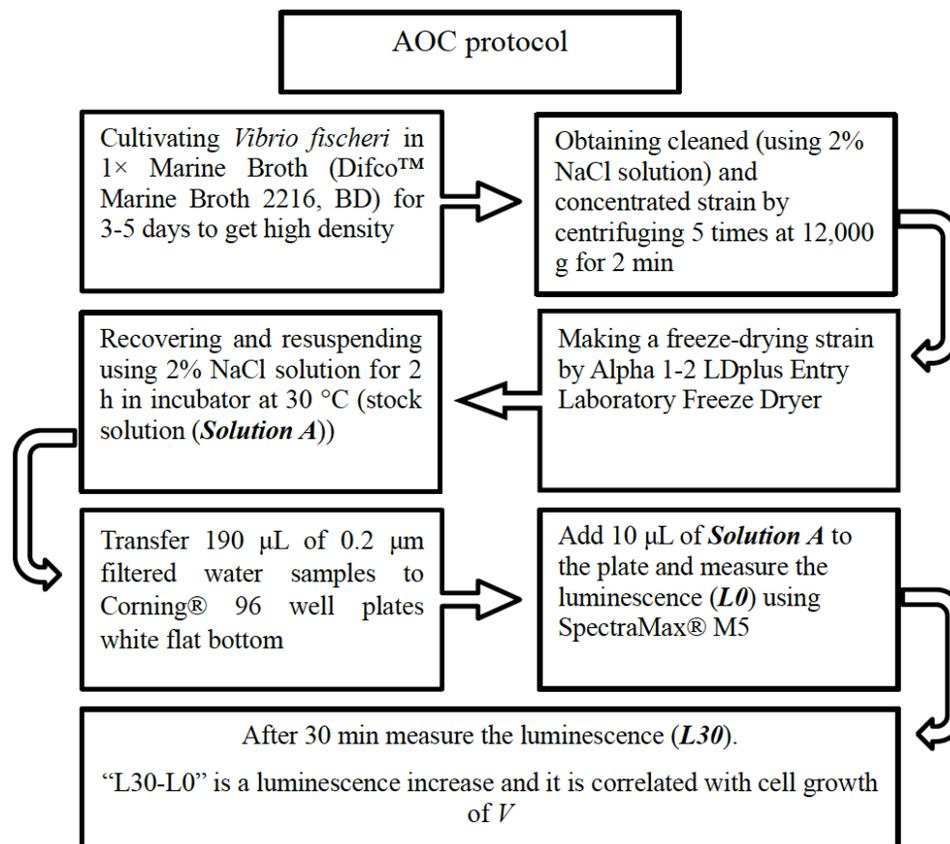


Figure 7-4: Assimilable Organic carbon protocol.

### 7.3.8 Field and lab analysis

The online parameters such as conductivity and pH were measured by using 3D TRASAR technology. This was designed for measuring the key system parameters for the PCT operation. Total organic carbon (TOC) was measured by using a Shimadzu analyzer after filtering through a Whatman filter (pore size = 0.45  $\mu\text{m}$ ).

## 7.4 Results and discussion

Results show that, the physical treatment of the seawater-cooling tower was able to successfully control the biofouling at actual full-scale plant condition. It was also able to maintain the targeted delta T  $10 \pm 2^\circ\text{C}$  at the heat exchanger sides. The PCTs were operated continuously 24/7. Successful operation of the pilot-cooling tower (PCT) was done for 30 days (d). For this study, the chemical disinfection practice of all PCTs was postponed during the experiment.

### 7.4.1 Microbial Analyses - Viable Cell count

Biofiltration (GAC column) and Ultrafiltration effectiveness was evaluated by determining the total live flow cell counts. In this study, this factor was quantified using flow cytometer. From Figure 9, rapid decrease in bacterial cell counts can be noticed after the physical pretreatment of the make-up water of the cooling tower.

Ultrafiltration achieved around 90% removal of the microorganisms, while the GAC column removed average around 39%.

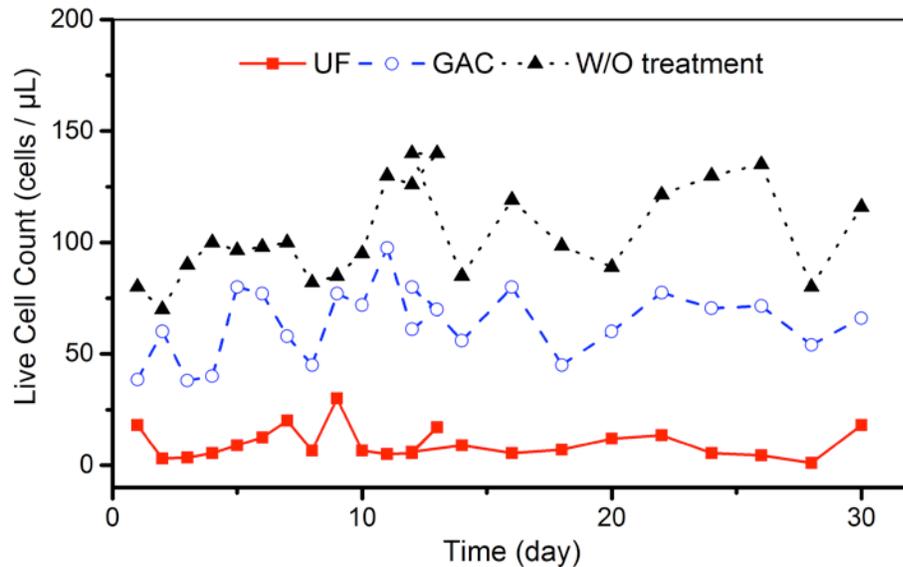


Figure 7-5: Total Live cell counts for granular activated carbon, ultrafiltration, and control.

UF managed to achieve viable cell counts lower than 3 cells/μl at the initiation of pre treatment. Viable cell counts for the other test conditions are shown in Table 7-5. It is interesting to note that, the backwash of UF and GAC are significantly reducing the viable cell counts during the experiment.

The total organic carbon (TOC) were measured due to physical treatment resulted in higher reducing level of TOC values (right after the GAC column) for all three PCTs as shown in Figure 7-6. This test showed the GAC column removing 71 % of total organic

carbon, while the ultrafiltration can remove around 11 %. Table 7 show that, GAC can significantly decrease the biological growth for cooling towers by removing the organic nutrients.

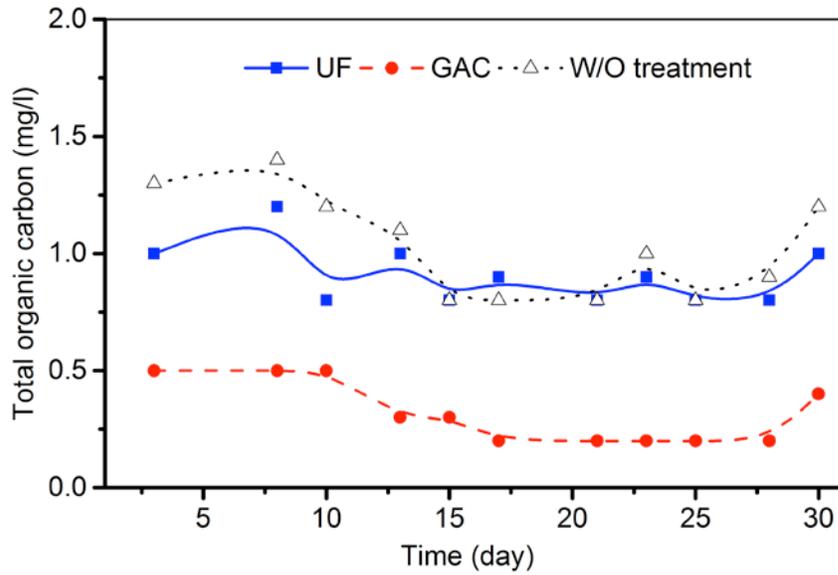


Figure 7-6: Total organic carbon data of granular activated carbon, ultrafiltration, and Control.

Table 7-5: Live Cell Count and Total organic carbon for granular activated carbon, ultrafiltration and, Control.

Parameters analysis	UF	GAC	Control
Live Cell Count (cells / $\mu$ L)	10	64	105
	$\pm 7$	$\pm 16$	$\pm 22$
TOC (mg/l)	0.91	0.32	1.03
	$\pm 0.13$	$\pm 0.13$	$\pm 0.22$

All of these above findings have relevance to the cooling tower operation treatment.

#### 7.4.2 Assimilable organic carbon

The possible for biofouling growth in the open seawater cooling tower was evaluated by assimilable organic carbon (AOC) bioassays. The changes in the nutrient concentration of the microorganism's growth and activity will assist to control the biofouling in the CT. Two GAC bio-filter were fixed in parallel before the makeup feed as given in Figure 7-7. GAC bio-filter achieved around 60 % removal of AOC than ultrafiltration during the 30th day as indicate in figure, this is due to the higher capacity for adsorption and greater surface area of GAC. Compared to the GAC bio-filter, the UF indicate less ability to remove AOC. The AOC of untreated seawater cooling tower (control) showed in Figure 7-7. The results demonstrate the capability of GAC bio-filter to remove AOC for the

seawater feed to minimize the microorganism's growth and biofouling on seawater cooling tower. The outcome data from this research suggest that, the GAC bio-filter media has possible to reduce AOC. This is a good pretreatment method selection standard to control biofouling.

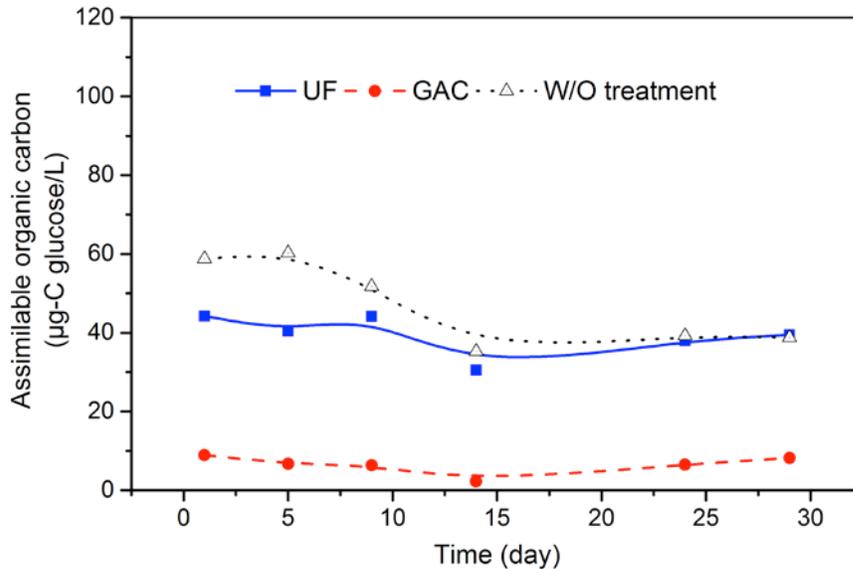


Figure 7-7: AOC data of granular activated carbon, ultrafiltration and, Control.

#### 7.4.3 Organic matter removal

The DOC removal efficiency of the GAC bio-filter was compared with membrane (Ultrafiltration) pretreatment of the cooling tower. The dissolved organic carbon concentration of raw seawater feed of makeup is  $1.0 \pm 0.14$  mg/L. The raw seawater was filtered through GAC bio-filter and was analyzed using the LC-OCD. The results showed that, GAC bio-filter was able to decrease the concentration of DOC to  $0.3 \pm 0.06$  mg/L (approximately 70%) during the 30<sup>th</sup> day run as showed in Figure 7-8.

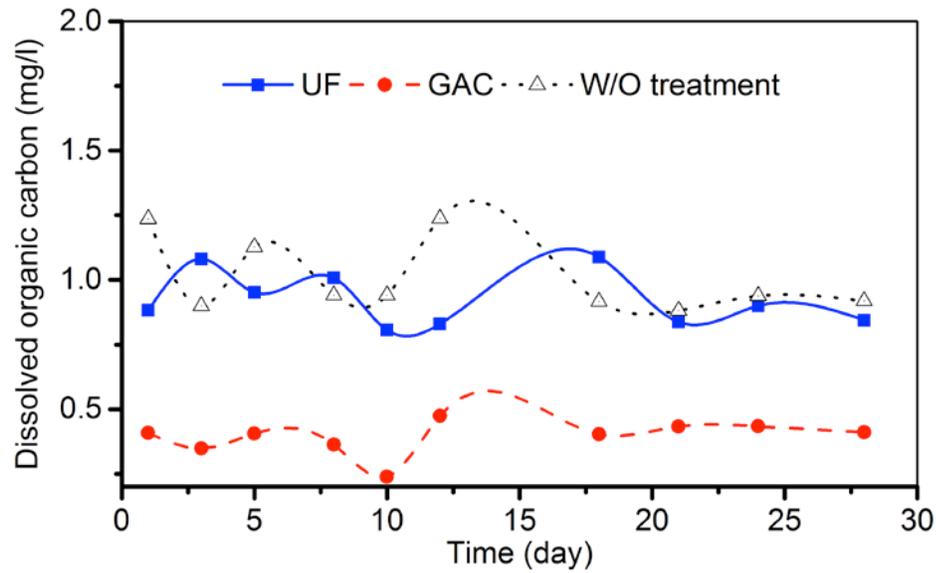
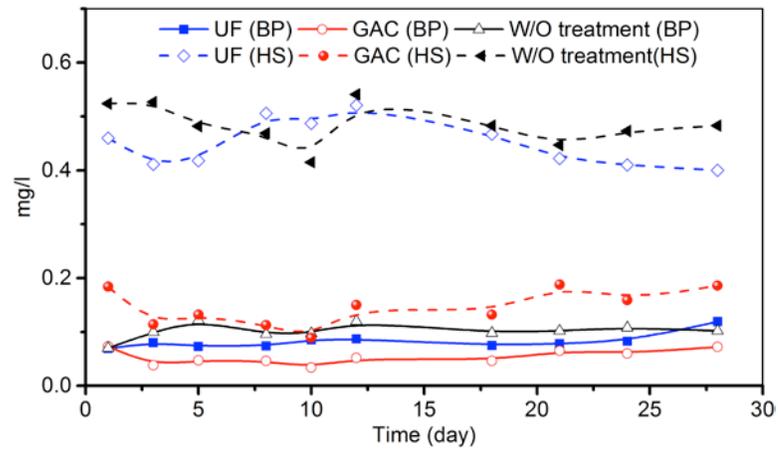
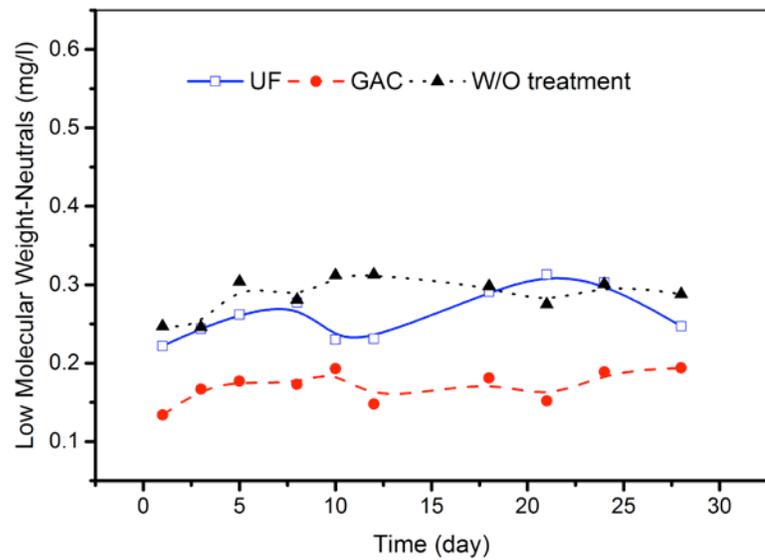


Figure 7-8: Dissolved organic carbon data of granular activated carbon, Ultrafiltration, and control.

This included removal of 50 % biopolymers, 71 % humic substance and 45 % LMW neutrals as shows in Figure 7-9A and Table 7-6. In last 10 day the organic concentration of GAC bio-filter remained stable at this stage ahead. This tendency might be due to the microbial growth.



A



B

Figure 7-9: (A) Humic substance and biopolymers data (B) LMW-N for granular activated carbon, ultrafiltration and, control.

Meanwhile, a parallel study of ultrafiltration membrane shows the results of DOC removal is very low around  $0.92 \pm 0.06$  mg/L, using the same seawater as that in this study was carried out. DO analysis (by LC-OCD) of UF membrane achieved 20 %

removal of the biopolymer fraction. However, the humic substances removal was only 6% as shows in Figure 7-9 B and Table 7-6. UF membrane was found ineffective to remove the LMW-N organic matter of seawater. In raw seawater the low molecular weight organic compounds is high and they are mainly responsible for biofouling [37]. Membrane UF pretreatment would not be able to successfully to control the biofouling growth. While GAC has high removal of LMW organics was achieved as indicate in Figure 7-10.

Table 7-6: LC-OCD organic matter data for granular activated carbon, ultrafiltration, and control.

Parameters analysis	UF	GAC	Control
BP (mg/l)	0.08 ± 0.01	0.05 ± 0.01	0.10 ± 0.01
HS (mg/l)	0.45 ± 0.04	0.14 ± 0.03	0.48 ± 0.04
BB (mg/l)	0.05 ± 0.04	0.02 ± 0.01	0.06 ± 0.03
LMW-N (mg/l)	0.32 ± 0.07	0.18 ± 0.07	0.33 ± 0.11
DOC (mg/l)	0.92 ± 0.10	0.39 ± 0.06	1.00 ± 0.14

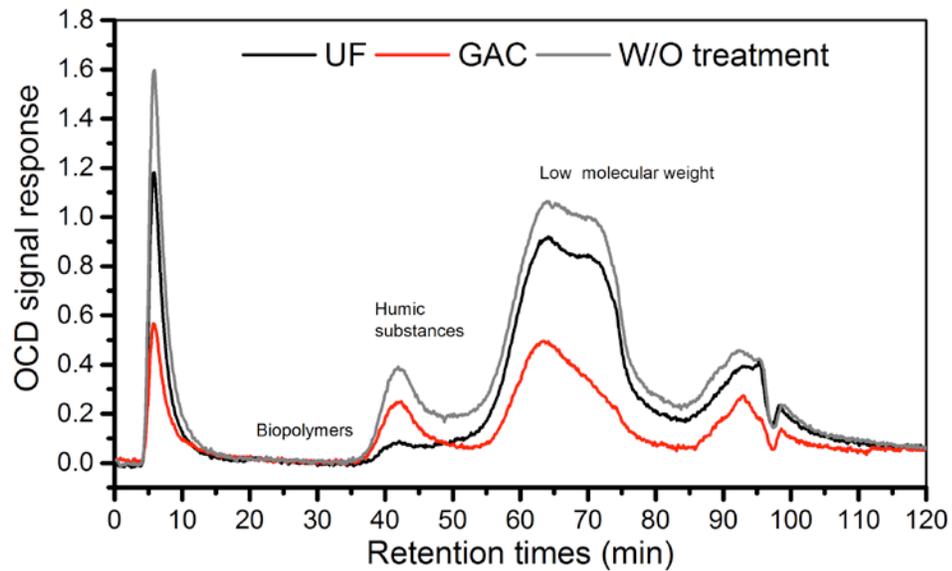


Figure 7-10: LC-OCD data analysis of the seawater-cooling tower using different treatment Ultrafiltration, Granule activated carbon and without treatment.

#### 7.4.4 pH and conductivity

In-situ pH measurements for all three PCTs showed that there was no pH change over the 30d of operational period and it was maintained at around pH 7.7. The conductivity values measured of UF and GAC CTs show a similar conductivity average value of around 65 mS/cm at PCT basins. The conductivity measurements on the control CT was around 57 mS/cm, Table 7-7 shows the overview of the pH and conductivity.

Table 7-7 : Overview of pH and conductivity for all cooling towers.

Parameters analysis	UF	GAC	Control
pH	7.68	7.72	7.61
	± 0.10	± 0.07	± 0.04
Conductivity	75	74	57
	± 6	± 3	± 1

## 7.5 Conclusions

This study investigated the organic removal and microorganisms of GAC bio-filter and membrane UF applied as pretreatment to seawater cooling tower makeup. Also, AOC was investigated to evaluate the effect of microbial biodegradation on organic removal. Based on the different physical pretreatment, the results led to following key findings obtained from the pilot-scale.

- GAC bio-filter has a high organic removal capacity was achieved (70%), including the LMW organic compounds removal (41%).
- The AOC concentration of the raw seawater was decrease significantly to 90% by the GAC bio-filter during the 30 days.
- Overall, this signified findings, that valuable to control the biofouling growth by reducing the organic nutrients concentration to the minimum.

## 7.6 Acknowledgements

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## **Chapter 8**

### **8 Publication No # 5**

The following publication, “Effect of (GAC/UF) Hybrid process pretreatment of industrial seawater cooling towers to minimizing biofouling”, written by Mohammed. Al-Bloushi, Jayaprakash. Saththasivam, Sanghyun. Jeong, Kim Choon NG, and TorOve Leiknes,

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## **Effect of (GAC/UF) Hybrid process pretreatment of industrial seawater cooling towers to minimizing biofouling**

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### 8.1 Abstract

Biofouling and organic fouling are one of the serious problems in industrial cooling tower processes. Chemical biocides such as chlorination have been used to control the cooling tower biofouling. However, the chlorination was found not be an effective enough to remove biofouling as well as the formation of harmful disinfection byproducts (DBPs) of high organic loading. Physical treatment such as ultrafiltration (UF), granule activated carbon (GAC) can prevent the cooling tower biofouling by removing the nutrients. This paper investigates the granule activated carbon (GAC) impact to the biofouling control by natural organic matter (NOM) removal in GAC/UF hybrid process. Removal of NOM from seawater is important to prevent the biofouling growth and Assimilable organic carbon (AOC) levels are linked with increased growth of biofouling potential in the feed seawater. So, AOC concentration can be used as an indicator of fouling of feed seawater. Therefore, the aim of this study was to evaluate the effect of the hybrid process, Granular activated carbon (GAC) adsorption/ ultrafiltration (UF)

approach, as a pretreatment of the makeup seawater. Also, to evaluate the performance in terms of organic matter removal and cooling tower biofouling. Experiments were performed in two transparent acrylic cylinder filter columns, which filled up granular activated carbon (GAC) as the media. Ultrafiltration membrane followed with to (1.5 L/min) constant permeates flux. Granular activated carbon achieved natural organic matter (NOM) removal by up to 67 %. Moreover, GAC adsorption with UF membrane increased the removal to 78% of NOM. The hybrid GAC / UF process performed in increase the performance of the NOM removal. However, GAC/UF hybrid promising processes contributed to minimizing the chemical biocides, mitigate the biofouling growth and, enhanced the AOM removal.

**Keywords:** Assimilable organic carbon; GAC/UF; Nutrient removal; total organic carbon; Biofouling control; biofiltration; seawater cooling system;

## 8.2 Introduction

Open recirculating seawater cooling tower is a great equipment to minimize thermal pollution of the seawater discharge. This device is used as an economically and environmentally method for disposing of surplus heat generated in the industrial process. The extra heat removal is achieved through the evaporation by using the cooling water system, which is the warm water contact with air into the cooling tower [1]. Scaling, biofouling and, corrosion are the challenges of the cooling water systems. The accumulation of organic deposits on the surfaces of heat exchangers is usually indicated to biofouling, this will require additional maintenance costs [2]. Biological fouling (or

biofouling) is a critical issue in the open recirculating cooling water, which decreases the performance of cooling water system. Also, biofouling cause issues such as Microbial Induced Corrosion (MIC), energy loss [3], clogging of cooling towers and, lower efficiencies of heat exchanger [4-7]. Biofouling of surfaces contains existing matter such as a single cell, bacteria, fungi, or algae. In some practices, such as seawater cooling equipment microorganisms could create operational problems [8]. A number of factors affect the growth of biofilms on the industrial cooling water equipment such as the availability of nutrients [9], temperature: the optimum temperature for maximum growth for bacteria found in cooling water process is around 40°C mostly in summer [10], and small particles that transferred with the makeup seawater [11]. Moreover, the water temperature in circulating cooling systems is an ideal environment for biological growth [12]. Biofouling in open recirculating cooling water system is a complex system affected the mechanical equipment features and the conditions of operation.

The most widely practiced approach used to minimize the biofouling in industrial water cooling systems is by using a disinfectant, commonly called a biocide. The role of the biocide is to kill microorganisms by using a continuous dose or intermittently. The use of oxidizing biocides is to control extreme biofouling formation in a cooling water process become the more common practice used in the industrial zone [5]. Among the various oxidants, chlorine has remained, Chlorine is one of a popular oxidizing biocides method used in the industrial cooling water system for many years of biofouling growth [6, 13, 14]. However, the chlorination is very reactive to natural organic matter, leading to the formation of disinfection by-products DBP such as trihalomethanes (THMs) and other

by-products concern due to possible toxicity [15-17]. Chlorinated blowdown introduced to coastal seawater is a great environmental concern because of major sources of hazardous compounds reaching to the marine environment [18]. Moreover, dead microorganisms of the biocides it can be nutrients and suitable surfaces for additional growth of cells introduced with the raw seawater [19]. For these reasons, the use of chlorination is not being recommended in favor of environmental standard regulations [8].

In water treatment process there is a trend to improve and apply more environmentally technologies and lower impact of chemicals to help to reduce overall water consumption. Non-chemical treatments methods were increasingly used in cooling water system, wastewater treatment and, drinking water disinfection [20]. Physical treatment (e.g., bio-filter, membrane filtration) has been recently reported as alternative disinfection methods [21]. Recently, A new technologies such as ultrasound, sand filtration, Granular activated carbon (GAC) and Ultrasonic technology have been applied in the cooling water system [20, 22]. Granular activated carbon (GAC) is one of the bio-filter becoming more common used in the removal of organic carbon. GAC has several advantages such as has a large and unequal surface which will increase the adsorption of the organic and microorganisms [23, 24]. Assimilable organic carbon (AOC) is one of the parameters linked directly to microbial growth in the seawater feed [25, 26]. The concentrations of AOC in industrial water systems are depending on the quality of the makeup water [27].

This study has been conducted to improve the ultrafiltration process performance by adding a bio-filter such as Granular activated carbon (GAC) in the pretreatment process

[28]. The hybrid GAC/UF technology has been used as a non-chemical approach to meet the environmental parameter. This process is very effective for removing the organic matter from seawater. UF can achieve a complete removal of cells, but less removal of natural organic matter NOM in water. By adding activated carbon to UF process treatment the removal of total organic carbon TOC and nutrients can be significantly improved [29]. The removal of (TOC) by UF around 7%, while when adding the activated carbon the removal increased to 70% [28]. Also, have been showing more than 95% of algae removal regarding chlorophyll [30]. The GAC/UF can improve the NOM removal rate have been reported [31]. The objective of the hybrid pretreatment is to protect and extend the lifetime of the cooling water system equipment.

### 8.3 Material and methods

#### 8.3.1 Experimental set-up

##### 8.3.1.1 Hybrid (GAC/UF) system:

The bio-filter was tested in a pilot-scale seawater cooling towers, these experiments were conducted to improve AOC and DOC removal efficiencies using Hybrid (GAC/UF) system as a bio-filter. Characteristics of Hybrid (GAC/UF) system bio-filter filling materials were presented in Table 8-1. The hybrid system biofiltration experimental set-up is demonstrated in Figure 8-1. Two transparent acrylic cylinder filter columns, which had a diameter of 12 cm and a height of 150 cm were connected together in parallel for makeup feed. The columns were filled up 100 cm in height (6 kg) respectively, and

following UF membrane module unit (WMZ-12521A-216) supplied by Applied Membrane INC, is a kind of hollow-fiber membrane module in a PVC membrane vessel.

Table 8-1: Characteristics of Hybrid (GAC/UF) system.

Specification (GAC)	Values	Specification (UF)	Values
Nominal size (d50, mm)	1.03	Nominal Capacity GPD	1600
Bulk density (kg/m <sup>3</sup> )	540	System Capacity m <sup>3</sup> /day	6.06
Surface area (m <sup>2</sup> /g)	1000 ± 50	Minimum/Maximum, dynamic psig	40/ 100
		System diameter cm	L 71, D 30, H 66
		Membran Element size, (Dia.*L)	2.5 * 21

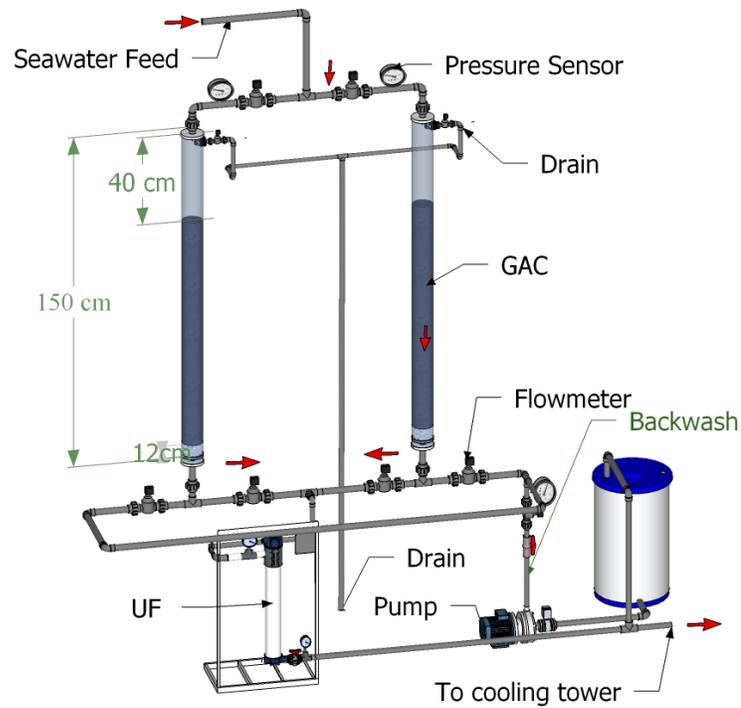


Figure 8-1: Hybrid (GAC/UF) system pretreatment diagram.

The empty bed contact time (EBCT) of the GAC bio-filter was about 7.5 min. The nominal size (d50) of GAC (1.03 mm) whereas surface area of GAC ( $1000 \pm 50 \text{ m}^2/\text{g}$ ). The GAC bio-filter was backwash infrequently at flow rate 3 l/m for 15 min. The UF unit consists of one membrane vessel 10.2 cm diameter by 51.5 cm length UF membrane module and control system. The Backwash of the UF membrane unit module (duration of 60 s) was made during a 48 h interval. The Hybrid (GAC/UF) systems were operated at flow rate  $1.5 \text{ l/min} \pm 0.3$  and the filtration rate was 8 m/ h.

### 8.3.2 Pilot plant seawater cooling towers

The pilot-scale facility was installed outside at King Abdullah University of Science and Technology (KAUST) Central Utility Plant (CUP) where can supply raw seawater from the intake system of RO desalination station and fed into Hybrid (GAC/UF) system fresh seawater and could be exposed to all types of environmental conditions. The PCTs diagram is depicted in Figure 8-2 and it is automated pilot operation runs were maintained by the LabView system. The basic components of PCTs are frame and casing made of fiber-reinforced plastic (FRP) with (height of 1550 cm and diameter of 750 cm), film filled with packing material made of PVC (height of 525 cm), cold-water basin with 52 L capacity that is located near the bottom of the tower and fans. The cooling towers specification and materials can be found in the supplementary information ( Table 8-2).

Certikin titanium plate heat exchangers were constructed with an electro seawater resistant heater (15 KW) (diameter length of 592 mm), worked by transferring the heated water from close loop to seawater open loop in a cooling tower. The temperature difference between inlet and outlet of heat exchanger remained at targeted temperature difference of  $10 \pm 2^\circ\text{C}$ .

The operation of the pilot-cooling tower (PCT), were lasted for 45 days (d). For this study the all three cooling towers operated by different pretreatment systems were: cooling tower no. 1 (**CT1, sodium hypochlorite**): 2,000 mg/l  $\text{Cl}_2$  stock of sodium hypochlorite (5.65–6 %), Cooling tower no. 2 (**CT2 run with using Hybrid (GAC/UF system) and**, cooling tower no. 3 (**CT3 run without treatment**).

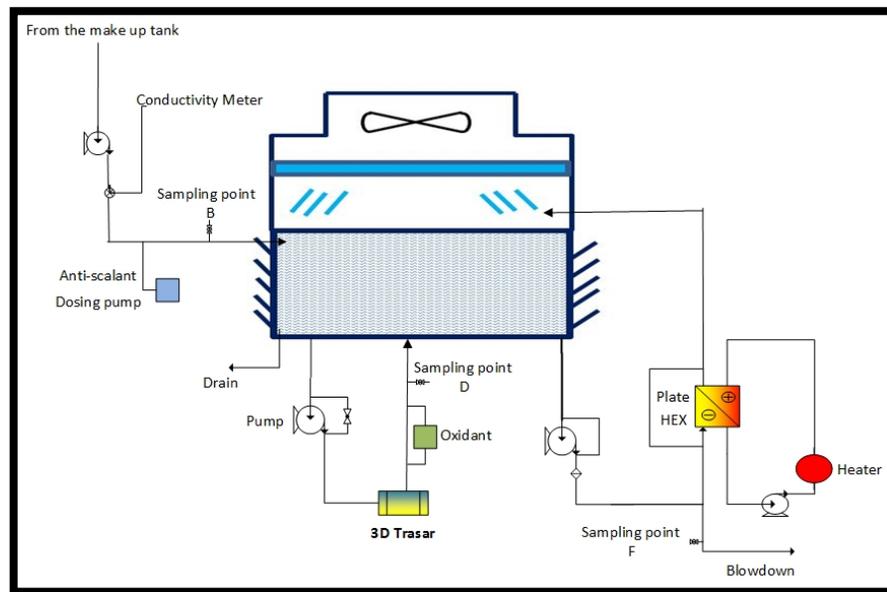


Figure 8-2: Flow diagram of a pilot plant cooling seawater system.

Table 8-2: Overview of the cooling Tower process parameters.

DESIGN, OPERATING AND CONSTRUCTION MATERIAL	SPECIFICATION
Tower pump head	1.5 m
Drift loss of water flow rate	0.10 %
Volume of cooling tower basin	52 L
Volume of water in system	10 L
Make-up water flow	1.5 L/min*
Recirculation water flow	24 L/MIN
Blow-down water flow	1 L/MIN
Concentration factor of process water	1.2 L/min
Heat water flow	21 L/min
Cycles of concentration	1.2

### 8.3.3 Flow Cytometer

The total live cell counts of algae and bacteria in seawater measured by using a BD Accuri™ C6 Flow Cytometer (FCM). 1X of SYBR® Green I + 10 µg/ml of Propidium Iodide (PI) were used to stain live and dead cells, respectively. A 495 µl of water sample was transferred to a sterile Eppendorf tube and 5 µl of the 100X of SYBR® Green + 1000 µg/ml Propidium Iodide (PI) was added to the water

sample. Then it was incubated at room temperature for 15 min. Then, 200  $\mu$ l of the incubate sample was transferred to a 96-well plate for measurement (pump speed = medium, and FL1 threshold = 600).

#### 8.3.4 Liquid Chromatography - Organic Carbon Detection

To characterize the natural organic matter (NOM), Liquid chromatography-organic carbon detection (LC-OCD) model 8 system was developed to identify quantitative information and qualitative results regarding organic compounds in natural water. Three chromatographic profiles are obtained, by measuring DOC, UV, and OND. The Organic Carbon Detector (OCD) measures a wide range of DOC, from 1 to 5 mg/L. The UV Detector (UVD) has a fixed wavelength of 254 nm and is operated with a low-pressure mercury lamp. The Organic Nitrogen Detector (OND) measures the dissolved organic nitrogen in the biopolymer fraction and the HS of NOM. In this study, the characteristics of different constituents of NOM identified are summarized in Table 8-3.

Table 8-3: Characteristics of different constituents of natural organic matter.

NOM	Size (Da)
Biopolymers (BP)	> 20,000
Humics (HS)	$\approx$ 1000
Building Blocks (BB)	300 - 450
LMW	<350

Seawater samples were filtered Whatman filter (pore size = 0.45  $\mu\text{m}$ ). in 20-mL glass vials. Then, Compounds were separated using two-column size (dimension: 250 mm x 20 mm, particle size: 20-40 $\mu\text{m}$ ). ChromCALC uni software was used to determine the concentration of each fraction in NOM sample. By integrating the defined area below each fraction.

### 8.3.5 Assimilable Organic carbon (AOC)

In this study, the asisimable organic carbon was measure to demonstrate the performance of the GAC removal [26]. Dr. Jeong developed the AOC method for improvement of accuracy and easiness of measurement. First, cultivating *Vibrio fischeri* in 1 $\times$  Marine Broth for 3-5 days to get high density. Then, Obtaining a clean by using 2% NaCl solution and concentrated strain via centrifuging 5 times at 12,000 g for 2 min and making a freeze-drying strain by Alpha 1-2 LDplus. Then, recover and suspend by using 2% NaCl solution for 2 h in incubator at 30  $^{\circ}\text{C}$  (**Solution A**). Transfer 190  $\mu\text{L}$  of 0.2  $\mu\text{m}$  filtered water samples to Corning $^{\circ}$  96 well plates white flat bottom. Then, add 10  $\mu\text{L}$  of **Solution A** to the plate and measure the luminescence (**L0**) using SpectraMax $^{\circ}$  M5 Microplate Reader from Molecular Devices LLC. Finally, after 30 min measure the luminescence (**L30**). “L30-L0” is a luminescence increase and it is correlated with cell growth of *V. fischeri* MJ-1 with utilizing AOC in the samples.

### 8.3.6 Field and lab analysis

The online parameters such as conductivity, pH and oxidation-reduction potential (ORP) were measured by using 3D TRASAR technology. This was designed for measuring the key system parameters for the pilot cooling tower operation. Total organic carbon (TOC) was measured by using a Shimadzu analyzer after filtering through a Whatman filter (pore size = 0.45  $\mu\text{m}$ ).

## 8.4 Results and discussion

During the 45 days testing period the operational reliability of the physical treatment of the seawater-cooling tower. Results show that the hybrid (GAC/UF) system of the makeup feed comparison with GAC column bio-filter and chlorination treatment was able to improve the nutrient removal successfully to control biofouling at actual full-scale plant condition. Also, the cooling tower process was able to maintain the targeted delta T  $10 \pm 2^\circ\text{C}$  at the heat exchanger sides. The PCTs were operated continuously 24/7.

### 8.4.1 Microbial Analyses - Viable Cell Count

The hybrid (GAC/UF) system effectiveness was evaluated by determining the total live flow cell counts. In this study, this factor was quantified using flow cytometer Accuri C6. From Figure 8-3, rapid decrease in bacterial cell counts can be noticed after the physical pretreatment of the make-up water of the cooling tower. Hybrid (GAC/UF) achieved around 97% removals of the microorganisms as well as the

chlorination inactivates cells around 89%, GAC column bio-filter removed average around 40%. While cooling tower No3 without treatment the live cell increased to 300 cells/ $\mu$ L.

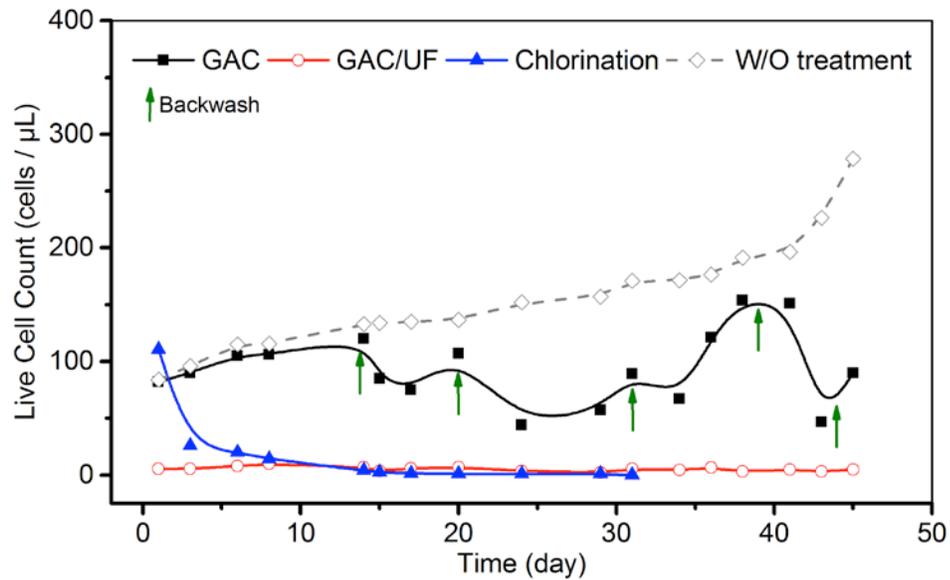


Figure 8-3: Total Live cell counts for GAC, GAC/UF, Chlorination, and without treatment.

Hybrid (GAC/UF) managed to achieve viable cell counts lower than 3 cells/ $\mu$ L at the initiation of pre treatment. Viable cell counts for the other test conditions are shown in Table 7. It is interesting to note that, the backwash of UF and GAC are significantly reducing the viable cell counts during the experiment as demonstrated in Figure 8-3.

The dissolved organic carbon (DOC) were measured due to physical treatment resulted in a higher reducing level of TOC values (right after the GAC column) for all three PCTs as shown in Figure 8-4. This test showed the Hybrid (GAC/UF) system removing 73 % of total organic carbon as will as GAC column, while the chlorination decreased the DOC around 18 %. Table 8-4 show that hybrid (GAC/UF) and GAC can significantly decrease the biological growth for cooling towers by removing the organic nutrients. All of these above findings have relevance to the cooling tower operation treatment.

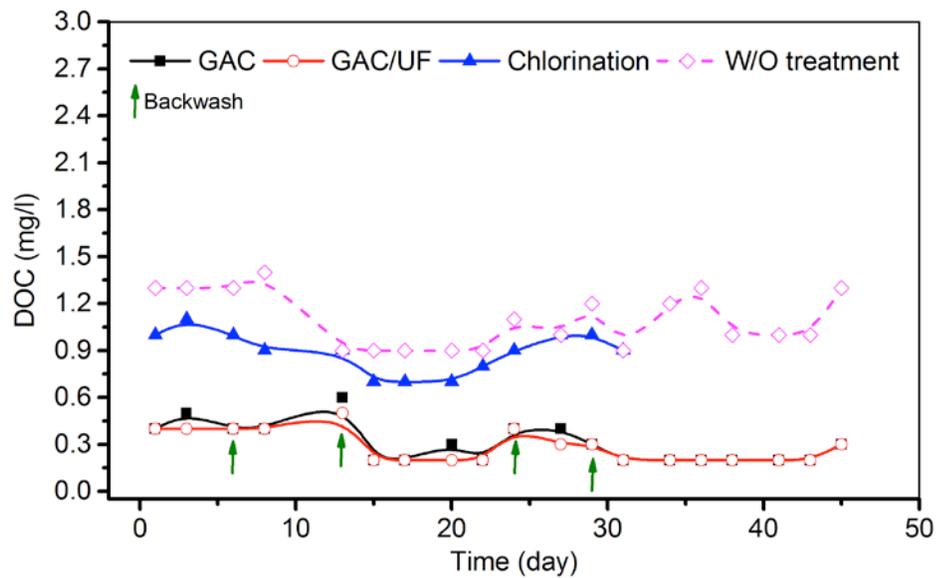


Figure 8-4: Total organic carbon data of GAC/UF, GAC, Chlorination, and without treatment.

Table 8-4: Live Cell Count and Total organic carbon for GAC/UF, GAC, Chlorination, and without treatment.

Parameters analysis	GAC	UF/GAC	Chlorination	W/O treatment
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	94	5	17	157
Live Cell Count (cells / $\mu$ L)	$\pm 32$	$\pm 2$	$\pm 32$	$\pm 49$
	0.4	0.3	0.9	1.1
DOC (mg/l)	$\pm 0.1$	$\pm 0.1$	$\pm 0.1$	$\pm 0.2$

#### 8.4.2 Assimilable organic carbon

The possible for biofouling growth in the open seawater cooling tower was evaluated by assimilable organic carbon (AOC) bioassays. The changes in the nutrient concentration of the microorganism's growth and activity will assist to control the biofouling in the CT. Hybrid (GAC/UF) system bio-filter achieved around 63 % removal of AOC than GAC bio-filter during the 45th day as indicated in Figure 8-5. Compared to the other treatments, the chlorination indicates less ability to remove AOC. The AOC of untreated seawater cooling tower (without treatment) also, showed in Figure 8-5. The results demonstrate the capability of GAC/UF to remove AOC for the seawater feed to minimize the microorganism's growth and biofouling on seawater cooling tower. The outcome data from this research suggest that, the GAC/UF media has possible to increase the removal of AOC. Table 8-5 demonstrates the average data of the AOC during the 45 days operation of the cooling towers. This is a good pretreatment method selection standard to control biofouling. From day 20 to 40 the AOC increased for all cooling towers due to a leak in the seawater intake system that, increase the organic contamination in the seawater intake line. The target level AOC 10 ug-C/L and the detection limit is 0.1 ug-

C/L.

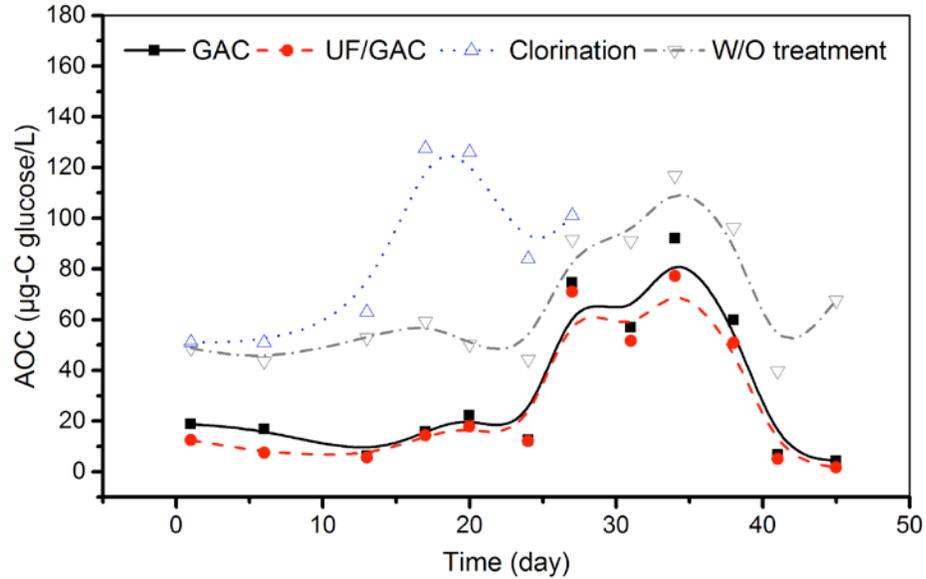


Figure 8-5: Assimilable organic carbon data analysis of GAC/UF, GAC, Chlorination, and without treatment.

Table 8-5: Assimilable organic carbon average data during the experiment of GAC/UF, GAC, Chlorination, and without treatment.

Parameters analysis	GAC	UF/GAC	Chlorination	without treatment
AOC (µg-C glucose/L)	32 ± 0.7	25 ± 1.1	92 ± 0.9	68 ± 1.5

### 8.4.3 Organic matter removal

The DOC removal efficiency of the GAC/UF system was compared with GAC bio-filter and chlorination pretreatment of the cooling tower. The dissolved organic carbon concentration of raw seawater feed of makeup is  $1.1 \pm 0.2$  mg/L. The raw seawater was filtered through GAC/UF media and, then analyzed by using the LC-OCD. The results showed that, GAC/UF media was able to decrease the concentration of DOC to  $0.3 \pm 0.1$  mg/L (approximately 73%) during the 45<sup>th</sup> day run as showed in Figure 8-6.

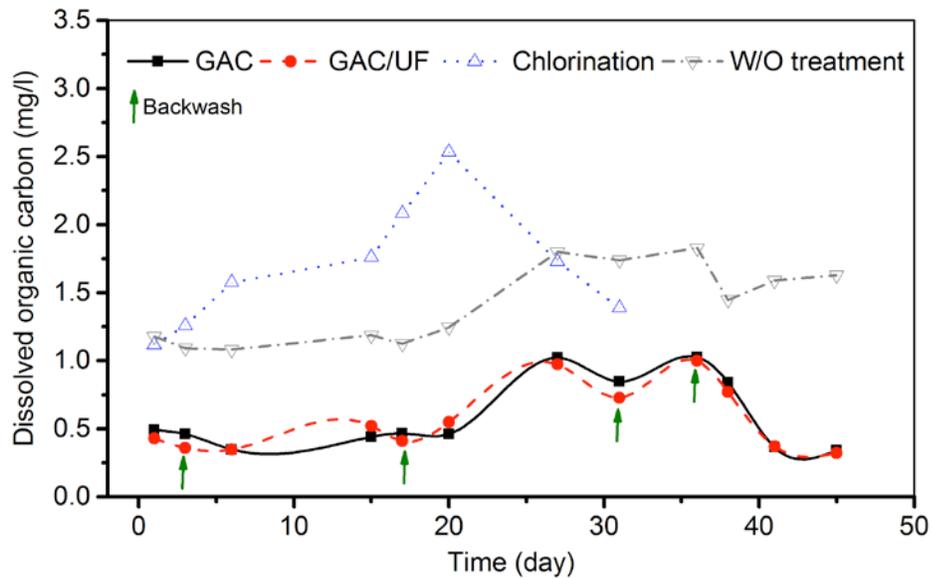
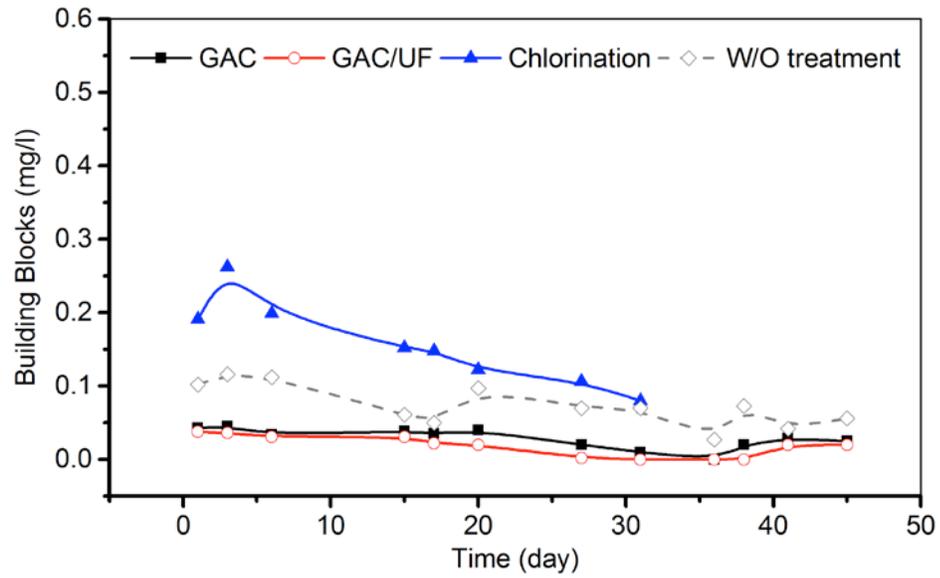


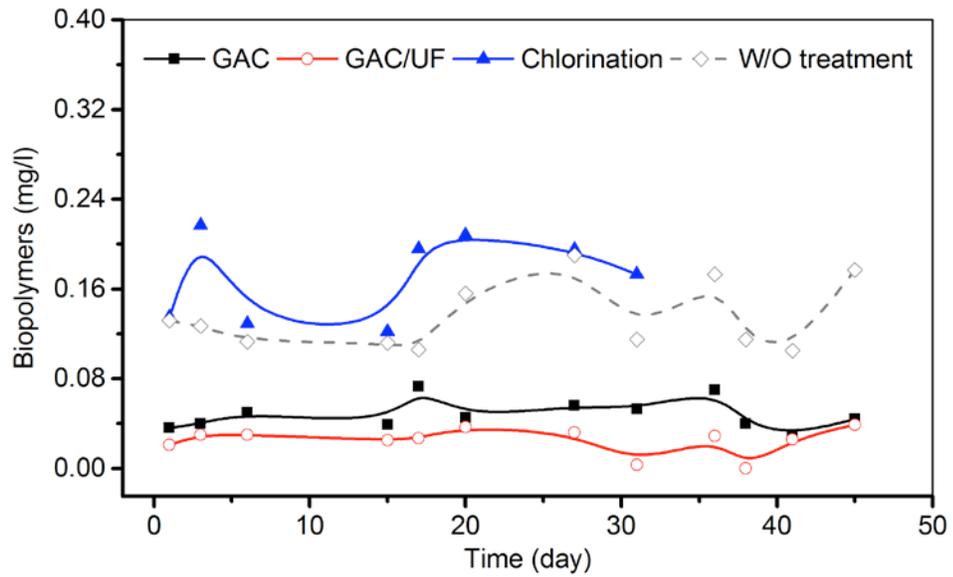
Figure 8-6: Dissolved organic carbon data of GAC/UF, GAC, Chlorination, and without treatment.

This included removal of 86% biopolymers, 74% humic substance and 89 % LMW-N as shows in Figure 8-7 and Figure 8-6. In last 20 day, the organic concentration remained

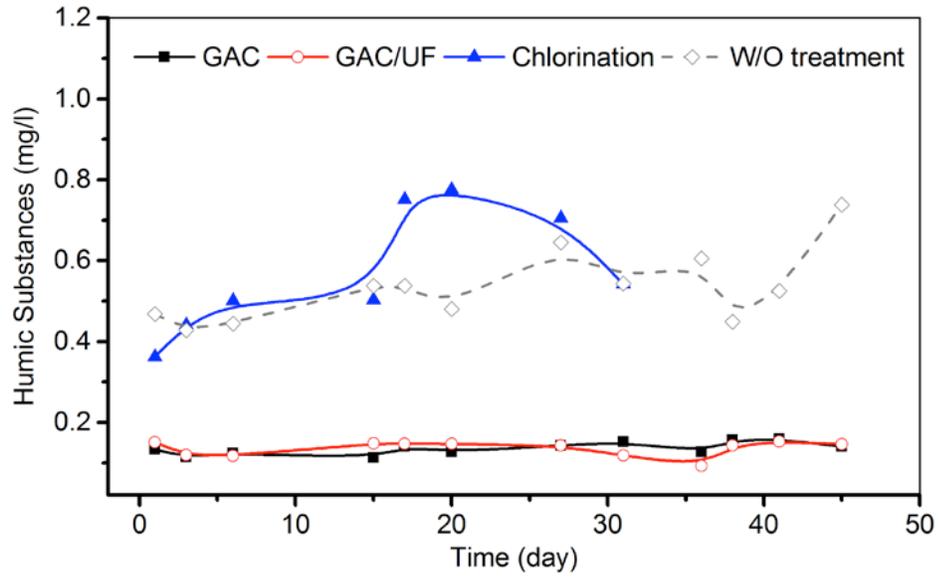
unstable at this stage ahead and this is due to the seawater intake leak.



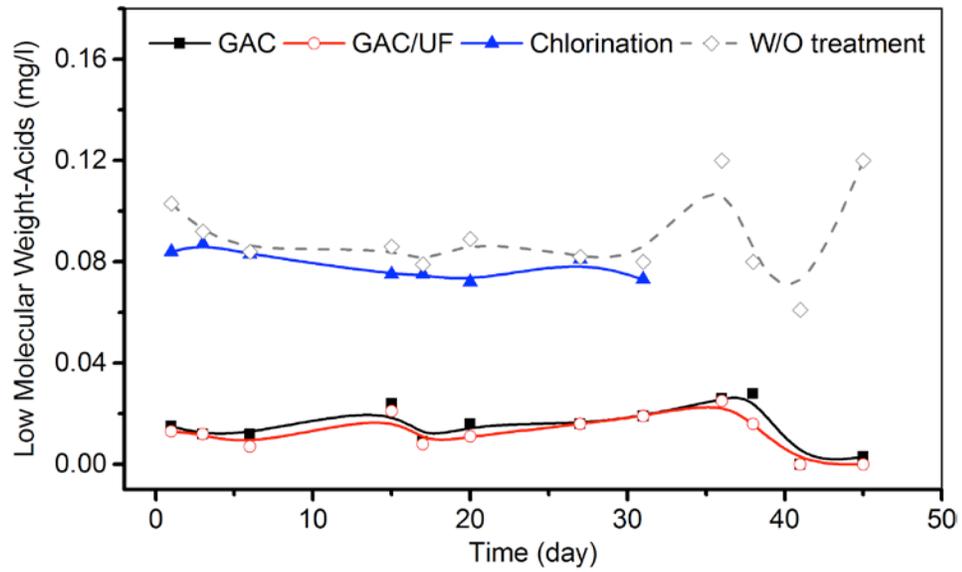
(A)



(B)



(C)



(D)

Figure 8-7: (A) Building blocks (B) Biopolymers (C) Humic substance and (D) low molecular-A data analysis for GAC/UF, GAC, Chlorination, and without treatment.

Meanwhile, a parallel study of GAC column bio-filter shows the results of DOC removal is close to the hybrid is around  $0.6 \pm 0.2$  mg/L, using the same seawater as that in this study was carried out. DO analysis (by LC-OCD) of the chlorination treatment shows increased on the biopolymer fraction, humic substances and, an LMW-N concentration of recycling seawater. In raw seawater the low molecular weight organic compounds are high and they are mainly responsible for biofouling [32].

Table 8-6: LC-OCD organic matter data for GAC/UF, GAC, Chlorination, and without treatment.

Parameters analysis	GAC	GAC/UF	Chlorination	W/O treatment
	0.05	0.02	0.17	0.14
BP (mg/l)	± 0.01	± 0.01	± 0.04	± 0.03
	0.14	0.14	0.57	0.53
HS (mg/l)	± 0.02	± 0.02	± 0.15	± 0.09
	0.05	0.02	0.17	0.14
BB (mg/l)	± 0.01	± 0.01	± 0.04	± 0.03
	0.38	0.33	0.65	0.51
LMW-A (mg/l)	± 0.25	± 0.24	± 0.19	± 0.20
	0.02	0.01	0.08	0.09
LMW-N (mg/l)	± 0.01	± 0.01	± 0.01	± 0.02
	0.6	0.6	1.7	1.3
DOC (mg/l)	± 0.26	± 0.24	± 0.46	± 0.28

#### 8.4.4 pH, oxidation-reduction potential, and conductivity

In-situ pH measurements for all three PCTs showed that there was no pH change over the 45 d of operational period and it was maintained at around pH 7.85. The conductivity average values measured of hybrid (GAC/UF), GAC column bio-filter and chlorination treatment show a similar conductivity average value of around 70 mS/cm  $\pm 3$  at PCT basins. The conductivity measurements on the control CT were around 57 mS/cm. The ORP results in demonstration the average value around 290 mV<sup>+</sup> for physical treatment and the ORP value increased up to 600 mV<sup>+</sup> for chlorination disinfection for CT No2. The disinfection residuals remained within the targeted levels after addition (TRO = 0.2 at ORP level of +600 mV) as in Figure 8-8. Table 8-7 shows the overview of the pH, ORP, and conductivity analysis data.

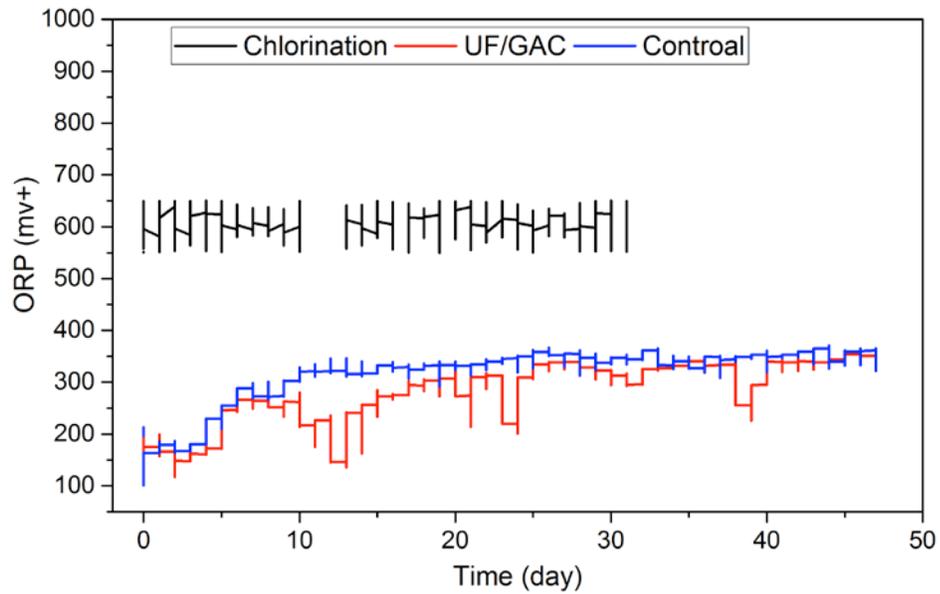


Figure 8-8: ORP data analysis for GAC/UF, GAC, Chlorination, and without treatment.

Table 8-7: Overview of pH, oxidation-reduction potential and conductivity for all PCTs.

Parameters analysis	Chlorination	UF/GAC	W/O treatment
pH	7.97 ± 0.09	7.86 ± 0.10	7.72 ± 0.02
Conductivity	69 ± 4	74 ± 6	67 ± 3
ORP	609 ± 14	281 ± 60	316 ± 55

## 8.5 Conclusions

The characteristics of a continuous hybrid (GAC/UF) system and GAC bio-filter as a pretreatment in an open recirculating cooling seawater process have been studied in terms of microorganisms and nutrient removal. AOC was investigated to evaluate the effect of microbial biodegradation on organic removal. Based on the different physical pretreatment, the results led to Hybrid (GAC/UF) has a high organic removal capacity was achieved (73%), including the LMW organic compounds removal (89%). GAC bio-filter achieved organic removal (73%), including the LMW organic compounds removal (78 %). The AOC concentration of the raw seawater was decreased significantly to 97% by the GAC bio-filter at the end of the 45 days trail. The chlorination was noticed to increase the AOC and this is due to the oxidation of chlorine with seawater. The Hybrid (GAC/UF) was enhanced to improve the removal of the nutrients and micro cell to control the biofouling growth. Also, achieving a disinfectant and more stable cooling water system, lower corrosiveness of the cooling water.

## 8.6 Acknowledgements

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## **Chapter 9**

### **9 Conclusions and future work**

#### 9.1 Conclusions:

This research work provides an analysis and evaluation of chemical and physical treatment of seawater cooling tower to control the biofouling growth in the process. The project was initiated in addressing several industrial seawater cooling tower facilities issues in KSA are using sodium hypochlorite (i.e., chlorine) generation systems in controlling the biofouling and microbial fouling at full-scale. The study was starting to evaluate two alternative oxidants, such as ozone and chlorine dioxide as effective disinfectant to an existing disinfectant type, the sodium hypochlorite (i.e., chlorine), which is widely used throughout this region. These oxidants were assessed for both at bench and pilot-scale assessment for the cooling tower application and operation. The research work was designed to investigate the wide ranges of treatment and operational options, scenarios and conditions for the cooling tower application. Also, these trails were performed in combination with the laboratory scale bench-scale as well as the field, pilot-scale modes in fulfilling the overall project goals. The detail analysis of the entire bench and pilot-scale work illustrating the differences among the oxidants and it types, and the difference in their behaviors for each disinfect type, in term of their efficacy and efficiency, performances and benefits. The following is an overview and key findings of the bench-scale and pilot-scale.

### 9.1.1 Bench-scale Study

The bench-scale study was conducted in assessing various key factors that are important to the cooling tower operation under laboratory condition. A customized true batch reactor was assembled and utilized in assessing comparative oxidant behaviors and decay behavior under well-defined controlled experimental conditions. The bench-scale testing was done for identifying some of these key parameters and factors that are critical, to provide greater insights into the cooling tower operations. Such as the impact of cycle of concentration on overall oxidant demand, temperature impact on decay kinetics, and residuals expectations with operational time during decay and, comparison of oxidant types and their performances. All of these were comparatively assessed for all three oxidants under these controlled experimental conditions to provide greater insights. The following are some of key factors assessed at the bench-scale conditions and findings.

#### 9.1.1.1 The Effect of Cycle of Concentration on Oxidant demands

As the concentration of seawater in the basin increases due to evaporation, or if larger portion of the incoming seawater is to be recycled within the cooling tower system in conserving seawater intakes for its operation, will lead into higher (TDS) concentration in the basin due to higher cycle of concentration. The experimental study covered three different COC levels, namely (i) COC = 1.0 (raw seawater) (ii) COC = 1.25 and (iii) and COC = 1.50. Tests were conducted at both 32°C and 48°C to simulate the cooling tower basin and return water temperatures. The TRO demand with different COCs at operating temperature of 32°C and 48°C were lower decay rates (or higher TRO values) are

observed for raw seawater (COC = 1.00) compared to the other COCs (i.e., COC of 1.25 and 1.50). Increment of residual organic as well as inorganic and loadings in seawater due to the evaporation or higher recycling leads to additional oxidant demand for the seawater. Thus, explaining the lower TRO values obtained at COC = 1.25 and COC = 1.50. However, no significant TRO or chlorine demand were observed between COC = 1.25 to COC=1.50 (with an exception of 0.5 mg/L Cl<sub>2</sub> dose at 32°C).

All of these results indicate as the seawater is concentrated to higher COC levels (COC=1.25 and COC=1.50), not significant differences are seen in chlorine demand or variation in temperature; nevertheless this difference is more significant as COC is increased from ambient (COC=1.0) to higher levels (COC>1.0), which was observed for all disinfectants, an important insight from this study.

#### 9.1.1.2 The Effect of Temperature on Oxidant Demands

As cooling towers operate at various temperature conditions (due to process load variation, day and night variation, summer and winter variation, etc.) A part from chlorine and ozone, the study also included chlorine dioxide in this temperature effect study where biocides were injected at different dosages and temperatures (32°C and 48°C) at constant COC of 1.2.

At higher oxidant dosages, all biocides exhibited lower TRO values at higher temperature. Higher positive residuals could be maintained at lower temperature due to lower first order reaction kinetics and decay. Such as low oxidant dosage could be too low to observe a clear TRO decay trend. All of these results indicate the effect of

temperatures on oxidant decays, which are important, especially in cooling tower operation and where residual levels can vary due to these variations. For example, above findings suggest, lower decay or higher residuals are expected if applied at basin than to after heat exchanger for an equivalent dosing, another important insight from the bench-scale study.

#### 9.1.1.3 Comparison of total residual oxidants between the oxidants

Comparisons between the oxidants were also carried out at different temperatures (32°C and 48°C) and dosages (eqv. 0.1 mg/l Cl<sub>2</sub> and 0.4 mg/l Cl<sub>2</sub>) at constant COC of 1.2. There is no significant difference between the chlorine and ozone at all conditions. This is an important finding for several reasons. This is expected as ozone and chlorine reacts with bromide in seawater to form a similar secondary disinfectant, which is hypobromous acid (HOBr, similar to hypochlorous acid, HOCl, as chlorine). Ozone forms some level of hypobromous acid which is similar to hypochlorous acid with chlorine; however, the levels of the former will be much lower and likely insignificant compared to the biocidal activity of the ozone itself. At lower dosage (eqv. 0.1 mg/l Cl<sub>2</sub>), the TRO decay for all the oxidants were more or less the same. This could be due to the fact that the oxidant dosages are too low and barely satisfy the seawater demand. However, at higher dosage (eqv. 0.4 mg/l Cl<sub>2</sub>) for both temperature conditions (32°C and 48°C), chlorine dioxide has higher TRO value (e.g., lower decay rate) than both chlorine and ozone, which seems to be another important finding from this study. As chlorine dioxide is a very selective oxidant, thus more positive residual are expected to be available for disinfection. All of

these above results have significance to the cooling tower operation in terms of oxidant and oxidant types. This also shows the ability of chlorine dioxide to have different reaction mechanism to chlorine and/or ozone, in keeping its residuals for longer time due to its selectivity.

#### 9.1.1.4 Microbial Analyses Due to Oxidants - Viable Cell count

Biocide effectiveness was also evaluated by determining the post treatment viable cell counts. In this study, this parameter was quantified using flow cytometer (FC). Where the test condition approximate the cooling tower basin (COC = 1.20 and T = 32°C), rapid decrease in bacterial cell counts were noted after each biocide dosing at bench-scale assessment. Despite the difference in mortality rates, all the biocides managed to achieve viable cell counts lower than 3 cells/ $\mu$ l within ten minutes of treatment. At higher dosage (eqv. 0.4 mg/l Cl<sub>2</sub>), all the three biocides achieved more or less comparable mortality rates. Temperature also plays a role in disinfection where higher mortality rates are observed at 48°C than 32°C for all the dosages. It is important to note that at very low dosage (eqv. 0.1 mg/l Cl<sub>2</sub>), chlorine dioxide treated seawater has significantly lower viable cell counts than ozone and chlorine. This is another important finding and insight to note. Following are some of the key findings from the bench-scale assessment.

- It was found that additional oxidant is demanded when the seawater is concentrated (due to cooling tower operation, i.e., at higher COC)
- Higher temperature also leads to the dissipation of TRO (implication of oxidant addition at various stages of cooling tower operation)

- Comparison between the three oxidants revealed that chlorine dioxide has a higher TRO values than chlorine and ozone at higher dosages
- As for viable cell counts, chlorine dioxide also yielded higher disinfection rate at very low oxidant dosage. However, at higher dosages (eqv 0.4 mg/l Cl<sub>2</sub>) all the oxidants have comparable mortality rates

All of these above findings and assessment of these oxidants at bench-scale study, especially under a more realistic condition was needed for the full-scale implementation.

#### 9.1.2 Pilot-scale Study (chemical treatment)

The next phase of seawater cooling tower treatment project is a pilot-scale cooling tower study, investigated chlorine along with chlorine dioxide and ozone as alternative disinfectants. The pilot-scale facility was set outside, such that it could be exposed to all types of environmental conditions. All the oxidants were evaluated at fixed cycle of concentration and under ambient temperature conditions. Among the three-oxidant types evaluated at the pilot-scale, chlorine is the existing or currently used disinfectant type at industrial full-scale facility. For comparative assessment of these disinfectants were assessed under various conditions and monitored for various water quality parameters, which included measurements by on-line, field analyzers along with lab measurements. The impact of water quality and disinfection practices and their effect toward biofouling, microbial activities and scaling, all were carefully monitored and assessed against the chlorine during this pilot-scale study. All of these key factors toward the cooling tower operation and their performances were carefully monitored and investigated as part of

this overall study. All three disinfectants were assessed in parallel mode and with different treatment tasks. The disinfectant residual for all three disinfectants, however were maintained on the same residual level, measured as total residual oxidant level (TRO, as mg/L).

Results show that all three trains were able to successfully mimic the actual full-scale plant condition. It was also able to maintain the targeted COC=1.2 and disinfectant residual level, the TRO of 0.2 ppm for all three oxidant types (i.e., chlorine, ozone and chlorine dioxide as Cl<sub>2</sub> equivalent) targeted. It was also able to successfully maintain the inlet to outlet temperature difference at the heat exchanger (Delta-T) sides at the targeted differential value (i.e., of 10°C as Delta-T). The pilot was also operated continuously, i.e., 24-hours and 7 days a week. Below is to provide an overview of the key pilot-scale findings.

#### 9.1.2.1 Cooling Tower after a period of disinfection postponement and robustness of disinfection (Task-1)

The disinfection practice of all three cooling tower were suspended for 30-days to promote bio-growth, only the antiscalant addition remaining. This is to assess effectiveness of these oxidants in controlling bio-growth after such postponement. During the first three weeks of pilot cooling tower operations under this task a higher level of biological growth were expected. However, after two weeks, no disinfection, no noticeable biological growth was observed for this trail. A small dose of methanol (2-5 mg-C/L as carbon) was added to the pilot-cooling tower to promote abundant needed

biological growth. The biological growth was observed within the few days of methanol dosing. Higher biological growth was noted (measured as Flow Cytometer) at higher concentration of methanol dosing for all three PCTs. This test suggests that the three cooling tower, in the absence of disinfection but in presence of nutrients (methanol) addition, can significantly increase the biological growth for all three cooling towers.

After a temporary postponement of the disinfection practices the disinfection was reinstated for additional 30-days. During the first week of the pilot operation the total microbial count (as FC) went down significantly by more than 90% due to the disinfection application. Therefore, the remaining three weeks it was decided, to continue and add the methanol at dose of 5 mg /L as carbon with the disinfection practices dosing. The purpose thus was to assess the efficacy of the disinfectant in controlling the biofouling after significant biological growth in the cooling tower operation.

During both trail of all three cooling towers in terms of the on-line data and monitoring behaved similarly. The pH, conductivity, COC levels of 1.2, temperature difference in the heat exchanger (Delta-T of 10°C) all remained similar. The disinfection residuals also remained within the targeted levels (TRO = 0.2 at ORP level of +600 mV). The total organic carbon due to methanol injection however resulted in slightly higher level of TOC values (right after the methanol injection). The DBPs and flow cytometer (FC) results are suggesting that all of the three disinfects were effective in keeping the active cell counts to minimal for all three pilot cooling towers, even under increase methanol dosing (5 mg-C/L) to a lower level. Among them ozone tends to be effective in keeping

the microbial count to lower value than to the chlorine and chlorine dioxide for the same TRO value.

#### 9.1.2.2 Cooling tower performance with algae addition to the cooling water basin (Task 2)

The oxidants of all three cooling seawater towers were again turned-off for another 30-days with algal addition as part of task 2. The intention for this task was similar to task 1 to promote higher level of algal growth by inoculating with actual algae (instead of methanol) for all three cooling towers followed by reinstatement of disinfection for another 30-day, in assessing robustness in tackling the higher level of biological growth in cooling tower operations. The first four weeks of the pilot cooling tower operations were conducted by inoculating the three pilot cooling towers with actual algae collected from industrial full-scale cooling tower facility. A higher level of biological growth was noted and higher level of the live cell counts (as compared to Task 1 with methanol addition).

Then, the disinfection practices was reinstated for the next 30-days and was noted the total microbial count went down significantly by more than 90 %. The pilot was able to maintain all of the targeted operational condition, with COC=1.2. The temperature difference between heat exchanger inlet and outlet remained at targeted (Delta-T) difference 10°C. The disinfection residuals also remained within the targeted levels after addition (TRO = 0.2). The addition of algae resulted in increase in TOC level. The flow cytometer (FC) results are suggesting that, the ozone tends to be effective in keeping the

microbial count to lower value than to the chlorine and chlorine dioxide for the same TRO value. In terms of the DBPs formation, particularly for this period, a significantly lower level of TTHMs was noted for chlorine dioxide. Finally, The pilot-scale cooling towers have some of the key findings.

- The pilot-scale cooling tower was found effective in replicating the full-scale pilot cooling tower in term of COC, differential (Delta-T) temperature at the heat-exchanger with residual chlorine as TRO level and maintenance.
- Ozone and ClO<sub>2</sub> oxidants were an effective in keeping the microbial growth to the minimum than chlorine (even after the algae).
- The amount of DBPs formed was low when used ClO<sub>2</sub> of seawater CT treatment.

The pilot-scale study was conducted in during this phase suggest all of three oxidants were effective when assessed in parallel modes and under the same environmental condition (temperature, seasons, humidity, etc.). These are based on two different tasks and for the two different challenging scenarios (methanol and algae addition). Among the disinfectants, chlorine dioxide was found to be effective in minimizing bioactivities for similar TRO level as compared to other oxidants in terms of cost benefit analysis, efficacy and efficiency along with ease of operations, treated water quality, and environmental impacts.

### 9.1.3 Pilot-scale Study (physical treatment)

The physical treatment can be applied to the cooling water tower process to reduce the growth of biofouling. Nutrient removal is another approach to control biofouling growth and prevent algae growing. The concentration limitation of the nutrients in seawater is one of the key strategies to growth biofouling in the system. This trail investigated the efficiency of nutrient removal in cooling seawater systems by using two conditions of treatment at pilot-scale bio-filter like GAC column and ultrafiltration. The GAC biofiltration column and Ultrafiltration (UF) experiments were used as pretreatment for the makeup feed of the seawater cooling towers basin conducted at pilot plant scale. The GAC column bio-filtration designed with two transparent acrylic cylinder filter columns were connected together and operated in parallel for makeup feed. The columns were filled up by granular activated carbon as media. The UF membrane module unit is a kind of hollow-fiber membrane module in a PVC membrane vessel was used in the experiment. Assimilable organic carbon levels and natural organic matter are linked with the growth of biofouling potential in the feed seawater.

Results show that, the physical treatment of the seawater-cooling tower was able to successfully control the biofouling at actual full-scale plant condition. It was also able to maintain the targeted delta T  $10 \pm 2^\circ\text{C}$  at the heat exchanger sides. For this study, the chemical disinfection practice of all PCTs was postponed during the experiment. Below is an overview of the key physical treatment findings.

#### 9.1.3.1 Minimizing the biofouling in seawater cooling towers by removing the Nutrient

This study investigated the organic removal and microorganisms of GAC bio-filter and membrane UF applied as pretreatment to seawater cooling tower makeup. Granular activated carbon bio-filter has a possibility of reducing biofouling potential in the pretreatment of seawater desalination by removing AOC. The test results showed that around 70 % removal was achieved of total organic carbon in seawater feed were effective in keeping the microbial growth to the minimum. Rapid decrease in bacterial cell counts can be noticed after the physical pretreatment of the make-up water of the cooling tower. Ultrafiltration achieved around 90% removal of the microorganisms, while the GAC column removed average around 39%. Based on the different physical pretreatment, the results led to following key findings obtained from the pilot-scale.

- GAC bio-filter has a high organic removal capacity was achieved (70%), including the LMW organic compounds removal (41%).
- The AOC concentration of the raw seawater was decrease significantly to 90% by the GAC bio-filter during the 30 days.
- UF managed to achieve viable cell counts lower than 3 cells/ $\mu$ l at the initiation of pre treatment.
- Overall, this signified findings, that valuable to control the biofouling growth by reducing the organic nutrients concentration to the minimum.

The measured results from this study enable designers of seawater cooling towers to manage the biofouling problems when such cooling towers are extrapolated to a pilot scale.

### 9.1.3.2 The performance of (GAC/UF) Hybrid process pretreatment to control the growth of biofouling in seawater cooling towers

The characteristics of a continuous hybrid (GAC/UF) system and GAC bio-filter as a pretreatment in an open recirculating cooling seawater process have been studied in terms of microorganisms and nutrient removal. Results show that the hybrid (GAC/UF) system of the makeup feed comparison with GAC column bio-filter and chlorination treatment was able to improve the nutrient removal successfully to control biofouling at actual full-scale plant condition. The following key findings obtained from this trail.

- Hybrid (GAC/UF) has a high organic removal capacity was achieved (73%), including LMW organic compounds removal (89%).
- AOC concentration of the raw seawater was decreased significantly to 97% by the GAC bio-filter at the end of the 45 days trail.
- Hybrid (GAC/UF) achieved 97% removals of the microorganisms as well as the chlorination inactivates cells around 89%, GAC column bio-filter removed average around 40%.
- Hybrid (GAC/UF) system bio-filter achieved around 63 % removal of AOC than GAC bio-filter.

The Hybrid (GAC/UF) was enhanced to improve the removal of the nutrients and micro cell to control the biofouling growth. Also, achieving a disinfectant and more stable cooling water system, lower corrosiveness of the cooling water.



## 9.2 Future work

Confirming the availability of freshwater for cooling tower plants is a matter of water quantity and quality. The freshwater capacity becomes less available for cooling tower use. The industrial cooling towers plants considering to use the seawater as media of the CTs because, of unlimited volume and free of coast. The new cooling system technologies are looking for a high quality of cooling towers equipment designed for seawater use. Seawater is required a treatment to protect the cooling equipment and increase the live time. For future work and to have a high quality of feed seawater to the cooling towers the use of subsurface intakes as pretreatment. The advantage of the subsurface intakes are provides a good quality supply seawater to the cooling towers, minimize the environmental impact, and reduce the nutrient. This will help to meet the environmental regulation of the TRO to reduces the need for the chemical biocides. For the chemical treatment, the chlorine dioxide recommended of seawater cooling tower treatment. Also, For future work recommended to designee a hybrid physical chemical treatment of seawater CT. for instance Hybrid (GAC column biofilter/ chlorine dioxide) system will be environmental-friendliness as well as cost effectiveness. Granular activated carbon becoming more common used in the removal of organic carbon. GAC bio-filter has a capability to reduce the biofouling with maintaining a stable microbial activity in the bio-filter. The effectiveness of chlorine dioxide is at least as high as that of chlorine at lower concentrations and effective over a wide range of pH. The aims of this hybrid system are to minimize the nutrient concentration and inactivated the microbiological in the cooling tower process and were proposed to future treatment users.