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

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Highlights

- Biofouling in seawater cooling systems depends on feed seawater quality.
- Alternative oxidants are studied to control biofouling in the cooling towers.
- Effects of oxidant dosage and cycle of concentration are studied.
- Chlorine dioxide yields higher disinfection rates even at low oxidant dosage.
- Chlorine dioxide performs the best TRO demand compared to chlorine and ozone.

Abstract

Biofouling can significantly hamper the efficiency of seawater cooling towers. The aim of this study was to investigate the effectiveness of alternative oxidants (i.e. ozone (O_3) and chlorine dioxide (ClO_2)) comparing with commonly being used chlorine in biofouling control. Effects of cycle of concentration, temperature and oxidant dosage along with residual decay and kinetics were studied. Even at lower oxidant dosage (total residual oxidant equivalent = 0.1 mg/L Cl_2), ClO_2 showed a better disinfection effect compared to chlorine and O_3 . Results of bench-scale studies will be helpful in the selection of appropriate oxidant for seawater cooling tower operation.

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

1 Introduction

The use of seawater as an alternative make-up water in cooling tower systems has rapidly increased over last decades, especially in the Gulf Cooperating Council (GCC) countries. 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 [6]. Moreover, organic and inorganic contents in seawater fed to cooling towers make them prone to corrosion and biofouling [7]. 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 [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. 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]. 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. [14,15]. Trihalomethanes (THM) formation can be reduced in the cooling tower by targeting appropriate dose of chlorination at certain times [16].

Ozone (O_3) has been used as an oxidant for drinking water disinfectant since the late 1800s [17]. O_3 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 O_3 in seawater intake pipes. Sugita et al. claimed that a residual O_3 equivalent of 1.0

mg/L of total residual oxidant (TRO) was sufficient to disinfect seawater for marine culture [19]. A study indicated that a high O_3 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 O_3 chemistry in seawater is significantly different than that in freshwater because of the presence of bromide [21]. Chlorine dioxide (ClO_2) is an alternative oxidant that has been used for microbial control in seawater and drinking water disinfection [22-24]. Agus et al. reported an increasing use of ClO_2 as disinfectant in distillation plants in the Gulf region, particularly in the UAE [24]. The effectiveness of ClO_2 can be similar to chlorine but applied at lower dosage concentrations. Key advantages compared to chlorine are; (i) less contact time and (ii) good solubility in water. In addition, ClO_2 does not react with bromides to form hypobromites and is more efficient at higher temperatures and pH [25, 26]. For these reasons, 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 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 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 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; O_3 and 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.

2 Methodology

2.1 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. (**Fig. 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 **Fig. 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, and 48 °C for outlet seawater) to emulate the cooling tower return water temperatures by using thermal baths and heat exchanger (HEX).

2.2 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 (in terms of 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 Cl₂) using suitable conversion factors for O₃ and ClO₂, respectively (e.g. 1 mg/L Cl₂ = 0.67 mg/L O₃ = 1.9 mg/L ClO₂). Different COCs of Red Seawater 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 Cl₂ for chlorination, 0.067 - 0.335 mg/L O₃ for ozonation and 0.19 - 0.95 mg/L ClO₂ for the use of ClO₂ 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. ClO₂ stock solution was prepared by adding sulfuric acid to sodium chlorite solution (Standard Method 4500-ClO₂) and then verifying the dosing rate by using DPD powder pillows (Method 10126).

Table 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.

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 (≤ 0.05) indicates strong evidence and large p-value (> 0.05) indicates weak evidence.

2.3 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 $\mu\text{g}/\text{mL}$ 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 $\mu\text{g}/\text{mL}$ 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 TROs. 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 **Table 2**.

3. Results and Discussion

Bench-scale studies was evaluated based on the following key factors; (i) the impact of 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.

3.1 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 and 48 °C, emulating the basin feed water and the return water to the cooling tower basin after the heat exchanger. **Figs. 3a** and **b** demonstrate the TRO profiles for the conditions tested at 32 and 48 °C, respectively. All profiles show a first-order response after oxidant injection, depicting a sharp and rapid drop in the initial two min before plateauing and stabilizing. The rapid decline represents the reaction of the oxidant meeting the oxidant demand in seawater (0.2 mg/L 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 **Figs. 3a** and **b**, positive TRO values (around 0.09 mg/L Cl₂) 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 3 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 Cl₂ at 32 °C.

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 O₃ 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]. **Figs. 4a** and **b** show the TRO decay profiles for seawater ozonation at 32 °C and 48 °C at O₃ dosages of 0.200 mg/L O₃ (0.3 mg/L Cl₂) and 0.335 mg/L O₃ (0.5 mg/L Cl₂), respectively. The statistical p values obtained from the paired t-test of this ozonation study are shown in **Table 4**.

From the p values reported in **Table 4** and TRO decay curves in **Figs. 4a** and **b**, 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 O₃ dosage 0.335 mg/L O₃ (0.5 mg/L Cl₂). This could be due to more rapid reaction of O₃ in seawater during the initial few seconds after injection (O₃ half-life time in seawater is 5.7 s).

3.2 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 O₃, ClO₂ was included in an assessment of temperature effects.

The oxidants were injected at two different dosages (eqv. 0.1 and 0.4 mg/L Cl₂) and temperatures (32 and 48 °C) at constant COC of 1.20±0.05. Decay curves for the three oxidants are presented in **Fig. 5**. Comparative statistics using p values at 95% confidence level are given in **Table 5**. 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.

3.3 Comparison of TRO among oxidants

Fig. 6 shows the decay profiles at two temperatures (32 and 48 °C) and dosages (eqv. 0.1 and 0.4 mg/L Cl₂) at constant COC of 1.20±0.05. A paired t-test analysis presented in **Table**

6 clearly indicates there is no significant difference between the chlorine (TRO 0.12 mg/L Cl₂ at 42 °C) and O₃ (TRO 0.13 mg/L Cl₂ at 42 °C) at all the conditions tested. This is probably due to O₃ and chlorine reacting with bromide in seawater and forming bromine, which is a secondary disinfectant. At lower dosage (eqv. 0.1 mg/L Cl₂), 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 Cl₂) the TRO value for ClO₂ was higher (e.g., lower decay rate) than for chlorine and O₃ for both temperature conditions (32 and 48 °C). As ClO₂ is a very selective oxidant, a more positive residual available for disinfection was expected. This is due to that ClO₂ has different reaction mechanisms compared to chlorine and O₃, 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.

3.4 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. Analyses were conducted for the operating condition COC = 1.20±0.05, and T = 32 and 48 °C, and equivalent dosages 0.1 and 0.4 mg/L Cl₂. A rapid decrease in bacterial cell counts was observed after injection of each oxidant at the lower temperature (32 °C) and higher oxidant dose (**Fig. 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 6**. At higher dosages (eqv. 0.4 mg/L Cl₂), 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 Cl₂) indicate insufficient disinfection efficiency of all oxidants, however, ClO₂ was found to be more effective than O₃ and chlorine. The findings in this study show the effect of residual oxidant concentrations on the biofouling control and its dependence on the temperature.

4. Conclusions

This research work analyzes and evaluates O₃ and ClO₂ 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_2 has a higher TRO values than chlorine and O_3 at higher dosages
- In terms of viable cell counts, ClO_2 also yielded higher disinfection rate at very low oxidant dosage. However, at higher dosages (eqv. 0.4 mg/L Cl_2) 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.

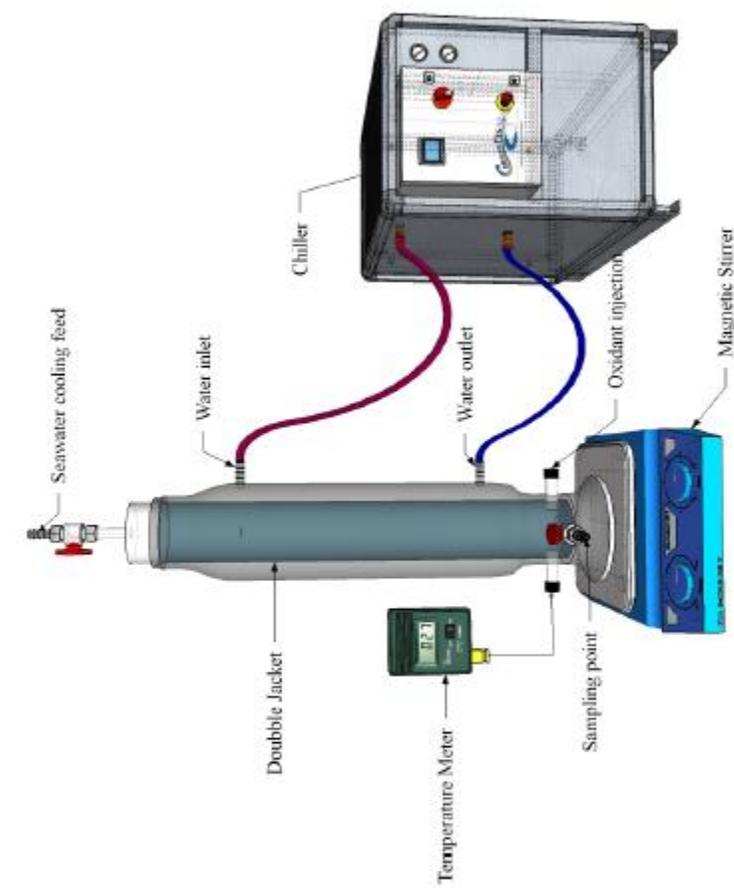
Acknowledgements

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List of Figures**Fig. 1.** Double jacket bench reactor for decay tests.

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Fig. 2. Equivalent TRO decay kinetics in cooling tower pipe network.

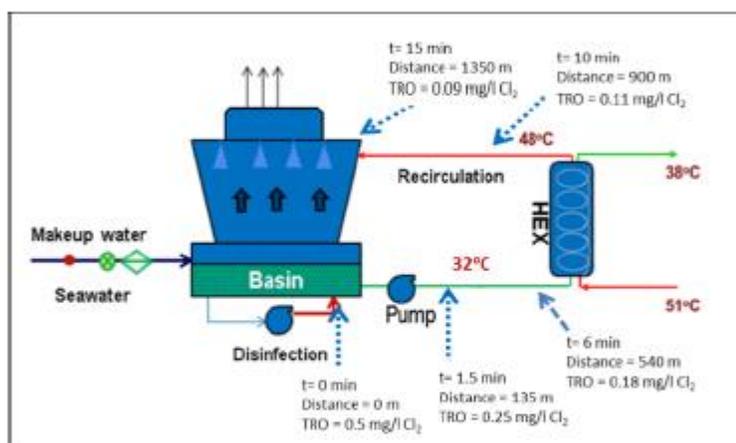


Fig. 3. TRO decay after seawater chlorination at (a) 32°C and (b) 48°C at different COCs and oxidant dosages.

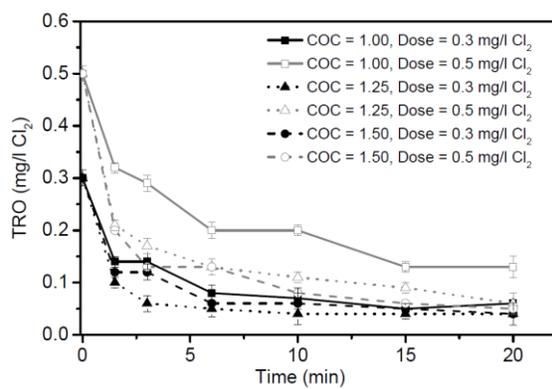
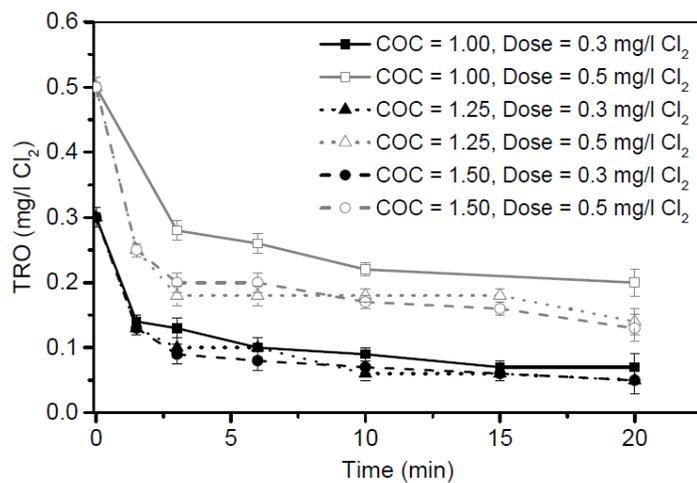


Fig. 4. TRO decay after seawater ozonation at (a) 32 °C and (b) 48 °C at different COCs and dosages.

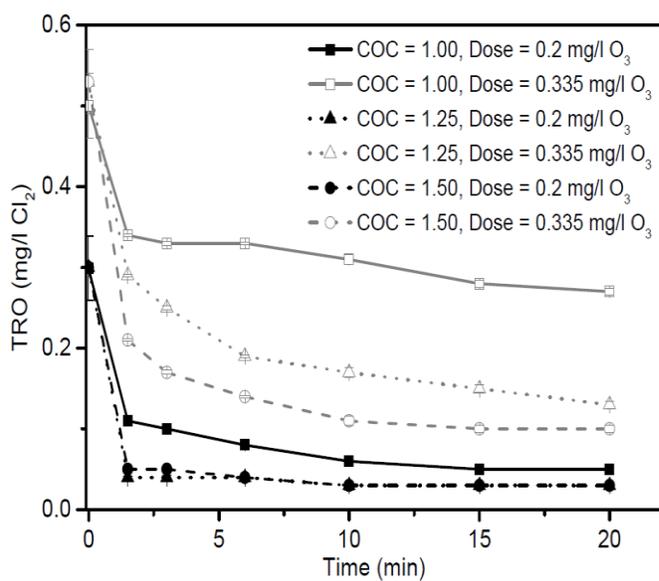
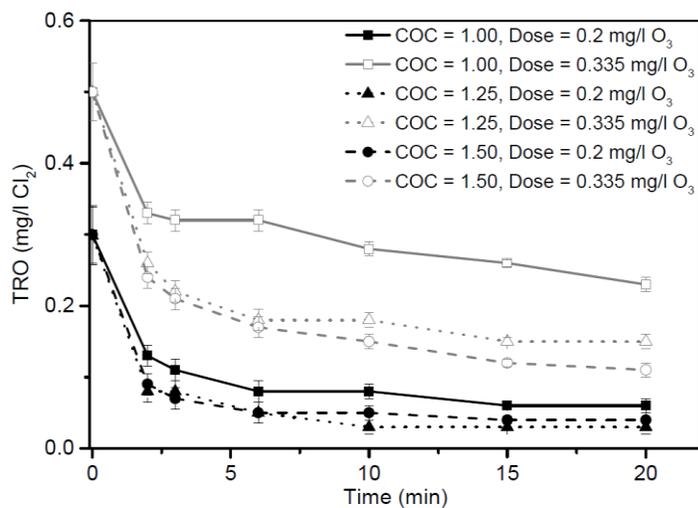
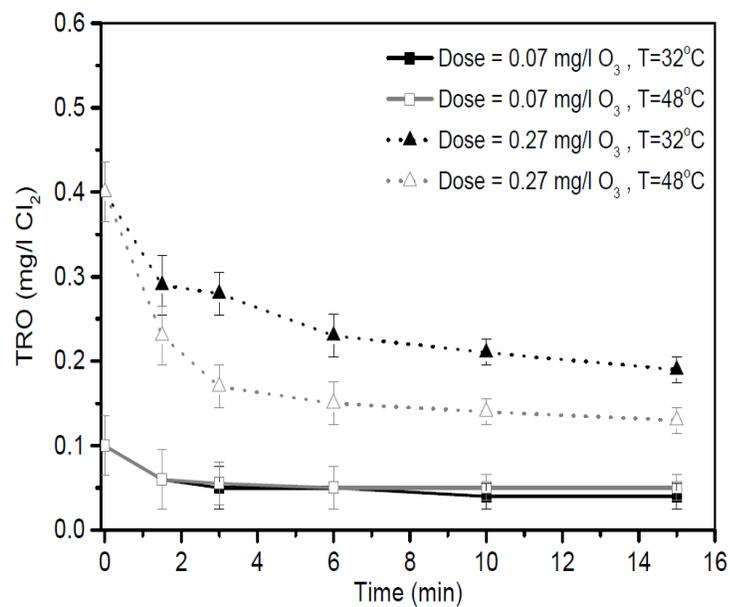
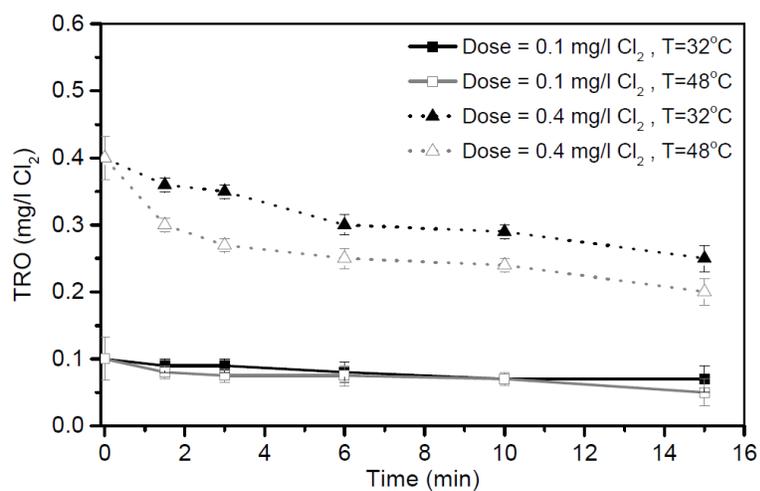


Fig. 5. TRO decay profile for (a) chlorine, (b) O₃ and (c) ClO₂ in seawater at different oxidant dosages and temperatures.



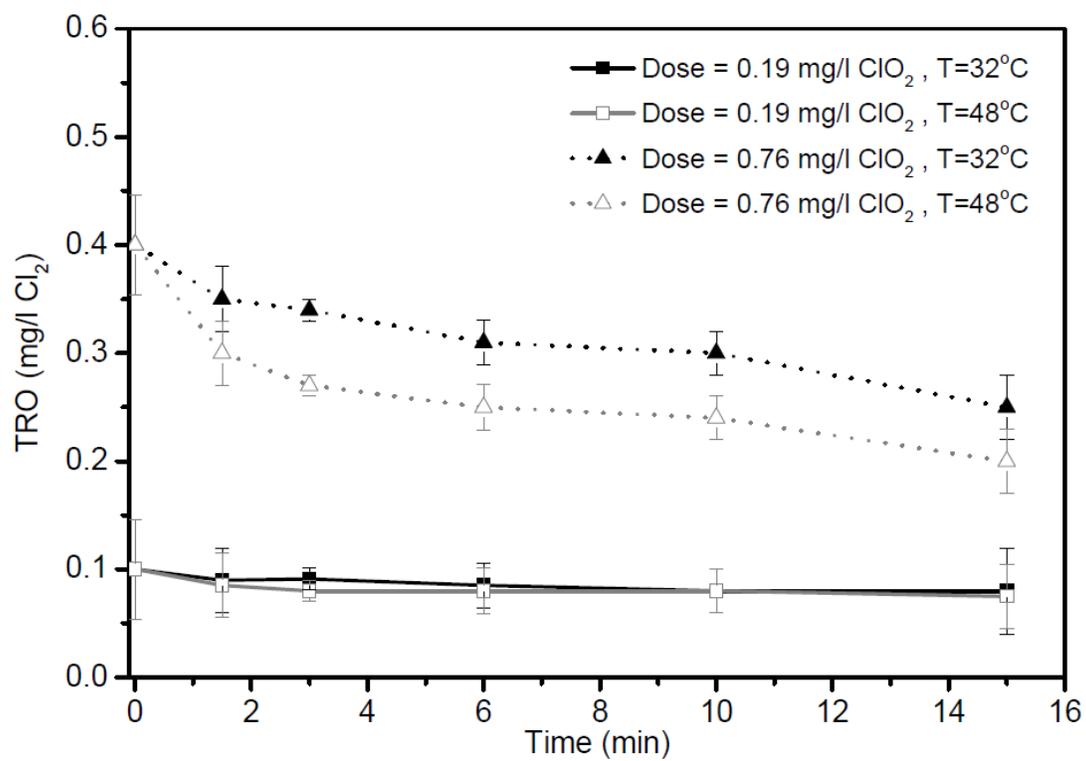


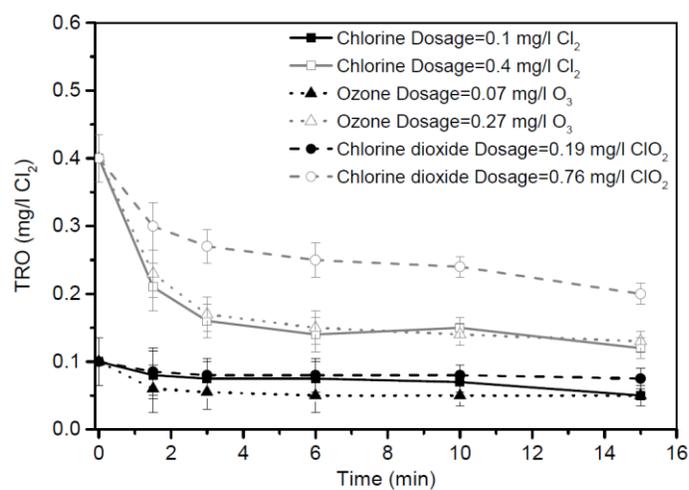
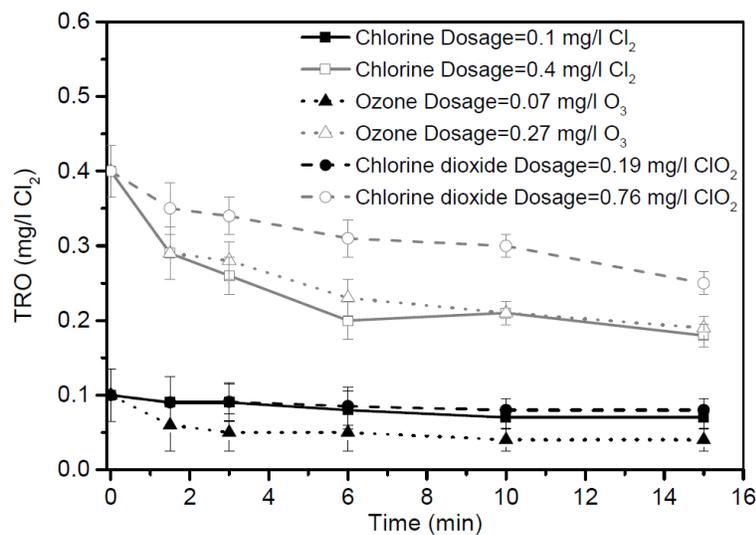
Fig. 6. TRO decay comparison for chlorine, O₃ and ClO₂ at (a) 32 °C and (b) 48 °C.

Fig. 7. Live cell counts after injection of chlorine, O₃ and ClO₂ into the seawater as function of time.

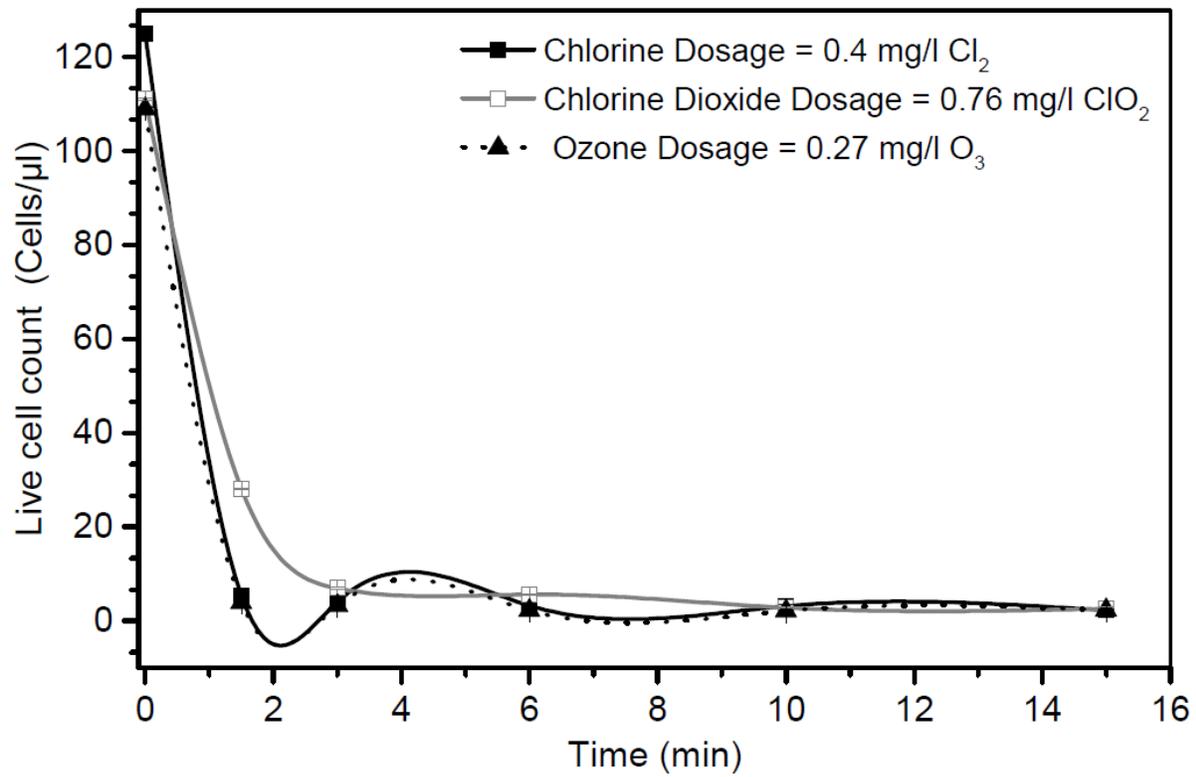


Table 1 TRO decay test matrix for each oxidant at different COCs, temperatures and oxidant dosages.

Tests	COC	Temperature (°C)	Dosage (eqv. mg/L Cl ₂)
1	1.00	32	0.30
2			0.50
3		48	0.30
4			0.50
5	1.25	32	0.30
6			0.50
7		48	0.30
8			0.50
9	1.50	32	0.30
10			0.50
11		48	0.30
12			0.50

Table 2 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 ₂ ⁻ (mg/l)	0.0047
Total Alkalinity (mg/l as CaCO ₃)	120	Ortho-P as PO ₄ ⁻³ (mg/l)	0.1
Total Hardness (mg/l as CaCO ₃)	7,500	Sulfate (mg/l)	2,650
Mg Hardness (mg/l as CaCO ₃)	6,300	Silica (mg/l)	0.13
Ca Hardness (mg/l as CaCO ₃)	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		

Table 3 Effect of chlorination at different COCs.

Dosage (mg/l Cl ₂)	Temperature (°C)	COC*	
		1.00 to1.25	1.25 to1.50
0.3	32	p = 0.025	p = 0.457
0.3	48	p = 0.022	p = 0.063
0.5	32	p = 0.005	p = 1.000
0.5	48	p = 0.004	p = 0.030

* p indicates statistically significant difference between cases.

Table 4 Effect of ozonation at different COCs.

Dosage (mg/l Cl ₂)	Temperature (°C)	COC*	
		1.00 vs1.25	1.25 vs1.50
0.2	32	p = 0.002	p = 0.154
0.2	48	p = 0.011	p = 0.500
0.335	32	p = 0.002	p = 0.010
0.335	48	p = 0.031	p = 0.003

* p values indicate statistically significant difference between cases.

Table 5 Effect of temperature at different oxidant dosages.

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

* p indicates statistically significant difference between cases.

Table 6 Comparison of oxidant residuals in seawater.

Dosage (mg/l Cl ₂)	Temperature (°C)	Oxidant*	
		Chlorine vs. O ₃	Chlorine vs. ClO ₂
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	p = 0.006
	48.0	p = 0.438	p = 0.006

* p values indicate statistically significant difference between cases.

Table 7 Viable cell counts after 10 min of oxidant dosing (unit: cells/ μ L).

Oxidant	Dosage (mg/L Cl ₂)	Temperature	
		32 °C	48 °C
Chlorine	0.1	34.3	25.2
O ₃	0.1 (0.07 mg/L O ₃)	56.0	24.5
ClO ₂	0.1 (0.19 mg/L ClO ₂)	19.2	8.1
Chlorine	0.4	2.8	2.5
O ₃	0.4 (0.27 mg/L O ₃)	2.1	1.5
ClO ₂	0.4 (0.76 mg/L ClO ₂)	2.8	1.8