

Use of chlorine dioxide as alternative to chlorination in reverse osmosis product water

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ABSTRACT

Enhanced bromate formation has been observed in desalination-derived drinking water containing bromide disinfected by chlorination under alkaline conditions. As an alternative to chlorine disinfection in drinking water, chlorine dioxide (ClO₂) was investigated to elucidate its performance in curtailing the bromate formation in the seawater reverse osmosis product water. The occurrence of disinfection by-products (DBPs), viz., chlorite, chlorate and trihalomethanes (THMs) was also monitored during the whole period of the tests at varying distances of 10, 50 and 3,500 m. Bromate concentrations throughout the trial were found to be <2 ppb indicating negligible or no bromate formation at the optimum residual ClO₂ in the range of 0.18–0.20 ppm. Chlorite (<0.01–0.1 ppm), chlorate (<0.05–0.14 ppm) and calculated total THMs were found to be within the range of the regulatory limits (<1) set by the World Health Organization (WHO). Biological analyses showed total coliforms and *E. coli* were negative indicating ClO₂ to be very efficient at the optimum residual in the range of 0.18–0.20 ppm. The chlorine dioxide generating system used in this test was found to be efficient in generating chlorine dioxide with minimum amounts of DBPs.

Keywords: Bromate; Chlorine dioxide; Disinfection; THMs; Disinfection by-products

1. Introduction

The major source of drinking water in the Kingdom of Saudi Arabia originates from seawater desalination. Saline Water Conversion Corporation (SWCC), a Government Agency responsible for producing desalinated water in the Kingdom, has installed several multistage flash distillation

(MSF) and reverse osmosis (RO) desalination plants along the coast of Red Sea and Arabian Gulf. MSF plants contribute the major share of the water being produced in the Kingdom. The distillates from MSF plants are normally blended with an adequate amount of groundwater in order to enhance the mineral content, followed by disinfection before sending to the distributing networks for domestic consumption.

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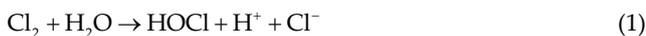
Disinfection of drinking water is an important procedure to control bacterial infection and maintain the water quality. Common disinfectants are ozone, chlorine, chloramines, chlorine dioxide, sodium hypochlorite (NaOCl), calcium hypochlorite (Ca(OCl)₂) and ultraviolet (UV). Chemical disinfectants are necessary in water treatment to inactivate pathogenic microorganisms. Unfortunately, these chemical disinfectants are found to produce disinfection by-products (DBPs) that pose threats to human health. Some by-products are known carcinogens to humans and therefore are regulated by the international and national water authorities. Studies [1] in understanding their toxicity and the kinetics of formation have been done to balance their potential risks against the need for disinfectants.

All chemical disinfectants produce organic and/or inorganic DBPs of potential health concern by oxidizing naturally occurring organic and inorganic material in water. DBPs are produced by the reaction of these precursors with disinfectants in drinking water [2]. Natural organic matter is the primary precursor comprising of approximately 50% carbon, and lower amounts of sulfur, nitrogen, phosphorous and trace metals. Bromide is another important parameter that is easily oxidized to aqueous bromine that can react further to form bromine substituted DBPs, that is, bromate (BrO₃⁻) [3].

Electrolysis of seawater to generate sodium hypochlorite (NaOCl) is popularly used in SWCC desalination plants to produce their own chlorinating agent. This crude chlorinating agent (NaOCl) generated from seawater, when dosed to product water, has been found to result in the formation of numerous DBPs and the product water getting contaminated. Toxic effects of some of these DBPs, THMs and haloacetic acids (HAAs), in small amounts, are known to have serious effects on human health. Of great concern are brominated DBPs which have been found to induce cancer [4].

Studies [5–11] have shown a link between the formations of bromate in drinking water produced by desalination when treated with sodium hypochlorite solution and reported significant amount of bromate formation explained by the following reaction. Product water produced from the desalination of seawater contains significantly more bromide than freshwaters, making this an issue of greater concern for desalination than for treatment of inland waters.

Chlorine gas hydrolyses in water almost completely to form hypochlorous acid (HOCl):



The hypochlorous acid reacts in waters containing bromide ion to produce hypobromous acid



Water containing bromide ion reacts with the hypochlorite solution resulting in the formation of bromate (BrO₃⁻).

Hypobromous acid (HBrO) is a weak acid (pK_a = 8.7) and hypobromite (OBr⁻) being metastable decomposes in alkaline solution to give bromate and bromide [9].



A very attractive alternative to chlorination, (NaOCl, Ca(ClO)₂ or Cl₂ gas) in drinking water disinfection is chlorine dioxide which is reported [12] to have several advantages in the treatment and distribution system of drinking water. ClO₂ is a very strong and selective oxidizing agent, approximately 2.5 times more powerful than chlorine gas. It is reported [13–16] to effectively inactivate bacteria and viruses over a broad pH range and it does not produce THMs or bromate. Final disinfection products of chlorine dioxide are chloride (Cl⁻) and chlorite (ClO₂⁻) ions.

Like other disinfectants, the relative efficacy of ClO₂ is reported to decrease at lower temperatures but comparing with chlorine it is highly effective over a broad pH range [17,18]. ClO₂ is reported to oxidize specific organic compounds such as phenols and other alcohols, as well as iron, manganese, sulfides, iodides, nitrites and it eliminates tertiary amino derivatives [19,20]. Previous research has reported [21] that it is necessary to maintain an appropriate chlorine dioxide residual concentration in distribution systems for control of microbiological regrowth.

Chlorate (ClO₃⁻) and chlorite (ClO₂⁻) ions formed as by-products are the major disadvantages of using chlorine dioxide because of their potentially harmful effects [22]. The levels of ClO₂⁻ and ClO₃⁻ have been reported to range between 30% and 70% of the initial ClO₂ concentration [16,23]. The combined residuals of ClO₂, ClO₂⁻ and ClO₃⁻ in the distribution system are regulated by the United States Environmental Protection Agency (USEPA) and should not exceed 1 mg/L [24,25]. WHO provisional guideline values in drinking water [26] for chlorite and chlorate are 0.7 mg/L per species. Investigations [27] carried out in Qatar for the occurrence of ClO₂ DBPs in drinking water samples have been reported to be within the WHO limits. However, many of the by-products formed by the reaction of chlorine dioxide with organics in drinking water are yet to be characterized [28]. A study [29] using chlorine dioxide as a primary disinfectant, carried out in Indiana, reported identifying more than 40 organic disinfection by-products whose toxicities require further investigation. A new group of polar halogenated DBPs, trihalomethanols, have been detected in ClO₂-treated drinking water sample [30].

One toxicological study [31] has raised concerns relating to the use of ClO₂ in drinking water treatment, although several other studies conducted in both controlled laboratory experiments and full-scale systems have failed to link the ingestion of ClO₂-treated water to any detrimental health effects in humans [32,33]. In addition, reports [34,35] on adverse birth outcomes on a study carried out on pregnant women drinking ClO₂-treated water have failed to prove a connection and found to be inconclusive.

Reports [36] of bromate formation in water distribution systems, containing bromide, disinfected by chlorination (sodium hypochlorite solution produced by seawater electrolysis) under alkaline conditions, resulted in this study to elucidate the performance of chlorine dioxide in curtailing

the bromate formation. This study also investigated the efficiency of the ClO_2 generating system by measuring the quantity of by-products chlorite and chlorate in the drinking water. The concentrations of chlorite and chlorate ion were monitored at several specific locations within the treatment facility to ensure compliance with WHO regulatory limits.

2. Research objectives

The main objective of this study was to evaluate the control of bromate formation in seawater reverse osmosis (SWRO) product water treatment using chlorine dioxide and the consumption of ClO_2 to optimize the required dosage for deactivating the bacteria. A further objective was to investigate the formation of chlorite, chlorate and THMs in the distribution system at distances of 10, 50 and 3,500 m after ClO_2 injection to the process. Efficiency of ClO_2 generating system in producing ClO_2 and determining the purity of ClO_2 product was also the objective of this study.

3. Experimental

All the experiments were carried out for treatment of RO permeate at the SWRO desalination plant having the design capacity of 20 MIGD (90,920 m^3/d) of potable water operating with single pass RO at a recovery ratio of 35% at SWCC Al-Jubail, Kingdom of Saudi Arabia.

The existing pretreatment comprised rapid mix/coagulation using ferric chloride (40%), flocculation, sedimentation and dual granular media (sand and anthracite) filtration. Coagulant was dosed at 2.0–3.5 ppm (mg/L) and pH was adjusted to 6.8 by adding sulfuric acid (98%). Chlorine was dosed from the electro-chlorinators at sea water intake and the residual chlorine was kept in the range of 0.3–1.5 ppm. Dechlorination of RO feed water was done by sodium metabisulfite solution to protect the membranes. However, to compensate for deficiencies and shutdowns at intake chlorination, separate chlorination lines from a calcium hypochlorite dosing system for RO plant have been provided. These dosing lines are located in the dosing pit upstream of dual media filters (Fig. 1). The RO permeate continuously flows to the backflow tanks (BFTs). Chlorine-free permeates then overflow from the upper area of the BFTs with a

capacity of 1,500 m^3 to the product water clearwell (PWC). An injection point for chlorine dosing (up to 0.5 mg/L of chlorine) is arranged in the common overflow pipe to the PWC. At this injection point chlorine dioxide dosing is arranged in place of chlorine.

Chlorine dioxide (ClO_2) generating system (SCOTMAS, UK, Fig. 2) was installed close to the injection point. This system is approved by the UK Drinking Water Inspectorate for installation onto drinking water treatment plants (EN 12679:2009). Both reagents (sodium chlorite and hydrochloric acid) are reacted within a submerged reactor that is installed within a bypass line of the water to be treated, avoiding storage or handling of free chlorine dioxide solutions on the site.

Dosing of ClO_2 was proportional to the water flow with additional control by an online analyzer. The sensors used to detect ClO_2 and ClO_2^- are ion-specific amperometric two-electrode systems, protected by a selectively permeable membrane, for accurate measurement of either chlorine dioxide or chlorite. The minimum detection limits of the ClO_2 probe and ClO_2^- probe are 0.005 and 0.05 ppm, respectively.

Five sample locations were selected as shown below (Fig. 3):

Sample #1: Intake seawater.

Sample #2: After RO (Before ClO_2 dosing).

Sample #3: 10 m after dosing of ClO_2 (before CO_2 and lime dosing).

Sample #4: 50 m after RO (after CO_2 and lime dosing).

Sample #5: 3,000–3,500 m after dosing of ClO_2 .

The samples were collected from sample points for analysis of residual ClO_2 , chlorate, chlorite, residual total chlorine, bromate, organics, THMs and biological analysis. Additional parameters, viz., residual sodium bisulfite (SBS), residual free chlorine and pH were analyzed at selected sample points.

4. Analytical techniques

4.1. Trihalomethanes (THMs) analysis by GC/MS

All samples were analyzed according to the Standard Methods based on the described procedures in APHA

SEA WATER REVERSE OSMOSIS PROCESS

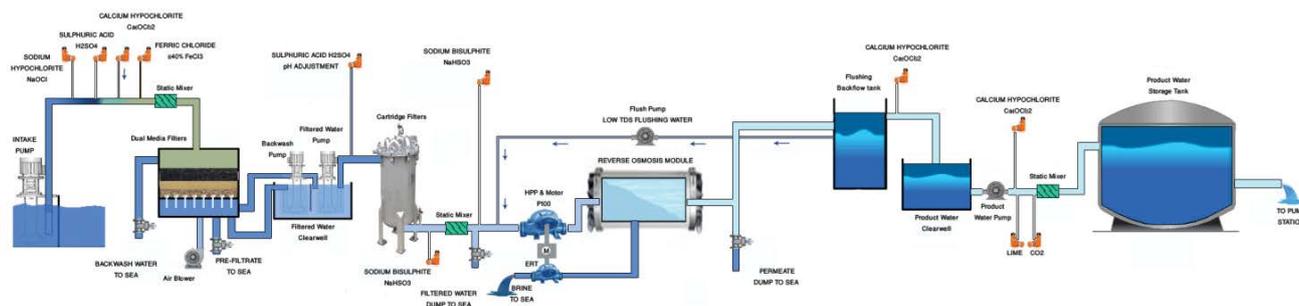


Fig. 1. Schematic diagram of seawater RO process at Al-Jubail plant.

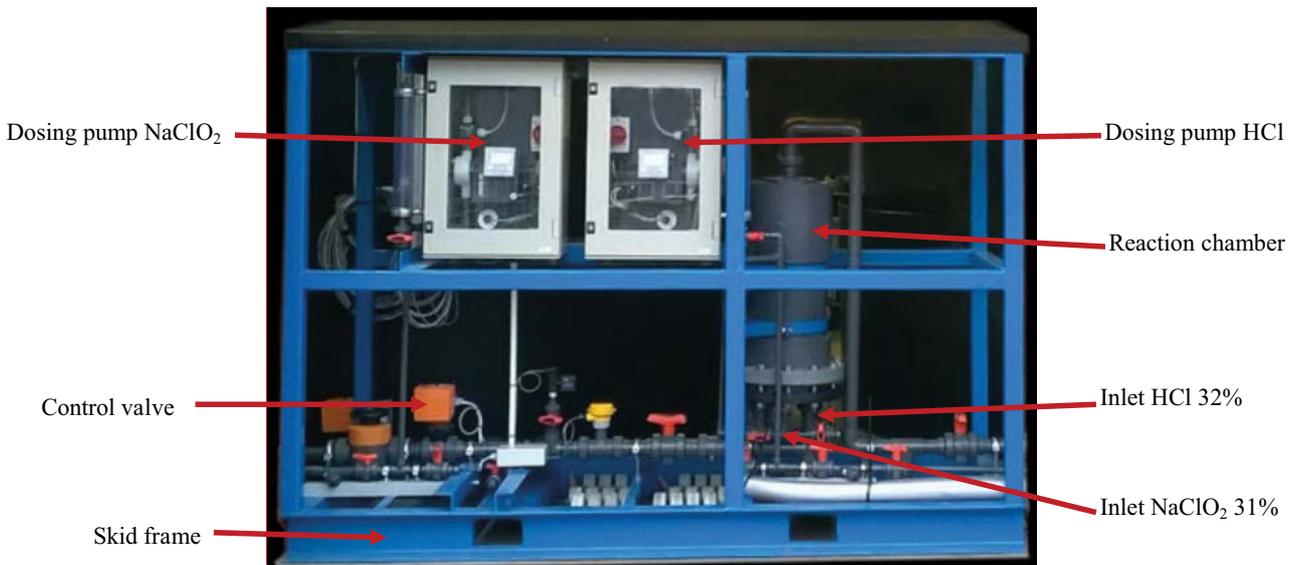


Fig. 2. Chlorine dioxide generating system.

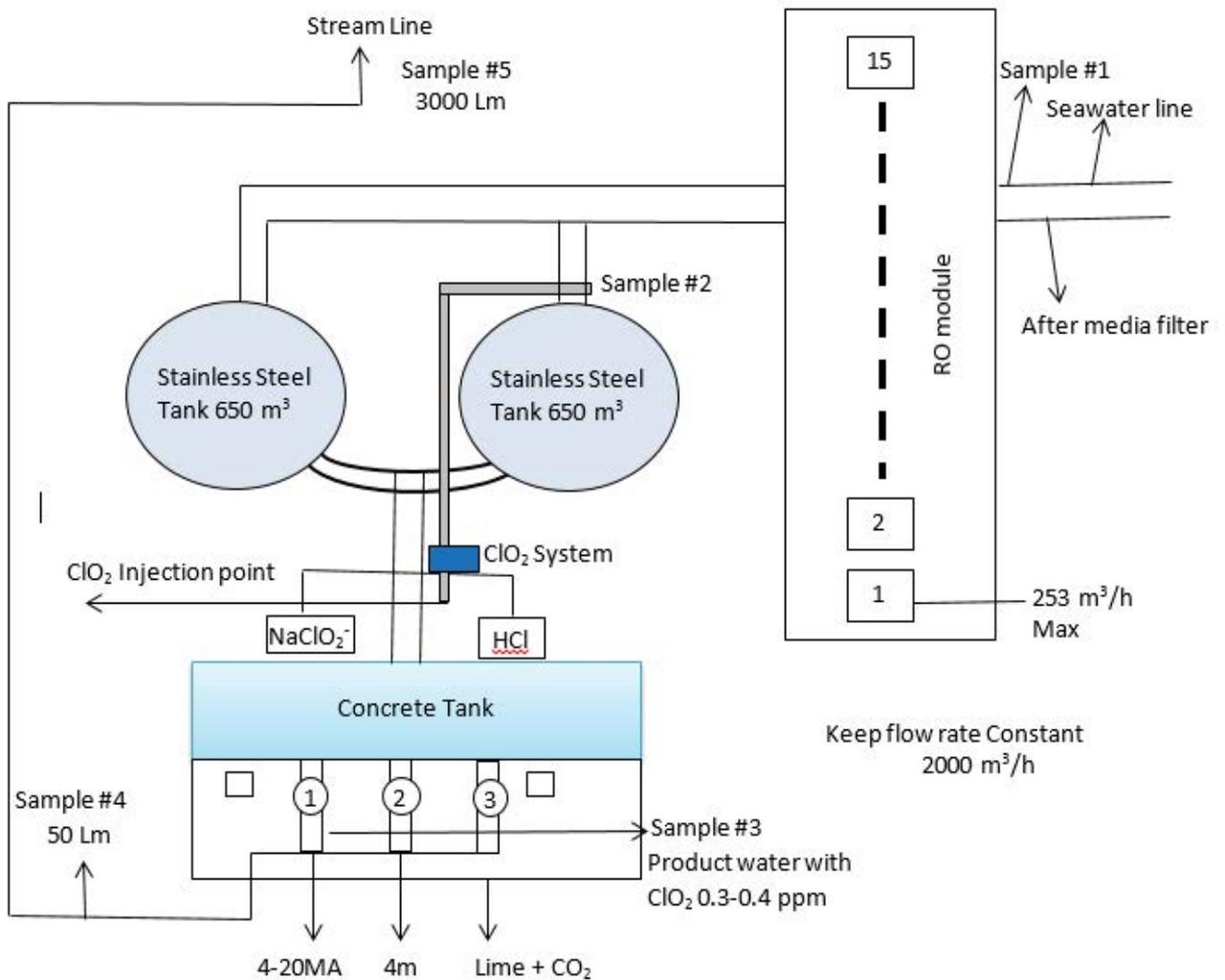


Fig. 3. Schematic diagram for sample points.

Standard Methods [37]. Based on the direct aqueous injection, an Agilent (HP-5890 series, USA), gas chromatography/high performance quadrupole mass spectrometer (GC-MS) using a Purge and Trap technique was used for the identification and quantification of THMs.

4.1.1. Analytical conditions and equipment

The GC oven temperature was programmed from 40°C (4 min) to 140°C at 8°C/min. Other GCMS parameters were as follows: Column: J and W-DB5, 60 m × 0.25 mm × 0.25 μm thickness; Carrier Gas: Helium at 1.2 mL/min; Injector T: 300°C; SIM mode (ions selected: 83, 85, 127, 129, 171 and 173); MS Quad. T: 150°C; MS Source T.

4.2. Bromate and chlorate analysis by ion chromatography

Bromate and chlorate in water were measured by ion chromatography using suppressed conductivity detection according to U.S. EPA Method 300.1 B [38]. An integrated Dionex ICS-3000 RFIC system equipped with an electrolytic eluent generator, an EluGen® EGC II KOH cartridge, a continuously regenerated anion trap column (CR-ATC), a dual piston pump with vacuum degas, with a 250 μL loop, a heated conductivity cell, and a column heater were all used in this work. An IonPac® AS19 (4 mm × 250 mm) with its respective guard column, AG19 (4 mm × 50 mm), was used for all separations. Analytes were detected by suppressed conductivity with an ASRS® ULTRA II (4 mm) operating at 130 mA in the recycle mode. Chromeleon® 6.6 chromatography management software was used for system control and data processing.

4.3. Chlorine dioxide and chlorite analysis

Residual chlorine dioxide and chlorite levels were measured by means of an online amperometric probe. The chlorine dioxide probe was calibrated using a chlorine dioxide solution free of free chlorine and bromine; calibration solution measurements were done using Prominent DT4 or Palintest ChlordioX Plus equipment. The chlorite probe was

calibrated by means of a degassing test kit (Prominent DT4 or Palintest ChlordioX Plus) which removes residual free ClO_2 from the sample prior to acidification and measurement of chlorite levels.

Chlorine dioxide and chlorite concentrations were also measured by manual grab sample and analysis as part of normal onsite test procedures using DPD or a Palintest ChlordioX Plus portable monitoring instrument calibrated for chlorine dioxide (Fig. 4). The ChlordioX Plus equipment is an electrochemical method based on chronoamperometry. In this method, a fixed voltage is applied to a working electrode and the resulting current-time dependence recorded. The magnitude of the current is directly proportional to the concentration of chlorine dioxide in the test sample. Glycine is added to the test sample to eliminate chlorine and bromine by combining with the chlorine and bromine to form non-reactive species [39].

4.4. Biological analysis

Total bacteria counts were determined by APHA Method 9215: Standard Methods for the Examination of Water and Wastewater [40].

5. Results and discussion

5.1. Conversion efficiency of the ClO_2 generating system

Table 1 shows the conversion efficiency of sodium chlorite to ClO_2 over a 2-week period during the month tuning period. Actual ClO_2 values were obtained from online daily charts generated by downstream analyzer installed onsite. The ClO_2 value is quoted daily as an average across the full 24-h period. Dosing control concentrations are generally 0.03–0.05 ppm lower than the downstream analyzer due to non-uniform mixing of dosed ClO_2 immediately after the dosing point. ClO_2 will react instantly with species in heavily contaminated water, this ClO_2 is, therefore, not detected when analyzing a sample taken a short distance after ClO_2 injection which results in a low “actual” ClO_2 concentration. In contrast, ClO_2 will remain stable and detectable in water with low levels of contamination. This justifies the lower than expected conversions.

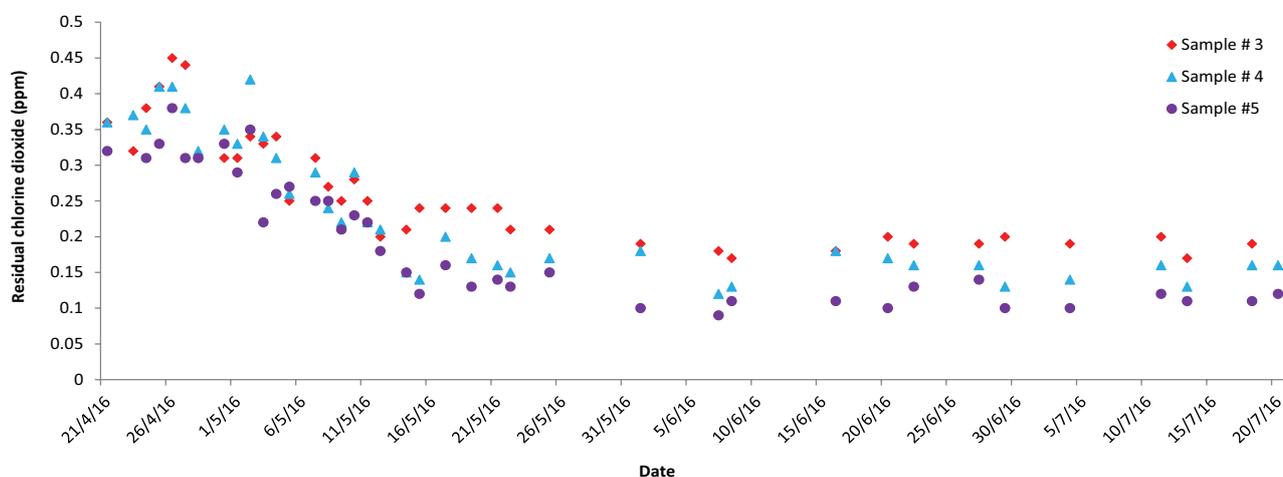


Fig. 4. Residual chlorine dioxide at sample point # 3, 4 and 5.

Table 1
Conversion efficiency of ClO₂ generator over a 2-week period within trial

Date	31% Sodium Chlorite (L h ⁻¹)	Equivalent ClO ₂ concentrations (ppm)		Conversion efficiency (%)
		Theoretical	Actual	
01/5/16	3	0.44	0.32	72.13
02/5/16	2.92	0.43	0.39	92.33
03/5/16	2.92	0.43	0.39	90.94
04/5/16	2.92	0.43	0.38	89.98
05/5/16	2.77	0.40	0.38	94.55
07/5/16	2.77	0.40	0.31	75.59
08/5/16	2.63	0.38	0.29	76.14
09/5/16	2.38	0.35	0.33	96.37
10/5/16	2.38	0.35	0.30	85.27
11/5/16	2.38	0.35	0.29	84.49
12/5/16	2.38	0.35	0.27	78.17
14/5/16	2.38	0.35	0.23	66.69

The efficiencies all fell within the range of 84% to 96%, excluding conversion from the 1st, 7th, 8th and 14th May. The values for these days show a sudden drop in chlorine dioxide concentration which subsequently increases over a period of time. This decrease does not follow the expected trend and can be presumed to be due maintenance work, and this value can be discarded.

Conversion efficiency is extremely dependent on several parameters, a slight adjustment in only one parameter can have a major effect on the calculated conversion. For example, if the percentage of sodium chlorite solution precursor is more/less than 31%, the theoretical ClO₂ concentration would be different to the calculated values shown in Table 1.

5.2. Optimization of dose rate and residual ClO₂

Results in Table 2 are the representative analysis for sample point # 1 (intake seawater). Since the seawater is treated with electrolytically generated calcium hypochlorite from seawater at the intake and intermittent chlorination by calcium hypochlorite before the membranes, it was necessary to investigate both organic (THMs) and inorganic (bromate and chlorite) DBPs at sample point # 2. Bromate,

Table 2
Average analysis values for intake seawater sample point #1 for the total trial period.

Parameters	Sample point #1
pH	6.4
Conductivity, μS/cm	61,000
TDS, ppm	44,000
Residual chlorine, ppm	0.3
M. alkalinity, ppm	75
Bromide, ppm	80

chlorite and chlorate were found to be negligible for the whole evaluation period (Table 3) for sample # 2, whereas THMs, predominantly bromoform (~40 ppb), were detected although the total THMs calculated were well below the regulated values of the WHO (≤1) [26].

The dosing control for chlorine dioxide was monitored at sample point # 3 (Fig. 4). A dosage of ClO₂ with a residual in the range of 0.3–0.4 ppm was controlled as per the requirement for initial disinfection. During the tests it

Table 3
Average values of chlorine dioxide, pH, bromate, TTHMs, organics and biological analysis for sample point # 2, 3, 4 and 5

Sample points	Chlorine dioxide residual	Bromate (BrO ₃ ⁻)	Organics	TTHMs ^a (total)	pH	Biological activity
	ppm	ppb	ppb	Calculated		CFU/mL
# 2	0.01	≤2	ND	0.27–0.40	5.2–5.65	0
# 3	0.17–0.45	≤2	ND	0.27–0.40	5.2–8.5	0
# 4	0.14–0.46	≤2	ND	0.26–0.40	8.2–8.95	0
# 5	0.11–0.38	≤2	ND	0.25–0.45	7.78–8.96	0

ND = Not detected.

^aFor TTHMs maximum permissible limit = Cchloroform + CBDCM + CDBCM + Cbromofrom ≤ 1.

300 60 100 100

was noticed that the pH at this point was high (7.2–8.55), which was attributed to the measurement being taken after lime and CO₂ treatment. The sample location was subsequently changed to a position before lime and CO₂ treatment (pH = 5.20–5.53) to ensure that this treatment did not affect the ClO₂ dosing control. No significant effect of pH on ClO₂ concentration was noticed. Once the performance of disinfection was determined with respect to the microbiological analysis, the ClO₂ dosage was reduced and optimized. A ClO₂ dose rate achieving residual ClO₂ in the range of 0.18–0.20 ppm at sample point # 3 was found to be optimum. The trial was continued with this dose rate monitoring microbiological analysis to ensure effective ClO₂ performance.

The average concentration of ClO₂ at the control dosing point was 0.18 ppm and the concentration decreased to 0.14 and 0.1 ppm at sample point # 4 (50 m) and sample point #5 (3,000 m), respectively (Fig. 4), indicating consumption of ClO₂ at these sample points.

5.3. Biological analysis

Biological analyses showed total coliforms and *E. coli* in all the sample points were negative (Table 3) indicating ClO₂ to be very efficient in killing the bacteria and an effective alternative to chlorination.

5.4. Disinfection by-products

The disinfection by-products chlorite, chlorate, bromate and THMs were monitored during the whole period of the trial at sample points # 3, 4 and 5.

5.4.1. Chlorite

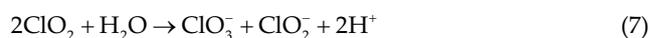
The concentration of chlorite ion (ClO₂⁻) and ClO₂ detected for total duration of test with variable dose rate and the optimized dose rate for all sample points was found to be well below the WHO regulation limit of 0.7 ppm (Fig. 5). Moreover, the values were typically very low (0.01–0.04 ppm) except for the sample point # 5 where the values were slightly higher

(0.04–0.1 ppm). The low concentrations are expected to occur as chlorite is the initial reaction product formed when chlorine dioxide reacts as an oxidizing agent with contaminants in the water (Eq. (6)). However, it is interesting to note that there was no significant effect on the concentration of chlorite detected with adjustment of the ClO₂ dose in this study.



5.4.2. Chlorate

Fig. 6 shows the concentrations of chlorate (ClO₃⁻) measured for total duration of test with variable dose rate and during the optimization of ClO₂ dose rate. The concentration of chlorate for all sample points was found to be well below the WHO regulation limit of 0.7 ppm. Initially at a higher dose rate (0.4–0.45 ppm) of ClO₂, chlorate concentrations were found to be a little higher (0.05–0.14 ppm). As the dose rate of ClO₂ reduced to the optimum dose rate of 0.19 ppm ClO₂, the chlorate concentrations at sample points # 4 and # 5 also reduced and were detected in the range of 0.02–0.06 ppm. At sample point # 3, the concentration detected was consistently 0.01 ppm. This slight increase in chlorate concentration observed at sample points # 4 and # 5 occurs after lime and CO₂ injection probably due to the disproportionation of ClO₂ under increased pH conditions (pH ~ 9, Table 2) to by-product ClO₃⁻ [41,42].



5.4.3. Bromate

Bromate concentrations determined were found to be below the detection limit (<2 ppb) for all the sample points (Table 3) indicating negligible formation of bromate with ClO₂ treatment during the whole trial period.

Bromate ion is of considerable concern with a great amount of research being carried out with respect to this ion [29,43–45]. The presence of bromide ion in hypochlorite solutions can lead to the formation of bromate through

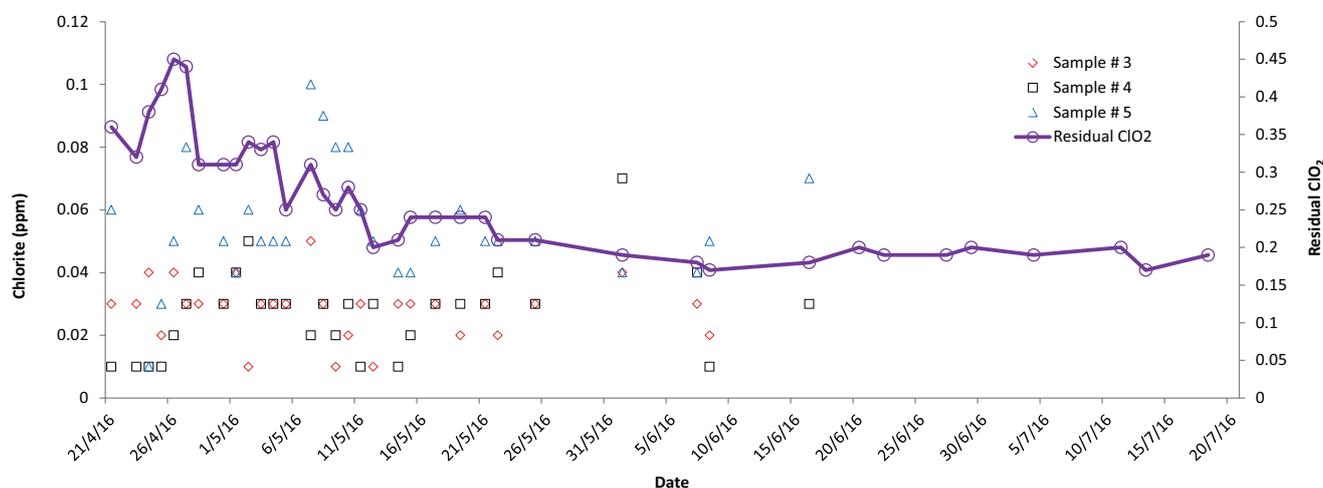


Fig. 5. Average values of chlorite and chlorine dioxide dose rate at sample points # 3, 4 and 5.

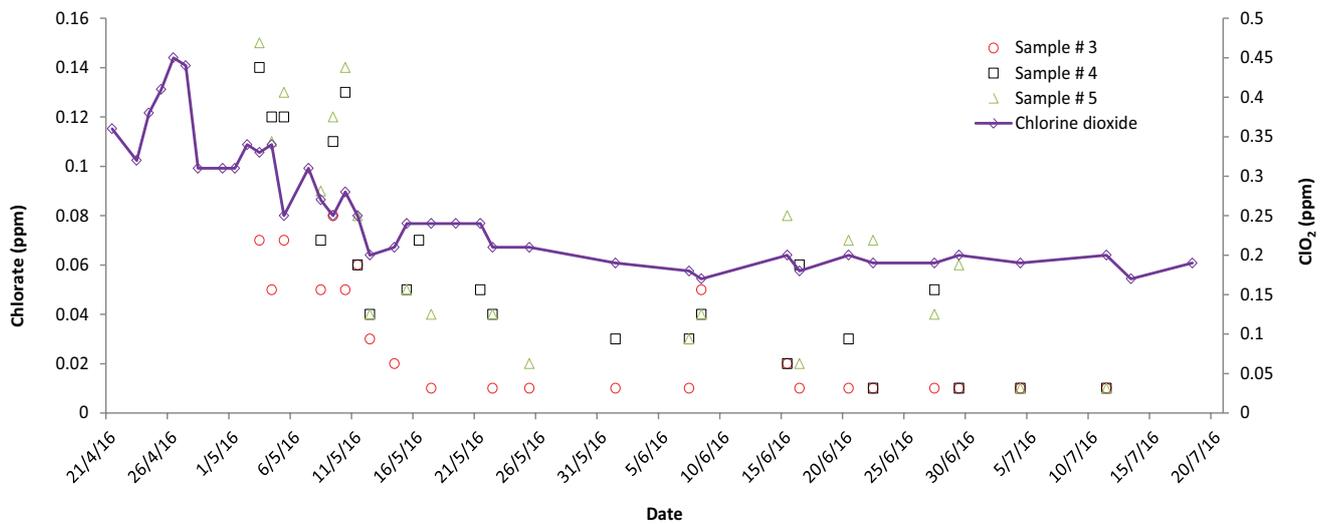


Fig. 6. Average values of chlorate and chlorine dioxide dose rate at sample points # 3, 4 and 5.

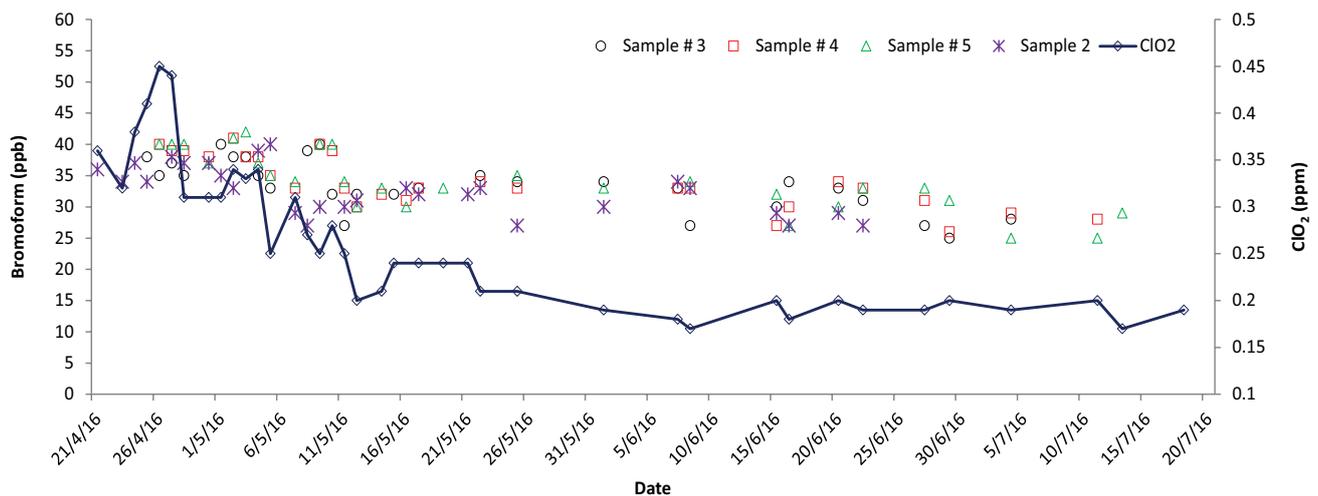


Fig. 7. Average values of bromoform (THMs) and chlorine dioxide dose rate at sample points # 2, 3, 4 and 5.

irreversible formation of hypobromous acid described in Eqs. (1)–(5) in section 1. It is reported that bromate concentrations range from <2 to 51 ppm in hypochlorite solution [41]. Bromate concentrations were found to be in high concentrations (16–81 ppb) in a study [36] conducted for desalinated waters disinfected with NaOCl generated from seawater. Bromate will not be removed through reverse osmosis, therefore, if it is formed at any stage of the water treatment process it will be likely carried through to the distribution network.

5.4.4. Trihalomethanes

Except for bromoform (~40 ppb) other species of THMs were not detected (Fig. 7). It should be noted here that the THMs detected as bromoform are carryover from the chlorination of sea water and intermittent chlorine dose before the membranes (Sample #2) and do not increase due to ClO₂ treatment. Total Trihalomethanes (TTHM) calculated

were also found to be well below the WHO regulated values of ≤1 (Table 3) at all sample points which confirms a major advantage of ClO₂ disinfection to control THMs formation.

6. Conclusions

Effective control of bromate concentrations with <2 ppb for all the sample points which are well below the WHO regulation values of 10 ppb confirmed that chlorine dioxide has good control in curtailing bromate formation.

The only trihalomethane detected throughout the trial was bromoform (~40 ppb) which was found to be carryover from the chlorination of seawater and intermittent chlorine dose due to its presence before the RO permeate with no significant change after ClO₂ injection; the amount found was well below the WHO regulated values for all the sample points.

The study also demonstrated that chlorine dioxide was able to achieve good disinfection with negative values

(0 CFU/mL) for total coliforms and *E. coli* in all the sample points (last sample point # 5 at a distance of 3,500 m) with an optimized dose rate in the range of 0.18–0.20 ppm as residual ClO_2 .

Chlorine dioxide generation with 95%–96% efficiency and minimum amount of disinfection by-products chlorite and chlorate (well below the recommended values by WHO, 0.7 ppm) confirmed the high-purity ClO_2 . The combined ClO_2 , chlorite and chlorate concentrations did not exceed the maximum limit of 1.0 ppm currently recommended by USEPA in all the sample points.

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