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# Ozone oxidation of desalinated seawater, with respect to optimized control of boron and bromate

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ABSTRACT

One of the two main objectives of this study is to use two pass membrane desalination system and to oxidize permeate of the first pass with ozone, as disinfection by products (DBPs) formed by ozone are rather limited. Second objective of this work; is to increase the pH levels to 10 in the permeate of the first desalination pass in order to promote dissociation of boric acid ($B(OH)_3$) to borate ($B(OH)_4^-$). Negatively charged borate can easily be removed by membrane systems because of the charge repulsion. Oxidation efficiency of ozone under pH 10 conditions and the buffer effect of borate were also focused on in this study. Double pass nanofiltration/reverse osmosis (NF/RO) membrane filtration systems were used for the desalination of model seawater. Permeate of the first membrane filtration was adjusted to pH 10 and oxidized with ozone for 30 mins. Oxidized permeate was then fed to the second membrane filtration in order to investigate boron removal and bromate formation and removal. Boron removal was improved effectively by all tested membranes at pH 10. Boron removal rates for NE70, NE90 and FL membranes increased from 4% to 7%, 11% to 28% and 37% to 84% respectively. Bromate was formed effectively with ozone oxidation at pH 10 and removed (>90%) by the RO membrane (FL) and (>75%) by one of the NF membranes (NE90) in the second pass.

*Keywords:* Desalination; Membrane filtration; Ozone oxidation; Boron removal; Bromate formation; Bromate removal

## 1. Introduction

Chlorine, chloramines, ozone and chlorine dioxide are the most common disinfectants, which are also used in desalination plants for pre-treatment and disinfection of desalinated water. In some cases disinfectants are dosed prior to sending the water into the distribution system. This may lead to the formation of DBPs when desalinated water and water from other sources mix in the presence of a residual disinfectant in the distribution system [1]. The formation and the chemical nature of DBPs formed are affected by the presence of bromide and iodide. Therefore enhanced production of brominated DBPs during chlorination and enhanced bromate production during ozone oxidation is expected in the case of seawater desalination, because of high bromide content in seawater even after desalination [2]. It might be difficult to monitor and control chlorinated and/or chloraminated DBPs due to the wide diversity of possible DBP formations [1]. Ozone oxidation typically minimizes the formation of conventional haloorganic DBPs like trihalomethanes and haloacetic acids. Ozone oxidation of high-bromide desalinated waters can

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produce $BrO_3^-$ at concentrations of one to two orders of magnitude, above its regulatory standard [3]. Ozone ($O_3$) was also found responsible for oxidization of aqueous Cl species ($Cl^-$, HOCl/OCl and $ClO_2^-$) to produce $ClO_4^-$ and $ClO_3^-$ as minor products [New]. Formation of DBPs after desalination might pose threats to human health or aquatic ecosystems, and additional treatment processes might be required. In our previous study, it was found that $BrO_3^-$ and two other anions (nitrate and perchlorate) can be effectively (90–95%) removed by NF/RO membranes due to the charge repulsion mechanism [4]. Therefore oxidation of the desalinated water prior to the second pass can be a promising method for both disinfection and DBP control.

It is well known that pH is an important factor for ozone oxidation. Ozone can be decomposed into active species by $OH^-$ ion and the primary radicals such as •OH can be formed [5]. In addition to accelerating ozone decomposition, high pH ozone (pH 9 and greater) is favourable for oxidation of ammonia to nitrate, cyanide destruction, and precipitation of heavy metals [6].

One of the biggest concerns over membrane based seawater desalination processes is the boron removal. It is well known that boron compounds in seawater do not dissociate into ions at low or natural pH. Therefore, boron removal in seawater reverse osmosis (SWRO) desalination systems is low and the process is not adequate enough to produce permeate, complying with the required quality standards (0.5 mg/l boron [7]). At elevated pH, the rejection increases up to 98–99% at pH 11 [8], as boric acid ($B(OH)_3$) shifts to borate ($B(OH)_4^-$) species, which can be rejected by the membrane due to charge repulsion. However, at high pH, precipitation of calcium carbonate and magnesium hydroxide must be avoided. The practical limit of the feed pH for a second desalination pass, desalination of the permeate of the first SWRO desalination pass, is about 10, which corresponds to a brackish membrane rejection rate of 90–95% [9]. Borate is also known as a buffer solution and has been widely used with ozone oxidation in order to keep pH constant during the oxidation processes [10,11].

In order to optimize removal of boron along with the formation and removal of bromate, we have attempted to develop a desalination system with a two pass membrane filtration, with increasing pH levels to 10 after the first pass and applying ozone after the pH levels were increased. We tested the efficiency of this system based on three hypotheses; (a) increasing pH levels to 10 after the first pass would promote the dissociation of boric acid to borate, (b) bromide would effectively be oxidized to bromate with ozone at pH 10 and previously formed borate would keep the pH levels relatively constant, (c) borate and bromate would be removed effectively on the second pass due to the charge repulsion mechanism.

## 2. Materials and methods

### 2.1. Membrane filtration

Membrane filtration tests were performed using one RO membrane (FL, Woongjin Chemical, Korea), two NF (NE70 and NE90, Woongjin Chemical., Korea) membranes, the properties of which are summarized in Table 1. A basic schematic diagram of the system is given in Fig. 1. FL membrane has a positive surface charge at neutral pH (7.00), therefore the removal of borate and bromate cannot be enhanced by the charge repulsion mechanism. Instead, the removal efficiencies of borate and bromate with FL membrane were assumed to be increased by size exclusion mechanism, as the molecular weight of boric acid and bromine were increased by dissociation and oxidation. Dissociation of boric acid to borate increases the molecular weight from 61.83 g/mol to 78.81 g/mol. Also the oxidation of bromide to bromate increases the molecular weight from 79.90 g/mol to 127.90 g/mol.

Flat-sheet membranes were used with an effective membrane area of 138.7 $cm^2$. The experiments were conducted in a semi-recycle mode for the first pass, where the retentates were returned to the feed water reservoir and permeates were collected for oxidation and second pass filtration. Second pass filtration experiments were conducted in recycle mode, where all retentates and permeates were returned to the feed water reservoir. Three different membrane combinations were selected (NE70-NE70, NE90-NE90 and NE90-FL) for first and second pass respectively. Model seawater was

Table 1
Specifications of the selected membranes

| Membrane | Type | Material | MWCO(Da) | Configuration | Surface charge(mV) | Sort |
|---|---|---|---|---|---|---|
| NE70 | Thin film composite | Polyamide | 320* | Flat sheet | –40* | NF |
| NE90 | Thin film composite | Polyamide | 110* | Flat sheet | –48* | NF |
| FL | Thin film composite | Polyamide | 70* | Flat sheet | 23* | RO |

*Data was taken from previous study [12].

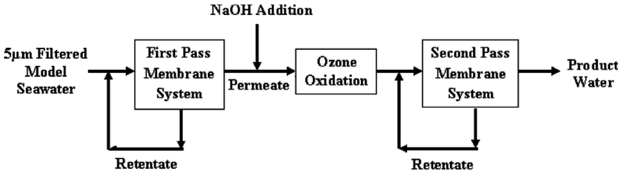


Fig. 1. Basic Schematic Diagram of the System.

Table 2
Model seawater characteristics

| | |
|---|---|
| Boron (mg/l) | 0.47–1.63 |
| Bromate (mg/l) | 0.0 |
| Bromide (mg/l) | 46.0 |
| Chloride (mg/l) | 27000 |
| Calcium (mg/l) | 113.7 |
| Magnesium (mg/l) | 33.4 |
| Potassium (mg/l) | 25.0 |
| Sodium (mg/l) | 15168 |
| pH | 7.2–7.8 |
| Conductivity (mS/cm) | 62.7 |

prepared by dissolving sea salts (Pure Ocean, SaltWorks Inc. WA) in water (Table 2). The retentate flow rate was adjusted to an appropriate value of 500 ml/min, with permeate fluxes adjusted to 12–25 µm/s for both the NF and RO membranes. Each membrane filtration test was conducted at ambient temperature (25 ± 2)°C. The membranes were washed with de-ionized pure water prior to a new series of experiments.

### 2.2. Ozone oxidation in elevated pH conditions

In order to increase pH levels (pH = 10) in permeate of the first membrane filtration, 0.1 M NaOH was added to the permeate. After pH levels were adjusted, $O_3$ (0.26 l/m oxygen, 6% w/w $O_3$) was fed to permeate through the air diffuser for 30 mins. Pure oxygen gas was used for ozone production and the ozone conversion rate was controlled by adjusting the power in the ozone generator to achieve stable ozone generation.

### 2.3. Analytical methods

Bromate samples were analyzed by using the method, which has been developed by Snyder et al., [13], which allows simultaneous measurement of sub-µg/l quantities of the oxyhalide anions in water samples. Boron samples were analyzed with ICP-MS (Agilent, 7500, US/An, octopole reaction system).

## 3. Results and discussion

### 3.1. Salt removal

Salt removal rates were calculated by using conductivity data. As expected NE70-NE70 system combination, with 27% overall conductivity removal, was not effective for salt removal. NE90-NE90 and NE90-FL combinations showed relatively high overall conductivity removals (90% and 96% respectively). It was found that after the ozone oxidation at pH 10, conductivity removal rates were improved in NE70-NE70 and NE90-NE90 combinations (from 10% to 19% and from 65% to 72% respectively) (Fig. 2). This phenomena could be explained by the oxidation of $Cl^-$ species by ozone and their increased removal rate as a result of charge repulsion with NF membranes and increase in the molecular weight with RO membrane ($Cl_2$ = 70.9 g/mol; $ClO_3^-$ = 83.45 g/mol; $ClO_4^-$ = 99.43 g/mol).

### 3.2. Boron removal

Boron concentrations were measured before (after high pH ozone oxidation) and after the second pass filtration for three different membrane combinations (NE70-NE70, NE90-NE90 and NE90-FL). Boron removal rates were calculated and compared with the data which was obtained from a previous study (Fig. 3) (Sarp et al., 2008). Boron removal rates were improved for all the membranes when ozone oxidation at pH 10 was used. Boron removal rates for NE70, NE90 and FL membranes increased from 4% to 7%, 11% to 28% and 37% to 84% respectively. Final permeate boron concentrations were 1.34, 1.04, and 0.23 mg/l for NE70-NE70, NE90-NE90, and NE90-FL combinations, respectively. WHO (1998) has a regulative value of 0.5 mg/l for drinking water boron concentration; therefore NE90-FL combination has matched the regulation values. Even though size

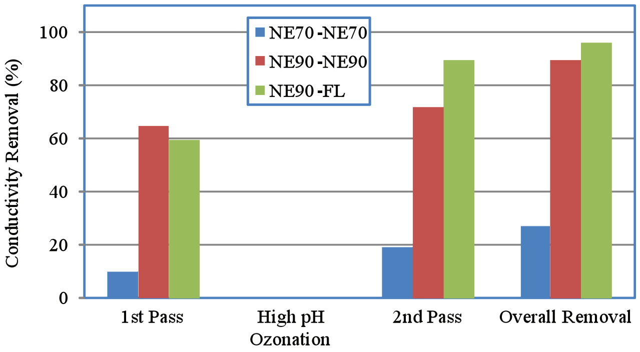
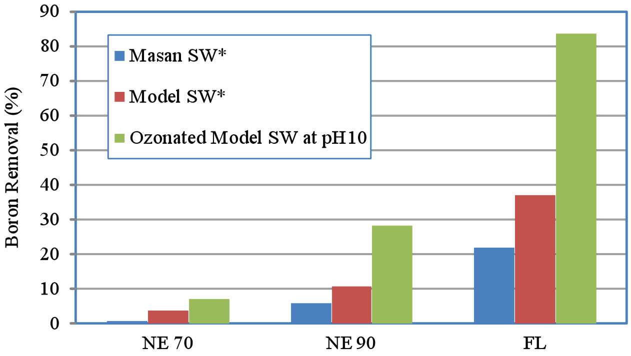


Fig. 2. Conductivity removal by selected membrane combinations (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ;ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).



*Data is taken from previous study [12]

Fig. 3. Comparison of boron removal efficiencies with three different membranes and water sources (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).

exclusion is still the major mechanism for the boron removal, it was found that charge repulsion mechanism can be improved dramatically by increasing the pH for negatively charged NF membranes. Also the removal of borate by RO membrane was increased by size exclusion mechanism, as a result of increased molecular weight.

### *3.3. Bromate formation and removal*

Bromide was effectively removed by the NE90 membrane in the first membrane filtration pass (Fig. 4) and the remaining bromide was oxidized with ozone oxidation at pH 10. After the ozone oxidation at pH 10, bromide concentration was under or equal to the detection limit (5 mg/l), thus it can be suggested that ozone oxidation at pH 10, along with the buffering effect of borate, effectively oxidized the remaining bromide. For the NE70-NE70 system combination, 14 mg/l of bromide was removed by the ozone oxidation at pH 10, but only 1.7 mg/l of bromate was formed. Similar results were obtained for NE90-NE90 and NE90-FL combinations (11 mg/l bromide to 3.1 mg/l bromate for NE90-NE90 and 13.1 mg/l bromide to 2.4 mg/l bromate for NE90-FL) (Figs. 5 and 6). The gap between removed bromide and formed bromate was even higher in terms of molarity. This unexpected gap can be explained by the formation of brominated DBPs with the effect of OH radicals and possible formation of chlorate species. Also lower bromate formation in NE70-NE70 combination might be explained by the salt effect on bromate formation, as first pass of the combination had a low salt removal rate (10%). Formed bromate was effectively removed by NE90 and FL membranes in the second pass filtration (78% and > 92%, respectively) (Fig. 7). Detection limit of bromate was 0.2 mg/l and permeate of NE90-FL configuration has a bromate concentration less than this value. WHO drinking water regulation (1998) for bromate is

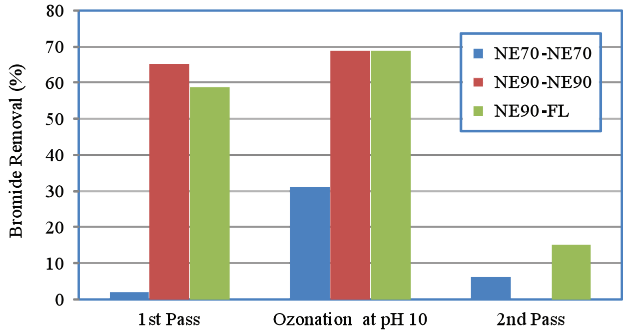


Fig. 4. Bromide removal for selected membrane combinations (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).

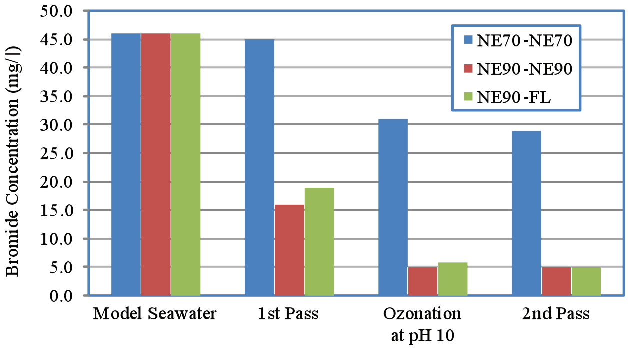


Fig. 5. Bromide concentrations throughout the system with different membrane combinations (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).

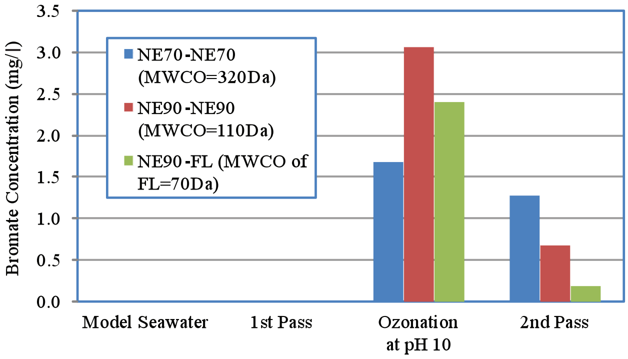


Fig. 6. Bromate concentrations throughout the system with different membrane combinations (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).

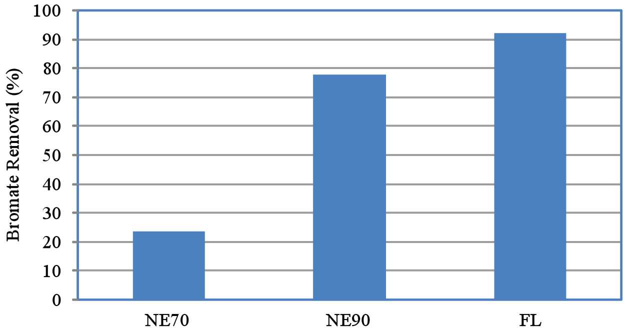


Fig. 7. Bromate removal rates of selected membranes on the second pass filtration after ozone oxidation at pH 10 (effective membrane area: 138.7 cm$^2$, retentate flow rate: 500 ml/min, permeate flux: 12 µm/s for NF and 25 µm/s for RO membranes).

0.01 mg/l, the bromate detection limit was much higher than this value to make a healthy comparison.

## 4. Conclusion

Two different membrane combinations (NE90-NE90 and NE90-FL) were determined efficient for the overall desalination process with respect to salt, boron and bromate removals. Even though the bromate detection limit was higher than regulatory values, it might be assumed that with certain membrane combinations and design parameters, these regulatory values can be matched. Boron was removed to under the regulation concentration by NE90-FL two pass membrane system. It has seen that with proper improvements, NF systems could be low pressure alternatives for RO systems. Salt removal efficiencies of NE70 and NE90 membranes were improved after ozone oxidation at pH 10. Increasing pH to 10 promoted the dissociation of boric acid to borate, thus effective boron removal was observed during the second pass filtration. Formed borate acted as a buffer solution and kept pH levels relatively constant (9.89–9.92). Therefore, ozone oxidation at constant pH (10) enhanced the oxidation of bromide to bromate efficiently, and formed bromate was removed by the second pass (by NE90 and FL membranes) due to the charge repulsion mechanism for NF membranes and enhanced size exclusion for RO membrane. High pH conditions increased the boron removal around two fold for all selected membranes.

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