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# Removal of fouling species from brackish water reverse osmosis reject stream

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**ABSTRACT**

Brine disposal from reverse osmosis (RO) systems remains a major challenge for the desalination industry especially in inland areas where discharge options are very limited. Solutions will entail the introduction of economic treatment processes that will alleviate the brine's negative impact on the environment and reduce its discharge volume. Such processes could act as an intermediary treatment process for the recycling of the brine through an additional RO stage which, for brackish water (BW) desalination, could lead to saving valuable water while reducing the amount of brine discharge. In this context, the study at hand attempts to evaluate the effectiveness of a one-step chemical process for the treatment of BWRO brine. This study seeks to determine optimal operating conditions relative to type, ratio, and dosage of alkalizing chemicals, pH and temperature, for substantially reducing the concentrations of scaling parameters such as calcium, magnesium, silica, and strontium. The results indicate that precipitation softening at pH = 11.5 using combined chemical dosages of NaOH and $Na_2CO_3$ in a ratio of 2:1 leads to substantial removal of calcium and magnesium (>95%) and moderately high removal of strontium and silica (>71%).

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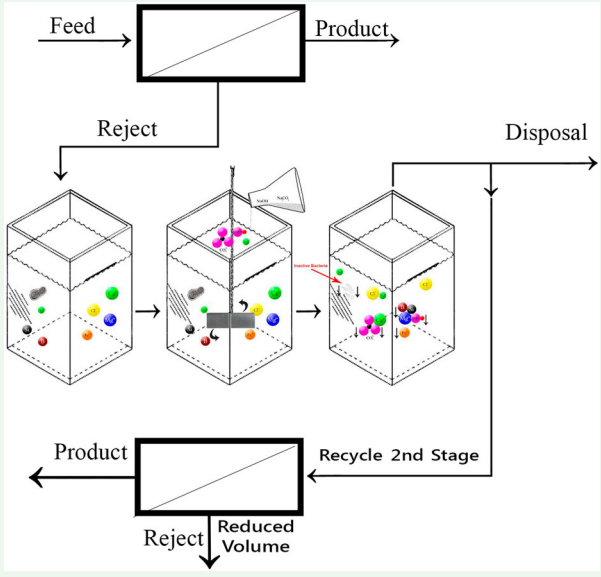
Reverse osmosis; brackish water brine; precipitation; sodium hydroxide; sodium carbonate; scaling




## Introduction

In response to the increasing demand for fresh water worldwide, water reuse and desalination have been successfully employed as alternative methods of freshwater supply over the last few decades [1]. Specifically, reverse osmosis (RO) has gained significant appeal as one of the major processes for desalination, representing up to 80% of the world's share of installed desalination plants [2,3]. Due to technological enhancements and reduction in cost, RO is one of the most commonly used desalination process, especially for the desalination of brackish water (BW) [1]. Nonetheless, the RO process has several limitations, such as relatively high energy consumption, moderately high operational costs, and environmental and

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cost constraints associated with brine disposal, especially for inland systems [4–9].

In brackish water reverse osmosis (BWRO) systems the concentrate (interchangeably referred to as reject or brine) stream usually constitutes 10–35% of the feed water as BWRO recovery rate varies between 65% and 90% [3,5,9]. As determined by the characteristics and pretreatment needs of the feed water, the concentrate streams rejected from the RO may contain high concentrations of salts (e.g. calcium, magnesium, boron, silica, barium, and strontium) coagulants, anti-scalants, anti-foaming agents, residues from membrane cleaning chemicals, and traces of heavy metals from equipment deterioration such as copper, nickel, and lead [3,10].

Several 'solutions' have been proposed, and employed, for concentrate disposal, such as evaporation ponds, irrigation, fish farming, discharge to surface water bodies, land disposal in unlined surface depressions, addition of the reject flow to a wastewater stream, further concentration into solid form, and injection below water aquifers [4,6,9,11,12]. All of these methods suffer from several disadvantages, such as high costs, contamination of surface and ground water, flooding, destabilization of aquatic ecosystems, and increased levels of salts in the soil [13,14].

It is important to add that in some cases, the brine undergoes treatment, depending on local environmental guidelines and on the disposal option selected. These include, but are not limited to, disinfection, aeration, degasification, and other processes [15]. The ideal target would be to minimize liquid effluent and recover useful or valuable products from the brine, transforming the waste into commodity [5,16–18]. Some efforts include selling recovered salts and byproducts, irrigating salt-tolerant crops, cultivating marine species such as brine shrimps, and applying the zero liquid-discharge (ZLD) concept [5,13,19,20]. ZLD can be achieved once the water recovery reaches 100% approximately, where all the salts are retrieved and good-quality water is produced [3,17].

Several processes have been proposed for concentrate minimization [4,6,9,12]. These processes are often integrated with a BWRO or other desalination processes. These include softening by pellet reactors [21], ion exchange [22], desalination using an additional RO stage [23–25], electrodialysis and electrodialysis reversal [9,26–29], oxidation combined with precipitation [30,31], vibratory shear enhanced process, electrocoagulation, micro-filtration, and ultra-filtration (UF) [7,9,32], microalgae [33], membrane distillation and forward osmosis [34,35].

Precipitation by lime and soda ash softening has also been tested for treating RO concentrate in order to aid in the removal of certain scaling precursors such as calcium, magnesium, and barium [17,22,24]. This is performed by direct addition of alkalizing chemicals to the concentrate [22,36], applying chemically enhanced seeded precipitation of concentrate using gypsum as an intermediate step prior to secondary RO units [37,38], seeded crystallization [39,40], and intermediate chemical demineralization [24,25]. Accelerated precipitation softening resulted in favorable reduction of major scalants such as silica, barium, and strontium [41,42].

The use of caustic and soda ash rather than lime and soda ash has been successfully tested by the authors as a pretreatment method for the removal of most if not all of the fouling/scaling species from seawater [43] and BW [44]. The limited use of chemicals to achieve this pretreatment process should result in a limited change in the types of pollutants that will appear in the brine, specifically the absence of disinfectants and their byproducts, conventional coagulants, antiscalents, antifoaming agents, with reduced quantities of biocides, ammonia, and hydrogen sulfide. As for heavy metals, precipitation softening is recorded to have been very effective in removing such metals [45,46]. The use of seawater bittern has also been found to be very effective in the removal of a variety of solids from alkalized effluents [47–49]. Whilst the use of chemicals for the removal of fouling species has been investigated for BWRO reject streams, a systematic evaluation of the most optimal conditions (type of chemicals, ratio of chemicals, pH conditions, and temperatures) necessary for the removal of fouling species from BWRO rejects has received scarce attention in the literature. The experimental study at hand attempts to address this issue and endeavors to (a) evaluate the effectiveness of a one-step process employing several pH-adjusting chemicals to remove precipitating constituents from the BWRO brine, (b) select the optimal combination of chemicals, and (c) determine the optimal operating conditions in terms of removing a large percentage of the scaling/fouling species. In this context the treatment of BWRO brine by the proposed method will serve as an intermediate treatment step prior to a second-stage BWRO leading to a higher water recovery for the overall RO system. This will reduce the total amount of reject water to be sent back to the environment and may prove to be a viable approach for the disposal of an end product which meets stringent brine discharge parameters.

## Materials and methods

### *BWRO brine sample collection and analysis*

All of the BWRO brine samples were collected from a pilot plant system located at the American University of Beirut's (AUB) Chemical Engineering Laboratory

**Table 1.** Composition of the BWRO brine samples collected for the experimental study.

| Parameter | Unit | Number of observations | Mean | Standard deviation |
|---|---|---|---|---|
| pH | pH units | 11 | 7.4 | ±0.1 |
| Temperature | °C | 11 | 25.5 | ±1.9 |
| Conductivity | mS | 2 | 15.3 | ±0.3 |
| TDS (gravimetric) | mg/L | 6 | 9053.3 | ±539.9 |
| TSS | mg/L | 4 | 44 | ±24 |
| VSS | mg/L | 5 | 20.0 | ±9.6 |
| Alkalinity (bicarbonate) | mg/L as $CaCO_3$ | 7 | 117 | ±59.1 |
| Ca hardness | mg/L as $CaCO_3$ | 18 | 1197 | ±130.7 |
| $Ca^{2+}$ | mg/L | 18 | 478.8 | ±52 |
| Mg hardness | mg/L as $CaCO_3$ | 18 | 2111 | ±182.0 |
| $Mg^{2+}$ | mg/L | 18 | 512.5 | ±44 |
| Total hardness | mg/L as $CaCO_3$ | 18 | 3273 | ±166.5 |
| Sulfate | mg/L | 6 | 125 | ±53 |
| Chloride | mg/L | 14 | 5489 | ±216.0 |
| Silica | mg/L as Si | 17 | 6 | ±1.4 |
| | mg/L as $SiO_2$ | 17 | 13.1 | ±4.6 |
| Fe | mg/L | 4 | 0.041 | ±0.004 |
| Boron | as B (mg/L) | 6 | 2.1 | ±0.2 |
| | as $H_3BO_3$ (mg/L) | 6 | 11.9 | ±1.4 |
| Strontium | mg/L | 7 | 7.5 | ±2.2 |
| Barium | mg/L | 4 | BDL[a] | BDL[a] |
| Na | mg/L | 5 | 2842.7 | ±349.7 |
| K | mg/L | 2 | 35.2 | ±1.4 |
| Fecal coliforms | CFU in 100 mL After 24 h | 3 | 0 | 0 |
| Total coliforms | CFU in 100 mL After 24 h | 3 | 0 | 0 |

[a]BDL, Below detection limits.

facilities. The pilot plant was desalinating water from a moderately saline BW well located in the vicinity of AUB, Beirut, Lebanon. The samples were collected on a weekly basis in 20 L containers that were cleaned and rinsed with the brine twice beforehand.

Tests conducted on the BWRO brine water samples were based on standard methods [50] where the following measurements were recorded: pH, temperature, conductivity, total dissolved solids (TDS), total suspended solids (TSS), volatile suspended solids (VSS), calcium, magnesium, silica, iron, boron, strontium, barium, sodium ions, potassium ions, and fecal and total coliform. The HACH method 8014 was used for measuring barium. The experimental study was carried out at the Environmental Engineering Research Center at AUB, over a year's time, with a total of 9 months of uninterrupted laboratory work. The characteristics of the collected BWRO brine are shown in Table 1.

## Selection of alkalizing chemicals

Three alkalizing chemicals, lime ($Ca(OH)_2$), caustic soda (NaOH), and soda ash ($Na_2CO_3$), as well as combinations of $Ca(OH)_2$ with $Na_2CO_3$ and of NaOH with $Na_2CO_3$, were used in testing for the removal of the components investigated in this study. To this effect, a preliminary investigation was conducted through a series of six titrations on the sample water with each of the proposed alkalizing agents, followed by the evaluation of Ca and Mg removal efficiencies. The water temperatures and pH values were recorded during the titrations, and the calcium and total hardness were analyzed. Ultimately, the agent or combination of agents that best achieved the required pH and optimal pollutants removal was selected for further evaluation as the final alkalizing agent/agents to be adopted for the consequent experiments.

Upon selection of the optimal chemical, which in this case was determined to be the combination of 1 N NaOH and 1 N $Na_2CO_3$ as noted in Table 2, further tests were performed to determine the optimal pH and chemical ratios needed to achieve maximum removals of the Ca and Mg. For this purpose series of tests were conducted to cover a range of pH values (9.5, 10.5, 11.0, 11.5, and 12) and a range of alkalizing chemical (NaOH:$Na_2CO_3$) ratios (1:1, 1.25:1, 1.5:1, 2:1, 2.5:1, 3:1, 3.5:1, 1:1.25, 1:1.5, 1:2, 1:2.5, 1:3). An additional series of titration tests were performed for the different alkalizing chemical ratios in order to determine the concentration of chemicals needed to attain different pH values. Figure 1 shows the amounts of alkalizing chemicals NaOH:$Na_2CO_3$ at a ratio of 2:1 and 25°C needed to attain different pH values, while the results recorded at all the ratios are shown in ESM Table S1 and Figure S1. For further clarification, ESM Table S2 is presented to indicate the ratios of a dosage of 1 mL of titrant and their equivalent in mg/L of NaOH and $Na_2CO_3$.

## Experimental procedure

The experiments were carried out using the standard jar-test apparatus (Phipps and Bird Model 7790–300 Six Paddle Stirrer). Starting with a rapid mixing phase of 1 min at 100 rpm, followed by slow mixing at 30 rpm for 20 min, alkalizing agents were added to the samples until the desired pH is achieved. The flocculated

**Table 2.** Results of preliminary study for the removal of Ca and Mg using different chemicals.

| Chemicals | $Ca(OH)_2$ | NaOH | $Na_2CO_3$ | 2NaOH:1$Na_2CO_3$ | 2$Ca(OH)_2$:1$Na_2CO_3$ |
|---|---|---|---|---|---|
| Concentration | 1 M | 1 N | 1 N | 1 N:1 N | 1 M:1 N |
| Sample temp. | 20.7 ± 0.5 | 23.7 ± 0.5 | 23.5 ± 1.8 | 23.6 ± 0.7 | 23.1 ± 1.3 |
| pH[b] | 12.1 ± 0.1 | 12.1 ± 0.2 | 11.33 ± 0.2 | 12.0 ± 0.1 | 12.02 ± 0.1 |
| Ca % removal | 0[a] | 65.5 ± 3.5 | 100 ± 0.0 | 99.9 ± 0.1 | 0[a] |
| Mg % removal | 84.8 ± 6.9 | 91.0 ± 6.0 | 66.4 ± 6.4 | 97.1 ± 0.4 | 73.5 ± 4.3 |
| Dose (mL/100 mL) | 2.56 | 5.51 | 265.92 | 8.34 | 4.26 |

[a]Higher concentrations for Ca were recorded.
[b]The selected pH is based on previous studies.

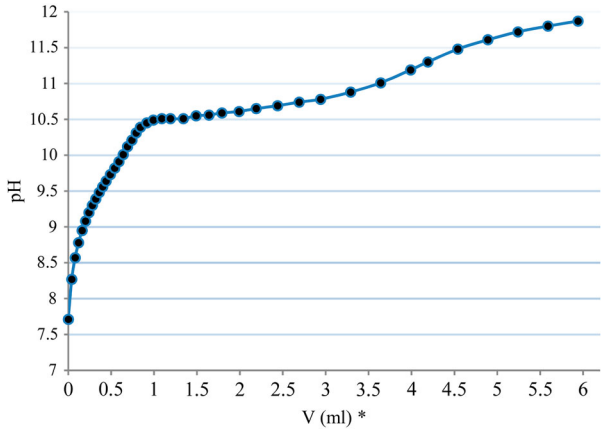


**Figure 1.** The variation of brine pH with volume of the alkalizing chemicals ($NaOH:Na_2CO_3$) at a 2:1 ratio.

Note: *For concentration of titrant expressed in mg/L refer to ESM Table 2.

samples were left to settle for around 60 min. When the jar tests were conducted at 10°C and 30°C, fitted polystyrene jackets were used so as to control possible variation to the test temperature. pH and temperature were monitored at regular intervals throughout the experimental time. In this regard, limited pH reductions were observed, which may be attributed to the presence of dissolved $CO_2$ in the form of carbonic acid ($H_2CO_3$) that results in reducing the pH [43,51].

The selected 'optimal' chemical combination ($NaOH:Na_2CO_3$) at a 2:1 ratio was used in successive tests at three different temperatures (10°C, 25°C, 30°C) and at three pH values (10.5, 11, 11.5) in order to determine the effect of temperature and pH on the removal efficiencies of the different pollutants. Additional tests were conducted at five different temperatures (10°C, 15°C, 20°C, 25°C, 30°C) for each of the five different pH values (9.5, 10.5, 11, 11.5, 12) to further elaborate these effects.

At the end of the settling period supernatant samples were withdrawn while ensuring that the settled layer was not disturbed and the samples were analyzed for the targeted parameters.

### *Analytical procedures*

The experimental data were analyzed using the software R: The R project for Statistical Computing. The Shapiro–Wilk test for normality of data was applied, along with the Bartlett test for the homogeneity of variances. One-way and two-way analysis of variance (ANOVA) tests were performed on every parameter as well, and the null and alternative/experimental hypotheses were defined as follows:

- $H_0$: The suggested treatment (pH and/ or temperature) has **no** effect on the parametric removal efficiency
- $H_a$: The suggested treatment (pH and/ or temperature) has **an** effect on the parametric removal efficiency

After significant findings were extracted from ANOVA, single and multiple linear regressions were conducted as well with the aim to assess the linear relationship between the predictor variables of pH and temperature and the response variable, which is the removal efficiency of the key contaminants.

The United States Geological Survey's modeling software, PHREEQC (version 2.18.3.570), was used for speciation and saturation-index calculations where at each pH experimental point, the initial concentrations and the concentrations of the alkalizing chemicals were inputted into the program to determine saturation levels and the nature of the precipitated compounds.

## Results and discussions

### *Optimal alkalizing chemical ratio*

Table 3 presents the results for the residual concentrations of $Ca^{2+}$ and $Mg^{2+}$ for experiments conducted at different chemical ratios of 1 N NaOH :1 N $Na_2CO_3$ and at five different pH values at a temperature of 25° C. The results indicate that there are several combination ratios and pH values that will lead to very low residuals of calcium and magnesium ions, that is, to good removal

**Table 3.** Residual concentrations of Ca and Mg ions at different pH and $NaOH:Na_2CO_3$ ratios.

| Ratio of[a] | pH = 9.5 | | pH = 10.5 | | pH = 11 | | pH = 11.5 | | pH = 12 | |
|---|---|---|---|---|---|---|---|---|---|---|
| $NaOH:Na_2CO_3$ | $Ca^{2+}$ | $Mg^{2+}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Ca^{2+}$ | $Mg^{2+}$ |
| (1/3) | 24.10 | 449.55 | 32.06 | 345.06 | 4.01 | 46.17 | 0.00 | 29.16 | 0.00 | 24.30 |
| (1/2.5) | 112.22 | 417.96 | 48.10 | 359.64 | 4.01 | 48.60 | 2.00 | 32.81 | 0.00 | 24.30 |
| (1/2) | 120.24 | 364.50 | 60.12 | 328.05 | 4.01 | 46.17 | 2.00 | 32.81 | 0.00 | 24.30 |
| (1/1.5) | 160.32 | 352.35 | 100.20 | 298.89 | 16.03 | 38.88 | 2.00 | 27.95 | 0.00 | 24.30 |
| (1/1.25) | 126.25 | 348.71 | 120.24 | 267.30 | 14.03 | 42.53 | 8.02 | 41.31 | 0.00 | 16.52 |
| (1/1) | 128.26 | 359.64 | 120.24 | 267.30 | 18.04 | 49.82 | 8.02 | 55.89 | 0.00 | 97.20 |
| (1.25/1) | 128.26 | 359.64 | 112.22 | 277.02 | 16.03 | 38.88 | 14.03 | 52.25 | 30.86 | 93.07 |
| (1.5/1) | 140.28 | 340.20 | 112.22 | 247.86 | 0.00 | 48.60 | 24.05 | 48.60 | 16.03 | 14.58 |
| (2/1) | 140.28 | 340.20 | 120.24 | 223.56 | 0.00 | 36.45 | 0.00 | 24.30 | 0.00 | 14.58 |
| (2.5/1) | 160.32 | 328.05 | 152.30 | 150.66 | 16.03 | 41.31 | 4.01 | 48.60 | 0.00 | 14.58 |
| (3/1) | 160.32 | 303.75 | 148.30 | 153.09 | 32.06 | 89.91 | 31.26 | 41.80 | 8.02 | 9.72 |
| (3.5/1) | 168.34 | 286.74 | 160.32 | 97.20 | 40.08 | 72.90 | 20.04 | 48.60 | 12.02 | 6.08 |

[a]Tests conducted at 25°C.

percentages of $Ca^{2+}$ and $Mg^{2+}$: 1.5:1 ratio at pH = 11, 2.5:1 ratio at pH = 12 and 2:1 ratio at pH values of 11, 11.5, and 12. Given that the 2:1 volumetric ratio of 1 N NaOH:1 N $Na_2CO_3$ yields excellent removal results over a range of pH values, this ratio was selected as the 'optimal' alkalizing combination to be used in the jar-test experiments.

### *Removal efficiencies of fouling species at various operating conditions*

The removal percentages of calcium, magnesium, silica, strontium, and boron at several temperatures and pH values are shown in Table 4, while a plot for the removal percentages of calcium and magnesium for a wider range of temperatures and pH values is shown in Figure 2.

It is evident from Table 4 that the percentage removals for Ca and Mg increase with the increase in pH from 10.5 to 11.5, reaching their maximum removals of 99.77% and 96.61%, respectively, at pH = 11.5. Consistently, the one-way ANOVA showed that pH had a major effect on the removal efficiency of Ca and Mg (*p*-values for all three parameters were <.05).

For a particular temperature, the percentage reduction of Ca and Mg increases as the pH of the system increases. It is depicted from Figure 2 that for the higher ranges of temperatures (25°C and 30°C), Ca precipitation starts at pH values lower than 9.5 while Mg precipitation is initiated at a pH of approximately 10.5. However, and for the higher temperature values, substantial removals of Ca and Mg (>80%) are achieved at a pH value around 11.0 with almost complete precipitation at pH = 11.5. The strong dependence of calcium carbonate solubility on the operating pH value is in agreement with previous research reported on BWRO brine, brackish, and seawater, while the precipitation of magnesium in the form of magnesium hydroxide at operating pH values larger than 10.5 has also been extensively reported [24,42–44].

Removal of strontium showed similar pH dependence to $Ca^{2+}$ and $Mg^{2+}$ removal where, for a particular temperature, the removal rate of strontium increased with the increase in pH with the highest removal rate of 71.6% recorded at pH = 11.5 and 25°C. This phenomenon is in line with the work of Rahardianto et al. [42], Gabelich et al. [24], and Gabelich et al. [25] for BW brine and is attributed to the co-precipitation of strontium (probably in the form of carbonate) with the increased precipitation of calcium carbonate at the higher pH values.

In contrast to observations for precipitation softening in seawater [43] where removal rates of calcium and

**Table 4.** Treated BWRO brine constituents at different temperatures and pH values.

| | | 10°C | | | 25°C | | | 30°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Initial brine | pH = 10.5 | pH = 11 | pH = 11.5 | pH = 10.5 | pH = 11 | pH = 11.5 | pH = 10.5 | pH = 11 | pH = 11.5 |
| pH | 7.4 ± 0.1 | 10.49 ± 0.1 | 10.91 ± 0.0 | 11.42 ± 0.0 | 10.4 ± 0.1 | 10.9 ± 0.1 | 11.4 ± 0.1 | 10.4 ± 0.1 | 10.9 ± 0.1 | 11.4 ± 0.1 |
| Temperature °C | 25.5 ± 1.9 | 10.3 ± 0.5 | 10.2 ± 0.7 | 10.5 ± 0.8 | 24.6 ± 1.8 | 24.5 ± 1.5 | 24.7 ± 1.5 | 30.4 ± 0.5 | 30.1 ± 0.7 | 29.8 ± 0.6 |
| Ca mg/L as $CaCO_3$ | 1197.2 ± 130.7 | 773.3 ± 30.6 | 733.3 ± 23.1 | 243.3 ± 49.3 | 537.5 ± 42.7 | 103.3 ± 10.0 | 2.8 ± 5.5 | 475.0 ± 7.1 | 111.0 ± 15.6 | 0.0 ± 0.0 |
| Ca removal % | N/A[a] | 35.4 ± 2.6 | 38.7 ± 1.9 | 79.7 ± 4.1 | 55.10 ± 3.6 | 91.38 ± 0.8 | 99.77 ± 0.5 | 60.3 ± 0.6 | 90.7 ± 1.3 | 100.0 ± 0.0 |
| Mg mg/L as $CaCO_3$ | 2110.6 ± 417.8 | 2110.0 ± 70.7 | 1139.5 ± 47.3 | 856.7 ± 25.2 | 1410 ± 130.8 | 244.0 ± 42.9 | 71.5 ± 13.1 | 1550.0 ± 84.9 | 200.0 ± 36.8 | 67.5 ± 2.1 |
| Mg removal% | N/A | 2.4 ± 0.0 | 46 ± 2.2 | 59.4 ± 1.2 | 33.19 ± 6.2 | 88.44 ± 2.0 | 96.61 ± 0.6 | 26.6 ± 4.0 | 90.5 ± 1.7 | 96.8 ± 0.1 |
| Silica mg/L as Si | 6.12 ± 2.1 | 4.8 ± 0.1 | 2.2 ± 1.0 | 0.5 ± 0.1 | 0.6 ± 0.4 | 0.6 ± 0.4 | 2.1 ± 0.9 | 91.0 ± 5.8 | 86.1 ± 5.8 | 78.8 ± 6.9 |
| Silica removal% as Si | N/A | 22.2 ± 1.9 | 64.1 ± 16.1 | 92.4 ± 1.9 | 90.61 ± 5.7 | 90.61 ± 6.0 | 66.52 ± 14.5 | 91.0 ± 5.8 | 86.1 ± 5.8 | 78.8 ± 6.9 |
| Silica mg/L as $SiO_2$ | 13.1 ± 4.6 | 10.2 ± 0.3 | 4.7 ± 2.1 | 1.0 ± 0.3 | 1.3 ± 0.8 | 1.2 ± 0.8 | 4.4 ± 1.9 | 1.1 ± 0.7 | 1.9 ± 0.6 | 2.8 ± 0.9 |
| Silica removal% as $SiO_2$ | N/A[a] | 22.1 ± 2.0 | 63.9 ± 16 | 92.6 ± 2.2 | 90.5 ± 5.9 | 91.0 ± 6.3 | 66.8 ± 14.2 | 91.6 ± 5.4 | 85.9 ± 4.9 | 79.0 ± 7.0 |
| Boron mg/L as B | 2.1 ± 0.6 | N/A[a] | N/A[a] | N/A[a] | 0.5 ± 0.3 | 0.4 ± 0.3 | 1.4 ± 0.5 | 0.3 ± 0.2 | 1.0 ± 0.2 | 1.9 ± 0.3 |
| Boron removal% as B | N/A[a] | N/A[a] | N/A[a] | N/A[a] | 77.4 ± 12.2 | 79.0 ± 12.2 | 33.9 ± 21.8 | 83.9 ± 7.4 | 50.0 ± 10.1 | 15.3 ± 3.4 |
| Boron mg/L as $H_3BO_3$ | 11.9 ± 3.1 | N/A[a] | N/A[a] | N/A[a] | 2.7 ± 1.3 | 2.4 ± 1.5 | 7.6 ± 2.5 | 1.8 ± 1.0 | 5.7 ± 1.1 | 10.1 ± 0.6 |
| Boron removal% as $H_3BO_3$ | N/A[a] | N/A[a] | N/A[a] | N/A[a] | 77.1 ± 10.6 | 80.1 ± 12.7 | 35.9 ± 20.6 | 84.9 ± 8.0 | 52.4 ± 9.5 | 15.2 ± 4.7 |
| Sr mg/L | 7.5 ± 2.7 | N/A[a] | N/A[a] | N/A[a] | 5.7 ± 0.8 | 3.9 ± 0.3 | 2.1 ± 0.2 | 6.1 ± 0.4 | 3.8 ± 0.6 | 2.2 ± 0.9 |
| Sr removal% | N/A[a] | N/A[a] | N/A[a] | N/A[a] | 24.16 ± 10.5 | 48.4 ± 3.4 | 71.6 ± 2.6 | 19.2 ± 4.7 | 49.7 ± 7.5 | 70.7 ± 12.1 |

[a]N/A, Not applicable.

magnesium at a temperature of 10°C and pH = 10.5 were relatively high (71% and 84%, respectively), removal rates of calcium and magnesium for the BWRO brine at the same operating point were much lower (35.4% and 2.4%, respectively). This difference may be explained by the fact that the ratio of Mg:Ca in the seawater system is much higher than that for the BWRO brine system (4.85 versus 1.77 on a molar basis) and the saturation indices for the potential precipitating species are higher for the seawater system. Nevertheless, and as can be seen from Table 4 and Figure 2, the increase in removal percentages of calcium with the increase in temperature was evident and, given the inverse solubility of the precipitating calcium salts, not surprising. On the other hand, and similar to precipitation of magnesium in seawater, the dependence of magnesium removal on temperature is not as evident as that for calcium. This may arise as a result of the interactions between competing or co-precipitating salts and is a phenomenon that is not, at present, very well understood. Statistically significant differences in Ca and Mg removals between different operating temperatures were recorded ($p$-value < .05)

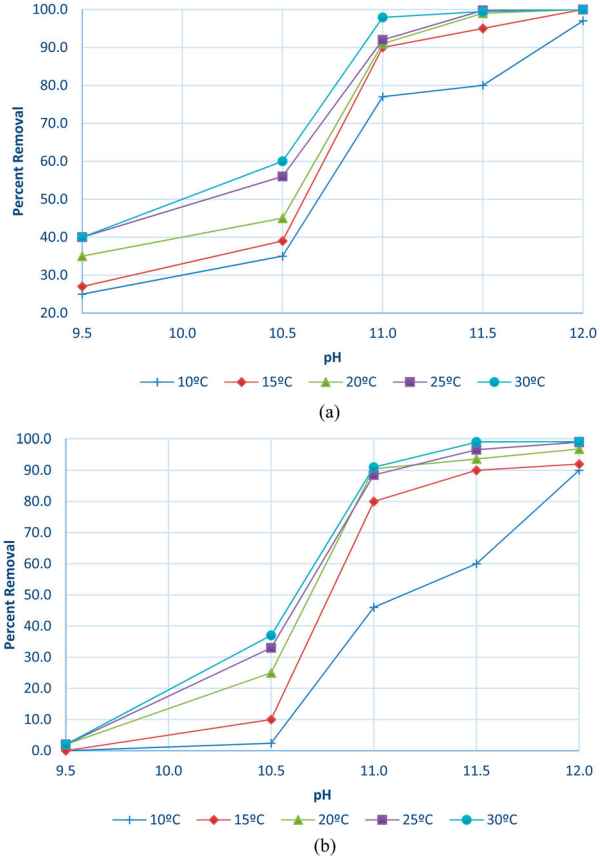


**Figure 2.** Removal of fouling species at various operating conditions (a) removal of calcium and (b) removal of magnesium.

For experiments conducted at 25°C, the percentage removal of silica increased with pH peaking at 91% removal at pH = 11 and dropping to 67% at pH = 11.5. A similar trend was observed for experiments conducted at 30°C. The trends for boron removal percentages were identical to those of silica where the percentage removals peaked at pH = 11.5. These observations are in line with a number of previously reported studies where, at pH > 10.0, boron and silica removal occur as a result of these compounds being adsorbed onto the surface of magnesium hydroxide, and becoming incorporated into the crystalline structure of magnesium hydroxide or by forming low solubility magnesium silicates [52–54]. The observations for the experimental results at pH ≤ 11.0 lend credence to the above postulates, however, fail to explain the experimental results at pH = 11.5, where highest percentage removal of magnesium occurs but the percentage removals of both boron and silica are lower than those observed at pH = 11.0. This reduction in the percentage removal of silica may arise as a result of repulsion forces and the formation of more soluble silicate and borate complexes. For experiments conducted at 10°C, the removal of silica followed the trend hypothesized in the literature, that is, percentage removal increased with the increase in pH reaching a very high 92.6% removal at pH = 11.5. According to the ANOVA test, no statistically significant differences were observed in $SiO_2$ removal efficiencies between the different pH values tested at $T = 25$°C, whereby the $p$-value was .868. However, the difference in $H_3BO_3$ removal between the experimental pH values was statistically significant ($p$-value = .0123).

## Saturation levels of the brine minerals

Table 5 summarizes the saturation levels, expressed as the log of the saturation index (logSI), for the minerals that may have precipitated from the brine at various pH values. It should be noted that a (logSI) value greater than 0.0 signifies a tendency for the salt to precipitate. The (logSI) values for the calcium carbonate minerals as shown in Table 5 indicate that these minerals will precipitate at all pH values, while strontium carbonate (strontianite) will precipitate at pH value greater than 8.5. Magnesium in the form magnesium carbonate (combined with calcium as Dolomite) will also precipitate at all pH values. The (logSI) of the sulfate compounds of calcium and strontium are negative throughout the pH range indicating that calcium and strontium minerals in the sulfates form will remain in solution. It is interesting to note that the (logSI) of $SiO_2$ is negative for all pH values, indicating that the silica is unlikely to precipitate in its pure form with the increase in pH.

**Table 5.** Log saturation indices (log SI) for minerals that may precipitate from BWRO brine.

| Mineral | Formula | Brine pH = 7.4 | Alkalized brine pH = 8.5 | Alkalized brine pH = 9.5 | Alkalized brine pH = 10.5 | Alkalized brine pH = 11.0 |
|---|---|---|---|---|---|---|
| Anhydrite | $CaSO_4$ | −1.74 | −1.74 | −1.74 | −1.74 | −1.74 |
| Aragonite | $CaCO_3$ | 0.13 | 0.17 | 0.87 | 1.25 | 1.3 |
| Calcite | $CaCO_3$ | 0.27 | 0.31 | 1.01 | 1.4 | 1.45 |
| Celestite | $SrSO_4$ | −1.43 | −1.43 | −1.43 | −1.43 | −1.43 |
| Dolomite | $CaMg(CO_3)_2$ | 0.95 | 0.98 | 2.38 | 3.14 | 3.24 |
| Gypsum | $CaSO_4{:}2H_2O$ | −1.54 | −1.52 | −1.52 | −1.52 | −1.6 |
| SiO2(a) | $SiO_2$ | −1.34 | −2.34 | −2.36 | −2.38 | −2.34 |
| Strontianite | $SrCO_3$ | −0.86 | −0.09 | 0.34 | 0.62 | 0.89 |

Note: (log SI) = (logIAP−log$K_{sp}$), where SI, IAP and $K_{sp}$ are the solubility index, ionic activity product and the solubility product of a particular salt in solution, respectively.

### *The impact of pH on the removal of calcium and magnesium ions*

Calcium carbonate precipitation has been reviewed by Morse et al. [55]. The mechanisms and rate of precipitation of calcium carbonate depend on a number of parameters such as temperature, saturation state, salinity, and concentration of other ions. Given the complexity of the brine solution, the synergistic, antagonistic, and competing effects of several co-precipitating salts, a discussion of the mechanisms involved and the order of the precipitation reaction rates (where they for calcium carbonate or magnesium hydroxide) will be limited to observations of the rates of precipitation.

The variation of the calcium and magnesium ion concentrations in the brine solution with time is shown in Figure 3. At the higher pH values (11.5 and 12), where the super-saturation values of calcium and magnesium ions are higher than the super-saturation values of these same ions at the lower pH values (8.5 and 9.5), higher removal percentages of calcium carbonate and magnesium hydroxide were observed. Additionally, the higher initial super-saturation levels lead to faster precipitation kinetics. However, at these elevated pH values the reduction in the calcium concentration occurred at a higher rate than that of magnesium where 93% of the calcium ions in solution were removed after 30 s compared to 75% for magnesium ion removal. This observation contrasts with the results of a previous study on seawater where similar removal percentages were achieved after 5 min and where magnesium exhibited the faster decline rate [43]. The precipitation rates recorded in this work are comparable to those reported by Rahardianto et al. [42] for a slightly less saline BWRO concentrate.

### *Advantages and limitations of the treatment process*

As a BWRO brine treatment option, the proposed chemical treatment scheme leads to the almost complete

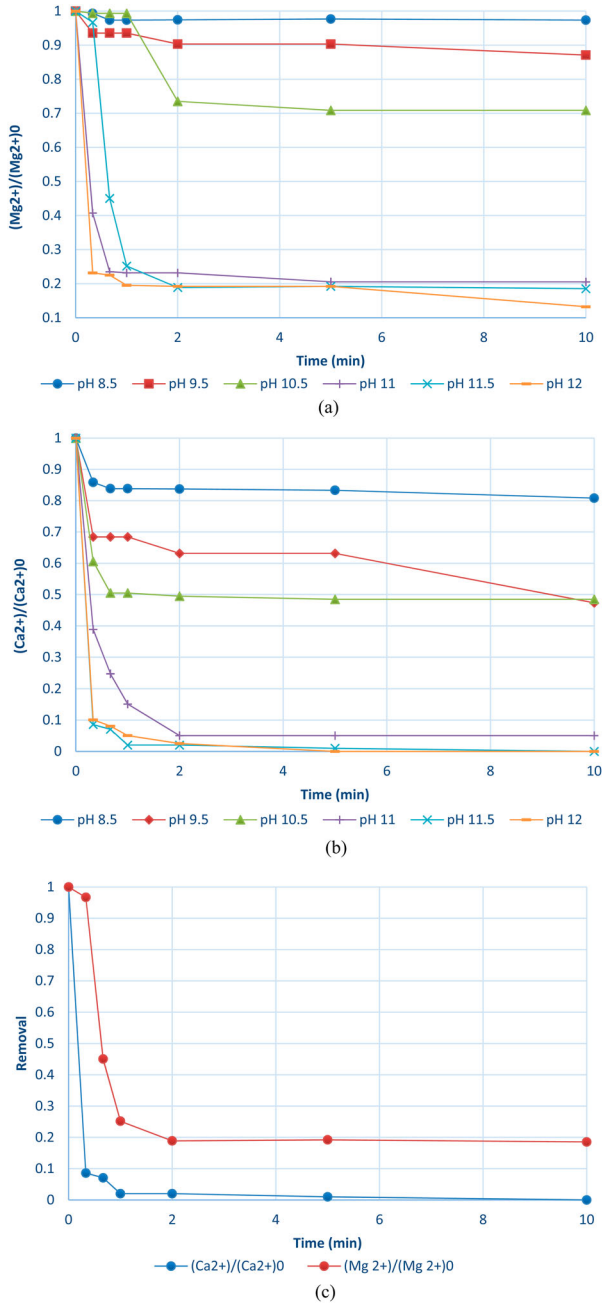


**Figure 3.** Precipitation kinetics for calcium and magnesium: (a) $Ca^{2+}$ at various pH values, (b) $Mg^{2+}$ at various pH values, and (c) $Ca^{2+}$ and $Mg^{2+}$ at pH11.5.

elimination and/or substantial reduction in the concentration of several contaminants and a number of potentially fouling species, conditions that will lead to an increase in the overall recovery of desalination systems, via the use of a high-recovery second-stage RO. This will lead to substantial reductions in the volume of the discharged brine. On the other hand, in the case of excessive chemical use, the process can incur further costs and render the sludge hard to manage. It would be interesting to further explore sludge considerations, since the presence of heavy metals like boron, iron, and others, can notably affect the quality of this end product [17,56]. Moreover, a cost–benefit analysis of this process as a BWRO brine treatment scheme is crucial in order to assess its effectiveness and feasibility as an alternative to other options.

## Conclusion

The purpose of this research was to evaluate the optimal conditions (alkalizing chemicals, dosages required, pH, and operating temperature) to be adopted for the removal of potential fouling species from BW RO concentrate using chemical addition. The key results of this work are summarized below:

- The use of a combination of 0.1 N-NaOH and 0.1 N-$Na_2CO_3$ in a 2:1 ratio at a pH = 11.5 and operating temperature of 25°C gave rise to the largest removal percentages for almost all of the potentially fouling species present in the BWRO concentrate. Silica was the only exception where the maximum removal percentage occurred at pH = 11.0
- At $T$ = 25°C, Ca, Mg, and Sr removals were the highest at pH = 11.5. As for silica and boron, their optimal removals were achieved at pH = 11, followed by pH = 11.5. pH showed a statistically significant effect on Ca, Mg, and Sr removal, but it did not significantly impact $SiO_2$ and $H_3BO_3$ removal.
- At $T$ = 10°C and for the pH range considered, Ca, Mg, and Sr removals percentages were unsatisfactory, compared to the removals achieved at higher temperatures.
- At $T$ = 30°C, Ca and Mg removals were at their absolute maximum levels at pH = 11.5. The highest silica removal was at pH = 10.5, while that of boron was recorded at pH = 11.5. The highest removal of Sr was accomplished at pH = 11.5, but it was slightly lower than that at 25°C.
- As well established results reconfirm Ca and Mg to have statistically significant trend of improvement of removal with temperature increase.
- Some inconsistencies were observed with regards to the expected variation of Si removal efficiency versus pH (in parallel to Mg removal) and temperature variation. Explanations for these observations are not possible at this stage; however, further experiments with a larger sample size are required to verify this phenomenon, to eliminate the possibility of experimental or instrumentation errors and to proffer a physico–chemical explanation.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

## References

[1] Elimelech M, Phillip WA. The future of seawater desalination: energy, technology, and the environment. Science. 2011;333:712–717.
[2] Valavala R, Sohn J-S, Han J-H, et al. Pretreatment in reverse osmosis seawater desalination: a short review. Environ Eng Res. 2011;16:205–212.
[3] Greenlee LF, Lawler DF, Freeman BD, et al. Reverse osmosis desalination: water sources, technology, and today's challenges. Water Res. 2009;43:2317–2348.
[4] Gabelich CJ, Xu P, Cohen Y. Chapter 10 concentrate treatment for inland desalting. In: Isabel CE, Andrea IS, editors. Sustainability science and engineering. Vol. 2. Amsterdam: Elsevier; 2010. p. 295–326.
[5] Ahmed M, Shayya WH, Hoey D, et al. Brine disposal from inland desalination plants. Water Int. 2002;27:194–201.
[6] Joo SH, Tansel B. Novel technologies for reverse osmosis concentrate treatment: a review. J Environ Manage. 2015;150:322–335.
[7] Khedr MG. Processing of desalination reject brine for optimization of process efficiency, cost effectiveness and environmental safety. In: Robert Y. Ning, editor. Advancing Desalination. Rijeka, Croatia: InTech. Chapter 6, p. 113–136.
[8] Malaeb L, Ayoub GM. Reverse osmosis technology for water treatment: state of the art review. Desalination. 2011;267:1–8.
[9] Pérez-González A, Urtiaga AM, Ibáñez R, et al. State of the art and review on the treatment technologies of water reverse osmosis concentrates. Water Res. 2012;46:267–283.
[10] Campbell RL, Jones AT. Appropriate disposal of effluent from coastal desalination facilities. Desalination. 2005;182:365–372.
[11] Sánchez AS, Nogueira IBR, Kalid RA. Uses of the reject brine from inland desalination for fish farming, spirulina cultivation, and irrigation of forage shrub and crops. Desalination. 2015;364:96–107.
[12] Mickley MC. Survey of high-recovery and zero liquid discharge technologies for water utilities. Alexandria (VA): Water Reuse Foundation; 2008.

[13] Sandia. Desalination and water purification roadmap – a report of the executive committee. Washington (DC): U.S. Department of the Interior, Bureau of Reclamation and Sandia National Laboratories; 2003.
[14] Subramani A, Cryer E, Liu L, et al. Impact of intermediate concentrate softening on feed water recovery of reverse osmosis process during treatment of mining contaminated groundwater. Sep Purif Technol. 2012;88:138–145.
[15] Mickley MC. Membrane concentrate disposal: practices and regulation. 2nd ed. Denver (CO): Department of the Interior, Bureau of Reclamation. Mickley Associates; 2006.
[16] Arnal JM, Sancho M, Iborra I, et al. Concentration of brines from RO desalination plants by natural evaporation. Desalination. 2005;182:435–439.
[17] Mohammadesmaeili F, Badr MK, Abbaszadegan M, et al. Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment. Water Environ Res. 2010;82:342–350.
[18] Ibáñez R, Pérez-González A, Gómez P, et al. Acid and base recovery from softened reverse osmosis (RO) brines. experimental assessment using model concentrates. Desalination. 2013;309:165–170.
[19] ESCWA. Role of desalination in addressing water scarcity (3rd ed.). United nations, economic and social commission for Western Asia; 2009.
[20] Ning RY, Tarquin A, Trzcinski M, et al. Recovery optimization of RO concentrate from desert wells. Desalination. 2006;201:315–322.
[21] van Houwelingen G, Bond R, Seacord T, et al. Experiences with pellet reactor softening as pretreatment for inland desalination in the USA. Desalin Water Treat. 2010;13:259–266.
[22] Comstock SE, Boyer TH, Graf KC. Treatment of nanofiltration and reverse osmosis concentrates: comparison of precipitative softening, coagulation, and anion exchange. Water Res. 2011;45:4855–4865.
[23] Al-Rawajfeh Aiman E, Araj K. Treatment of wastewater to meet the requirements for cooling water systems in Jordan's nuclear plants. Chem Process Eng. 2013;34:253–267.
[24] Gabelich CJ, Williams MD, Rahardianto A, et al. High-recovery reverse osmosis desalination using intermediate chemical demineralization. J Membrane Sci. 2007;301:131–141.
[25] Gabelich CJ, Rahardianto A, Northrup CR, et al. Process evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting. Desalination. 2011;272:36–45.
[26] Jiang C, Wang Y, Zhang Z, et al. Electrodialysis of concentrated brine from RO plant to produce coarse salt and freshwater. J Membrane Sci. 2014;450:323–330.
[27] Medina V, Johnson J, Waisner S, et al. Development of a treatment process for electrodialysis reversal concentrate with intermediate softening and secondary reverse osmosis to approach 98-percent water recovery. J Environ Eng. 2015;141:04015002.
[28] Turek M, Was J, Dydo P. Brackish water desalination in RO–single pass EDR system. Desalin Water Treat. 2009;7:263–266.
[29] Wang M, Wang K, Jia Y, et al. The reclamation of brine generated from desalination process by bipolar membrane electrodialysis. J Membrane Sci. 2014;452:54–61.
[30] Greenlee LF, Testa F, Lawler DF, et al. Effect of antiscalant degradation on salt precipitation and solid/liquid separation of RO concentrate. J Membrane Sci. 2011;366:48–61.
[31] McCool BC, Rahardianto A, Cohen Y. Antiscalant removal in accelerated desupersaturation of RO concentrate via chemically-enhanced seeded precipitation (CESP). Water Res. 2012;46:4261–4271.
[32] Subramani A, DeCarolis J, Pearce W, et al. Vibratory shear enhanced process (VSEP) for treating brackish water reverse osmosis concentrate with high silica content. Desalination. 2012;291:15–22.
[33] Wang X-X, Wu Y-H, Zhang T-Y, et al. Simultaneous nitrogen, phosphorous, and hardness removal from reverse osmosis concentrate by microalgae cultivation. Water Res. 2016;94:215–224.
[34] Martinetti CR, Childress AE, Cath TY. High recovery of concentrated RO brines using forward osmosis and membrane distillation. J Membrane Sci. 2009;331:31–39.
[35] Qu D, Wang J, Wang L, et al. Integration of accelerated precipitation softening with membrane distillation for high-recovery desalination of primary reverse osmosis concentrate. Sep Purif Technol. 2009;67:21–25.
[36] Almasri D, Mahmoud KA, Abdel-Wahab A. Two-stage sulfate removal from reject brine in inland desalination with zero-liquid discharge. Desalination. 2015;362:52–58.
[37] McCool BC, Rahardianto A, Faria JI, et al. Evaluation of chemically-enhanced seeded precipitation of RO concentrate for high recovery desalting of high salinity brackish water. Desalination. 2013;317:116–126.
[38] Sanciolo P, Ostarcevic E, Atherton P, et al. Enhancement of reverse osmosis water recovery using interstage calcium precipitation. Desalination. 2012;295:43–52.
[39] Omar WS. Experimental study of pretreatment of brackish reverse osmosis concentrate streams using seeded precipitative softening process for improvement of water recovery. Desalin Water Treat. 2016;57:13916–13923.
[40] Pervov AG. Precipitation of calcium carbonate in reverse osmosis retentate flow by means of seeded techniques – a tool to increase recovery. Desalination. 2015;368:140–151.
[41] Zhu A, Rahardianto A, Christofides PD, et al. Reverse osmosis desalination with high permeability membranes – cost optimization and research needs. Desalin Water Treat. 2010;15:256–266.
[42] Rahardianto A, Gao J, Gabelich CJ, et al. High recovery membrane desalting of low-salinity brackish water: integration of accelerated precipitation softening with membrane RO. J Membrane Sci. 2007;289:123–137.
[43] Ayoub GM, Zayyat RM, Al-Hindi M. Precipitation softening: a pretreatment process for seawater desalination. Environ Sci Pollut Res Int. 2014;21:2876–2887.
[44] Korban L. A treatment process for brackish water and brine desalination [Masters of Sciences, Civil and Environmental Engineering]. American University of Beirut; 2015.
[45] Ayoub GM, Merhebi F, Acra A, et al. Seawater bittern for the treatment of alkalized industrial effluents. Water Res. 2000;34:640–656.
[46] Ayoub G, Semerjian L, Acra A, et al. Heavy metal removal by coagulation with seawater liquid bittern. J Environ Eng. 2001;127:196–207.

[47] Ayoub GM, Koopman B. Algal separation by the lime-seawater process. Vol. 58. Washington (DC): ETATS-UNIS: Water Pollution Control Federation; 1986.
[48] Ayoub GM, Merehbi F, Abdallah R, et al. Coagulation of alkalinized municipal wastewater using seawater bittern. Water Environ Res. 1999;71:443–453.
[49] Ayoub GM, BinAhmed SW, Al-Hindi M, et al. Coagulation of highly turbid suspensions using magnesium hydroxide: effects of slow mixing conditions. Environ Sci Pollut Res Int. 2014;21:10502–10513.
[50] A. American Public Health, A. American Water Works, F. Water Pollution Control. Standard methods for the examination of water and wastewater. Standard methods for the examination of water and wastewater, 1905.
[51] Al-Rawajfeh AE, Al-Garalleh M, Al-Mazaideh G, et al. Understanding $CACO_3$-$Mg(OH)_2$ scale formation: a semi-empirical mindo-forces study of $CO_2$-$H_2O$ system. Chem Eng Commun. 2008;195:998–1010.
[52] Chao P-F, Westerhoff P. Assessment and optimization of chemical and physicochemical softening processes. J Am Water Works Ass. 2002;94:109–119.
[53] Sheikholeslami R, Al-Mutaz IS, Tan S, et al. Some aspects of silica polymerization and fouling and its pretreatment by sodium aluminate, lime and soda ash. Desalination. 2002;150:85–92.
[54] Parks J, Edwards M. Boron removal via formation of magnesium silicate solids during precipitative softening. J Environ Eng. 2007;133:149–156.
[55] Morse JW, Arvidson RS, Lüttge A. Calcium carbonate formation and dissolution. Chem Rev. 2007;107:342–381.
[56] Mohammadesmaeili F, Badr MK, Abbaszadegan M, et al. Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation. Water Res. 2010;44:6021–6030.