Dual pretreatment-concentration hybrid process of salty water feed and reject of desalination plants

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ABSTRACT

Among the frequent problem encountered in seawater desalination is scales formation. Scale may form because of the composition of the make-up, but mostly develops as a result of further change occurring during the desalination process from the hardness causing salts (i.e., Ca^{2+} and Mg^{2+} that deposit as scale). An ion exchange unit containing natural aluminum silicate or synthetic magnesium silicate materials is used as a pretreatment step, and utilized to split the feed water into two streams; the first is NaK-rich and the second is CaMg-rich in a so called "Auto-regeneration (AR) process". The NaK-rich stream is then pumped to a desalination unit either thermal unit (MED or MSF) or membrane unit (RO), while the CaMg-rich stream is either recycled or pumped to a nanofiltration (NF) unit to soften the Ca and Mg ions in the stream, and additionally to partially remove the bicarbonate and carbonate ions. This makes the NF step to serve also as a CO_2 deareation unit, which consequently decreases the release rates of carbon dioxide in the thermal unit. Additionally, these steps concentrate the salty water of two streams; that is, NaK-rich or CaMg-rich streams. The NaK-rich stream can be also used in a forward osmosis (FO) step for further water recovery and brine concentration. The pretreatment process is very cost-effective because it uses a control unit to send a signal to open the control valve for splitting the treated water to the target stream.

Keywords: Desalination; Scale prevention; Pretreatment; Softening; Splitting the feed; brine concentration, Brine mining

1. Introduction

Desalination is widely used to face the problem of water lack in many countries. Desalination is a process that removes salts and minerals from saline water in order to produce fresh water suitable for human consumption or irrigation [1]. Desalination has become a promising alternative and viable way to shrink the deficit in fresh water supply and has been adopted by 120 countries in the world [2]. Different techniques have been used to achieve desalination, the used techniques are classified into three process-based categories; distillation such as the multi-stage flash, adsorption based on chemical bonds such as ion exchange, and membranes processes such as reverse osmosis or electrodialysis [3]. All these methods differ in advantages, disadvantages, and their

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challenges. Ion exchange is a process by which high content dissolved inorganic salts such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} are exchanged with more innocuous ions such H^+ and OH^-. For membrane processes, there are two common membrane materials; the cellulose acetate membrane and thin film composite membrane based aromatic polyamide polymers [4]. Economically, ion exchange is more beneficial than reverse osmosis (RO) for producing pure water at low salinities. However, it is not appropriate for brackish or concentrated waters [5]. One of substances that used for ion-exchange is zeolite. Zeolites are microporous crystalline solids with well-defined structure, consisting of a three-dimensional network of SiO_4 and AlO_4 tetrahedral linked together by common oxygen atoms [6]. Commonly, the negative charge is compensated by additional non-framework cations like sodium (Na^+) [7,8].

The most frequent problem encountered in seawater desalination is scales formation [9]. Scaling is the deposition of sparingly soluble salts that are dissolved in water. The most common encountered scales are; calcium carbonate, calcium sulfate, silica, aluminum hydroxides, and aluminum oxides. The other less encountered scales include; calcium fluoride, barium sulfate, and strontium sulfate [10]. Scale formation is mainly caused by crystallization of alkaline scales, for example, $CaCO_3$ and $Mg(OH)_2$ and non-alkaline scale, for example, $CaSO_4$. The formation of $CaCO_3$ scale strongly depends on operating conditions and surface properties in desalination system. $CaCO_3$ scale formation and CO_2 release occur simultaneously from the thermal decomposition of bicarbonate ions [11]. A number of methods exist to control scale formation include: (i) acid addition to reduce the pH, (ii) increasing the solubility of scale-forming substances, (iii) removing calcium and magnesium hardness from water, and (iv) precipitating the scale-forming substances [12]. Calcium and magnesium can be removed by lime soda softening, ion exchange or membrane filtration (nanofiltration or reverse osmosis) [13]. Also, addition of anti-scalant substances is one of methods that used for solving desalination accompanied problems. Anti-scalants adsorb onto the nuclei of solids and inhibit the crystal growth process [14].

The problems associated with the use of water or brines can be attributed to one or more of impurities such as hardness causing salts (i.e., Ca^{2+} and Mg^{2+} that deposit as scale on heat transfer surfaces), silica, iron, microbiological species, oils and dissolved gases [15].

Softening is the removal of calcium, magnesium, and certain other metal cations in hard water (contains high levels of calcium and magnesium ions) [16]. Water can be made soft using what is called water softeners which consists of ion exchange resins. When water passes through the ion exchange resins, calcium and magnesium ions replace sodium ions that are loaded on the resin material due to the stronger attraction of hardness ions to the resin negative charges [17].

Automatic water softeners are usually programmed to recharge at specific times that will not disrupt the occupants. It is used to remove temporary hardness resultant of the existence of (Ca^{2+}) and (Mg^{2+}) ions by using the resins [18]. Based on Fig. 1, the alternative attachment of sodium ions on one hand and magnesium and calcium ions on the other hand for the sites of the zeolite was reported as sine-wave consisting of alternating steps of saturation-regeneration of the zeolite [19].

The advantages of this method are that softening of materials don't reach the breakthrough behavior of zeolite and ion-exchange materials. When the ion exchange material is used for a column process, the operation is often discontinued at breakthrough, that is, when the ion or substance that is targeted to be trapped by the column appears at the outlet. The value of breakthrough capacity of the column is always lower than that of an ion exchange capacity characterizing the material loaded in this column, where C_o is the initial concentration of the targeted ion, C is the targeted ion concentration in the effluent. The breakthrough capacity depends on the operating conditions and on the properties (including capacity) of the material [20].

Many studies were conducted on desalination and its problems. Some of problems that accompanied desalination based on reversed osmosis RO were elaborated by Liyanaarachchi et al. [21]. Examples on such problems; rust problem in the intake step, high concentration of Br^- in produced water, boron removal, and etc. Ceramic membranes made from zeolites (MFI-type silicalite membrane) were synthesized on a α-Al_2O_3 support by the direct in situ crystallization [22]. Desalination performance of the prepared silicalite membrane was carried out with a seawater solution (0.3wt.% TDS) over a long period of around 180 d at a constant pressure of 700 kPa at various temperatures. The prepared silicalite membrane achieved a high rejection (>93%) for all major seawater ions including Na^+. Permeation flux of the zeolite membrane is significantly increased with an increase in temperature. Ca^{2+} and Mg^{2+} ions were less responsive to temperature than smaller Na^+ and K^+ ions [22]. Due to high concentrations of calcium and silica in the contaminated groundwater, the feed water recovery of the RO process was restricted to less than 60% [23]. To enhance feed water recovery, a primary RO followed by intermediate concentrate treatment and a secondary RO process, was tested [23]. For intermediate concentrate treatment, electrocoagulation was compared to chemical softening. Chemical softening and electrocoagulation were both effective in reducing the concentration of calcium and silica by more than 90% in the primary RO concentrate [23].

Awerbuch [24] filed an improved desalination process including blending a first stream of softened water with a second stream of water containing a higher concentration of hardness ions to form a feed to a desalination system, wherein the source of the first and second streams were different. The feed was then passed through the desalination system to form a water product of potable quality. The improvement comprises the introduction of a feed of variable proportions of the softened and second stream of water to the desalination system to increase the top operating temperature of the system and increase recovery of potable water. SenGupta and Sarkar [25] used ion-exchange in prior to a nanofiltration step to exchange the monovalent ions such as sodium and chloride to polyvalent ions such as magnesium and sulphate. The resultant solution has lower osmotic pressure and requires less transmembrane pressure. Mathiesen [26] reported a patent
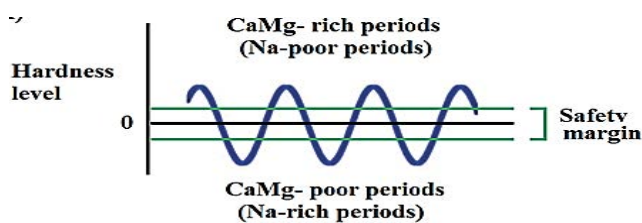
Fig. 1. Auto-regeneration (AR) process.

for the utilization of cation-exchange resins as continuous simulated moving bed potassium exchange calcium in a previously regenerated bed to bind with nitrate to form potassium nitrate. Howe and his [27] presented a system of ion-exchange to improve water recovery in desalination systems by the removal of cations and/or anions. The system was useful for water recovery in brackish ecosystems and included recycling, regeneration, and recovery of key components. Komer and Ikehata [28] provided a method of regenerating ion exchange medium. It included of an ion exchange medium involving at least one first multivalent cation, an effluent comprising at least one monovalent cation and optionally at least one multivalent cation where the ratio of the multi-to-monovalent was at least 200, and contacting the ion exchange medium for regeneration medium. A steam production facility comprising a filter and exchange resin to remove at least 80% of divalent cations in the feed water was presented.

The purpose of this study is to cost-effectively softening the feed water of desaliantion processes or any process that uses hard water or brines containing hardness species using a novel auto-regeneration step of natural zeolites, synthetic materials, and a synthesized organic ligand that is covalently bonded to silica sol–gel glass.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals and reagents

All seawater samples were bought form the Gulf of Aqaba at the south of Jordan. All reagents used in this study were analytical reagent-grade and were used without any further purification. Anhydrous salts, for example, NaCl, KCl, $CaCl_2$ and $MgCl_2$ (purity > 99%) were used for the preparation of all solutions. Disodium ethylenediaminetetraacetic acid (EDTA), NaOH, KCl, NaCl, ammonia solution, ammonium chloride, and HCl were purchased from Sigma–Aldrich (Germany). Murexide and Eriochrome Black T, were purchased from Alfa Aesar (Taiwan). All salts were dried at 120°C for suitable time before use. Stock solutions were prepared by using doubly distilled water which was previously deionized.

2.1.2. Physical and chemical analysis

Based on standard methods of analysis, all water samples were tested for physical and chemical parameters. The pH was measured using HI 254 pH/ORP meter (USA). A conductivity meter (pH/ION/Cond 750 (Germany)) was used to measure electrical conductivity (EC). Total dissolved solids (TDS) were calculated based on conductivity measurements. Total hardness (TH), calcium and magnesium ion concentrations were measured using the EDTA titrimetric method. Sodium and potassium ions were determined using flame emission photometric method (Jenway PFP7 Flame photometer (England)). The seawater sample was analyzed for sodium, potassium, calcium, magnesium, bromide, chloride, fluoride, sulfate, nitrate, and phosphate using an inductively coupled plasma [ICPE-9800 (ICP-AES) (Japan)]. Shimadzu FT-IR-8400 (Japan) and X-Ray powder diffraction [(XRD) Seifert 3003 TT (USA)] were used for the characterization of natural zeolite. Zeta potential analyzer [MICROTRAC Zetatrac NPA152-31A (USA)] was used for determination of particle size. All instruments were calibrated according to the manufacturer recommendations.

2.1.2.1. Determination of total hardness, $[Ca^{2+}]$ and $[Mg^{2+}]$

Total hardness was obtained by reported titrimetric method 2340 C [29]. An EDTA disodium salt was standardized against zinc sulfate. A 5.0 mL of water sample was titrated against the standardized 0.010 M EDTA-disodium salt solution until reaching the Eriochrome Black-T (E.B.T) end point where color changed from red to blue. Buffer solution of pH = 10 (NH_3/NH_4Cl) was used to adjust the pH of the solution. The same procedure was used for the determination of calcium ion concentration but the end point was recorded to murexide indicator endpoint in which color changed from red to violet. Concentration of calcium and magnesium ions in addition to TH were then calculated.

2.1.2.2. Determination of sodium ions concentration

A 1,000 ppm sodium ion reference solution from Jenway was used to prepare diluted standard solutions with different concentrations of sodium ion. Standard solutions with different concentrations ranging from 20 to 200 ppm were prepared and used for the calibration curve construction. Jenway PFP7 Flame photometer was used to measure the emission intensity of all standard solutions and water samples. The constructed calibration curve was then used to determine the concentration of Na+ ion in each sample. Excel Microsoft program was utilized to do the calculations.

2.1.2.3. Determination of potassium ions concentration

A 1,000 ppm potassium ion reference solution from Jenway was used to prepare standard solutions with different concentrations of potassium ions. The prepared standard solutions were then used for the purpose of calibration curve construction. Jenway PFP7 Flame Photometer was used to measure the emission intensity of all standard solutions and water samples. The constructed calibration curve was then used to determine the concentration of K+ ions in water samples. Excel Microsoft program was utilized to do the calculations.

2.2. Ion exchange with natural zeolite and conditions optimization

A 10.0 g of natural zeolite was packed in a glass column (Type A: 100–300 mg load mass, 1.8 cm diameter, 32.5 cm

length. Type B: 2.5 cm diameter, 10 cm length for ultrasonic uses). A solution of sodium ions with 1,000 ppm concentration was passed through the natural zeolite column employing 4–5 mL/min flow rate at pH 7. About 10 mL sample was collected at the column outlet every 2 min. All collected samples were subjected to chemical analysis for sodium concentration using a flame photometer, until the column was fully saturated with sodium ions.

A 100 ppm of Ca^{2+} (0.28 g of $CaCl_2$ in 1L DDW) solution was passed through the sodium- natural zeolite loaded column at the same conditions of flow rate and pH values. The same procedure was repeated with 100 ppm of Mg^{2+} (0.39 g of $MgCl_2$ in 1 L DDW) solution.

All collected samples were subjected to chemical analysis for concentration of Mg^{2+} and Ca^{2+} ions. The same procedure was repeated with a new natural zeolite sample using different flow rates (3–4, 4–5, and 5–6 mL/min) and different pH values (5 and 9) in order to optimize the best conditions for ion exchange. The efficiency (capacity factor) for the ion exchange process for zeolite resin was calculated using the following equation:

$$R_{rem} = \frac{C_o - C_e}{C_o} \times 100$$

where R_{rem}: is the removal efficiency; C_o is the initial ions concentration in ppm, C_e is the concentration of ions at equilibrium (ppm).

The same procedure was repeated employing a pH of 5 and a flow rate of 3–4 mL/min. Two different experiments were conducted, in the first experiment a solution of 1,000 ppm Na^+ was employed through Mg^{2+} natural zeolite loaded column and in the second one a solution of 1,000 ppm Na^+ was employed through Ca^{2+} natural zeolite loaded column.

2.3. Experimental setup

Our experimental results showed an alternate ion exchange process between sodium ions in one hand and Mg^{2+}, Ca^{2+} on the other hand. In other words, when the Na^+ reached maximum attachment to the resin while the Ca/Mg was at the minimum. Immediately after that the process was inverted and Ca/Mg ratio reaches a maximum and Na ion concentration reaches a minimum, the results obtained were similar to a wave sign.

The same elution process was repeated under the effect of ultrasound waves as shown in Fig. 2.

The experiments were conducted using a certain amount of the material (natural zeolite or synthetic glass resin) in "a flow system" containing 10 g of the material in a glass column. A seawater sample of 5,000 mL feeding tank was passed through the system with and without ultrasound waves. Samples were collected from the column outlet at constant time interval. The samples were then filtered and kept in polyethylene bottles for chemical analysis.

2.4. Nanofiltration

Ca-Mg-rich streams were then passed through a nanofilter (Hydranautics NITTO DENKO ESNA1-LF2

Fig. 2. Treatment study under effect of ultrasonic waves.

nanofiltration) in order to reduce the amount of Mg^{2+} and Ca^{2+} ions (divalent ions).

3. Results and discussion

3.1. Characterization of seawater

Table 1 shows the concentration of common ions in seawater sample from Gulf of Aqaba analyzed by ICP-9800. As a result, seawater contains about 440, 1,650 and 13,100 ppm of Ca^{2+}, Mg^{2+} and Na^+ ions, respectively. Over 70 elements are present in natural seawater. However, only six ions make up over 99% by weight of all the dissolved solids in seawater. Sodium and chloride ions are not only account for seawater salty taste, but also make up slightly more than 87% of all the dissolved solids in seawater. Sodium accounts for about 33% and chloride accounts for about 54% by weight of all dissolved solids in seawater. The other four ions include calcium, magnesium, potassium and sulfate which are divalent ions. Potassium is a monovalent ion accounting for only 1.0% by weight of seawater and the TDS of the seawater sample that used in this study equal 39,348 ppm.

3.2. Characterization of ion exchange materials

3.2.1. Natural aluminum silicate materials

Zeolites are one of the inorganic ion exchange materials. Ion exchange properties are defined by cavity-containing or layered structures with exchangeable cations located on the internal surfaces of these voids, Fig. 3 shows the zeolite chemical structure. The use of zeolite minerals to remove hardness ions (namely calcium and magnesium) from water is well known in the historical sense; zeolites were replaced long ago with synthetic organic, ion-exchange resins [30].

Infrared spectroscopy was used to investigate the structural properties of natural zeolite. Fig. 4 shows the Fourier-transform infrared spectrum of natural Jordanian Al-silicate (obtained from the south of Jordan). In general, a broad band between 3,000 and 3,700 cm^{-1} was assigned to the fundamental stretching vibrations of O–H hydroxyl groups.

Table 1
Chemical analysis of seawater of the Gulf of Aqaba

Species	Initial concentration (ppm)
Na^+	13,100
K^+	376
Mg^{2+}	1,650
Ca^{2+}	440
F^-	79
Cl^-	21,150
Br^-	52

Another peak related to O–H hydroxyl groups was found at 1,640 cm^{-1}. In details, the spectrum indicates that the peak at 3,600 cm^{-1} was characteristic to Al–OH stretching. The broad peak near 3,334 cm^{-1} was attributable to H-bonding of coordinated water and a weak peak at 1,641 cm^{-1} may be ascribed to the hydroxyl bending of zeolitic water. The strong peak at 1,200 with shoulder at 1,100 cm^{-1} was ascribed to Si–O stretching vibrations. The peak at 660 cm^{-1} was due to Si–O bending vibrations, while the Mg–O vibrations occur at lower wave numbers [31].

To further characterize the zeolite resin material, X-ray powder diffraction (XRD) was used as a powerful tool for characterization. The basic experiment is relatively easy to perform and can be done in most labs on standard diffractometers; and the data obtained was easy to analyze for many applications. Perturbations in the framework structure, crystal morphology, extra framework material, phase purity, crystallite size, and the setting and occupation of cation sites can produce differences in the X-ray diffraction patterns. Amorphous and less stable components can be removed from zeolite samples by NaOH treatment [32]. Fig. 5 shows the X-ray diffraction of a natural zeolite sample from the south of Jordan.

The three basic things to look for in a diffraction pattern are peak positions, peak intensities and peak shapes. The peak positions of a crystalline material are determined solely by the size and shape of the unit cell. Since all zeolite framework types have unique unit cells, the peak positions will be a fingerprint for each zeolite type. Peak intensities are determined by the positions and types of atoms in the unit cell. So, variations in intensities give information about the chemical composition and siting of atoms in the unit cells. Peak shapes and widths give an idea of the quality of the crystallites. In general, small crystallite size and high crystallite strain lead to peak broadening. For hydrated Na-exchanged faujasite zeolites the unit cell size, *a*, increases from about 24.6° to 25.1° as the number of Al atoms in the unit cell increases from about 48 to 96. The broad peak at 18°, 21°, 23° and 36° give the highest peak intensity of faujasite type zeolite [33].

3.3. Optimization conditions and ion exchange of natural zeolite

A 10.0 g of natural zeolite was packed in a glass column and rinsed with a concentrated brine of sodium chloride (1,000 ppm). The sodium-saturated zeolite was then eluted with a solution containing 100 ppm Mg^{2+} and
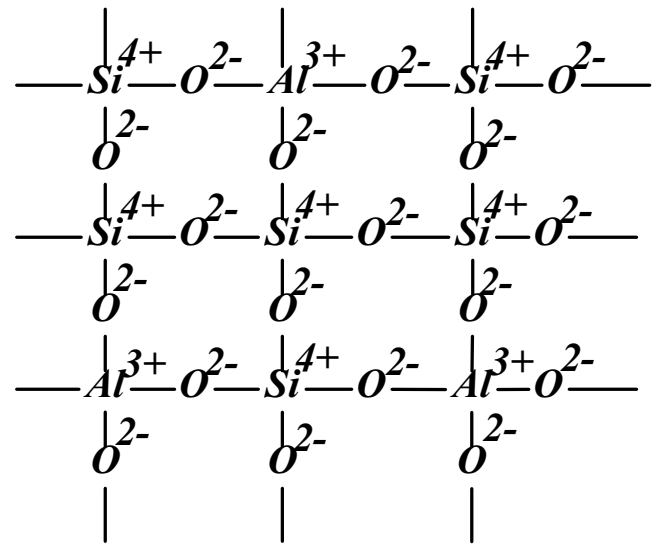

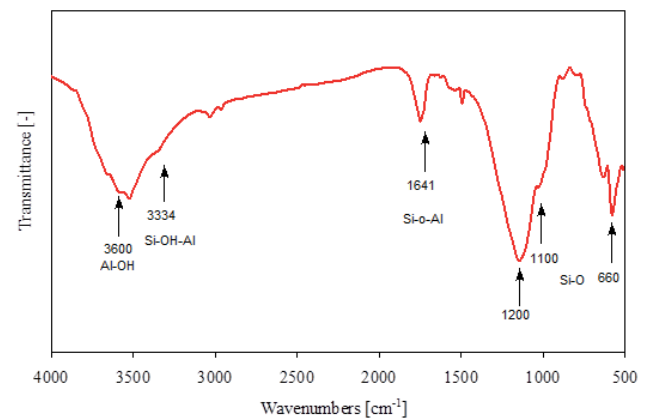Fig. 3. Structure of zeolite.

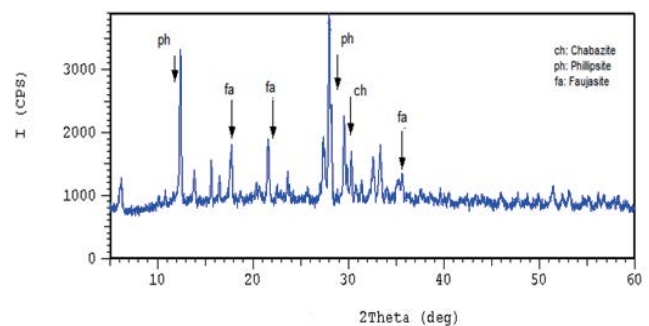Fig. 4. Fourier-transform infrared spectra of the natural zeolite.

Fig. 5. X-ray diffraction of a natural zeolite sample from the south of Jordan.

100 ppm Ca^{2+}. This experiment was carried out four times with different flow rates and at pH 7 in order to obtain the best flow rate for the exchange process. A sample of the eluate was collected in a polyethylene bottle every 10 mL eluted. All collected samples were analyzed for

sodium, calcium, and magnesium ions. Fig. 6 shows that 4–5 mL/min. was the best flow rate for the exchange process which is related to the allowable contact time between the exchangeable ions, in addition to the suitable mobility of the brine to be treated through zeolite multiple paths.

The same experiment was then repeated three times with a new sample of natural zeolite (saturated with sodium) using different pH's while the flow rate was kept constant at 4–5 mL/min. Fig. 7 shows the obtained results of calcium behavior eluted through the zeolite column at different pHs.

Based on Fig. 7, pH 5 was selected as the best pH for the softening process. In addition to the monovalent sodium ions which was basically responsible on the exchange process with both calcium and magnesium ions, the high concentration of H^+ further enhances the removal process of Ca^{2+} ions.

After passing 1,000 mL of 100 ppm Ca^{2+} solution through 10 g of natural zeolite resulted in a percentage uptake of 69.5% at pH 5, while 52.4% and 10% were obtained at pH 7 and 9, respectively. The removal efficiency was calculated as follow:

At pH 5:

$$\frac{100-30.5}{100} \times 100\% = 69.5\%$$

At pH 7:

$$\frac{100-47.6}{100} \times 100\% = 52.4\%$$

At pH 9:

$$\frac{100-90}{100} \times 100\% = 10.0\%$$

The behavior of sodium ion during the exchange process at pH 5 and flow rate of 4–5 mL/min is shown in Fig. 8 which is compatible with the results in Fig. 7.

Similarly, 100 ppm solution of magnesium chloride was passed through a freshly prepared sodium-saturated zeolite column. Fig. 9 shows similar behavior to calcium ion at pH 5.
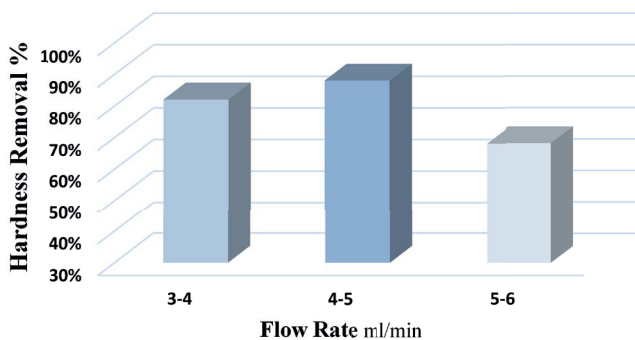
It was noticed that the exchange between Ca^{2+} and Na^+ on zeolite surface was better than the exchange between Mg^{2+} and Na^+.

The same calculations of removal efficiency (% uptake) were performed for Mg^{2+} ion and the results were 62.10% at pH 5, while 43.12% and 7.00% were obtained at pH 7 and 9, respectively.

The behavior of sodium ion during the exchange process with Mg^{2+} ions at pH 5 and a flow rate of 4–5 mL/min is displayed in Fig. 10.

Finally, the loaded calcium and magnesium natural zeolite column was rinsed with a solution of 1,000 ppm NaCl and the concentrations result of Ca^{2+}, Mg^{2+} and Na^+ ions are shown in Figs. 11 and 12.

3.4. Softening by ion-exchange and auto-regeneration

To prepare zeolite minerals for water softening, they first of all must be rinsed with a concentrated brine of sodium chloride. This high concentration of sodium ions would cause the removal of any ions bonded within the crystal lattice and replace them.

The water to be softened would then be flowed through a bed of the zeolite-sodium mineral. The sodium ions held in the zeolite crystal lattice are replaced by the hardness ions (Mg^{2+} and Ca^{2+}). The replaced sodium ions flow out with the new softened water and the hardness ions
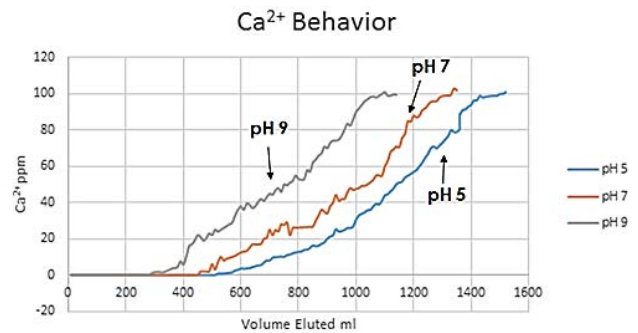

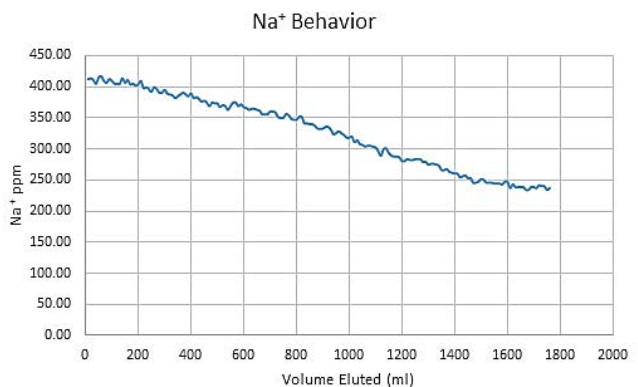Fig. 7. The behavior of calcium ion during the exchange process at three pH; 5, 7 and 9.

Fig. 8. The behavior of sodium ion during the exchange process with Ca^{2+} ions at pH 5.

Fig. 6. The percentage of hardness removal vs. flow rate of elution.

would preferentially be held by the zeolite. Fig. 13 shows the auto-regeneration curve of treated feed seawater from the Gulf of Aqaba on a 10g of ion-exchange material (natural zeolite). Such pretreatment process can be used for all processes that needs softening, such as, but not limited to, cooling water system in power plants, NaOH–Cl_2–H_2 production from salty water, and produced water in oil industry, and others [34].

The curve shows continuous sine-wave alternating steps of high Ca-Mg wave (saturation) that is accompanied by a low Na^+ wave followed by a low Ca-Mg wave (high Na^+ wave) of regeneration of the ion-exchange material.

3.4.1. Effect of ultrasound waves on auto regeneration process

Fig. 14 shows the influence of ultrasonic (US) waves (35 kHz) on the removal of mono and divalent ions. The ion exchange ratio of sodic to calcic ions (Na+K)/(Ca+Mg) was higher without US and lower with US. This means that US enhances the removal of monovalent ions; which may be attributed to the ability of US in forcing the ions to penetrate inside the pores of zeolite and enhance the ion exchanging process.

In the case of the synthetic glass resin, the (US) waves increased the capacity of the ligand toward Ca^{2+} and Mg^{2+} ions by 28.0% and the life of auto-regeneration cycle had increased to about 200 mL of treated brine before the breakthrough occurred.

3.4.2. Effect of nanofiltration on auto-regeneration process

To exploit the output of the auto-generation process, the produced CaMg-rich stream can be recycled or treated by nanofiltration, while the sodium rich segment can be treated by desalination. Fig. 15 shows the concentrations at which the product water requires desalination (cycle A) and recycling or NF (cycle B).

3.4. Forward osmosis unit: approach for efficient recovery and ZLD

In this part of the study, the CaMg-rich stream was passed through a nanofilter in order to remove the multivalent ions including Ca^{2+} and Mg^{2+} from the stream, while the high Na^+ stream was pumped to a desalination unit, either thermal; multiple-effect distillation (MED) or multistage flash (MSF) distillation, or membrane; reverse osmosis (RO) or forward osmosis (FO).

The high Na^+ stream was about 50.0% of the feed which reduces the NF-treated stream to lower percentages; hence reduces the cost of NF step. Our results indicated that the nanofilter rejected about 62.0% of Ca^{2+} and 65.0% Mg^{2+} ions. The Ca-Mg concentrated segment could either be recycled or sent directly to the nanofilter as shown in Fig. 16.
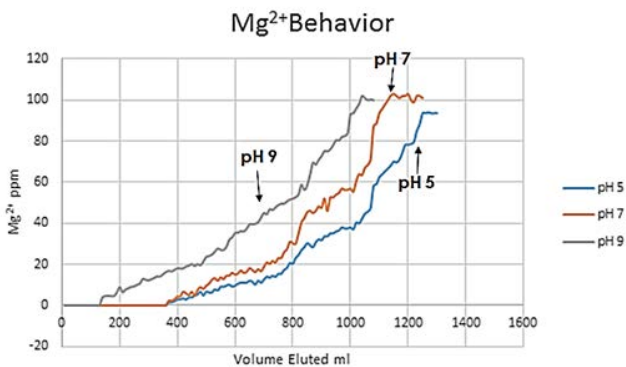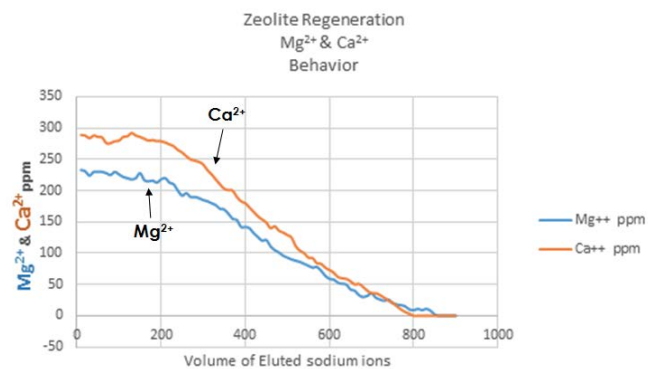

Fig. 9. The behavior of magnesium ion during the exchange process at three pH; 5, 7 and 9.

Fig. 10. The behavior of sodium ion during the exchange process with Mg^{2+} ions at pH 5.

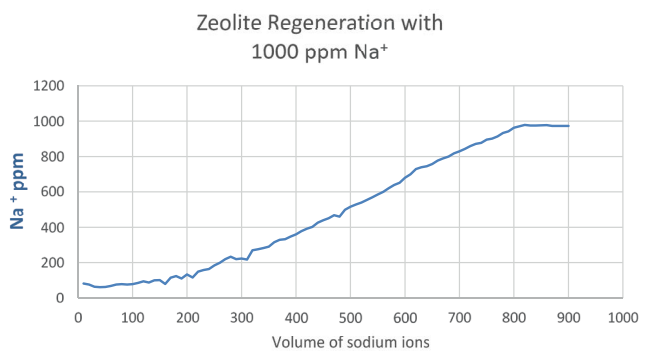Fig. 11. The behavior of Mg^{2+} and Ca^{2+} during the regeneration with 1,000 ppm sodium solution.

Fig. 12. The behavior of Na^+ during the regeneration with 1,000 ppm sodium solution. From Figs. 9–12, it was noticed that there was a repeatable the cycle of ion exchange between sodium and the hardness ions.
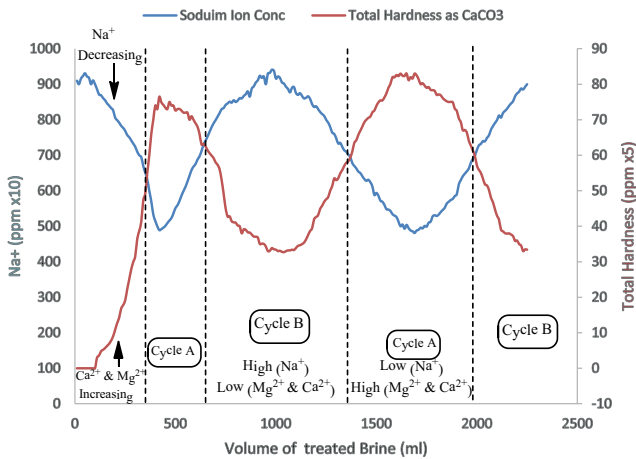
Fig. 13. The auto-regeneration curve of treated feed seawater from Gulf of Aqaba on natural zeolite.
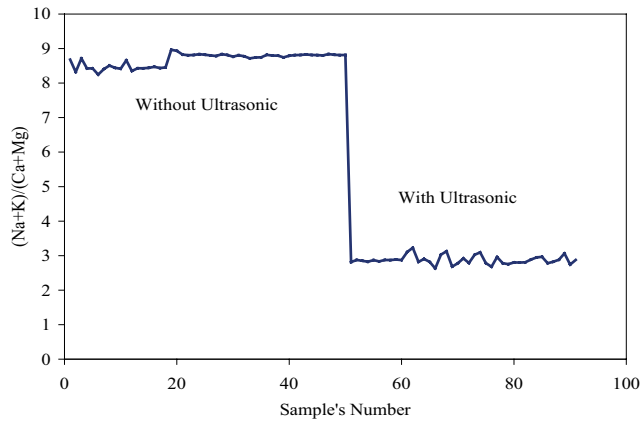

Fig. 14. The influence of ultrasonic (US) waves (35 kHz) on the removal of mono and divalent ions using natural zeolite.
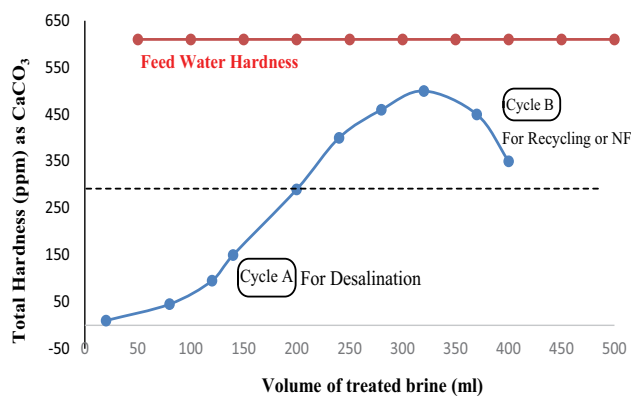

Fig. 15. The auto-regeneration curve of different samples of seawater from the Gulf of Aqaba on natural zeolite.

The recycling of CaMg-rich stream gave results shown in Fig. 17. It shows the decrease in total hardness ions concentrations that reached zero from the first loop and the concentrations reached 25.0% after 3 loops (i.e., 75.0% removal).
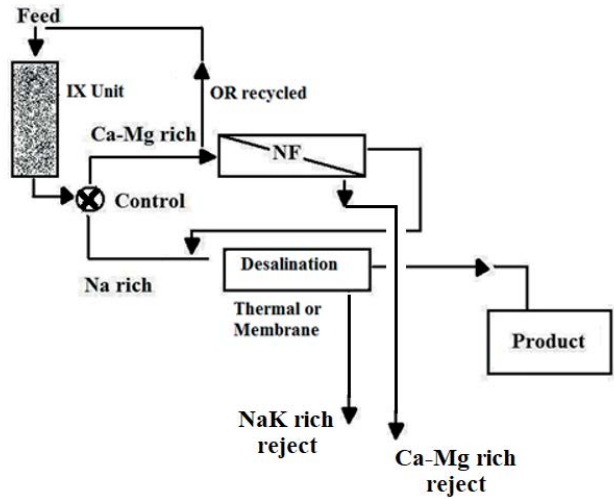

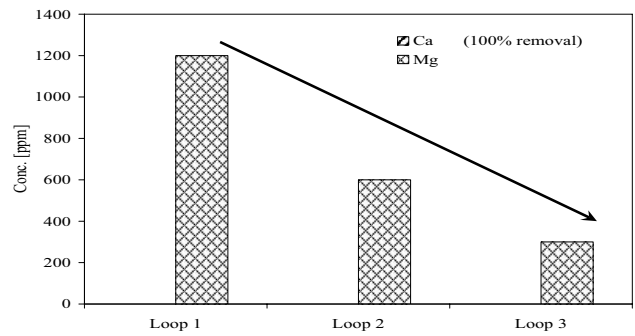Fig. 16. Hybrid ion-exchange-nanofiltration pretreatment of desalination feed.

Fig. 17. The concentration decreases to reach zero and 25.0% after 3 loops of Ca^{2+} and Mg^{2+}, respectively.

The results obtained in this part of the study could be beneficial in using a complete unit such as that show in Fig. 16, in which a sensor can be used to split water based on the amount of hardness. This sensor could be an ion selective electrodes of calcium, magnesium, and sodium ions.

The NaK-rich stream can be also used as a draw solution in a forward osmosis (FO) step for further water recovery and brine concentration for zero-liquid discharge (ZLD) and Ca-Mg recovery (Fig. 18).

3.5. Splitting control unit

A control unit (Fig. 19) can be used to send a signal for the pumps and to open the control valve for splitting the treated water to the target stream. Smart water ions monitoring system can be used for this purpose.

The control valve is normally used for proportional control on flow splitting applications. The valve has two outlets and a common inlet branch. It is used for proportional flow splitting, diverting a portion of the process medium from one part of the system to another. A typical application is on the upstream side of heat exchangers, to control the temperature of the process fluid. The valve action is – pull stem to open upper port, close lower port.
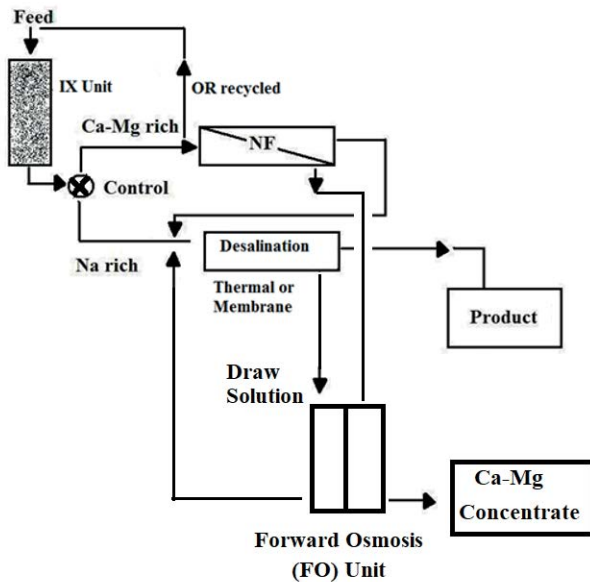
Fig. 18. Forward osmosis (FO) can be used to concentrate the nanofiltration (NF) reject.
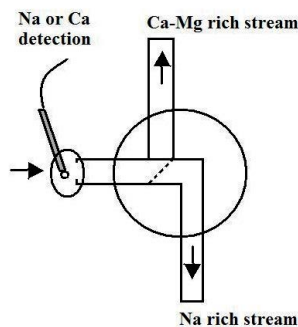

Fig. 19. The controller for splitting the product of the ion-exchange step.

Fig. 20 shows a simple control system for separating the flow of the water depending on the concentration of Na, Ca or Mg. The water flow over the concentration sensor (CS) which gives a continues signal indicating the concentration for Na, Ca or Mg for the on/off control unit. The control unit compares the incoming signal with an adjustable set point. If the value is below the set point, no signal is sent to the three-way control valve (3WV) which stays open and water flows normally from exit 1. If the signal is equal or above the set point, a signal is sent to the three-way control valve (3WV) to close and water will flow through exit 2. Fig. 21 shows a sample run of the control depending on the results showed in Fig. 20. The following is a simplified algorithm used for the control unit and a sample run.

Loop for ever
Get sensor reading
If sensor reading below set point
Set control valve flow to output on
Else if sensor reading above or equal to set point
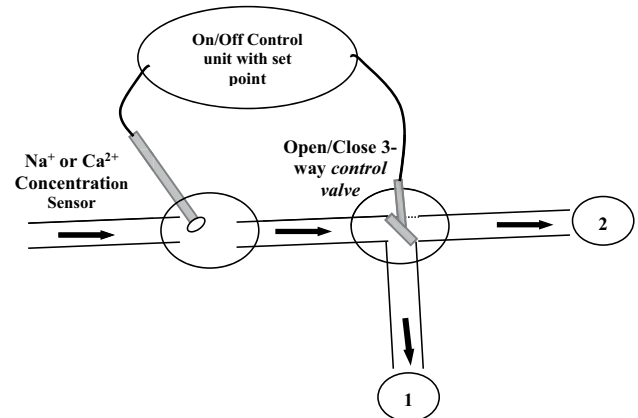*Set control valve flow to output two.*

Fig. 20. The control details.

Fig. 21. Sample run of the control unit.

4. Conclusion

In the sight of this lab-scale study, the following remarks could be concluded:

- An ion exchange unit containing natural aluminum silicate or synthetic glass resin were used as a pretreatment step, and utilized to split the feed water into two streams; the first was Na-rich and the second was CaMg-rich.
- This step was referred to as called "Auto-regeneration (AR) process" because it had been found to be continuous sine-wave alternating steps of saturation-regeneration of the ion-exchange material. The Na-rich stream was pumped to a desalination unit either thermal unit (MED or MSF) or membrane unit (RO), while the CaMg-rich stream was pumped to a nanofiltration (NF) unit to soften the Ca^{2+} and Mg^{2+} ions in the stream and get rid of the bicarbonate and carbonate ions to serve also as a CO_2 deareation unit, to decrease the release rates of carbon dioxide in the thermal unit.
- The "Auto-regeneration" pretreatment process by composite materials is very cost-effective because the regeneration of the softening materials was performed without the need of using costly chemicals which add more Na^+ ions and hence needs extra-effort for removal (i.e., high pressure in RO) in the next desalination steps.
- A pH of 5 and flow rate of 4–5 mL/min were found as the most efficient parameters in the optimization process for natural.

- "Auto-regeneration process" can be achieved by either looping the feed certain times or staging the feed.
- A control unit is used to send a signal for the pumps to open the control valve for splitting the treated water to the target stream. Smart water ions monitoring system can be used in this study.
- Ultrasound increases the efficiency of the process significantly.
- Pilot plant and full cost analysis should be performed once the required fund is secured.

Acknowledgement

Dedication

Dedicated to the soul of my M.Sc. Professor: Prof. Dr. Hassan Al-Salah.

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