Removal of Ca(II) and Mg(II) hardness by ion exchange resins and soda ash for seawater pretreatment to reduce scale formation in evaporators multi-stage flash desalination

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ABSTRACT

Softening pretreatment by removal of calcium and magnesium from seawater using cation exchange resins and soda ash was examined with the long term aim of reducing scale formation in multi-stage flash plants. Infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy analyses were employed to characterize the resins before and after pretreatment to demonstrate the presence of Mg^{2+} and Ca^{2+} on the resin surface. The changes in the composition and properties of seawater were also assessed. The results of this study revealed that the pretreatment achieved by a mixture of ion exchange and soda ash was successfully removed of 75% total hardness and reducing the concentration of Ca^{2+} and Mg^{2+} to 5 and 200 mg L^{-1}, respectively.

Keywords: Seawater; Hardness; Scale; Evaporator; Ion exchange resin

1. Introduction

Many countries in the world suffer from a shortage of freshwater due in part to a rapid rise in population as well as climatic factors [1–3]. One solution to the water scarcity problem is desalination [1–4]. Desalination processes are divided into two main categories, thermal and membrane, several limitations remain in the use of a membrane for the seawater treatment such as membrane fouling bay biological growth, colloids, organic and inorganic compounds which deteriorate the membrane and allow the passage of salt through the membrane and the pressure drop across the membrane [5–8], where the multi-stage flash (MSF) is the most used in thermal process [4]. The MSF process

which produces 60% of the desalinated water in the world consists of evaporators and brine heaters [9–11]. MSF plants operate at a top brine temperature of 120°C which increases efficiency but also increases the potential for scale formation; a major problem. Alkaline scale results from the interaction between the decomposition and hydrolysis products of the bicarbonate ions of seawater with calcium and magnesium ions generating carbonate calcium ($CaCO_3$) and hydroxide magnesium ($Mg(OH)_2$), respectively [12]. The appearance of sulfate scales in distillers using the MSF process is also a major problem. Non-alkaline sulfate minerals are composed principally of calcium sulfate, resulting from crystallization of anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$), or gypsum ($CaSO_4 \cdot H_2O$)

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[13,14]. While it is difficult to remove sulfate scales, it may be prevented running the plant at lower temperatures and reducing the concentration of components such as $CaSO_4$ to below saturation [15–17].

Plants cannot operate without using the antiscalant, which has a negative impact on heat transfer surfaces and reduces plant performance by lowering the yield and quality of potable water [15,18]. Seawater composition and operating temperature are amongst the factors leading to precipitation of salts and thus resulting in scaling and reduced efficiency. Scale control in MSF desalination units is thus essential and may be accomplished by the addition of acid to reduce the susceptibility to alkaline scale and the addition of antiscalant to mitigate alkaline and non-alkaline scaling. The top brine temperature should also be maintained below 120°C in MSF evaporators [19,20].

Precipitation softening through the use of a variety of chemicals, such as lime, sodium bicarbonate, sodium carbonate, and sodium hydroxide, whether individually or in combination, has been utilized for the removal of calcium and magnesium ions from seawater and brine water [21]. Elimination of calcium and magnesium increases the performance ratios in the thermal process by reducing energy consumption and decreasing the need for antiscalants. This allows the desalination plant to operate at a higher temperature and thus greater efficiency [20–22].

Many studies have analyzed non-alkaline scale developments in seawater distillers. The formation of sulfate scales begins, in multi-stage flash distillers, when the top brine temperature exceeds 130°C. Sulfate scale potential decreases with increasing salt precipitation and with nano-filtration pretreatment of the feed water. The Skillman index can be employed for the estimation of the probability of calcium sulfate scaling [19]. Furthermore, Al-Rawajfeh et al. [20] presented a model for the development of scale formation in once-through and brine recycles multi-stage flash (MSF) evaporators. They indicated that the fouling factor increases with a rise in the temperature along the tube from the first stage to the final stage. In addition, Andritsos and Karabelas [23] observed the augmentation of the $CaSO_4$ deposition rate, on a heated metal surface, covered by a film in the presence of particles. There was a co-precipitation of $CaSO_4$ and $CaCO_3$. However, while much has been learned there is still a need to gain a better understanding of how to minimize scale formation in evaporators.

In the current study, ion exchange resins and soda ash were used to remove a maximum amount of calcium and magnesium from seawater. Thus, softening pretreatment of seawater to avoid the scale formation in (MSF) evaporators. The composition and properties of seawater, including pH, conductivity, total hardness, calcium (Ca^{2+}), and magnesium (Mg^{2+}) concentration were measured before and after pretreatment to determine the optimal parameters for the ion exchange process.

2. Materials and methods

2.1. Materials

Soda ash (Na_2CO_3) from Sigma-Aldrich Co., (USA), sodium hydroxide (NaOH) from Biochem Chemopharma

Co., (France), and hydrochloric acid (HCl) from Sigma-Aldrich Co., (USA) used for pH adjustment. Cationic resin Lewatit® S100 was obtained from Bayer CEDEX (South Africa) used to remove Ca^{2+} and Mg^{2+} from seawater.

The seawater used in this study was from the KAHRAMAA desalination plant with a capacity of 29,629 m^3 d^{-1} of distillate water and located on the Mediterranean Sea in Algeria. Seawater samples were collected from the beach. The pH, total hardness, and calcium Ca^{2+}, and magnesium Mg^{2+} ion concentrations were monitored. The seawater composition and properties are described in Table 1.

2.2. Resin characterization

Cationic resin Lewatit® S100 was evaluated by various analyses. Infrared spectroscopy analysis of cationic resin before and after treatment was carried out using a Perkin Elmer Spectrum Two FTIR (Fourier-transform infrared spectroscopy) with a UATR sampling accessory (PerkinElmer Inc., France). Scanning electron microscope (HIROX SH 400M, Bruker, Germany) analysis was used to identify the morphology of the resin before and after Ca^{2+} and Mg^{2+} removal. The chemical composition of the resin surface also is characterized by a scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) with accelerating voltage at 15 kV.

2.3. Ion-exchange experiments

The removal of Ca^{2+} and Mg^{2+} experiments were investigated in batch operation type. The experiments were performed by introducing a precisely weighed amount of cationic resin into a volume of 100 mL of seawater at the different condition to study the effect of contact time, initial doses of resin, pH, and the presence of soda ash on the elimination of Ca^{2+} and Mg^{2+}, then the mixture was filtered and analyzed to determine the pH, conductivity (ms cm^{-1}), total hardness (TH; mg L^{-1}), calcium hardness Ca^{2+} (mg L^{-1}) and magnesium hardness Mg^{2+} (mg L^{-1}).

3. Results and discussion

3.1. Resin characterization

3.1.1. Infrared spectroscopy of cationic resin

FTIR spectroscopy of the cationic resin Lewatit® S100 before and after seawater pretreatment is illustrated in Fig. 1. Shown strong broadband at 3,382 cm^{-1} attributed to the stretching vibration OH of the hydroxyl groups, the vibration of the OH group's external plane identified at 1,638 cm^{-1}, bands at 2,850 and 2,923 cm^{-1} related the symmetric and asymmetric stretching of C–H in the methylene groups, respectively [24–28]. Other peaks to 1,600, 1,490 and 1,450 cm^{-1} indicated the existence of conjugated vibration C=C bonds (aromatic nucleus) which are related to the phenyl skeleton [29,30]. Three peaks at 1,123, 1,031 and 1,003 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of SO_3^{3-} [29], also a weak peak at 1,598 cm^{-1} corresponding to the phenyl groups [31]. However, after pretreatment (Fig. 1b), an appearance of new peaks at 1,169 and 1,633 cm^{-1} due to the presence

of Ca^{2+}, Na^+, and Mg^{2+} from seawater [32]. There is also a decrease in the intensity and a displacement of peaks 3,382 and 1638 cm^{-1} towards 3,477 and 1633 cm^{-1} due to the interactions with the ions present in seawater and the resin.

3.1.2. Resin analysis by SEM and EDX

The SEM photos of cationic resin Lewatit® S100 at 0 min showed a smooth surface on the beads Figs. 2a and b. But

Table 1
Seawater composition and properties

Parameters	Value
Total hardness (mg L^{-1})	4,200
Ca^{2+} (mg L^{-1})	620.00
Mg^{2+} (mg L^{-1})	644.00
Cl^- (mg L^{-1})	20.412
HCO_3^- (mg L^{-1})	40.00
CO_3^{2-} (mg L^{-1})	50.00
Conductivity (ms cm^{-1})	54.50
pH	08.15
Temperature (°C)	22.00
Na^+ (mg L^{-1})	12.32
TDS, at 180°C (mg L^{-1})	39.13

TDS – total dissolved solids.

after 60 min of contact with seawater solution, a roughness in surface morphology can be clearly observed in Figs. 5c and d. This roughness due to the fixation of calcium and magnesium on the surface of the resin.

Fig. 3 shows the EDX of cationic resin before and after pretreatment. This characterization was done to determine the chemical composition of the resin. The EDX spectrum of the ion exchange resin surfaces indicated that the elemental composition of unused resin was mostly Mo, O, and Ca, after using the resin for the pretreatment seawater we observe the appearance of a new element which Na, and the increase in the quantity of Ca and Mg due to the migration of these elements from seawater to the surface of resin, which confirms the SEM analyses Figs. 2c and d.

Another essential property of this resin is shown in Table 2.

The overall ion exchange process can be defined by the following equation:

$$4R - SO_3H + Ca^{2+} + Mg^{2+} \rightarrow 2R - SO_3Ca + 2R - SO_3Mg + 4H^+$$

(1)
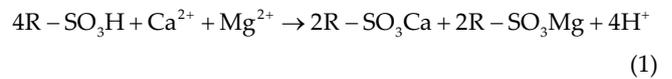
3.2. Ion exchange studies

3.2.1. Effect of contact time

To study the time effect on the Ca^{2+} and Mg^{2+} exchange, we introduce an amount of 2 mg of cationic resin (Lewatit® S100) into a series of beakers containing 100 mL of
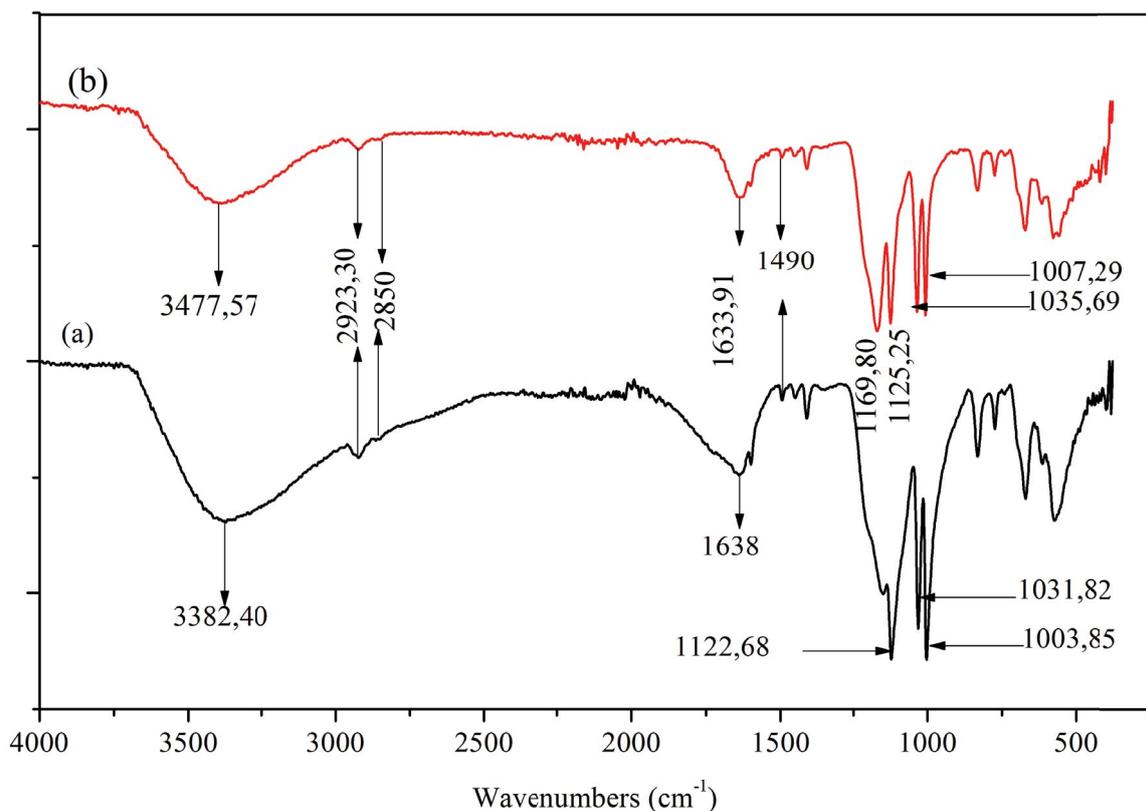
Fig. 1. The infrared spectrum of cationic resin (a) before and (b) after 60 min of seawater pretreatment.
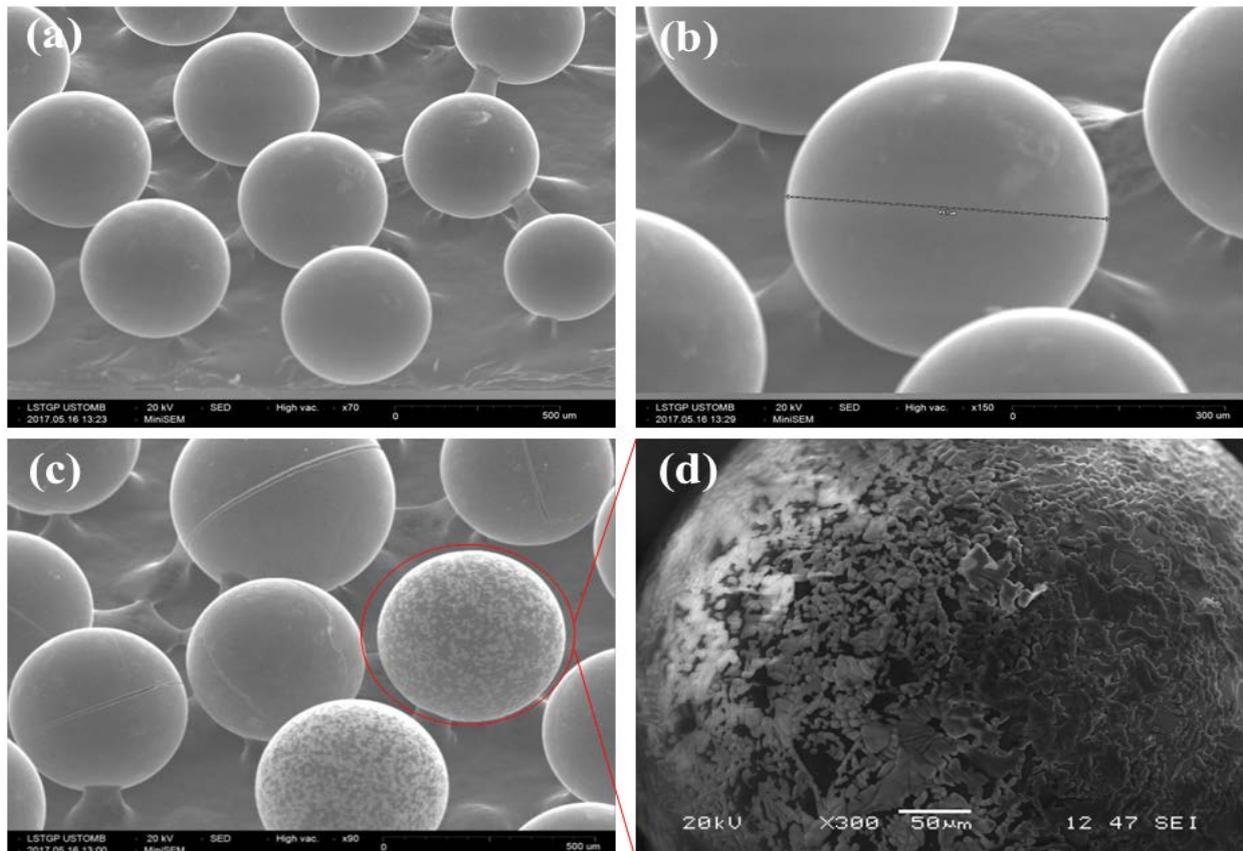
Fig. 2. SEM micrograph of cationic resin (a and b) before and (c and d) after seawater pretreatment.

seawater. The mixture was stirred for various times; 30, 45, 60, and 120 min. Then, the solution is filtered and analyzed to determine the concentration of Ca^{2+} and Mg^{2+}. Calcium and magnesium concentrations are highly time-dependent Fig. 4, a decrease in the concentration from 620 to 410 mg L^{-1} for calcium and 644 to 577 mg L^{-1} for magnesium corresponds with an equilibrium time of 60 min for the Ca^{2+} and Mg^{2+}.

3.2.2. Effect of resin dose

The resin dose also affects the efficiency of the ion exchange process. The optimal amount of cationic resin was determined by introducing introduce increasing concentrations of resin from 10 to 60 mg L^{-1} (equivalent to an amount of 10–60 mg) in 1 L of seawater, the mixture was stirred for 60 min (at equilibrium time). Then, the solution is filtered and analyzed to determine the concentration of Ca^{2+}, Mg^{2+} and the conductivity.

Fig. 5 shows the variation in calcium and magnesium content as a function of the resin concentration at an optimal contact time of 60 min. As the resin dose increased in the seawater solution, a decrease in the calcium and magnesium concentrations was observed, the Ca^{2+} concentration dropped from 620 to 300 mg L^{-1}, Similarly, the Mg^{2+} concentration decreased to 486 mg L^{-1}. This means a decrease in the TH of the seawater, these results correspond to a 45 mg L^{-1} resin dose.

The pH value of seawater decreased quickly after mixing with the cationic resin from 8.15 to 4.13 within 60 min at 10 mg L^{-1} resin dose Fig. 6. The cationic resin fixed the calcium and magnesium ions from seawater at the same time releases H^+ into seawater which lowers the pH, which results in an increase in conductivity from 54 to 97 ms cm^{-1} Fig. 6.

3.2.3. Effect of soda ash on the seawater pretreatment

The effect of soda ash in the pretreatment of seawater was study determined by adding an amount between 0.5 and 3.5 g of soda ash and 40 mg of resin to 1 L of seawater. The mixtures were stirred for 60 min, and the solutions were filtered and analyzed, the results are shown in Fig. 7.

With the increase in the mass of soda ash, the concentration of Ca^{2+} ions decreases rapidly from 620 to 200 mg L^{-1} by the addition of 2 g of soda ash, on the other hand, the ion of Mg^{2+} decreases slowly in the range (0–2) g of soda ash, from 644 to 631 mg L^{-1} due to the competition with Ca^{2+}. When the weight of soda ash exceeds 2 g, the ion exchange between the resin and the Ca^{2+} ions is reached, the concentration of Mg^{2+} rapidly decreases to 218.7 mg L^{-1} with 2.5 g of soda ash.

When soda ash is added to seawater, it dissolves and produces two sodium ions $[Na^+]$, and one carbonate ion $[CO_3^{-2}]$ Eq. (2). The carbonate of soda ash [Eq. (2)] reacts with the calcium and magnesium ions existing in seawater to give
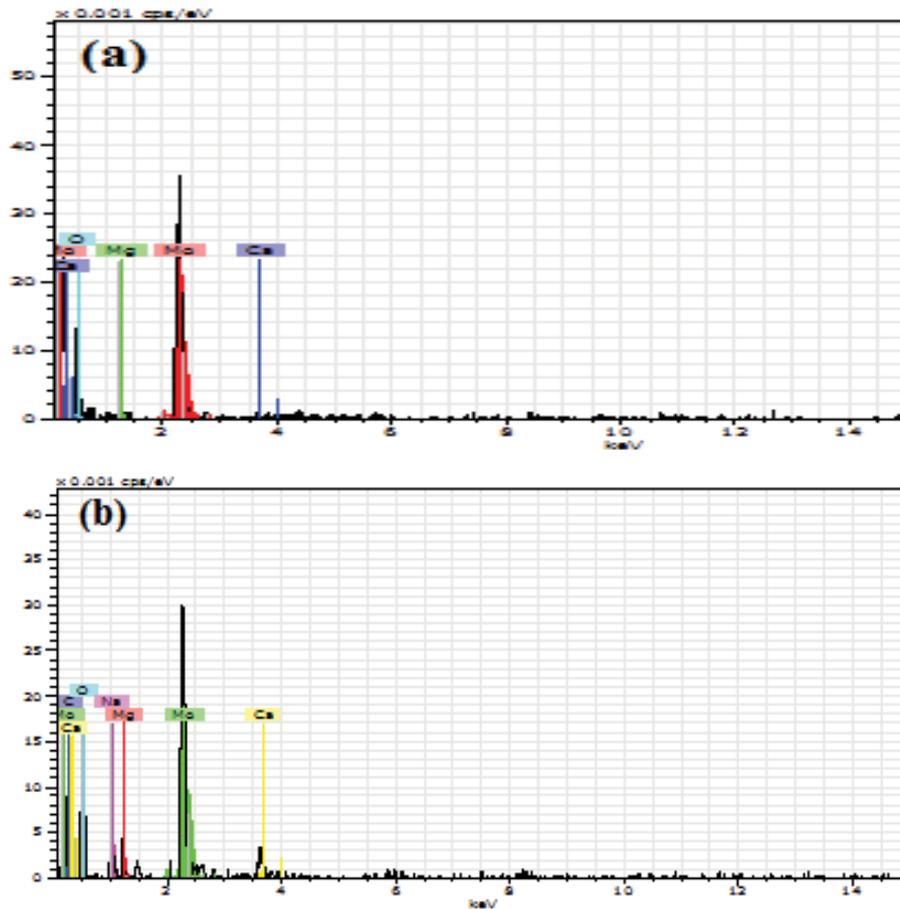
Fig. 3. EDX spectrum of cationic resin (a) before and (b) after seawater pretreatment.

Table 2
Properties of Lewatit® S100 resin

Property	
Ionic form	H^+
Functional group	SO_3^-
Matrix type	Styrene-DVB
Resin type	Cation
Effective size (mm)	0.47(±0.06)
pH	0–14
Temperature max. (°C)	120
Total capacity min. (eq L⁻¹)	2.0

the insoluble precipitates of calcium carbonate $CaCO_3$, and magnesium carbonate $MgCO_3$, respectively [Eqs. (3) and (4)]. The soda ash precipitation process is also used for the treatment of the eluted solutions which are saturated with Ca^{2+} and Mg^{2+} ions after resin Lewatit® S100 regeneration.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{-2} \tag{2}$$

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3 \downarrow \tag{3}$$

$$Mg^{+2} + CO_3^{-2} \rightarrow MgCO_3 \downarrow \tag{4}$$

The decrease in the concentration of Ca^{2+} and Mg^{2+} ions has a direct influence on the total hardness which reaches a value of 1,050 mg L⁻¹ when compared with 4,200 mg L⁻¹
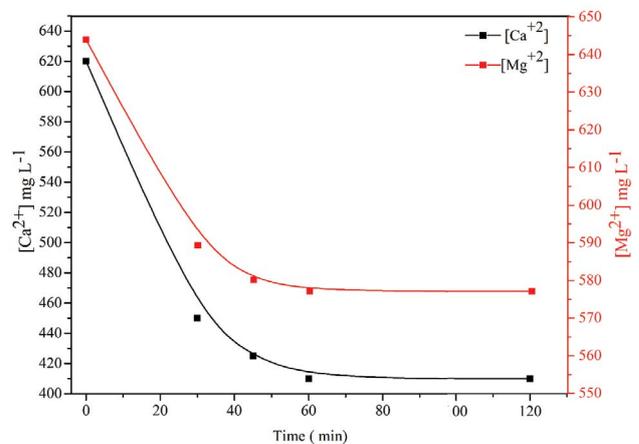
Fig. 4. Effect of the contact time on the Ca^{2+} and Mg^{2+} ion exchange ($T = 22$°C; $m = 2$ mg).

seawater without treatment. The soda ash increases the pH from 8.15 to 8.84. The pretreatment of seawater with cationic resin in the presence of sodium removal of 69% of Mg^{2+}, 99% of Ca^{2+}, and 75% of total hardness Table 3.

In Table 4 we have presented a brief comparative study of the removal of Ca^{2+} and Mg^{2+} from the literature by various materials.
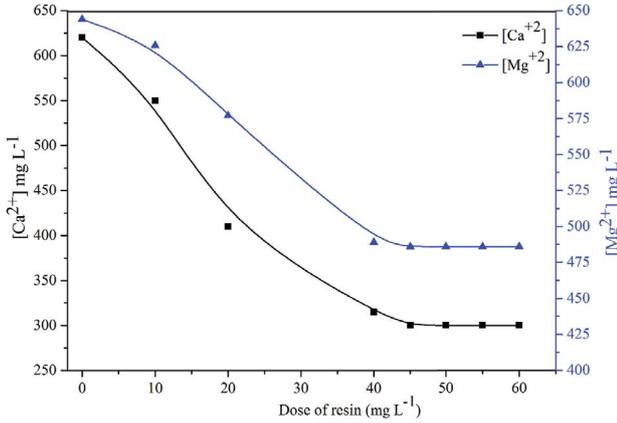
Fig. 5. Effect of the resin dose on the Ca^{2+} and Mg^{2+} ion exchange (T = 22°C; t = 60 min).
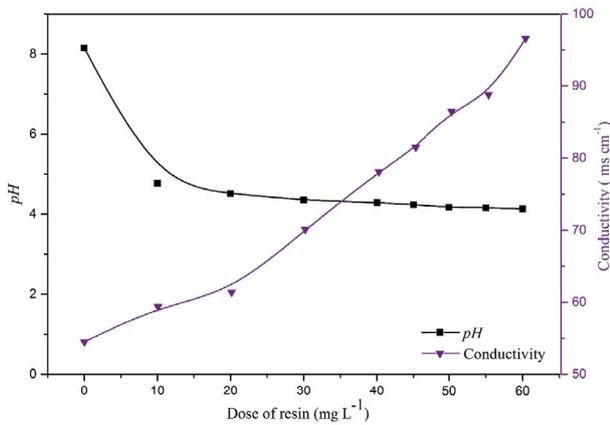
Fig. 6. Effect of the resin dose on the pH and conductivity of seawater (T = 22°C; t = 60 min).

3.3. Elution study

Elutions of Ca(II) and Mg(II) from the loaded resin were studied using hydrochloric acid solutions as eluent with concentrations ranging from 5 to 15% w/v (Fig. 8). Desorption of Mg(II) and Ca(II) increased with increasing hydrochloric acid concentration. Results show that 75% of Ca(II) was eluted in three stages using 15% hydrochloric acid solution while only 54% of Mg(II) was eluted under the same conditions. This may be due to the formation of Mg(II) salts, which are difficult to elute under normal conditions. The same finding was reported in the literature [36].
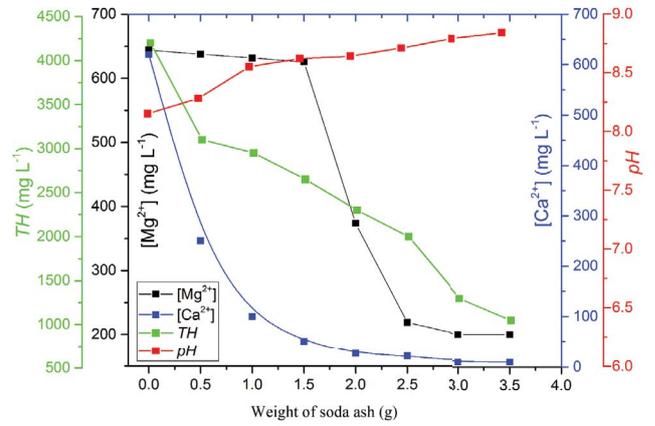
Fig. 7. Effect of soda ash on the [Ca^{2+}], [Mg^{2+}], TH, and pH of seawater pretreatment (t = 60 min; resin dose = 40 mg L^{-1}; T = 22°C).

Table 3
Removal rate of Mg^{2+}, Ca^{2+} and TH by the cationic resin (weight of soda ash = 3 g; T = 22°C; t = 60 min)

Parameters	Before pretreatment	After pretreatment	% Removal
TH (mg L^{-1})	4,200.00	1,050.00	75.00
[Ca^{2+}] (mg L^{-1})	620.00	5.00	99.19
[Mg^{2+}] (mg L^{-1})	644.00	200.47	68.87
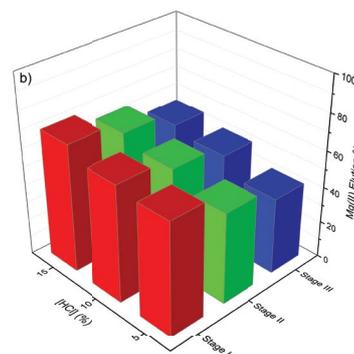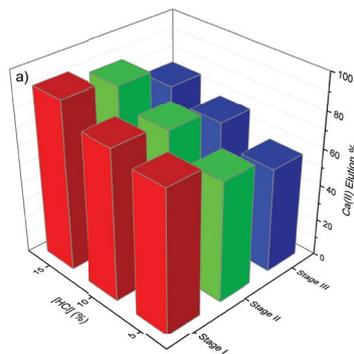
Fig. 8. Elution study for (a) Ca(II) and (b) Mg(II) from loaded Lewatit® S100 resin.

Table 4
Comparison of the removal of Mg²⁺ and Ca²⁺ by different materials

Material used	Elements	Value before treatment (mg L⁻¹)	References
SEPA Cell (OSMONICS, Minnetonka, Minnesota)	Magnesium	0.20	[33]
Resin Amberlite IRN-77	/	0.19	[34]
Resin Lewatit® S100	/	200.47	This work
SEPA Cell (OSMONICS, Minnetonka, Minnesota)	Calcium	15.00	[33]
Amberlite IRN-77 resin	/	0.10	[34]
Resin S930	/	2.92	[35]
Resin Lewatit® S100	/	5.00	This work

4. Conclusions

In this study, seawater was treated to remove Ca^{2+} and Mg^{2+} ions with the cationic resin Lewatit® S100, this resin is characterized by various analyzes such as FTIR, SEM, and EDX. The results of this study revealed the enhanced effectiveness of coupling two methods softening by cationic resin and precipitation by soda ash. Pretreatment achieved by a mixture of 40 mg L⁻¹ ion exchange resin and 3.5 g L⁻¹ soda ash in seawater gave the best results an equilibrium time of 60 min of contact, the calcium and magnesium ion concentrations in seawater were reduced from 620 and 644 to 5 and 200 mg L⁻¹, respectively. Under optimal conditions, there was the removal of 75% in total hardness and a decrease in calcium and magnesium ion concentration of 99.19% and 68.87%, respectively.

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