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Separation of calcium and magnesium using dual precipitation/chelation scheme from saline solutions

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ABSTRACT

A process scheme has been developed for the selective separation of calcium (Ca) and magnesium (Mg) from the Red Sea water and reverse osmosis (RO) brine using combined dual precipitation/chelation units. Two precipitation stages have been adopted for sequential Ca and Mg removal using sodium carbonate and sodium hydroxide, respectively. Calcium removal using sodium carbonate approached 96.6 and 93.2% for Red Sea (pH 9) and RO brine (pH 9.2), respectively. Maximum Mg removal efficiencies achieved using sodium hydroxide at pH 12 for both Red Sea and RO brine were 99.6 and 74%, respectively. The decalcified filtrate of the second precipitation stage was further processed for Mg removal using ethylene glycol bis(2-aminoethyl ether)-N,N,N´,N´-tetra acetic acid (EGTA), diethylenetriaminepentaacetic acid (DTPA), and N-(2-Hydroxyethyl) ethylene diamine-N,N,N´-triacetic acid (HEDTA) as selected chelating agents. Almost complete removal of Mg was achieved using the three tested chelating agents with maximum Mg adsorption capacity of 490 mg/g. The final rich monovalent effluents could be directed to thermal or membrane desalination plants or selective monovalent ion separation/salt recovery units. The purified streams after Ca and Mg removal could be utilized immediately for lithium, potassium, and sodium chloride separation.

Keywords: Seawater; Brine; Sequential precipitation; Calcium; Magnesium; Chelation

1. Introduction

The need for water is rapidly increasing and current freshwater resources will not be able to meet all requirements. Thermal systems and membrane schemes are now operating successfully for commercial production of desalted water in Egypt. Economic evaluation of water desalination in Egypt seawater, brackish groundwater, and agriculture wastewater is based on Egyptian experience in technology, field characteristics, energy, and materials [1–5]. Brine management is one of the challenging problems in most large-scale seawater desalination plants. Recovery of salts from brines improves both sides of the problem and avails opportunities for new state of the art desalination/salt production complex [6–8]. Numerous purification steps are undertaken to precipitate

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seawater feed for desalination, and limited benefits are currently achieved from discharged brines [9,10]. Salts recovery methods can be generally classified in the chemical precipitation processes, extraction methods, ion exchange resins, as well as, advanced membrane processes [8,11–14]. Calcium and magnesium are precipitated from seawater and brines by addition of alkali (sodium carbonates, sodium hydroxides, lime, etc.) [15–17]. Ion exchange chelators and polymers were utilized by a number of authors to selectively separate heavy metals from aqueous solutions. It was reported that sorption of heavy metals onto polyacrylate anion exchangers could be effective when the metals are complexed with amino polycarboxylic acids [18,19]. Silica-based chelating exchangers as well as polymeric-based ones where used for Ca and Mg removal [20]. Other workers utilized chromatography columns packed with polystyrenes impregnated with chelating dyes [21–23]. In other studies, mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD) were tested for hardness removal, they exhibited maximum adsorption capacities ranging from 15.6 to 54.1 mg/g for Ca and Mg, respectively [24]. Optimum chelation conditions for Ca and Mg removal from saline solutions have been experimentally tested as a standalone process by the authors for the adsorption of some different chelating agents using Red Sea water and reverse osmosis (RO) brine [25].

It is worth mentioning that in spite of the previous published work on precipitation or adsorption, very little work has been done to develop a process combining precipitation and adsorption on continuous basis. Thus, the current study is a proof of concept for gearing precipitation and adsorption for selective calcium and magnesium removal from the Red Sea water and RO brine through a developed integrated process scheme. The proposed scheme serves either as a pretreatment stage for performance enhancement of thermal or membrane desalination plants or as a preliminary stage in integrated salt recovery schemes from desalination brines. This scheme mainly comprises combined dual precipitation/chelation units. Optimum conditions for Ca and Mg precipitation and chelation were selected for experimental investigations.

2. Materials and methods

2.1. Materials

Selected types of chelating agents were purchased from Sigma-Aldrich: ethylene glycol bis (2-aminoethyl ether)-N,N,N´,N´-tetraacetic acid (EGTA) ($C_{14}H_{24}N_2O_{10}$, purity ≥ 98.5%, MW 380.35), diethylenetriaminepentaacetic acid (DTPA) ($C_{14}H_{23}N_3O_{10}$, purity 98%, MW 357.32), and N-(2-hydroxyethyl) ethylene diamine-N,N,N´-triacetic acid (HEDTA) ($C_{10}H_{18}N_2O_7$, purity > 99%, MW 278.26). Analytical grade precipitants, sodium carbonate from Merck and sodium hydroxide ADWIC, were used for alkaline treatment and pH adjustment for seawater and brine.

Natural seawater samples were collected from the Red Sea and RO brine sample was collected from Safaga desalination plant located on the Red Sea in Egypt. Chemical and physical properties for natural seawater and RO brine are presented in Table 1 [17].

2.2. Methods

2.2.1. Approach

An integrated scheme has been developed for Ca and Mg removal from Red Sea water and RO brine. The proposed scheme, shown in Fig. 1, mainly comprises combined dual precipitation/chelation units.

Experimental investigations of the proposed scheme were conducted on three stages based on previous experimental studies of the authors [17,25] and in addition to other reported indicators [15]. Two precipitation stages were adopted for selective Ca and Mg removal using sodium carbonate and sodium hydroxide, respectively. The clarified stream or supernatant after chemical precipitation will be directed to ion exchange column, after pH adjustment, for the removal of divalent ions. The stream after ion exchange will enable production of high purity monovalent ions.

Table 1
Chemical and physical characteristics of Red Sea water and RO brine

Parameter	Red Sea water	RO brine
Ca^{2+} (mg/L)	473	727
Mg^{2+} (mg/L)	1,649	2,444
Na^{+} (mg/L)	13,038	19,118
Cl^{-} (mg/L)	23,950	36,700
SO_4^{2-} (mg/L)	3,152	5,588
k^{+} (mg/L)	551	766
CO_3^{2-} (mg/L)	28.8	28.8
HCO_3^{-} (mg/L)	102.5	126.9
Alkalinity (mg/L)	132	152
TDS (mg/L)	43,500	65,500
Conductivity (μs)	60,900	91,700
pH	7.7	7.3

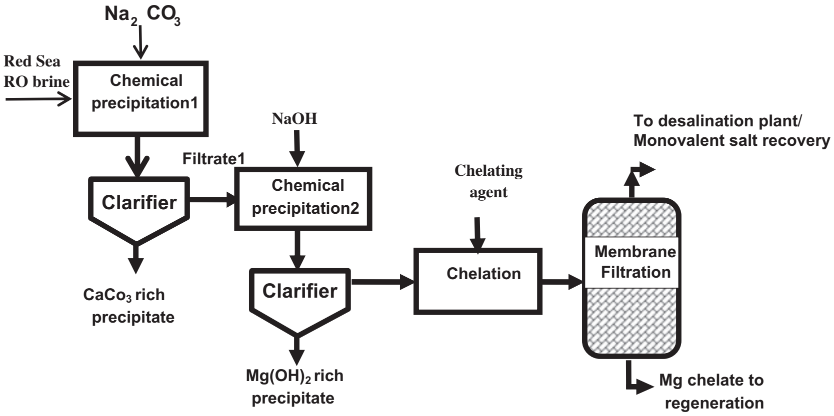

Fig. 1. Schematic diagram for the developed dual precipitation/chelation scheme for selective separation of Ca and Mg.

Experimentally investigated stages are described as follows:

(1) Stage (1): Ca precipitation experiments using sodium carbonate from both Red Sea water and RO brine at selected optimum conditions based on previous experimental studies of the authors [15,17].
(2) Stage (2): Mg precipitation experiments using sodium hydroxide from the filtrate of stage (1) [15].
(3) Stage (3): Ca and Mg chelation experiments, where the filtrate of stage (2) will be treated with selected successful types of chelating agents previously tested for raw seawater and RO brine for Ca and Mg removal based on previous experimental studies of the authors [25].

2.2.2. *Experimental investigations*

Selective precipitation of Ca from Red Sea as well as RO brine was conducted using sodium carbonate (pH 9 and 9.2, respectively) based on previous experimental studies of the authors [17], while the filtrate from Ca precipitation (magnesium rich filtrate) was then directed to another chemical precipitation stage for magnesium hydroxide precipitation using sodium hydroxide at pH 12 for both Red Sea and RO brine [15]. Settling was conducted after mixing the saline solutions with the precipitant (sodium carbonate and sodium hydroxide) for 30 min and then transferred to a graduated cylinder during which a suspension is allowed to settle for 30–120 min, and the height of the supernatant–suspension interface is measured as a function of the settling time.

Selected chelating agents have been tested for the remaining Ca and Mg chelation from the filtrate of the second precipitation stage based on previous experimental studies of the authors [25]. Batch mode adsorption was conducted in 250-mL flask by adding 0.1 g of each of the employed chelating agents to a specific volume (100 ml) of the saline solutions (Red Sea and RO desalination brine) at 28°C and pH 6.6, adjusted using hydrochloric acid [25]. Flasks were sealed and constantly shaken using a water bath shaker (Julabo, SW-20C) with a constant agitation rate (150 rpm) and at room temperature for 24 h to attain equilibrium. The supernatant was filtered using a Whatman filter paper no. 4.

The filtrate from Ca and Mg precipitation stages as well as after chelation treatment was analyzed to determine the concentration of Ca and Mg in the treated solutions using an atomic absorption flame spectrometer (AAS) (GBC Avanta).

The adsorption capacity (Q) of the chelating agents was calculated using the following equation [26]:

$$Q = \frac{C_o - C_e}{m} \times V \tag{1}$$

where Q is the amount of metal ions adsorbed in (mg/g adsorbent), C_o and C_e are the initial and equilibrium ion concentrations (mg/L), respectively; V is the volume of metal ions solution used (L) and m is the weight of dry adsorbent (g).

3. Results and discussion

3.1. *Chemical precipitation using sodium carbonate (Stage 1)*

3.1.1. *Ca removal*

Fig. 2 shows the reduction in Ca concentration in stage (1). It is clear that high Ca removal efficiencies

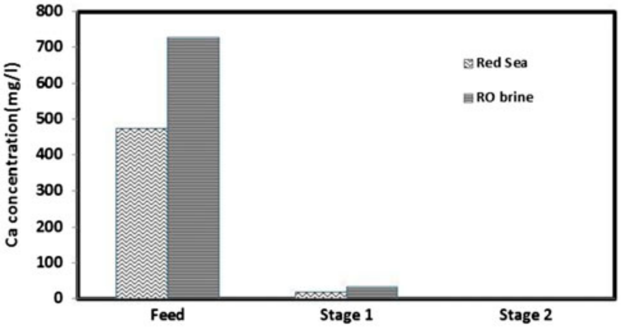

Fig. 2. Concentration of Ca in the effluent of each precipitation stage.

from Red Sea and RO brine were attained in this stage using sodium carbonate (96.6 and 93.2%, respectively) as shown in Table 2, which agrees with Sorour et al. [17].

3.1.2. Mg removal

Fig. 3 shows the reduction in Mg concentration in stage (1). Lower Mg removal efficiencies from the Red Sea and RO brine were attained using sodium carbonate in this stage (24.8 and 22.8%, respectively) as shown in Table 2. This may be attributed to the high initial Ca concentration in the brine which agrees with Sorour et al. and Ghosh et al. [25,27].

It is worth mentioning that both Ca and Mg removal efficiencies from Red Sea were higher than those of the RO brine [17].

The filtrate of this stage contains low Ca concentration for both the Red Sea and RO brine (16 and 32 mg/L, respectively). Higher corresponding Mg concentrations were 1,240 and 1,877 mg/L, respectively. This filtrate was then subjected to another chemical precipitation stage for Mg removal using sodium hydroxide.

3.2. Chemical precipitation using sodium hydroxide (Stage 2)

3.2.1. Ca removal

It is clear from Fig. 2 that complete Ca removal was achieved from both the Red Sea and RO brine in this stage which may be attributed to the low initial Ca concentrations.

3.2.2. Mg removal

Maximum values of Mg removal from the Red Sea and RO brine were attained using sodium hydroxide in this stage (99.6 and 74%, respectively) as shown in Table 2 and Fig. 2. Both Ca and Mg removal efficiencies from Red Sea were higher than those of RO brine. It is worth mentioning that theoretical analysis would require almost full removal of Mg in case of brine (Mg recovery from brine after 2 stages precipitation: 80%). However, the obtained results might be explained by hindered settling due to the possible use of antiscalants in the desalination plant (Safaga desalination plant located on the Red Sea in Egypt). This agrees with Greenlee and Greenlee et al. [28–30].

The filtrate of this stage is free of Ca and contains high Mg concentration (490 mg/L) for the RO brine and much lower Mg concentration (5 mg/L) for the Red Sea.

Fig. 4 presents the settling curves for Ca and Mg precipitates from the Red Sea and RO brine using sodium carbonate (for Ca precipitation) and sodium hydroxide (for Mg precipitation). It is clear that settling of Ca is faster than Mg in both saline sources,

Table 2
Characteristics of each precipitation stage in the integrated scheme

	Stage (1): Na_2CO_3		Stage (2): NaOH		Total precipitation stages	
Source	Ca (mg/L)	Mg (mg/L)	Ca (mg/L)	Mg (mg/L)	Ca (mg/L)	Mg (mg/L)
Red Sea						
Feed	473	1,649	16	1,240	473	1,649
Filtrate	16	1,240	0	5	0	5
Removal (%)	96.6	24.8	100	99.6	100	99.7
RO brine						
Feed	727	2,444	32	1,887	727	2,444
Filtrate	32	1,887	0	490	0	490
Removal (%)	93.2	22.8	100	74	100	80

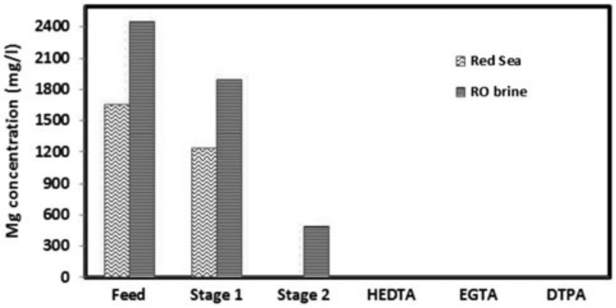

Fig. 3. Concentration of Mg in the effluent of each precipitation stage.

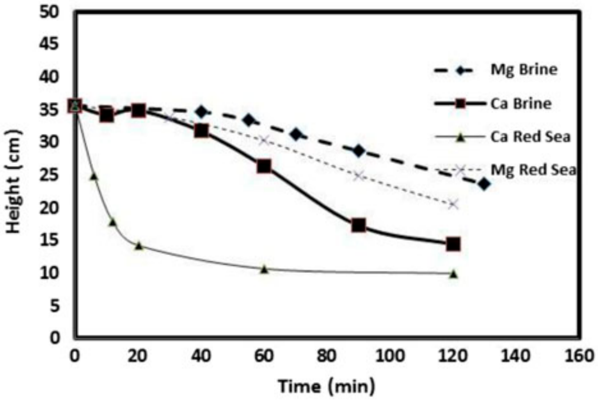

Fig. 4. Settling curve for Ca and Mg precipitation from saline solutions using sodium carbonate and sodium hydroxide.

and in general, settling of both Ca and Mg is faster in Red Sea rather than RO brine. These data are important for settler design.

3.3. Chelation of Mg (Stage 3)

The filtrate of the stage (2) is subjected to chelation for further Mg removal from the decalcified second precipitation effluent.

Chelation using the selected chelating agents resulted in complete removal of the residual Mg in both Red Sea and RO brine filtrates, as shown in Fig. 2. It is obvious that all chelating agents revealed higher tendencies for Mg adsorption at lower Ca concentration found in Red Sea filtrate subjected to chelation which agrees with Sorour et al. [25]. The Mg adsorption capacities using the tested chelating agents form Red Sea and RO brine filtrates were 5 and 490 mg/g, respectively. The later value is higher than the reported values, as mentioned by Sorour et al. [25]. High magnesium adsorption capacity may be attributed to that decalcified saline solutions offer enough magnesium ions to the accessible vacant adsorption sites. The adsorption is also enhanced by the lack of divalent ions interference due to the total calcium removal in the previous stage. Obviously, in spite of these promising results, additional endeavors are still needed to explore data reproducibility after successive loadings. Regarding the regeneration of the chelating agents, very little work is presented in the literature for regeneration of the Mg-bound chelating resins. Experiments for regeneration are ongoing.

Furthermore, with the exception of the author's previous work [25], the used adsorbents have not been reported (to our knowledge) on softened seawater or desalination brines. Further work is ongoing to optimize the proposed scheme, especially minimization of chemical usage and impact on downstream. Thus, the financial aspects should be addressed within the context of integrated salt recovery and desalination.

4. Conclusions

Sequential separation of Ca and Mg from Red Sea water and RO brine was investigated using a dual precipitation/chelation scheme. It was possible to separate Ca-rich precipitate using sodium carbonate with removal efficiencies of 96.6 and 93.2% for Red Sea (pH 9) and RO brine (pH 9.2), respectively. The filtrate obtained after Ca precipitation was subjected to a second precipitation stage using sodium hydroxide to separate Mg with efficiencies of 99.6 and 74% from the Red Sea and RO brine, respectively. After the second precipitation stage, Ca has been completely removed where the corresponding Mg removal efficiencies from both Red Sea and RO brine were 99.7 and 80%, respectively. Chelation was then conducted to remove residual Mg using EGTA, DTPA, and HEDTA as selected chelating agents. It was found that Mg has been completely removed using all the tested chelating agents with maximum Mg adsorption capacity of 490 mg/g. The developed scheme serves either as a pretreatment stage for performance enhancement of thermal or membrane desalination plants or as a preliminary stage in integrated salt recovery schemes from desalination brines. Ca/Mg softened seawater or RO brine is thus amenable for further processing to separate monovalent ions such as lithium, potassium, and sodium chloride. Investigations are currently underway to come up with optimized financial indicators of the precipitation and chelation scheme for Ca and Mg removal.

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