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Experimental screening of some chelating agents for calcium and magnesium removal from saline solutions

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ABSTRACT

Removal of hardness-causing ions from seawater and desalination brines improves the performance of water treatment units and provides economic and environmental benefits. Chelation of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in saline solutions has been experimentally investigated as a stand-alone separation process. In the current study, ethylene glycol bis(2-aminoethyl ether)-N,N,N´,N´-tetraacetic acid (EGTA), diethylenetriaminepentaacetic acid (DTPA), N-(2-Hydroxyethyl) ethylene diamine-N,N´,N´-triacetic acid (HEDTA), ethylene diaminetetraacetic acid (EDTA), polyacrylic acid (PAA), boric acid (BA), and sodium tripolyphosphate (STP) were selected as chelating agents. It was found that DTPA exhibited the maximum Ca^{2+}-loading capacity of 128 mg/g and minimum Mg^{2+}-loading capacity at pH 3 for the Mediterranean Seawater. The corresponding values for EGTA in Red Seawater were 117 and 2 mg/g and were obtained at pH 3 and 6.6, respectively, with an EGTA optimum dose of 1 g/L. Maximum Ca^{2+} and Mg^{2+} loading capacities (153 and 72 mg/g, respectively) were attained using EDTA with reverse osmosis brine. On the other hand, EDTA exhibited the highest calcium and magnesium loadings (158 and 76 mg/g) with Red Seawater at pH 7.5. Among the investigated chelating agents, EGTA and EDTA were found to be the most suitable for softening of Red Seawater, whereas EGTA proved to be the most selective for calcium ions. Both calcium and magnesium adsorption onto EGTA have been best described by Langmuir isotherm indicating monolayer coverage of ions on the outer surface of the chelating agent.

Keywords: Chelation; Seawater; Brine; Adsorption; Calcium; Magnesium; Isotherm

1. Introduction

Chelating agents have been widely used for softening and water treatment applications. The majority of conventional chelators can be classified into two main groups, namely aminopolycarboxylates (APCAs) and polyphosphonates [1–3]. In addition, a new generation of biodegradable ligands has been recently introduced to avoid the environmental issues associated with the

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presence of chelating and metal-binding agents in water systems [4]. Ion-exchange chelators were utilized by a number of workers 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. Amberlites IRA 458, 958, and 67 were found to be potential suitable exchangers for the removal of heavy metals complexed with ethylenediaminetetracetic acid (EDTA) or nitrilotriacetic acid (NTA) and could hence be applied for wastewater treatment [4]. In addition, Amberlite IRC-748 showed potential applicability for enriching trace metals, such as Cd, Zn, and Pb, in complex water samples [5]. Biophosphonates proved to efficiently bind coordinately with Cu to form mono- and bis-chelates [6]. Polymer-supported UF studies showed that the modified chelators (water-soluble N-benzoyl thiourea) successfully removed Cu and Ni from aqueous solutions containing high sodium nitrate concentration [7]. Other studies were conducted on the separation of heavy metals via high-performance chelation ion chromatography using silica-and polymer-based chelating ion exchangers [8,9].

As for the removal of Ca^{2+} and Mg^{2+} ions from aqueous solutions, silica-based chelating exchangers as well as polymeric-based ones were used for hardness removal [10,11]. Other workers utilized chromatography columns packed with polystyrenes and impregnated with chelating dyes [12,13]. In other studies, mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD) exhibited maximum adsorption capacities ranging from 15.6 to 54.1 mg/g for Ca^{2+} and Mg^{2+}, respectively [14]. Furthermore, a model was proposed to describe polymer-enhanced UF of Ca^{2+} ions complexed with poly (acrylic acid–maleic anhydride) sodium salt (PAA-Na) to predict Ca^{2+} rejection at different operating conditions [15]. Chelation/UF of Ca^{2+} and Mg^{2+} ions using polyethylene imine (PEI) and polystyrene-based membranes revealed that the separation is enhanced by increasing polymeric ligand/metal ion ratio. In addition, better separation was achieved for Ca^{2+} relative to Mg^{2+} under the same operating conditions [16]. The present paper investigates the potential of using different chelating agents for Ca^{2+} and Mg^{2+} removal from different seawater sources such as Mediterranean Sea and Red Sea, and reverse osmosis (RO) desalination brine. Effect of the different operating conditions was studied for the chelators possessing the highest calcium adsorption capacities. Furthermore, equilibrium studies were conducted for the most efficient adsorbent.

2. Materials and methods

2.1. Materials

Two different groups of chelating agents investigated in this study were purchased from Sigma Aldrich. Group (I); acidic chelating agents with pH 3 ± 0.5 and group (II); neutral chelating agents with pH 7 ± 0.8 in saline solutions. Group (I) includes ethylene glycol bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA), diethylenetriaminepentaacetic acid (DTPA) and N-(2-hydroxyethyl) ethylene diamine-N,N′,N′-triacetic acid (HEDTA). While group (II) includes ethylene diaminetetraacetic acid free acid (EDTA), poly acrylic acid (PAA), boric acid (BA), and sodium tripolyphosphate (STP). Characteristics of the chelating agents, including formula, molecular weight, purity, and stability constants, are presented in Table 1.

Different sources of saline solutions were tested; natural seawater from the Mediterranean Sea and Red Sea as well as RO desalination brine obtained from Safaga city located on the Red Sea in Egypt. Chemical and physical characteristics of these saline solutions are presented in Table 2 [17]. Sodium carbonate and hydrochloric acid were used for pH adjustment. It is worth mentioning that the pH of the slightly alkaline saline solution (pH ≅ 8), decreased with increasing the EDTA dose due to protonation.

2.2. Methods

2.2.1. Adsorption experiments

Batch-contacting experiments were conducted in 250-mL flasks by adding 0.1 g of each of the employed chelating agents to a specific volume (100 mL) of the saline solutions (Mediterranean Seawater, Red Seawater, and RO desalination brine). Flasks were sealed and constantly shaken on a water bath shaker (Julabo, SW-20C) with constant agitation speed (150 rpm) and for 24 h at room temperature in order to attain equilibrium. The supernatant was filtered using a Whatman filter paper no. 4 and then analyzed to determine the equilibrium concentration of Ca^{2+} and Mg^{2+} in the treated solution. It is to be noted that the addition of the chelating agent to the saline solution varied its pH. Therefore, experiments were conducted with and without pH adjustment in order to understand the effect of pH. The pH was adjusted using either hydrochloric acid or sodium carbonate via a pH meter HANNA apparatus model-211.

Adsorption experiments were conducted for Ca^{2+} and Mg^{2+} uptake onto a number of chelating agents at different pH and initial concentrations of the tested

Table 1
Characteristics of chelating agents used

Chelating agent	Formula	Molecular weight	Purity (%)	Stability constant, pK_a
Ethylene glycol bis(2-aminoethyl ether)-N,N,N´, N´-tetraacetic acid: (EGTA)	$C_{14}H_{24}N_2O_{10}$	380.35	≥98.5	<2, 2.7, 8.8, 9.5
Diethylenetriaminepentaacetic acid: (DTPA)	$C_{14}H_{23}N_3O_{10}$	357.32	98	1.68, 2.1, 2.6, 4.15, 8.2, 9.9
N-(2-Hydroxyethyl) ethylene diamine-N,N´,N´-triacetic acid: (HEDTA)	$C_{10}H_{18}N_2O_7$	278.26	>99	2.64, 5.33, 9.73
Ethylene diaminetetraacetic acid free acid: (EDTA)	$C_{10}H_6N_2O_8$	292.24	≥98.5	1.5, 2, 2.7, 6.13, 10.37
Poly acrylic acid: (PAA)	$C_3H_3NaO_2$	5,100	≥98.5	4.2
Boric acid: (BA)	H_3BO_3	61.83	≥99.5	9.23
Sodium tripolyphosphate: (STP)	$Na_5O_{10}P_3$	367.86	85	0.9, 1.9, 5.3, 7.7

Table 2
Chemical and physical characteristics of Mediterranean, Red Seawater and brines

	Seawater		
Parameter	Mediterranean	Red Sea	RO brine
Ca^{2+} (mg/L)	400	473	727
Mg^{2+} (mg/L)	1,460	1,649	2,444
Na^+ (mg/L)	11,000	13,038	19,118
Cl^- (mg/L)	20,000	23,950	36,700
SO_4^{2-} (mg/L)	2,700	3,152	5,588
k^+ (mg/L)	500	551	766
CO_3^{2-} (mg/L)	20	28.8	28.8
HCO_3^- (mg/L)	90	102.5	126.9
Alkalinity (mg/L)	110	132	152
TDS (mg/L)	36,320	43,500	65,500
Conductivity (μs)	57,500	60,900	91,700
pH	7.6	7.7	7.3

saline solutions. The effect of chelating agent dose was studied for selected chelators that showed simultaneous maximum Ca^{2+}- and Mg^{2+}-loading capacities from Red Seawater; in addition to those that exhibited maximum Ca^{2+}-loading with minimum Mg^{2+}-loading capacities. Furthermore, isotherm investigations were performed for the chelating agent that possessed the highest Ca^{2+}-and lowest Mg^{2+}-loading capacities at concentrations of (Ca^{2+}: 45–727 mg/L, Mg^{2+}: 152–2,444 mg/L) using diluted brine. All experiments were carried out in duplicate, and the mean values are presented. Experimental data were fitted to the Langmuir, Freundlich, and Dubinin–Radushkviech (D–R) isotherm models.

Regarding the solubilities of these chelating agents in saline solutions, it was found that HEDTA, BA, and PAA were soluble using the specified doses in the entire range of examined pH (3–7.7). However, DTPA, EDTA, and STP were insoluble within the pH range (5–7.5). EGTA was insoluble at pH 2.9 and started to become soluble at pH 5.

Langmuir sorption isotherm describes the monolayer coverage of the sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent where all the sorption sites are energetically identical. The linear form of Langmuir isotherm is given by the following:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{1}$$

where C_e is the equilibrium aqueous metal ion concentration (mg/L), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g), q_m and b are the Langmuir constants related to the maximum adsorption (saturated monolayer) capacity and the free energy of adsorption, respectively. The values of q_m (mg/g) and b (L/g) can be respectively determined from the slope and intercept of the linear plot [18,19].

Freundlich isotherm describes multilayer sorption on heterogeneous surfaces. The logarithmic form of the equation may be written as:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \tag{2}$$

where K_F is a rough indicator of the adsorption capacity ((mg/g)/(L/mg)^n) and $1/n$ indicates the sorption intensity. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption [18–20].

Dubinin–Radushkviech (D–R) isotherm is applied for micro porous adsorption and pore filling. The linearized D–R isotherm can be expressed in the form [21,22]:

$$\ln q_e = \ln Q_{\max} - B \times \zeta^2 \tag{3}$$

where $Q_{\max}$ is the maximum concentration in the solid phase, i.e. ion-exchange capacity (mol/g), q_e is the concentration in solid at equilibrium (mol/g), B is a constant related to the ion sorption energy (mol^2/kJ^2), and ζ is the Polanyi potential (kJ/mol) and this is equal to

$$\zeta = RT \ln(1 + 1/C_e) \tag{4}$$

where R is the gas constant (kJ/mol K), T is the absolute temperature in degrees Kelvin, and C_e is the concentration in solution at equilibrium (mol/l). The D–R plots of $\ln Q_e$ vs. ζ^2 at different temperatures are used to estimate the slope and intercept. The mean sorption energy E (kJ/mol), defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in the solution, is calculated according to:

$$E = \frac{1}{\sqrt{-2B}} \tag{5}$$

where B is calculated from the D–R equation. The values of E are obtained from the slope of the D–R plots. The magnitude of E is useful for estimating the type of occurring sorption reaction [18,19,23].

2.2.2. Spectrophotometry analysis

The concentrations of Ca^{2+} and Mg^{2+} in the saline solutions were analyzed using an atomic absorption flame spectrophotometer (GBC Avanta). The adsorption capacity (Q) was calculated by mass balance using the following equation [24]:

$$Q = \frac{C_o - C_e}{m} \times V \tag{6}$$

where Q is the amount of Ca^{2+} or Mg^{2+} ions adsorbed (mg/g adsorbent), C_o and C_e are the initial and equilibrium ion concentrations (mg/L), respectively; V is the volume of saline solution used (L) and m is the weight of dry chelating agent (g).

3. Results and discussion

3.1. Adsorption of Ca^{2+} and Mg^{2+} from different saline solutions

Fig. 1(a) and (b) depict Ca^{2+} and Mg^{2+} adsorption capacities using different chelating agents with three tested saline solutions without pH control. The figures reveal that the maximum loading range of Ca^{2+} for all the tested saline solutions (124–153 mg/g) was attained using EGTA-, HEDTA-, and DTPA-chelating agents from group (I) as well as EDTA from group (II). The corresponding range of Mg^{2+}-loading capacities for all saline solutions (71–91 mg/g) was achieved using STP and EDTA. It is worth mentioning that simultaneous maximum Ca^{2+}- and minimum Mg^{2+}-loading capacities of 128 and 0 mg/g, respectively were obtained from Mediterranean Seawater using DTPA, as well as 117 and 2 mg/g, respectively from Red Seawater using EGTA. Maximum and minimum removal efficiencies achieved by Ca^{2+} and Mg^{2+} using DTPA were 30 and 0%, respectively. The corresponding values for EGTA were 24 and 0.2%, respectively. For RO brine, it was not possible to maximize Ca^{2+} and minimize Mg^{2+} uptakes simultaneously, Nevertheless, EDTA was found to provide a reasonable compromise between Ca^{2+}- and Mg^{2+}-loading capacities; being 153 and 72 mg/g, respectively. The adsorption uptake capacities of Ca^{2+} from Mediterranean and Red Seawater onto DTPA- and EGTA-chelating agents were comparable within the acceptable experimental error of 5%. In view of these findings and in addition to the strategic importance of the geographic site of the Red Sea peninsula and the need for its future development, Red Seawater has been selected for further investigation. Furthermore, the screening results at different pH values indicated the promising features of EGTA, which will be discussed in the next section.

In general, it is clear from Fig. 1 that EGTA, DTPA, HEDTA, and EDTA have higher adsorption capacities for Ca^{2+} than Mg^{2+} ions. This is in agreement with previous results [16,25–27]. EDTA, for example, exists predominantly in the deprotonated form (HY^{3-}) at pH 7. Hence, it binds Ca^{2+} and Mg^{2+} ions by chelation, and it has been reported that the formation constant for the EDTA–Ca^{2+} complex is higher than its Mg^{2+} counterpart [27].

However, EGTA, DTPA, and HEDTA exist predominantly in their protonated forms at pH 3 as can be inferred from their pK_a values [26,28–31]. Therefore, they probably bind to metal ions via ion exchange. Their higher Ca^{2+} adsorption capacity relative to Mg^{2+} could thus be owed to the fact that Ca^{2+} by virtue of its smaller hydrated radius, is more competitive than Mg^{2+} [27].

3.2. Effect of pH on Ca^{2+} and Mg^{2+} adsorption from Red Seawater using different chelating agents

The effect of pH on adsorption of Ca^{2+} and Mg^{2+} from Red Seawater using chelating agents of groups

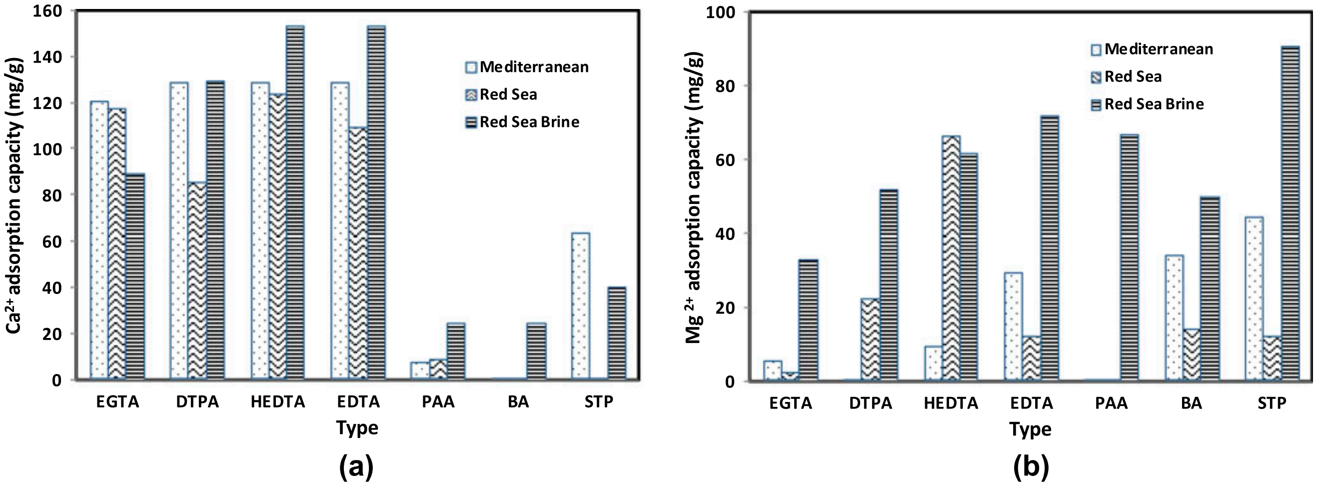

Fig. 1. Adsorption capacities of (a) Ca^{2+} and (b) Mg^{2+} using 1 g/L of different chelating agents from three types of saline solutions. Adsorption was conducted without pH adjustment.

(I) and (II) is shown in Figs. 2 and 3, respectively. Chelating agents of groups (I) and (II) were tested at pH ranges of (3–7.7) and (5–7.5), respectively. Solubilities of different chelating agents may vary according to the experimental conditions, as illustrated in Section 2.2.1. However, no precipitation was observed with any of the chelating agents at any of the studied pH values. Previous work by the authors did not reveal precipitation of calcium or magnesium within the adopted experimental conditions [17]. It is worth mentioning that pH variation will affect the protonation and deprotonation of chelating agents, and hence, this may change the mechanism of ions removal by either chelation or ion exchange.

For group (I), Fig. 2 shows that EGTA exhibited simultaneous highest Ca^{2+} (117 mg/g)- and lowest Mg^{2+} (2 mg/g)-loading capacities at pH 6.6 and 3.0 as compared to other chelating agents. The corresponding removal efficiencies were 25 and 0.12%, respectively. Working at such pH values is worth further investigation as it will incur additional costs of neutralization before and after the treatment. As for group (II), Fig. 3 shows that EDTA exhibited the highest Ca^{2+} (109 mg/g) and lowest Mg^{2+} (12 mg/g) loading capacities at pH 6.5,

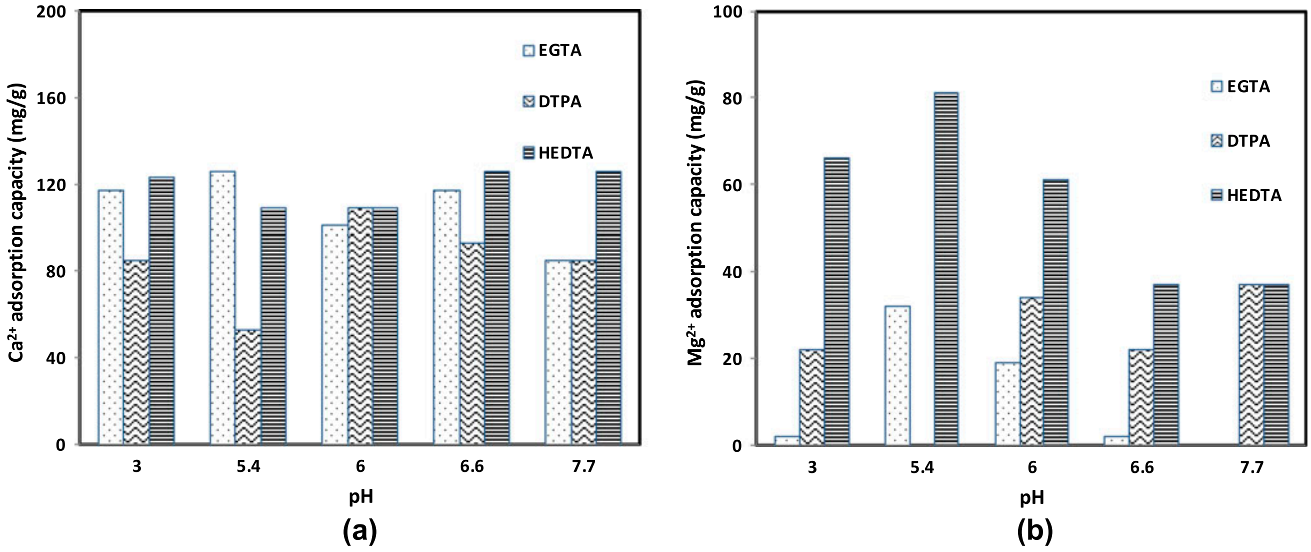

Fig. 2. Effect of pH on (a) Ca^{2+} and (b) Mg^{2+} adsorption from Red Sea using Group (I) chelating agents at a dose of 1 g/L.

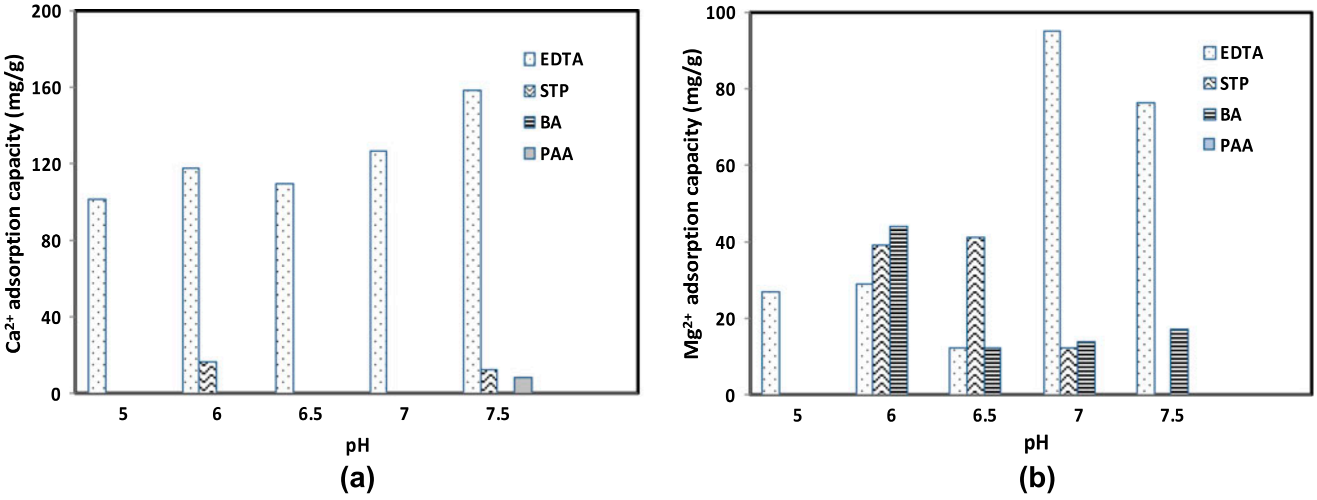

Fig. 3. Effect of pH on (a) Ca^{2+} and (b) Mg^{2+} adsorption from Red Seawater using group (II) chelating agents at a dose of 1 g/L.

with removal efficiencies of 23 and 0.7%, respectively. From the separation performance point of view, it is clear that EGTA achieved better selectivity for Ca^{2+} (highest Ca^{2+}- and lowest Mg^{2+}-loading capacities) than EDTA. On the other hand, EDTA exhibited the highest calcium and magnesium loadings (158 and 76 mg/g) at pH 7.5. It is also clear from the figure that EDTA capacity for adsorbing Ca^{2+} increases with increasing pH due to its successive deprotonation that yields more chelating ligands.

The values of pK_a shed light on the dissociation of target chelators; however, the dissociation behavior of these agents in seawater would differ due to the combined effect of high ionic strength, the presence of competing ions and variability in the compositions of seawater and brines. Sample calculations have been attempted to determine the amount of Ca^{2+} bound to EGTA. This chelating agent has been selected since it provided the highest Ca^{2+} and lowest Mg^{2+} adsorption. Calculations were performed using "Ca^{2+}-EGTA Calculator v1.3" using constants from Theo Schoenmakers' Chelator. The calculator uses the pK_a value of the chelator, pH, ionic strength, and molarity of calcium and the chelator to determine the amount of bound Ca^{2+} [32]. Values obtained were compared to the experimental results as shown in Fig. 4, and they were in good agreement.

3.3. *Effect of EGTA and EDTA doses on Ca^{2+} and Mg^{2+} adsorption from Red Seawater*

Fig. 5 represents the effect of chelating agent dose (1–4 g/L) on the Ca^{2+}(Fig. 5(a)) and Mg^{2+} (Fig. 5(b)) uptakes of two chelators selected for their high performance; EGTA from group (I) at pH 6.6 and EDTA from group (II) at pH 6.5 and 7.5. Data revealed that comparable calcium and magnesium adsorption capacities were achieved for group (I) at all the tested doses.

EGTA at a dose of 1 g/L achieved maximum and minimum adsorption capacities of 117 and 2 mg/g for Ca^{2+} and Mg^{2+}, respectively. The corresponding values for EDTA at pH 6.5 were 143 and 61 mg/g, respectively. In addition, EDTA exhibited the highest adsorption capacities of 158 and 76 mg/g, respectively for both Ca^{2+} and Mg^{2+} at pH 7.5.

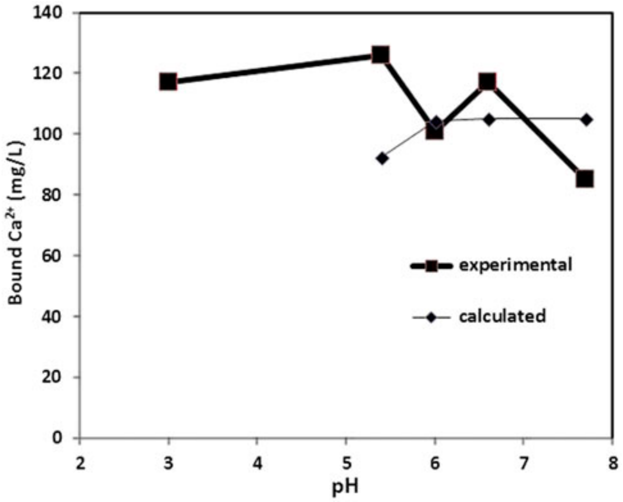

Fig. 4. Experimental and calculated bound Ca^{2+} using EGTA (1 g/L) at different pH values.

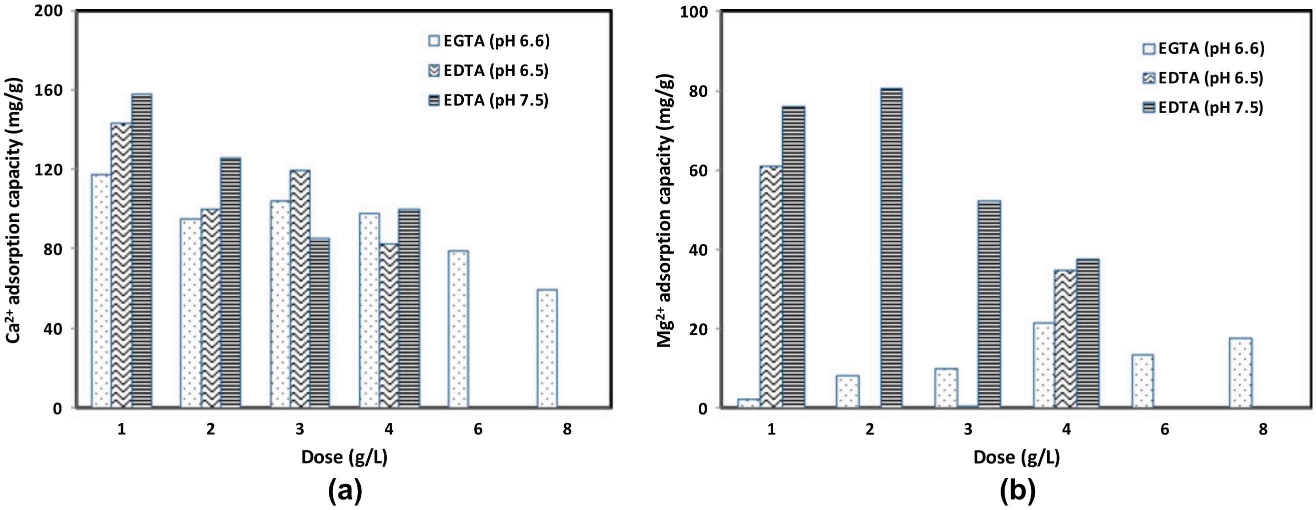

Fig. 5. Effect of EGTA and EDTA doses on (a) Ca^{2+} and (b) Mg^{2+} adsorption from Red Seawater at different pH values.

3.4. Effect of initial ion concentration

Fig. 6 illustrates the effect of Ca^{2+} and Mg^{2+} initial ion concentration on the adsorption using 1 g/L EGTA at pH 6.6 for a range of initial concentrations from 45 to 727 mg/L and from 152 to 2,444 mg/L for Ca^{2+} and Mg^{2+}, respectively.

It is clear that the adsorption capacities of both Ca^{2+} and Mg^{2+} ions increase with increasing initial ion concentration. Adsorption capacity of Ca^{2+} increased from 11.4 to 101 mg/g with increasing initial Ca^{2+} concentrations by about 16-fold (from 45.4 to 727 mg/L), whereas the adsorption capacity of Mg^{2+} increased from 14 to 36 mg/g with increasing initial Mg^{2+} concentrations by about 16-fold (from 152.7 to 2,443.5 mg/L). This manifests the selectivity of EGTA to calcium, a result consistent to that of Gosh et al. using polyethyleneimine (PEI) [16].

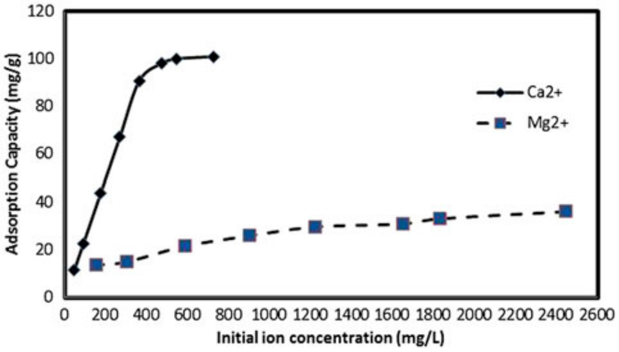

Fig. 6. Effect of initial Ca^{2+} and Mg^{2+} concentrations on adsorption capacities using 1 g/L EGTA at pH 6.6.

The increase in uptake capacity of EGTA with increasing initial ion concentration may be due to higher probability of collision between the metal ion and EGTA particles. The variation in the extent of sorption may also be due to the fact that initially all sites on the surface of EGTA were vacant and the metal ion concentration gradient was relatively high.

3.5. Adsorption isotherms

Sorption isotherms for the removal of Ca^{2+} and Mg^{2+} ions from saline solutions onto EGTA at pH 6.6 and 301 K are depicted in Fig. 7(a) and (b), respectively. Experimental data as well as data fitted by Langmuir, Freundlich, and Dubinin–Radushkviech (D–R) isotherm models are shown. The isotherms are regular, positive, and concave to the concentration axis for both ions.

The graphical representation of (C_e/q_e) vs. C_e yields straight lines for both Ca^{2+} and Mg^{2+} ions, as shown in Fig. 8(a) and (b), respectively, confirming a Langmuirian type behavior. The monolayer sorption capacity (q_m) values for Ca^{2+} ions onto EGTA are higher than those of Mg^{2+}.

Linear plots of Freundlich isotherms for Ca^{2+} and Mg^{2+} are depicted in Fig. 9(a) and (b), respectively. The figure suggests that only the sorption of Mg^{2+} ions follows Freundlich isotherm over the entire range of investigated sorption concentrations. It is also clear from the figure that the Freundlich intensity constant (n) is greater than unity for Mg^{2+} ions. This indicates an increase in tendency for sorption with increasing solid phase concentration [33,34]. Fig. 10(a) and (b) represent the linear D–R isotherm plots pertaining to

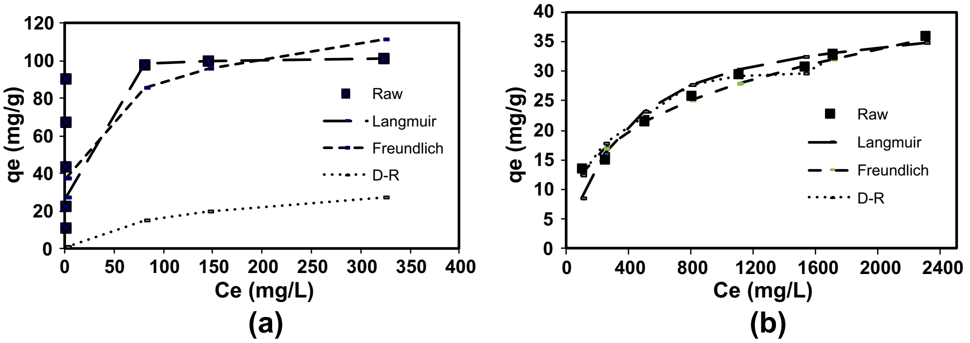

Fig. 7. Sorption isotherms of (a) Ca^{2+} and (b) Mg^{2+} ions onto EGTA at pH 6.6 and 301 K. The solid and dashed lines represent the fitted data by Langmuir, Freundlich, and D–R isotherm models.

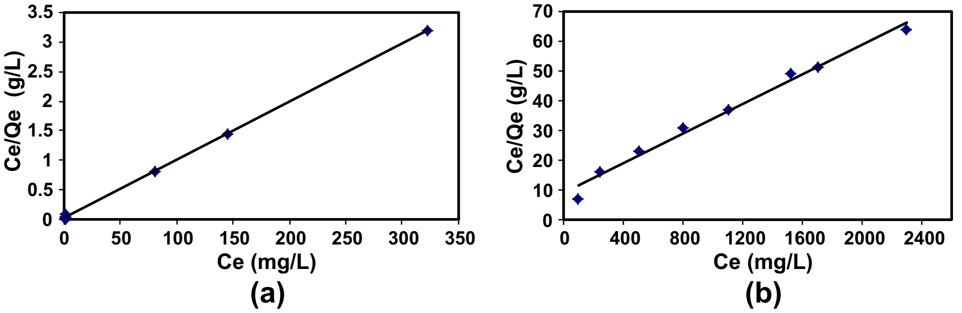

Fig. 8. Linear plots for Langmuir isotherms of (a) Ca^{2+} and (b) Mg^{2+} onto EGTA at pH 6.6 and 301 K.

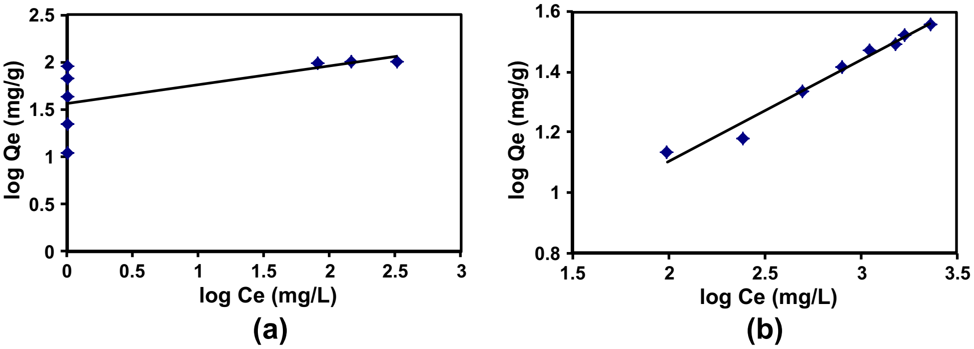

Fig. 9. Freundlich isotherm linear plots for the sorption of (a) Ca^{2+} and (b) Mg^{2+} onto EGTA at pH 6.6 and 301 K.

calcium and magnesium, respectively. As shown, only sorption of Mg^{2+} ions follows D–R isotherm over the entire range of employed sorption concentrations. Value of E calculated using Eq. (6) for magnesium is 8.84 kJ/ mol, indicating an endothermic nature of the adsorption process.

The numerical values for the different isotherm constants and R^2 values are given in Table 3. It is concluded that calcium and magnesium adsorption is best described by Langmuir isotherm indicating monolayer coverage of ions on the outer surface of EGTA.

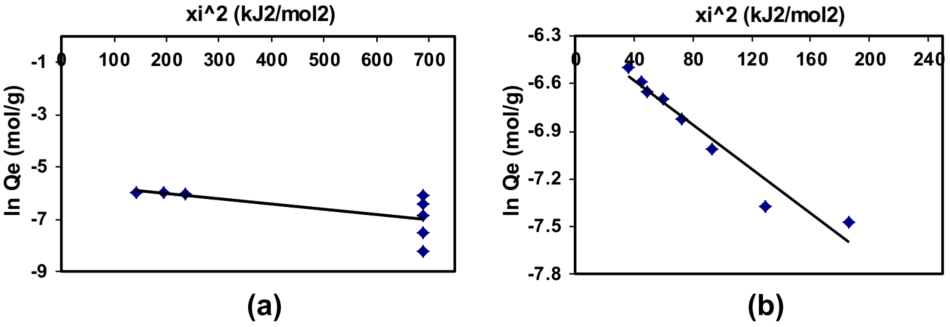

Fig. 10. D–R isotherm linear plots for the sorption of (a) Ca^{2+} and (b) Mg^{2+} onto EGTA at pH 6.6 and 301 K.

Table 3
Langmuir, Freundlich, and D–R isotherm parameters for the sorption of Ca^{2+} and Mg^{2+} onto EGTA at pH 6.6 and 301 K

Isotherm	Ca^{2+}	Mg^{2+}
Langmuir		
Q_m (mg/g)	102	40.3
B (L/g)	0.36	0.0027
R^2	0.9995	0.9853
Freundlich		
K_F ((mg/g)/(L/mg)^n)		2.754
n		3.03
R^2	0.39	0.97
D–R		
B		−0.0069
Q_m (mol/g)		0.001821 (43.7 mg/g)
E (kJ/mol)		8.51
R^2	0.393	0.94

4. Conclusions

This paper investigated the potential of using different types of chelating agents for Ca^{2+} and Mg^{2+} removal from saline solutions. Selected chelating agents, including EGTA, DTPA, HEDTA, EDTA, PAA, BA, and STP, were tested for softening of Red and Mediterranean Seawaters and RO brine. It was found that the maximum Ca^{2+}- and minimum Mg^{2+}-loading capacities (128 and 0 mg/g, respectively) were achieved using DTPA from Mediterranean Sea, as well as EGTA (117 and 2 mg/g, respectively) from Red Sea. Maximum Ca^{2+}- and Mg^{2+}-loading uptakes (153 mg/g and 72 mg/g, respectively) were attained for RO brine using EDTA. Adsorption from Red Seawater has been further investigated using the target-chelating agents to identify the effect of pH and chelating agent dose on the efficiency of chelation. Results revealed that EGTA-chelating agent at pH 6.6 and 3 and dose of (1 g/L) exhibited the highest Ca^{2+}-loading (117 mg/g) and lowest Mg^{2+}-loading (2 mg/g) capacities. Furthermore, EDTA exhibited the highest Ca^{2+}-loading (109 mg/g) and lowest Mg^{2+}-loading (12 mg/g) capacities at pH 6.5. In addition, EDTA exhibited the highest calcium and magnesium loadings (158 and 76 mg/g) from Red Seawater at pH 7.5. EGTA at a dose of (1 g/L) has proved to be the most suitable dose among the tested ones. Adsorption of Ca^{2+} and Mg^{2+} onto EGTA was best described by Langmuir isotherm, indicating monolayer coverage of ions on the outer surface of the chelating agent. In view of the above, both EDTA and EGTA could be potential candidates for softening saline solutions via a stand-alone separation process.

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