# Effect of Magnetic Treatment on Seawater Determined by Quartz Crystal Microbalance: Mechanisms of Crystal Deposition

**Fathi Alimi**
Department of Chemistry, College of Science, University of Ha'il, Saudi Arabia
f.alimi@uoh.edu.sa (corresponding author)

*Received: 14 April 2024 | Revised: 5 May 2024 | Accepted: 12 May 2024*

## ABSTRACT

**This study investigated the effect of a magnetic field on the crystal deposition of treated seawater to determine the mechanism of calcium carbonate deposition on the quartz surface. Several samples of standard seawater (43 g/L) were circulated through a permanent magnetic field of 0.16 T at a fixed temperature, pH, and flow rate. Scaling experiments showed that magnetic treatment of seawater enhanced the precipitation of calcium carbonate and that two superposed phases were deposited. A first layer formed with crystals of aragonite covering the whole surface of the quartz, and then a second phase of calcite was deposited. In the untreated solutions, only homogeneous agglomerates of aragonite were deposited.**

***Keywords-seawater; magnetic treatment; calcium carbonate; quartz crystal microbalance; deposition***

## I. INTRODUCTION

Magnetic treatment of water is an attractively simple approach in which the water to be treated flows through a magnetic field and consequently changes some of its physicochemical properties. The most claimed benefits are in the suppression or reduction of scale formation [1-9]. Until now, the efficiency of this treatment has been a controversial question without a clear explanation of the phenomenon. Previous studies have shown that the field strength, composition, and flow velocity of water have significant effects on scaling rate [1, 10-13]. The investigations on the influence of the magnetic field on scaling focused mainly on the process of nucleation and/or crystallization of $CaCO_3$, the crystal structure of $CaCO_3$ [14-17], the stability of colloidal aqueous dispersions [18], the change of the zeta potential of the colloidal particles [15, 16] and the physicochemical properties of water or its solutions [10-11]. Magnetic treatment of calcocarbonic water increases its precipitation potential. This effect is more pronounced for homogeneous nucleation than for heterogeneous nucleation [1]. However, the magnetic treatment of water is strongly dependent on the physicochemical properties of the pipe material [5] and on the composition of the treated water [4]. However, only a few experimental and theoretical investigations can be found on saline water treatment [19-23] and the effect of magnetic treatment on seawater [24-26].

In [24], it was shown that passing seawater solutions through a permanent magnetic device increased their conductivity and pH, enhancing the separation of salt from water by reverse osmosis. In [25], a new method was proposed to intensify the production of drinking water from seawater in a membrane distillation system. For this purpose, the feed water passed through a strong magnetic field and then entered the membrane unit. As the strength of the magnetic field increased, the size and rate of the scale particles formed in the complete solution increased, but the analysis showed that the accumulation on the membrane surface decreased because of the magnetic treatment. In [26], it was deduced that magnetic brine treatment causes various changes in the treated water, such as a weakening of hydrogen bonds between water and dissolved ions, which simplifies the separation process. This study aimed to systematically investigate the mechanisms of crystal deposition from synthetic seawater treated through a magnetic device, using Quartz Crystal Microbalance (QCM) to trace the adhesion of formed crystals (calcium carbonate) on the solid surface. The mechanisms of adhesion (scale formation) on the solid surface during the precipitation and transformation of calcium carbonate were determined.

## II. EXPERIMENTS

Considering the complexity of the real seawater, this study used standard seawater, as described in ASTM D1141 and given in Table I.

TABLE I. COMPOSITION OF THE SYNTHETIC SEAWATER

| **$NaCl$ (g/L)** | **$Na_2SO_4$ (g/L)** | **$MgCl_2 \cdot 6H_2O$ (g/L)** | **$CaCl_2 \cdot 2H_2O$ (g/L)** | **$KCl$ (g/L)** | **$NaHCO_3$ (g/L)** |
|---|---|---|---|---|---|
| 24.544 | 4.0907 | 11.1007 | 1.5437 | 0.6948 | 0.2345 |

Synthetic seawater was prepared in the laboratory as follows:

- Solution 1: 24.5448 g NaCl and 4.0907 g $Na_2SO_4$ dissolved in 0.8 L of pure water.
- Solution 2: 11.1007 g $MgCl_2 \cdot 6H_2O$ and 1.5437 g $CaCl_2 \cdot 2H_2O$ dissolved in 0.05 L of pure water,
- Solution 3: 0.6948 g KCl and 0.2345 g $NaHCO_3$ in 0.05 L of ultra-pure water.

Stirring was performed during the dissolution of the different salts. The mixing process started by mixing solutions 1 and 2 before adding solution 3 and making up to 1 L. The pH was subsequently adjusted to 8.2 with a few drops of NaOH (2N). The prepared seawater had an ionic strength of 0.7 $mol.L^{-1}$. Standard seawater adjusted at pH = 8.2 was kept at ambient temperature in a separate tank and circulated by a pump through a 0.16 T magnetic device in a Tygon pipe for 30 minutes. The magnetic field was the same as that described in [1]. The conductivity and pH values were recorded every 5 minutes. The same test was conducted in the absence of the magnetic device. There were no significant differences in the pH and conductivity of the circulated seawater solutions. Once magnetically treated, standard seawater was put in a reservoir and the scaling power of the treated water was evaluated using an electrochemical test. The magnetic treatment was carried out by inserting the pipe into the air gap of a group of alternating permanent magnets (opposite north-south poles) for a specific time. The seawater to be treated was circulated in a Tygon pipe with an internal diameter of 7 mm using a variable-speed circulation pump, as shown in Figure 1. The Tygon used was a Tygon R3603, which is a PVC plasticized with 51% phthalate by mass (the phthalate used was di-2-ethylhexyl known as DEHP). Phthalates are additives commonly used in plastics and other materials, primarily to make them soft and flexible. They have a hydrophobic character under normal conditions, which makes the surface of Tygon also hydrophobic.

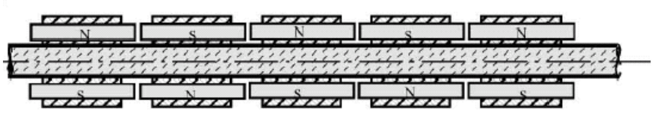

Fig. 1. The magnetic device used for the treatment of seawater.

For electrochemical tests, shown in Figure 2, a SOTELEM-VINCI potentiostat was used in connection with an ammeter to plot the chronoamperometric curves. A 6 MHz quartz crystal microbalance was used. All experimental setup was computer-controlled. The current passing through the electrode and the frequency of the microbalance were measured simultaneously during the calcareous deposition, while the electrode was polarized at the diffusion-limiting current of the oxygen reduction (-1 V). The reduction of oxygen increased the pH at the electrode, which caused calcium carbonate to precipitate on it. Mass transport was controlled using an impinging jet cell with a flow of 0.95 L/min. Figure 3 shows the jet cell and the schematic of the working electrode. The deposited mass was recorded over time (chronoelectrogravimetric curve). The comparison of the quantities of deposited mass allows the scaling power of the water to be assessed by evaluating the scaling time and the nucleation time. The nucleation time was defined when the mass neatly increased after some delay. The characterization of the calcium carbonate crystals adhered to the gold surface after the electrochemical test was performed using a Scanning Electron Microscope (SEM) and X-Ray powder Diffraction (XRD).

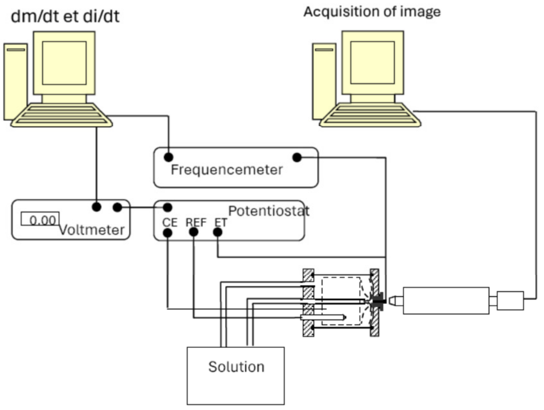

Fig. 2. Experimental setup of the electrochemical tests.

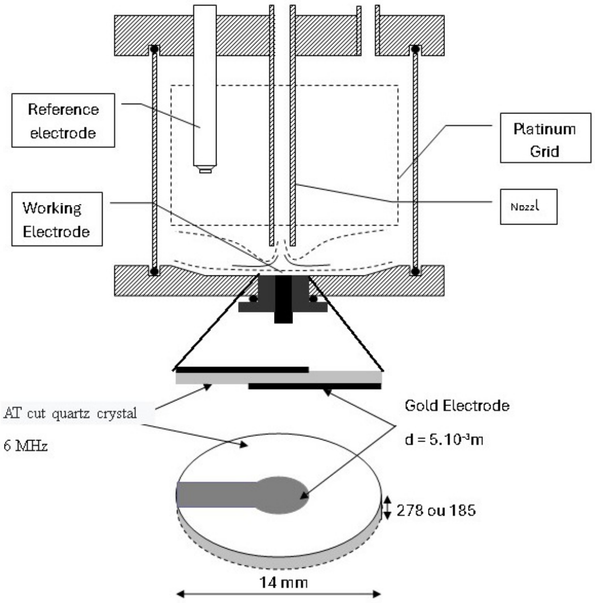

Fig. 3. Cell jet and working electrode.

## III. RESULTS AND DISCUSSION

The scaling power of standard seawater, treated and untreated through the magnetic device, was examined. Figure 4 shows the chronoelectrogravimetric curves recorded. Various characteristic parameters concerning the scale formation, in the presence or not of a magnetic device, such as the mass, rate, and time of scale, were obtained. These curves show that the application of magnetic treatment to standard seawater had a significant effect on the kinetics of crystal deposition. This magnetic treatment increased the nucleation time of calcium carbonate from 7.5 to 12 hours and the scaling time from 19 to 23 hours.

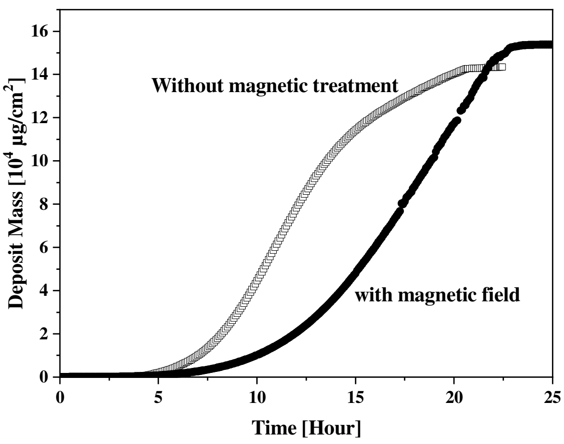

Fig. 4. Amount of adhesion against time.

The adhesion rate of the crystal formed on the surface of the quartz increased from $1.4\times10^{-3}$ µg.cm$^{-2}$h$^{-1}$ for untreated seawater to $1.6\times10^{-3}$ µg.cm$^{-2}$h$^{-1}$ with the application of the magnetic field. The number of adhered particles shows a significant variation. These results were confirmed by observing precipitation on the solid surface by SEM images. Figure 5 shows some selected scanning electron micrographs of crystals disposed on the quartz surface. Figures 5(a,b) present the SEM images of seawater with magnetic treatment after 23 h. In this case, it was observed that two superposed phases were deposited. During the first stage of electrodeposition, a thick homogeneous stable layer of aragonite crystals formed, with an average crystal size of needle-like shapes of 1.4 × 1 µm.

The second phase was deposited on the first layer, where the predominant polymorph was calcite with a rhombohedra shape (50 µm). The presence of the two polymorphs was confirmed by XRD examination of the deposits. Figure 5(c,d) shows the SEM images obtained for the electrode surface without magnetic treatment. Most of the quartz surface is not covered by the $CaCO_3$ precipitate and is still free. The totality polymorph is aragonite, as observed in [27, 28]. The adhered crystals grew as homogeneous aragonite agglomerates to an average size of 100 µm after 20 hours. These agglomerates were well separated. This effect is because when calcium carbonate is precipitated from seawater, the formation of aragonite alone is favored because of the strong influence of the magnesium in the water on the polymorphic crystallization of calcium carbonate. In the absence of magnesium, only calcite was formed [29].

The presence of a magnetic field increases the mass and the total number of crystals formed. However, the average size of the crystals is found to be small due to the impact of the field. This effect can be caused by the weakening of the hydrogen bonds between water and dissolved ions. The changes in the kinetics of calcium carbonate deposition and its morphology could be due to physical alteration, such as clustering or nucleation of certain types of ions and particulates formed from the treatment step and subsequently adhered to the gold surface by the electrochemical process.

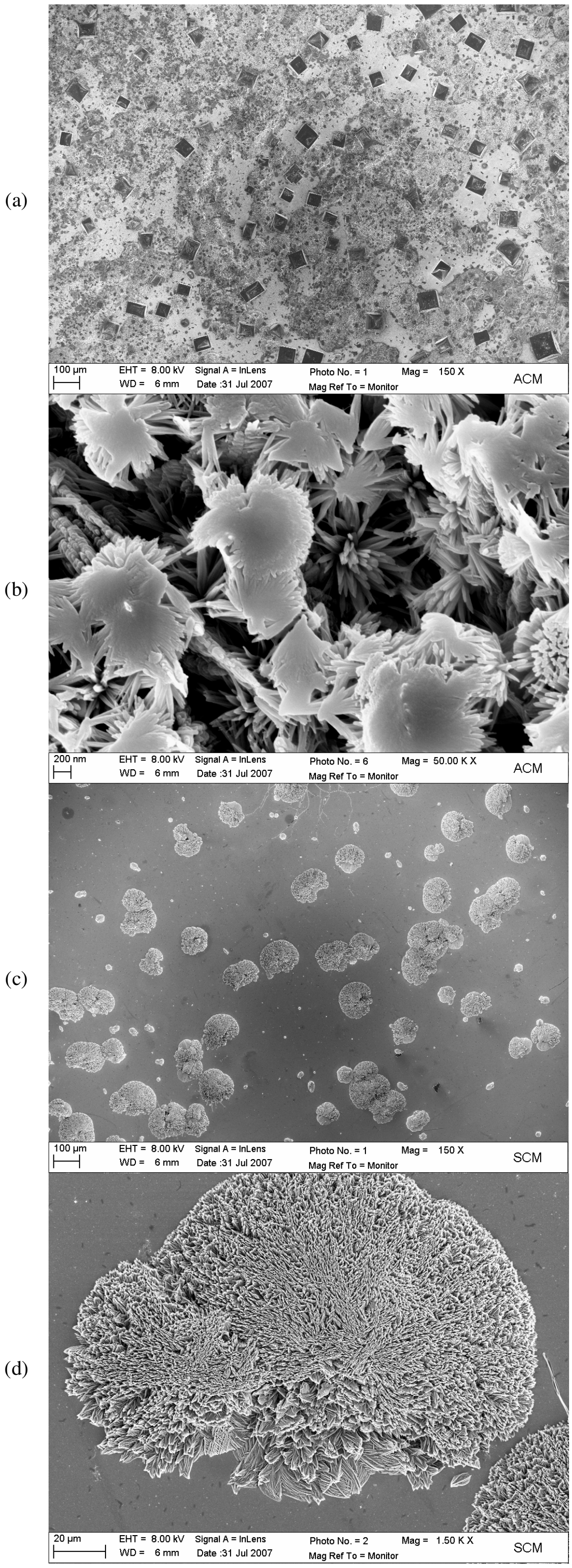

Fig. 5. SEM pictures of the solid surface: (a) with magnetic treatment, two layers, (b) with magnetic treatment, the first layer deposited, (c) without magnetic treatment, magnification 1, (d) without magnetic treatment, magnification 2.

From the formation of two superposed layers observed, it can be postulated that different forms of $CaCO_3$ clusters exist in the supersaturated solution after the application of a magnetic field. Thus, calcite was deposited on the aragonite layer because the clusters favorable for the calcite were not adsorbed by the crystal surface as those of the aragonite.

These observations were confirmed by the XRD spectrum for the calcium carbonate formed with and without magnetic treatment, shown in Figure 6.

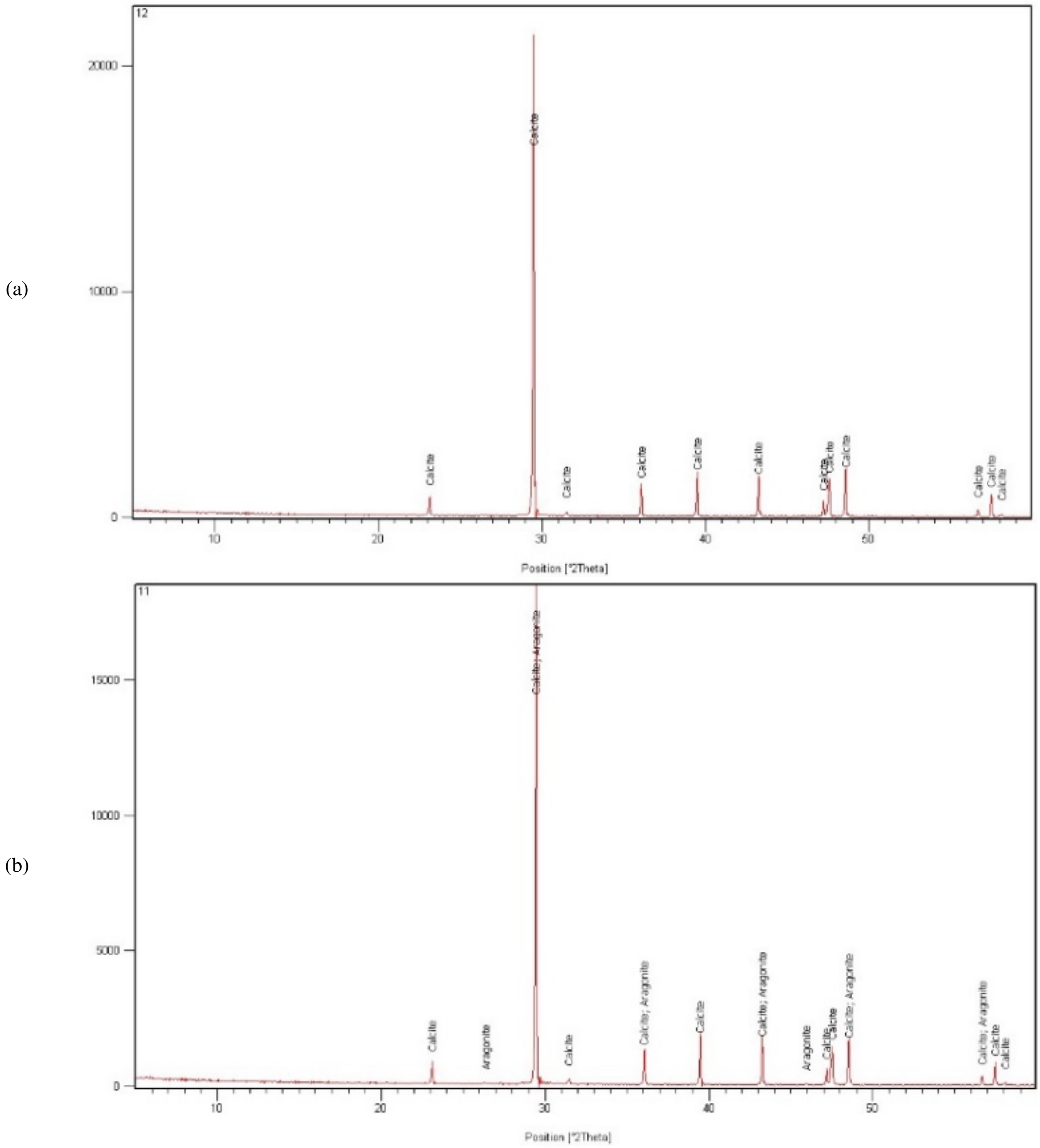

Fig. 6. XRD spectra of $CaCO_3$ formed (a) without magnetic treatment and (b) with magnetic treatment.

## IV. CONCLUSIONS

In summary, this study came to the following conclusions:

- The nucleation time and the amount of scale were affected by the application of the magnetic field.
- $CACO_3$ was formed in the presence and absence of a magnetic device.
- The adhesion rate and morphology of $CaCO_3$ on the surface were particularly influenced by the magnetic field.
- In the absence of a magnetic field, the adhesion of $CaCO_3$ on the solid surface was not homogeneous across it, and only agglomerates of aragonite formed.
- With magnetic treatment, the main adhesion process was the direct growth of aragonite on the surface, on which a second phase of calcite was deposited. The surface was entirely covered by the aragonite layer.

## REFERENCES

[1] A. Fathi, T. Mohamed, G. Claude, G. Maurin, and B. A. Mohamed, "Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate," *Water Research*, vol. 40, no. 10, pp. 1941–1950, Jun. 2006, https://doi.org/10.1016/j.watres.2006.03.013.

[2] F. Alimi, A. Boubakri, M. M. Tlili, and M. Ben Amor, "A comprehensive factorial design study of variables affecting $CaCO_3$ scaling under magnetic water treatment," *Water Science and Technology*, vol. 70, no. 8, pp. 1355–1362, Sep. 2014, https://doi.org/10.2166/wst.2014.377.

[3] F. Alimi, M. Tlili, M. Ben Amor, C. Gabrielli, and G. Maurin, "Influence of magnetic field on calcium carbonate precipitation," *Desalination*, vol. 206, no. 1, pp. 163–168, Feb. 2007, https://doi.org/10.1016/j.desal.2006.02.064.

[4] F. Alimi, M. Tlili, M. Ben Amor, G. Maurin, and C. Gabrielli, "Influence of magnetic field on calcium carbonate precipitation in the presence of foreign ions," *Surface Engineering and Applied Electrochemistry*, vol. 45, no. 1, pp. 56–62, Feb. 2009, https://doi.org/10.3103/S1068375509010104.

[5] F. Alimi, M. M. Tlili, M. B. Amor, G. Maurin, and C. Gabrielli, "Effect of magnetic water treatment on calcium carbonate precipitation: Influence of the pipe material," *Chemical Engineering and Processing: Process Intensification*, vol. 48, no. 8, pp. 1327–1332, Aug. 2009, https://doi.org/10.1016/j.cep.2009.06.008.

[6] C. Y. Tai, M. C. Chang, R. J. Shieh, and T. G. Chen, "Magnetic effects on crystal growth rate of calcite in a constant-composition environment," *Journal of Crystal Growth*, vol. 310, no. 15, pp. 3690–3697, Jul. 2008, https://doi.org/10.1016/j.jcrysgro.2008.05.024.

[7] E. Chibowski and A. Szcześ, "Magnetic water treatment–A review of the latest approaches," *Chemosphere*, vol. 203, pp. 54–67, Jul. 2018, https://doi.org/10.1016/j.chemosphere.2018.03.160.

[8] Y. Liang, Y. Xu, M. Jia, and J. Wang, "Experimental study on the influence of an alternating magnetic field on the CaCO3 fouling of a heat transfer surface," *International Journal of Heat and Mass Transfer*, vol. 183, Feb. 2022, Art. no. 122156, https://doi.org/10.1016/j.ijheatmasstransfer.2021.122156.

[9] A. S. Kote and D. V. Wadkar, "Modeling of Chlorine and Coagulant Dose in a Water Treatment Plant by Artificial Neural Networks," *Engineering, Technology & Applied Science Research*, vol. 9, no. 3, pp. 4176–4181, Jun. 2019, https://doi.org/10.48084/etasr.2725.

[10] L. Hołysz, M. Chibowski, and E. Chibowski, "Time-dependent changes of zeta potential and other parameters of in situ calcium carbonate due to magnetic field treatment," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 208, no. 1, pp. 231–240, Aug. 2002, https://doi.org/10.1016/S0927-7757(02)00149-8.

[11] M. O. Karkush, M. D. Ahmed, and S. M. A. Al-Ani, "Magnetic Field Influence on The Properties of Water Treated by Reverse Osmosis," *Engineering, Technology & Applied Science Research*, vol. 9, no. 4, pp. 4433–4439, Aug. 2019, https://doi.org/10.48084/etasr.2855.

[12] C. Y. Tai, C. K. Wu, and M. C. Chang, "Effects of magnetic field on the crystallization of CaCO3 using permanent magnets," *Chemical Engineering Science*, vol. 63, no. 23, pp. 5606–5612, Dec. 2008, https://doi.org/10.1016/j.ces.2008.08.004.

[13] C. Gabrielli, R. Jaouhari, G. Maurin, and M. Keddam, "Magnetic water treatment for scale prevention," *Water Research*, vol. 35, no. 13, pp. 3249–3259, Sep. 2001, https://doi.org/10.1016/S0043-1354(01)00010-0.

[14] K. Higashitani, A. Kage, S. Katamura, K. Imai, and S. Hatade, "Effects of a Magnetic Field on the Formation of CaCO3 Particles," *Journal of Colloid and Interface Science*, vol. 156, no. 1, pp. 90–95, Mar. 1993, https://doi.org/10.1006/jcis.1993.1085.

[15] M. Colic and D. Morse, "Mechanism of the Long-Term Effects of Electromagnetic Radiation on Solutions and Suspended Colloids," *Langmuir*, vol. 14, no. 4, pp. 783–787, Feb. 1998, https://doi.org/10.1021/la970979a.

[16] M. Colic and D. Morse, "Effects of Amplitude of the Radiofrequency Electromagnetic Radiation on Aqueous Suspensions and Solutions," *Journal of Colloid and Interface Science*, vol. 200, no. 2, pp. 265–272, Apr. 1998, https://doi.org/10.1006/jcis.1997.5367.

[17] J. S. Baker and S. J. Judd, "Magnetic amelioration of scale formation," *Water Research*, vol. 30, no. 2, pp. 247–260, Feb. 1996, https://doi.org/10.1016/0043-1354(95)00184-0.

[18] E. Chibowski, L. Hołysz, A. Szcześ, and M. Chibowski, "Precipitation of calcium carbonate from magnetically treated sodium carbonate solution," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 225, no. 1, pp. 63–73, Sep. 2003, https://doi.org/10.1016/S0927-7757(03)00133-X.

[19] F. B. Mainier, A. M. Coelho, and E. F. Barros, "Corrosivity Evaluation of Copper-Nickel Alloy (90/10) in Pumps Used in Offshore Platforms for Seawater Pumping," *Engineering, Technology & Applied Science Research*, vol. 9, no. 5, pp. 4636–4639, Oct. 2019, https://doi.org/10.48084/etasr.3016.

[20] H. A. Maddah, "Predicting Flux Rates against Pressure via Solution-Diffusion in Reverse Osmosis Membranes," *Engineering, Technology & Applied Science Research*, vol. 11, no. 2, pp. 6902–6906, Apr. 2021, https://doi.org/10.48084/etasr.4059.

[21] A. A. Mahessar, A. N. Laghari, S. Qureshi, I. A. Siming, A. L. Qureshi, and F. A. Shaikh, "Environmental Impact Assessment of the Tidal Link Failure and Sea Intrusion on Ramsar Site No. 1069," *Engineering, Technology & Applied Science Research*, vol. 9, no. 3, pp. 4148–4153, Jun. 2019, https://doi.org/10.48084/etasr.2686.

[22] M. ben Mosbah, A. K. D. Alsukaibi, L. Mechi, F. Alimi, and Y. Moussaoui, "Ecological Synthesis of CuO Nanoparticles Using Punica granatum L. Peel Extract for the Retention of Methyl Green," *Water*, vol. 14, no. 9, Jan. 2022, Art. no. 1509, https://doi.org/10.3390/w14091509.

[23] I. M'barek *et al.*, "Cellulose from *Tamarix aphylla*'s stem via acetocell for cadmium adsorption," *Arabian Journal of Chemistry*, vol. 15, no. 3, Mar. 2022, Art. no. 103679, https://doi.org/10.1016/j.arabjc.2021.103679.

[24] H. Al-Qahtani, "Effect of magnetic treatment on Gulf seawater," *Desalination*, vol. 107, no. 1, pp. 75–81, Sep. 1996, https://doi.org/10.1016/0011-9164(96)00152-X.

[25] A. Kargari and A. Yousefi, "Process intensification through magnetic treatment of seawater for production of drinking water by membrane distillation process: A novel approach for commercialization membrane distillation process," *Chemical Engineering and Processing - Process Intensification*, vol. 167, Oct. 2021, Art. no. 108543, https://doi.org/10.1016/j.cep.2021.108543.

[26] A. A. Alwan, S. Ahmed, A. Nwokoye, A. A. Alhendi, O. Ibrahim, and E. Alhseinat, "Recent advances in the application of magnetic/electromagnetic field for water desalination," in *Current Trends and Future Developments on (Bio-) Membranes*, A. Basile and E. P. Favvas, Eds. Elsevier, 2024, pp. 427–459.

[27] A. Neville and A. P. Morizot, "A combined bulk chemistry/electrochemical approach to study the precipitation, deposition and inhibition of CaCO3," *Chemical Engineering Science*, vol. 55, no. 20, pp. 4737–4743, Oct. 2000, https://doi.org/10.1016/S0009-2509(00)00046-4.

[28] Ch. Barchiche *et al.*, "Characterization of calcareous deposits in artificial seawater by impedance techniques: 3-Deposit of CaCO3 in the presence of Mg(II)," *Electrochimica Acta*, vol. 48, no. 12, pp. 1645–1654, May 2003, https://doi.org/10.1016/S0013-4686(03)00075-6.

[29] C. Deslouis, D. Festy, O. Gil, G. Rius, S. Touzain, and B. Tribollet, "Characterization of calcareous deposits in artificial sea water by impedance techniques—I. Deposit of CaCO3 without Mg(OH)2," *Electrochimica Acta*, vol. 43, no. 12, pp. 1891–1901, May 1998, https://doi.org/10.1016/S0013-4686(97)00303-4.