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Process Optimization on Brine Pre-treatment to Enhance Magnesium and Calcium Recovery

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Membrane technologies have been recently used for brine management following the Zero Liquid Discharge approach. However, the main challenge about these technologies is fouling from inorganic and organic matters which limits membrane efficiency. Thus, pre-treatment is required to remove scaling ions to enhance environmental and economic performance of membranes. In addition, pre-treatment can present opportunities for resource recovery such as nutrients (e.g. Magnesium) for further reuse in different industrial sectors. In this study, possible effects of thermal and chemical pre-treatments on seawater brine were investigated to both remove scaling compound and recover nutrients. Lab-scale tests were performed to optimize the selective precipitation of Ca^{2+} and Mg^{2+} from brine. Chemical precipitation was initially conducted with NaOH at different dosages (from 4.5 to 18 mL/L). Further, chemical coagulation was tested using Aluminium Sulphate and PolyAluminium Chloride (PAC) at concentration of 3 g/L. The addition of an anionic flocculant (between 7 - 21 mg/L) was also evaluated for further improvements in the precipitation process. Finally, thermal pre-treatment was performed, focusing on the effect of pH and temperature on the Ca^{2+} and Mg^{2+} concentration as well as on other main anions and cations. Tests were further upscaled in the demonstrative environment to optimise operating temperature and pressure conditions (110 - 150 °C and P_{Atm}, -0.3 and -0.4 bar vacuum). The results showed that Mg^{2+} and Ca^{2+} recovery increased with increasing NaOH dosage, while increments were less than proportional compared to the dosage increase. Thus, the best recovery rates were considered at 9 mL NaOH/L with yields up to 69 % of Mg^{2+} and 60 % of Ca^{2+}. Following the PAC addition and the highest pre-dosed NaOH, no remarkable improvement was detected even when the flocculant was added. From the lab-scale evaporation tests, the results indicated that the temperature was more effective on ions concentrations than the pH of brine samples since a higher variation in ion concentration was detected between evaporations at 40 °C, 60 °C and 100 °C. Finally, at pilot scale, temperature was found to be a more effective parameter than pressure in terms of evaporation yield. The highest evaporation yield was achieved for the evaporation at 150 °C with vacuum of -0.4 bar. This test led to an evaporation time reduction of 30 % compared to evaporation at atmospheric pressure, with Mg^{2+} and Ca^{2+} recovery rates up to about 95 % and 55 %, respectively.

1. Introduction

Nowadays, water scarcity has become a critical issue to tackle in several Mediterranean countries, particularly in the Southern Mediterranean region where the economy is strictly related to water resources. Specifically, in coastal areas around 180 million people face water stress with less than 1000 m^3/y/p available, while 80 million people can count on less than 500 m^3/y/p. Moreover, water-related problems can become even more intense when considering an expected reduction in average precipitation of about 10 to 25 % in summer and 10 to 60 % in spring by the end of the century (Khordagui, 2014). This water stress is progressively underlining the need to implement innovative technologies for closing the water loop and thus using alternative sources (e.g. drinking water from seawater) (Mavukkandy et al., 2019) as a sustainable water resource. Thus, seawater desalination may represent a valuable and economically viable option to provide safe drinking water from alternative water resources. In terms of technologies, reverse osmosis represents the most diffuse desalination treatment, ranging average water recovery rates up to 40 - 55 %. Rejected water (the remaining 45 - 60 %) is then discharged as "brine" (Panagopoulos et al., 2019), which is commonly disposed as waste flow. However, brine disposal into surface water cannot be considered a sustainable brine management option anymore, as it can negatively affect the water quality in terms of alkalinity, salinity and average temperature. Furthermore, the more stringent prescriptions on discharge quality standards highlighted the need to adopt appropriate brine management methods, which involve zero or minimized volume to be disposed. In this context, the Zero Liquid Discharge (ZLD) or Minimal Liquid Discharge (MLD) approaches promote the reduction of brines to be disposed while providing high-quality freshwater and supporting resource recovery.

To embrace these approaches, different solutions can be implemented such as membrane-based technologies (e.g. reverse osmosis, forward osmosis, nanofiltration, electrodialysis etc.) and thermal-based treatments (e.g. multi-effect/stage distillation, brine concentrator/crystallizer, spray dryer etc.). However, the selection of the most appropriate solution must be evaluated by considering operating conditions (e.g. the salinity of the brine to be treated) which can influence the performance of selected technology (Panagopoulos and Haralambous, 2020). Concerning membrane-based technologies, these systems can recover high quality water with relatively low energy demand (Panagopoulos, 2020) in all these cases when low-salinity influent is fed. In fact, when high-salinity brine is treated, inorganic (scaling) and/or organic fouling can negatively affect the membrane efficiency (Semblante et al., 2018). Meanwhile, thermal-based technologies are usually characterized by higher energy consumption (compared to membrane-based solutions) (Son et al., 2020), which are often needed to remove precursor ions and possible organic foulants from brine to optimize performance of the downstream membrane technologies. However, pre-treatment methods can also be implemented to selectively remove precursor ions for fouling reduction, such as chemical precipitation of Ca^{2+} (Semblante et al., 2018). Recently, great importance is also detected in recover resources from brine, such as magnesium, not only due to its relevant value as critical raw material, but also because of the growing demand in the global market (Cipollina et al., 2014). Given the importance to handle not only the waste disposal reduction, but also the need to achieve circularity objectives in the brine sector, further efforts need to be made in assessing proper integrated systems (e.g. chemical/thermal pre-treatment coupled with membrane-based treatment) for delivering resource recovery and ZLD. Thus, in this study possible chemical and thermal pre-treatment methods to achieve both scaling ion removal and nutrient recovery from brine were investigated.

2. Materials and methods

In the first phase of the experimental activities, lab-scale tests were conducted to optimize the selective precipitation of Ca^{2+} and Mg^{2+}. Seawater desalination brine was obtained from the Capraia desalination plant (Tuscany, Italy). The average characterization of the main ions in the raw brine is reported in Table 1. Ion Chromatography was used to determine anions and cations with DX-120 and ICS-1000, respectively. pH was measured with Hannah "Edge" portable pH-meter provided with HI2300 pH electrode. In table 1, the raw brine characterization is reported and used as references for the removal percentages calculations.

Table 1: Average characterization of the raw brine

Sample	pH	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
	-	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Raw Brine	7.5	26193 ± 42	2793 ± 32	14713 ± 87	617 ± 113	2271 ± 471	1576 ± 776

Dosage intervals for each chemical and operating test condition were established according to the literature data (Ordo´n˜ez et al., 2012). Chemical precipitation was conducted in a jar test equipment by the addition of different dosages of NaOH at 30 % w/v, from 4.5 to 18 mL per litre of brine. Samples were rapidly stirred for 2 min and then slowly mixed for 15 min at room temperature (Dong et al., 2018). Then, a settling period was maintained until a complete phase separation was observed. Main parameters such as pH and conductivity were monitored before and after the addition of NaOH together with the settling capacity. Further, the settling velocity of the precipitate was evaluated.

Chemical coagulation and flocculation were latter performed at room temperature (Azadi Aghdam et al., 2016), for a possible improvement in settling velocity and Mg^{2+} and Ca^{2+} recovery. Specifically, Aluminium Sulphate ($Al_2(SO_4)_3 \cdot 16H_2O$) and PolyAluminium Chloride (PAC) coagulants were separately dosed at a concentration of 3 g/L (Ho et al., 2015), while anionic flocculant (IDRAPOL A) was added at varying concentrations between 7 - 21 mg/L. Specifically, PAC and $Al_2(SO_4)_3 \cdot 16H_2O$ coagulants were dosed to reach the same Al^{3+} equivalent concentration in the batch tests. For coagulation and flocculation, the samples were initially rapidly mixed for 2 min when the coagulant was added and followed by 15 min of slow stirring after the flocculant addition (Yang et al., 2007). Finally, the settling phase was monitored. All the chemical precipitation tests were carried out at room temperature. "TESCAN VEGA3 LMU" Scanning Electron Microscope (SEM) was used to detect Mg^{2+} and Ca^{2+} inside the precipitates.

In thermal-based processes, preliminary batch evaporation tests were performed at the lab-scale using a rotary evaporator equipped with vacuum and manometer to ensure monitor evaporation condition. 500 mL of raw brine samples were evaporated for 30 minutes. Different temperature (i.e. 40, 60 and 100 °C) and pH (i.e. 7.5, 8, 9 and 10) conditions were tested at the vacuum condition of -0.55 bar. pH was adjusted by adding NaOH solution (30 % w/v) to the raw brine. The effect of pH and temperature on the Ca^{2+} and Mg^{2+} concentration as well as on the other ions (e.g. Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}) were further analysed. The evaporation tests were further scaled-up and tested at pilot scale in the wastewater treatment plant (WWTP) of Falconara Marittima (Italy) to optimise operating conditions using a 30 L "Formeco DiQ 20 AX" evaporation system at the temperatures ranging from 110 °C and 150 °C and at different pressure conditions (i.e. atmospheric pressure, vacuum at -0.3 and -0.4 bar). The batch tests were performed with 15 L of raw brine. A summary of the tests is reported in Table 2.

Table 2: Summary of experimental operative conditions on raw brine

Chemical Tests	Unit	1	2	3	4	5	6	7	8	9	10	11
Scale	-	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
NaOH	mL/L	4.5	9	13.5	18	9	13.5	18	18	18	18	18
PAC	g/L	-	-	-	-	-	-	-	3	-	-	-
$Al_2(SO_4)_3$•$16H_2O$	mL/L	-	-	-	-	3	3	3	-	3	3	3
IDRAFLOC	mg/L	-	-	-	-	7	7	7	7	0	14	21

Thermal Tests	Unit	1	2	3	4	5	6	7	8	9
Scale	-	Lab	Lab	Lab	Lab	Lab	Pilot	Pilot	Pilot	Pilot
pH	-	9	10	9	10	9	7.5	7.5	7.5	7.5
Temperature	°C	60	60	100	100	40	150	150	150	110
Pressure	bar	-0.55	-0.55	-0.55	-0.55	-0.55	1	-0.3	-0.4	-0.4

3. Results and discussion

3.1 Chemical Tests

Results from tests 1 – 4 showed that Mg^{2+} precipitation increased with the increasing NaOH concentration up to 98 %. As shown in Figure 1, the first dosage of 4.5 mL/L NaOH resulted in a minimal precipitation of the Ca^{2+} and Mg^{2+} as hydroxide (Quintero et al., 2020). This was mainly due to the increase of pH of the solution from 7.5 to 10.1, with the consequent reduction of hydroxyls available for the precipitation of cations. However, when the NaOH dosage increased (from 4.5 to 9.0 mL/L), a considerably increase in the Mg^{2+} and Ca^{2+} recovery rates was detected up to 89 % and 79 % respectively, compared to the lowest dosage. From this point, different removal trends were obtained for the two cations with the increment of NaOH dosage. Specifically, Ca^{2+} reached a plateau with the highest precipitation at 61 %, achieved at 18 $mL_{NaOH}/L_{rawbrine}$, while Mg^{2+} precipitation continued increasing. However, the increase of Mg^{2+} recovery was less than proportional compared to the increment of the dosage (achieved by doubling the NaOH from 9 to 18 mL/L). This was most probably due to higher Mg^{2+} concentration in the raw brine.

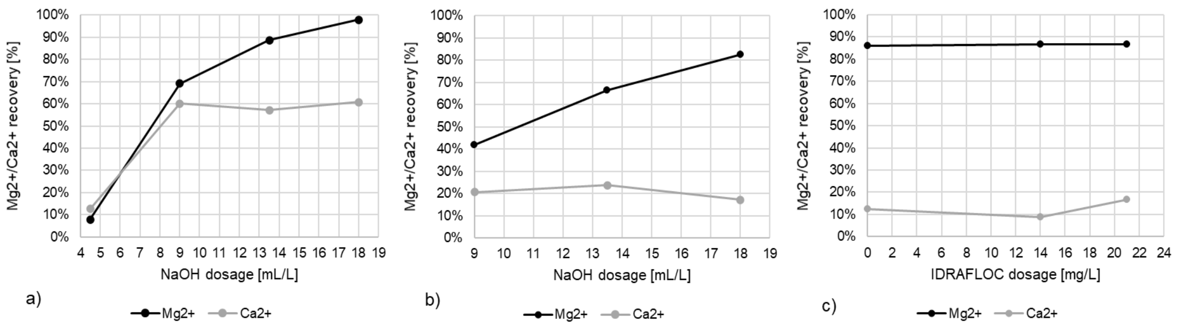

Figure 1: Magnesium and Calcium recovery rates with a) different dosages of NaOH; b)different dosages of NaOH, 3 g/L $Al_2(SO_4)_3$•$16H_2O$ and 7 mg/L IDRAFLOC; c) 18 mL/L NaOH, 3 g/L $Al_2(SO_4)_3$•$16H_2O$ and different dosages of IDRAFLOC

Chemical pre-treatment was also assessed in terms of the sedimentation yield. The NaOH dosage of 4.5 mL/L showed the fastest precipitation, reaching 53 % of the volume after an hour of settling. Plateau conditions were reached after 5 h (73 %) while the sedimentation yield was equal to 75 % at the end of 24 h. Similar trends were also observed at the other dosages (9-18 mL/L). The maximum sedimentation velocity was achieved within 2 h reaching to 14 ± 3 % (maximum value of 18 % for 9 mL/L dosage) while the final sedimentation yield was 54 ± 8 % (maximum value of 63 % for 18 mL/L dosage) at the end of 24 h.

Given the fact that hydroxide species made a colloidal suspension, which settled slowly, further investigation was carried out with coagulant and flocculant addition in tests 5-11. Due to the recovery increment (in tests 1 - 4) between different NaOH dosages, NaOH was added only in the range 9 - 8 mL/L. Mg^{2+} precipitation highlighted an increasing trend with the addition of $Al_2(SO_4)_3 \cdot 16H_2O$, with the recovery rates of 42 % and 83 % (test 5 and 7), respectively. Instead, no clear trend was detected for Ca^{2+} precipitation with a decreasing of the recovery rates from 21 % to 17 % for the same NaOH dosage. When PAC was used as coagulant (test 8), the maximum Mg^{2+} and Ca^{2+} recovery rates were achieved at the highest dosage of NaOH (18 mL/L) as 90 % and 14 %, respectively. Thus, when comparing the results of test 7 and 8 with the two different coagulants, PAC was found to be slightly more effective on Mg^{2+} recovery than Ca^{2+} recovery. Averagely, PAC and $Al_2(SO_4)_3 \cdot 16H_2O$ as coagulants did not considerably enhance the recovery yields compared to the softening with NaOH. Specifically, Ca^{2+} recovery was substantially lower during the coagulation than conventional softening (NaOH addition). This could be due to the decrease in pH caused by the addition of both coagulants of which in turn led to a consumption of alkalinity (Um et al., 2014) and thus resulting in a re-solubilization of Ca^{2+} compounds in the liquid phase. Based on the SEM results that were conducted in the precipitated fractions obtained from the chemical tests with the addition of NaOH and NaOH and coagulation with $Al_2(SO_4)_3 \cdot 16H_2O$, Mg^{2+} and Ca^{2+} percentages did not differ with the dosage of NaOH in tests 1 - 4, reaching average values of 26 ± 1.9 % Mg^{2+} (maximum of 28.3 % at lowest NaOH dosage) and 3.4 ± 1.4 % Ca^{2+} (maximum of 5.3 % at lowest NaOH dosage). Similarly, Mg^{2+} % and Ca^{2+} % did not differ among the tests 6 - 7, reaching average values of 25.1 ± 0.7 % Mg^{2+} (maximum of 25.9 % at middle NaOH dosage) and 0.8 ± 0.2 % Ca^{2+} (maximum of 1 % at lowest NaOH dosage). Comparing the two coagulants, PAC and $Al_2(SO_4)_3 \cdot 16H_2O$ did not considerably enhance the recovery yields.

The results from combining flocculation with $Al_2(SO_4)_3 \cdot 16H_2O$ coagulation (tests 9 - 11) did not highlight any remarkable improvements in terms of Mg^{2+} and Ca^{2+} recovery rates. Average recovery for Mg^{2+} was 86 ± 2 % (maximum value equal to 86.8 % for 21 mg IDRAPOL/L) while that of were 14 ± 4 % for Ca^{2+} (maximum value equal to 17.2 % for 7mgIDRAPOL/L). The addition of the anionic flocculant did not further enhance the sedimentation yield. This could be due to the fact that precipitated compounds with NaOH addition are neutrally charged species so that they are not easily aggregated by ionic flocculant.

3.2 Thermal evaporation tests

The results of the evaporation tests highlighted that the highest ions concentrations were observed at 100 °C, -0.5 bar vacuum. When brine was evaporated at 100 °C, Mg^{2+} was found to be increased by 2.11 folds (pH 9) and by 2.13 folds (pH 10) in the concentrated brine compared to the raw brine sample. Meanwhile, Ca^{2+} increased by 1.63 folds (pH 9) and by 1.41 folds (pH 10). A slight increment was also detected for Cl^- and Na^+ concentrations, which increased from 5.36 (pH 9) to 5.92 (pH 10) and from 2.20 (pH 9) to 2.21 (pH 10) folds, respectively. The concentration increment was more noticeable for SO_4^{2-} which increased from 5.57 (pH 9) to 6.17 (pH 10) folds. Moreover, the results highlighted that the temperature was a more effective parameter than pH on ions concentration since a higher variation in ion concentration was detected between the evaporation tests at 40 °C, 60 °C and 100 °C. In fact, between 60 °C and 100 °C, a considerable increment was achieved. Specifically, at the highest pH (pH 10), Cl^- concentration was 3.5 folds higher at 60 °C and 5.92 folds higher at 100 °C; SO_4^{2-} 3.53 times higher at 60 °C and 6.17 folds higher at 100 °C and; Na^+ 3.05 folds higher at 60 °C and 2.21 folds higher at 100 °C; Mg^{2+} 1.45 times higher at 60 °C and 2.13 times higher at 100 °C; Ca^{2+} 2.08 times higher at 60 °C and 1.41 times higher at 100 °C. When lower evaporation temperature (40 °C) and vacuum conditions (-0.5 bar) were tested, no distillate flow and no concentration effects was achieved. Given the low influence of pH compared to temperature, further experimental tests were conducted at pilot-scale without any preliminary NaOH addition before the evaporation. A summary of the results obtained from pilot the-scale evaporation tests is given in Table 3.

Table 3: Summary of evaporation results at pilot scale

Evaporation Test	Unit	8) T 110 °C P -0.4 bar	9) T 150 °C P Atm	10) T 150 °C P -0.3 bar	11) T 150 °C P -0.4 bar
Evaporation Flowrate	L/30 min	0.7 ± 0.08	1.2 ± 0.6	1.5 ± 0.5	1.6 ± 0.7
Evaporated volume*	%	91	91	91	91
Evaporation time**	h	10	5	4	3.5
Time saving***	%	65	30	12.5	-
Energy saving***	%	45	26	11	-

*with respect to the initial raw brine
**to reach the 91 % of evaporation
***with respect to the optimal condition (T 150 °C and P -0.4 bar) for 91 % of evaporation

The pilot-scale tests showed that, at 150 °C and vacuum at -0.4 bar (test 11), the highest evaporation flow rate was detected with value of 1.6 ± 0.7 L/30min together with the highest evaporation volume of 91 % of the initial raw brine volume that was achieved after 3.5 h of evaporation. The evaporation volume of test 11 was used as the reference performance for the other tests. Furthermore, a reduction of 30 % in the evaporation time was also achieved compared to the evaporation at atmospheric pressure (test 9). Specifically, at the latter conditions, the evaporation flowrate during the entire evaporation test was averagely equal to 1.2 ± 0.6 L/30min and the volume reduction was detected at 5.5 h. When the vacuum condition was increased (test 10), the flowrate was raised up to 1.5 ± 0.5 L/30min and the evaporated volume was gained after 4 h. Finally, when the temperature was decreased (test 8), the evaporation flowrate dropped down to 0.7 ± 0.08 L/30min and longer time (around 10 h) were required. Thus, test 11 led to an evaporation time reduction of 65 % compared to test 8. Moreover, when energy consumption is considered, vacuum condition (test 11) led to a 26 % of energy saving compared to atmospheric pressure, while 45 % of energy reduction was gained when the temperature was increased from 110 °C to 150 °C (test 11) at the same vacuum condition. In the optimal conditions, Mg^{2+} and Ca^{2+} recovery rates in the precipitated salts reached up to about 95 % and 55 %, respectively.

4. Conclusions

Chemical precipitation conducted at different NaOH (30 % w/v) concentrations in raw brine was found to be effective both in Ca^{2+} and Mg^{2+} precipitation and recovery. Specifically, highest recovery rates were achieved at the addition of 18 mL NaOH/L. PAC and $Al_2(SO_4)_3{\bullet}16H_2O$ as coagulants did not considerably enhance the recovery yields most probably due to the decrease in pH caused by coagulant addition which led to a re-solubilization of chemical compounds. Furthermore, flocculant addition did not further enhance Ca^{2+} and Mg^{2+} recoveries, probably due to the neutral charge present on the surface of precipitated compounds which poorly reacted with flocculant. The lab-scale evaporation tests indicated that the highest ions concentrations were obtained at 100 °C with no significant difference between pH 9 and 10. Moreover, the experimental tests highlighted that the temperature was more effective than the pH since a higher variation in ion concentration was detected between different evaporation temperatures. At the pilot-scale, the maximum evaporation yield was obtained at 150 °C with the vacuum at -0.4 bar and noticeable reductions in evaporation time and energy consumption were detected respect to other test conditions. The temperature was more effective on the evaporation than the pressure, while Mg^{2+} and Ca^{2+} recovery rates were up to 95 % and 55 %, respectively in the case of 91 % of volume reduction. It can be concluded that both chemical and thermal pre-treatments can be valuable options for both Ca^{2+} and Mg^{2+} recovery from brine; however, it has to be noted that further assessments should be done using Life Cycle Assessment and/or Life Cycle Costing for evaluating techno-economic viability of the treatments.

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