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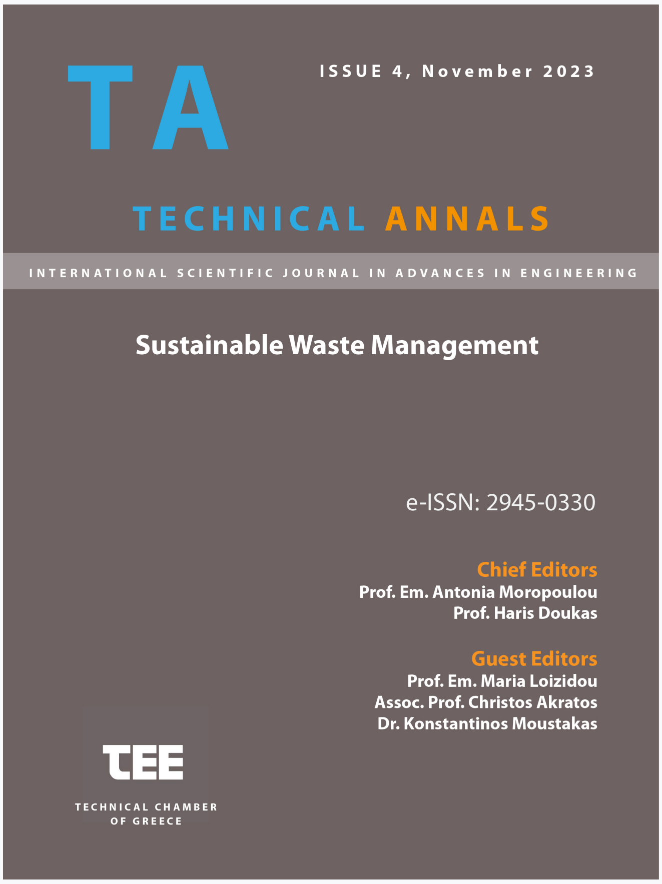

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Nanofiltration and selective crystallisation for the recovery of bio-based fertilizing products from seawater desalination brine

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Abstract. The majority of companies that operate desalination units produce significant quantities of brine, a hypersaline product whose disposal in the sea contributes to the degradation of local fauna and flora. The proposed framework for the valorisation of seawater brine in its entity and recovery of high purity water unveils a sustainable zero liquid discharge strategy consisting of two precipitation steps for the recovery of $Mg(OH)_2$ and $CaCO_3$. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to nanofiltration unit for Na_2SO_4 separation from the NaCl - KCl rich stream. Monovalent salt stream is further concentrated by multiple effect distillation evaporator and crystallizer and KCl is separated from NaCl by flotation using sodium dodecyl sulfate as floating agent. The outcomes of this exploratory effort validate that the process upscaling is feasible. The aforementioned micronutrients have readily been tested for their part in enhancing the agronomic performance of fertilising products, so they possess market potential to support local/national/European fertilisation purposes. Last but not least, such a nutrient recovery approach can ensure capital recovery within the expected time limitations of an investment and in some cases offset completely the treatment cost.

Keywords: nutrient recovery, seawater desalination brine.

Table 1. List of abbreviations

Abbreviation	Name	Abbreviation	Name
BBFs	Bio-based fertilisers	N	nitrogen
Ca	calcium	NR	nutrient recovery
$CaCO_3$	calcium carbonate	C	organic
KCl	potassium chloride	P	phosphorus
$Mg(OH)_2$	magnesium hydroxide	K	potassium
MED	multiple effect distillation	RO	reverse osmosis
NF	nanofiltration	WW	waste water

1 Introduction

Climate change, climate immigrants, and the global population growth challenge the future of crop production [1] by intensification [2] and compliance with strict environmental rules at a local/national/international level [3]. This trend demands that mineral-based fertilizers be replaced because of variations in nutrient availability across different regions, intermittent restrictions on nutrient transfer, and growing awareness of ore depletion [4].

To both combat these challenges and make agriculture sustainable and greener, several organisations are currently committed to the application of nutrient recovery (NR) strategies for the production of fertilising products [4]. The nutrients in solid waste and waste water (WW) streams are considered as raw material for obtaining Bio-based fertilisers (BBFs) to replace mineral-based fertilisers. The feedstock [5] can be anything from solid (all ashes with phosphorus (P) content >7%, precipitated phosphate salts (struvite [6] (after calcining to remove organic contaminants, with ammonia recovery), calcium phosphate), food waste, food industrial by-products (food processing wastes) or bone meal, secondary materials e.g. wood chips, organic fibres, biomass ash, sewage sludge digestates, ashes from sewage sludge incineration or liquid waste streams, thought attempts have shifted towards the valorisation of nutrient-based, commercially significant products found in WW streams. The WW feedstock candidates for NR practices can be liquors with a high ammonium concentration, and food industrial WW, any type of industrial WW (paper, food processing, bottle water and cosmetics), urban WW, as well as brine, the target of the presented work.

Currently, NR technologies involve the recovery of both P and nitrogen (N) and there are cases in which micronutrients are also recovered from the input streams. As an example of crystallization as calcium silicate-hydrate, mono or diammonium phosphate can be recovered by precipitation with phosphoric acid by reacting with ammonia gas [7]. Other examples of process technologies can include microbial fuel cells [8] or any kind of hybrid systems of photoautotrophic and heterotrophic microalgal cultivation [9], nanofiltration (NF), multiple effect distillation (MED). In order to validate the market of recovered nutrients and the nutrient recovery technologies, SuSPhos® 'has built and validated a kilogram-scale prototype reactor and is now ready for the compilation of the industrial pilot' [10]. Using a hollow fibre liquid-liquid membrane contactor (HF-LLMC) is a promising technology capable of transforming recovered nitrogen into several ready-to-use fertilisers (ammonium salts). This technology is capable to produce ammonium salts in solution with a concentration like conventional fertilisers present in market [11].

Regarding the recovered products, they should be part in the fertilisers market either by replacing an existing product or by complementing its performance. In some countries, struvite from NR practices, already has an EU 2003/2003 fertiliser validation and an end-of-waste status [7]. The market share for organic and mineral fertilisers could be complemented by a BBF with an organic (C) and mineral (N, P) base. A substitute for nitrate fertilisers could be a BBF with a mineral base and a high N content. A BBF enriched in Ca/P with better properties (organic content) than mineral fertilisers of phosphate origin has the capacity to share the market for phosphate fertilisers. Another example of WW-based NR product is Ammonium salts with plant growth promoting bacteria. These fertilisers can provide the inorganic nutrients required by the plant while the organic part can act as a bio-stimulant [12].

Any series of recovered micro-nutrients that are proven to complement plant growth can increase the yield of BBFs or replace micronutrient fertilisers on the market. A mixture of inorganic (N) and organic components could compete with products that are currently present in the market of organic and inorganic fertilisers. Hence, the relevance of the positioning in the market of this type of products is of utmost importance [13]. All in all, it has to be kept in mind that NR and the production of bio-based fertilisers, and WW-based fertilisers, in particular, are innovative practices [14]. The valorisation however of bio-based input streams (Urban WW, sewage sludge, food, Industrial WW and brine) into marketable fertilizing products or components is urgent and is guided and directed by accurate legislation for such products to enter the EU market. Still, the market for products from practices of recovery remains scarce [15].

Desalination of seawater is widely used to produce high-purity water to deal with water scarcity throughout Europe and the other continents. It is carried out in specialized plants using different techniques. The principal method for high-purity water production is reverse osmosis (RO). The application of this method results in fresh water and brine; a hypersaline by-product considered waste with a high concentration of minerals and metals [16]. Since seawater brine represents a potential alternative source for raw materials production and some salts are already being recovered, the development of suitable technologies for the selective recovery of a broad spectrum of salts as marketable products is imperative. Membrane-based separation processes, bioprocesses along with electrochemical and other hybrid processes represent technologies that have shown potential for metals recovery/removal [17]. The precipitation of minerals from brine reduces the fresh water production cost as well as minimises the brine disposal problem [18]. Despite their encouraging performance in lab-scale studies, these processes have not reached commercialisation yet, due to several associated challenges.

Current practice in countries using large-scale desalination plants is to reject brine back to the sea, leading to the degradation of local fauna and flora. However, further processing of brine could result in the recovery of economically prime important materials such as magnesium, calcium, and potassium salts and high-purity water. Brine treatment can contribute to the minimization of the environmental footprint of desalination plant [19].

Given its limited geological sources, Mg^{2+} has been qualified as a critical raw material by the European Union Commission [20]. Thus, its recovery from brine could be an alternative source. Another salt with an increasing consumption rate is KCl. It is estimated that under current consumption, world stocks of KCl will last until 2111. KCl is another salt that can be recovered from seawater desalination brine, as mentioned in the previous paragraph.

Due to its low cost and higher potassium (K) content than most other sources (50–52 % K, 60–63 % K_2O and 45–47 % Cl^-), potassium chloride (KCl) is the most often used K fertilizer [21]. In addition to achieving a sustainable circular economy, recovery and reuse of potassium are necessary since its current consumption rate will soon lead to the depletion of its reserves.

The aim of this study is to investigate the process parameters for the optimization of $Mg(OH)_2$, limestone calcium carbonate $CaCO_3$ and KCl recovery in terms of valorization of brine as a wastewater stream from the desalination plants. The main targets are the recovery of high purity water and salts. This work is the predecessor of the design of a pilot system for the treatment of the waste stream produced from a RO desalination plant. These salts are economically prime important nutrient resource-based micro and macro nutrients to be valorised in/as Bio-based fertilisers. Potassium can be reused as a primary macronutrient, while Mg^{2+} and Ca^{2+} as micronutrients for the manufacturing of bio-based fertilizers [22, 23]. The parameters examined are reagents quantity and stirring time to optimize the purity and quantity of the recovered salts that are obtained as marketable ingredients of BBFs. The experiments are analyzed and organized through a 2^2 factorial design [24] in order to make a statistical evaluation of the tests and results.

2 Methodological approach

2.1 Brine sampling

Brine samples were collected during three different periods of time from the outlet of a small-scale desalination plant applying reverse osmosis (RO) of a hotel in Sounio, south-east Athens. The samples were stored at ambient conditions.

2.2 Brine characterisation

Analyses were performed according to standard methods (APHA). Every experimental measurement is preceded by the analysis of a brine sample, from the same day as the experiment. The results of seawater desalination brine applying reverse osmosis (RO) and seawater (inlet of RO) characterisation are presented in **Table 8**. There are variations depending on the local composition of brine, therefore the measured ion concentrations are likely to slightly vary in different brine samples.

2.2.1 Materials

Sodium hydroxide-NaOH(2M), calcium hydroxide-$Ca(OH)_{2(s)}$, nitric acid-HNO_3 1.5%, sodium carbonate-$Na_2CO_{3(s)}$, potassium chloride-KCl, NaCl, sodium dodecyl sulfate-$CH_3(CH_2)_{11}OSO_3Na$ and hexadecyl trimethyl ammonium bromide were all supplied by Sigma Aldrich (Merck).

2.2.2 Methods

A Spectroquant® UV-VIS spectrophotometer Pharo 300 was used to measure the chlorides (Cl^-), the sulfate ions (SO_4^{2-}), the nitrates (NO_3^-) and the phosphates (PO_4^{3-}).

The concentration of K^+, Na^+, Ca^{2+} and Mg^{2+} in the brine samples was measured using the Agilent Technologies® 200 Series AA 240 FS AA flame atomic absorption spectrometer (FAAS). All samples were analysed in triplicate. The setting for the examples was: wavelength 248.3 nm, slit width 0.2 nm, flame type: acetylene-air with a flow of 2.0 L/min with 13.5 L/min flow of air. The calibration curve, with deuterium used for the background correction, ranges between 0.1–10 mg/L. The limit of detection (LOD) is 0.002 mg/L and 0.007 mg/L and the limit of quantification (LOQ) is 0.005 mg/L and 0.025 mg/L for the instrument and the method, respectively.

Bicarbonate ions (HCO^{3-}) were measured with titration and neutralization up to pH=4.4.

Analyses on recovered dried samples with X-ray Diffraction (XRD) were performed using a Cu X-ray tube (λ=1.5418 Å) BRUKER D8-ADVANCE (twin/twin) diffractometer (40kV, 40 mA). The recorded range of angles was 2θ=10-60 ° and the recording speed 0.02 °/sec.

2.3 Brine treatment process

The first step of the brine treatment train is the precipitation of Mg^{2+} in the form of $Mg(OH)_2$. The addition of two reagents NaOH and $Ca(OH)_2$ for Mg^{2+} recovery is studied. Two series of experiments are carried out under different values of stirring time and quantity of reagent to recover the best combination regarding the highest quantity and purity of Mg^{2+} recovery. Na_2CO_3 is added to the brine after Mg^{2+} removal for $CaCO_3$ precipitation. As in the former experiments series, stirring time and quantity of the reagent are the two parameters examined to achieve maximum recovery of $CaCO_3$. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to NF unit for Na_2SO_4 separation. The stream rich in monovalent ions such as Na^+, K^+, and Cl^- is further concentrated by a rotary evaporator for the reclamation of high-purity water. Then, KCl is separated from the mixed salt of NaCl-KCl using a flotation technique. Sodium dodecyl sulfate and hexadecyl trimethyl ammonium bromide are used as flotation agents. The efficiency of each floating agent is examined in terms of KCl recovery and purity. The bench-scale experiments of the proposed seawater brine treatment are described in **Fig. 1**.

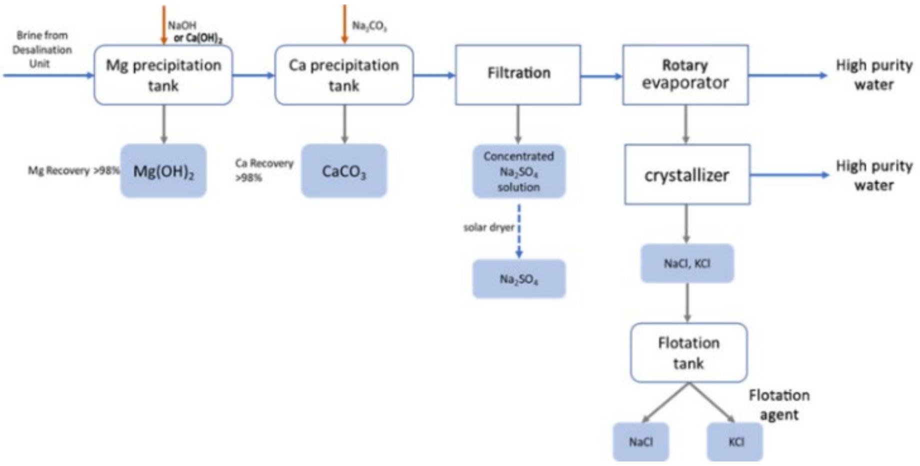

Fig. 1: Process flow diagram of the proposed seawater brine treatment

2.3.1 Mg^{2+} Removal

For the Mg^{2+} removal, samples of 200ml characterized brine are used. Chemical precipitation of Mg^{2+} is realised by using two different reagents. The first one is NaOH (2M) solution and the second one is solid $Ca(OH)_2$. Firstly, in every experimental series, the reagent is added under magnetic stirring. Different quantities of the reagent and different reaction times are examined. Sedimentation curves for magnesium hydroxide precipitation are also examined between 0-24 h. After the reaction, solid $Mg(OH)_2$ is separated through centrifugation (10min, 3500rpm) and then the liquid samples are collected. Liquid brine samples are diluted with nitric acid 1.5% and then are analyzed through AAS method to measure the final concentration of Mg^{2+} and calculate its removal percentage (%). Solid is washed out with deionized water, then collected in a crucible and left at 105 °C until dry. Finally, the dry solid is weighted, ground and analyzed through XRD method to determine its composition.

2.3.2 Ca^{2+} Removal

Solid sodium carbonate (Na_2CO_3) is added to brine samples without Mg^{2+} and the mixture is stirred. As a product of the reaction, a new solid is produced, $CaCO_3$, which is separated from the liquid solution through centrifugation (10min, 3500rpm). The liquid solution is filtered and then diluted with nitric acid 1,5% to be analyzed using AAS method. Through this analysis the concentration of Ca^{2+} is measured and the percentage (%) of Ca^{2+} removal is calculated. Solid $CaCO_3$ is washout out with deionized water. Finally, it is left at 105° C to dry and is analysed through XRD method.

After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to a rotary evaporator for water and salt recovery. Recovered salt is led to flotation for the separation of KCl from NaCl.

2.3.2.1 Factorial experimental design

Recovery of Mg^{2+} and Ca^{2+} is designed through a 2^2 factorial experiment of two parameters (reagent's quantity and stirring time). Experiments are realized under various conditions and combinations of the upper and lower levels of the parameters. The experiments with the conditions that refer to level 0 were repeated 4 times for statistical evaluation. The parameters selected are quantity of the reagent and different reaction times; a series of experiments are carried out under different conditions and combinations of the two parameters. X_1 refers to reagent's quantity and X_2 to stirring time. Stoichiometric quantity of the reagent is used as centre of the factorial design and based on the symmetry are defined the upper and lower extreme values of the levels. Specifically, at the upper level (+1) 110% of reagent's quantity is added with a stirring time of 45 min while at the lower (-1), 90% of the stoichiometric quantity is added with 15 min stirring time (**Table 2**).

Table 2: Parameters and levels of the factorial design

Factorial parameters			Factorial levels		
	unit		-1	0	1
Reagent's quantity	g/ml	X_1	90% of stoichiometry	stoichiometry	110% of stoichiometry
Stirring time	min	X_2	15	30	45

2.3.2.2 *Factorial design for the recovery of Mg^{2+} from brine using NaOH (2M) as reagent*

Experiments for the recovery of Mg^{2+}, using NaOH (2M) as reagent are based on the chemical reaction (1):

$Mg^{2+}_{(aq)} + 2\ NaOH_{(aq)} = Mg(OH)_{2\ (s)} + 2\ Na^{+}_{(aq)}$ (1)

The initial sample is 200ml brine with 2,74g/L concentration in magnesium. Based on the above reaction, the stoichiometric quantity of NaOH (2M) for the precipitation of magnesium is 22.5ml; mixing time for this level is settled at 30'. Conducting all possible combinations of the levels of the two parameters (**Table 3**), resulted in 12 experiments in total. For the upper and lower level, 4 trials take place with two replicates for each level. As for the center, 4 replicates are realized for statistical validation.

Table 3. Factorial design for Mg^{2+} recovery from brine using NaOH (2M) as reagent

Experiments A/A	Quantity NaOH (2M) (ml)	Mixing time (min)
1	20.25	15
2	20.25	15
3	24.75	45
4	24.75	45
5	20.25	45
6	20.25	45
7	24.75	15
8	24.75	15
9	22.50	30
10	22.50	30
11	22.50	30
12	22.50	30

2.3.2.3 *Factorial design for the recovery of Mg^{2+} from brine using $Ca(OH)_2$ as reagent*

Experiments for the recovery of Mg^{2+}, using $Ca(OH)_2$ as reagent are based on the chemical reaction (2):

$Mg^{2+}_{(aq)} + 2\ Ca(OH)_{2\ (s)} = Mg(OH)_{2\ (s)} + Ca^{2+}_{(aq)}$ (2)

Similarly to the latter process, 200ml of brine sample are used and based on the stoichiometry of the reaction, the quantity of $Ca(OH)_2$ for the $Mg(OH)_2$ precipitation is

1.356g under 30 min stirring time; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (**Table 4**), resulted in 12 experiments.

Table 4. Factorial design for Mg^{2+} recovery from brine using $Ca(OH)_2$ as reagent

Experiments A/A	Quantity $Ca(OH)_2$ (g)	Mixing time (min)
1	1.220	15
2	1.220	15
3	1.492	45
4	1.492	45
5	1.220	45
6	1.220	45
7	1.492	15
8	1.492	15
9	1.356	30
10	1.356	30
11	1.356	30
12	1.356	30

2.3.2.4 Factorial design for the recovery of Ca^{2+} from brine

Experiments for the recovery of Ca^{2+}, using Na_2CO_3 as reagent are based on the chemical reaction (3):

$Ca^{2+}{}_{(aq)} + Na_2CO_{3\ (s)} \rightarrow CaCO_{3\ (s)} + 2Na^{+}{}_{(aq)}$ (3)

Using 200ml of brine sample and based on the stoichiometry of the reaction (3), the quantity for the $CaCO_3$ precipitation is 0.48g Na_2CO_3 by stirring the mixture for 30'; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (**Table 5**), resulted in 12 experiments.

Table 5. Factorial design for Ca^{2+} recovery from brine

Experiments A/A	Quantity Na_2CO_3 (g)	Mixing time (min)
1	0.43	15
2	0.43	15
3	0.53	45
4	0.53	45
5	0.43	45
6	0.43	45
7	0.53	15
8	0.53	15
9	0.48	30
10	0.48	30
11	0.48	30
12	0.48	30

2.3.3 KCl recovery from brine

After magnesium and calcium removal and pH conditioning from 10.5 to 7, the resulting brine is forwarded to a rotary evaporator for concentration and then to the oven for salt crystallization. KCl is more soluble at high temperatures than NaCl, so every 2 min, brine is separated from the crystallized salt. The separated brine is expected to be more enriched in KCl, upon full evaporation. Three types of salt resulted and are named A, B and C; C is expected to be the most KCl-rich, while A is the least KCl-rich fraction. Mixed (NaCl-KCl) salt is led to a flotation cell for the separation of KCl from NaCl. For this purpose, a saturated solution of KCl and NaCl is prepared by dissolving 342g KCl and 514g NaCl in 2L of deionized water. In every flotation trial, 10g of the mixed salts are added into 40 ml of the saturated solution and then Sodium Dodecyl Sulfate 1% is used as flotation agent. The mixture is stirred for 10 min and air is provided through a pipe to create froth; KCl crystals are attached on bubbles and then are collected. Finally, crystals are left to dry. A quantity of salts is diluted with nitric acid 1.5% for further qualitative analysis through AAS method. XRD analysis is performed for each kind of salt, to study their composition qualitatively. The results obtained are given in **Fig. 2** to **Fig. 4**.

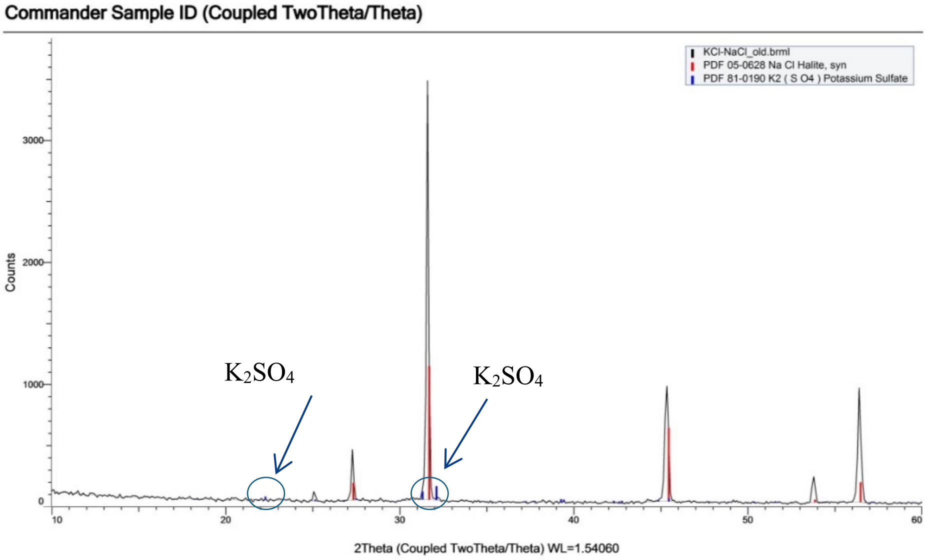

Fig. 2: Mixed salt A XRD analysis

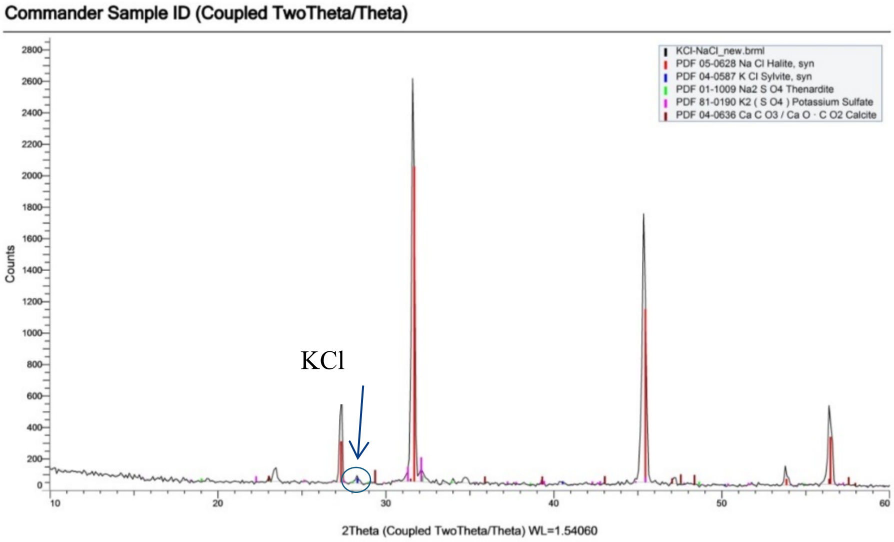

Fig. 3: Mixed salt B XRD analysis

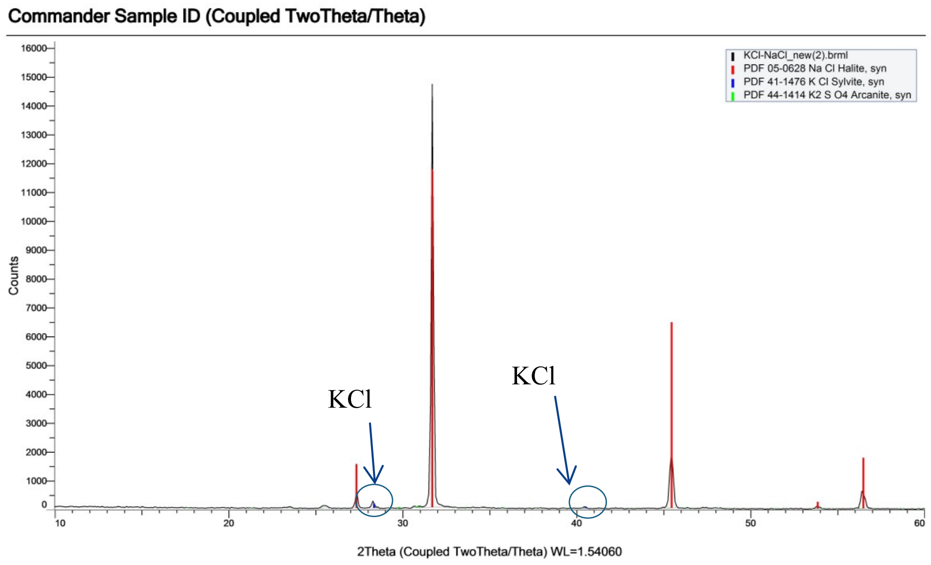

Fig. 4: Mixed salt C XRD analysis

Peaks corresponding to NaCl in the form of halite (red peaks) are visible in all three plots. In **Fig. 2**, which corresponds to salt A, some smaller peaks appear which are probably due to K_2SO_4 presence, while no peaks corresponding to KCl are found, due to the very low concentration of KCl in salt A. However, in Fig. **3** and in **Fig. 4** (mixed salt B and C) a small peak (blue in color) is visible due to the presence of KCl (sylvite). Other peaks probably correspond to the compounds K_2SO_4, Na_2SO_4 and $CaCO_3$.

To achieve a quantitative estimate of the composition of mixed salt, the analytical AAS is used (**Table 6**).

Table 6. Mixed salt analysis using AAS

K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)
0.034	1.724	0.208	0.012	0.028

The concentration measured for potassium corresponds to 1.63 % KCl in salt B. There are also small concentrations of Mg^{2+} and Ca^{2+} which are probably not completely removed in the previous stages of the experiment. A total of 195 g of salt is collected where 52 g is salt A (less rich in K), 100 g salt B and 43 g salt C (richest in K). For the recovery of potassium by flotation method, 17 experiments are carried out where 10 g of salt are used for each one. The effect of the flotation agent addition is mainly studied keeping the amount of saturated KCl – NaCl solution constant; 40 mL are used in every experiment. In addition, tests are performed on how flotation time, mass of added salt and granulometry of the salt affect the recovered amount of KCl and its purity. **Table 7** shows the conditions for each experiment [25] and the recovered mass of solid.

Table 7. Conditions of the flotation experiments and the recovered solid mass

Experiments	Pre-treatment time (min)	Flotation time (min)	Concentrated solution volume (mL)	Added salt (g)	Floating agent volume (mL)	Granulometry (μm)	Recovered solid (mg)
A1	5	5	40	10	5.0	-	360
A2	5	5	40	10	5.0	-	150
A3	5	5	40	10	2.5	-	200
A4	5	5	40	10	2.5	-	80
A5	5	5	40	10	1.0	-	70
B1	5	5	40	10	1.0	-	110
B2	5	5	40	10	5.0	-	180
B3	5	5	40	10	0.5	-	140
B4	5	5	40	10	0.5	-	80
B5	5	5	40	10	1.0	<180	60
B6	5	5	40	10	1.0	<180	60
B7	5	5	40	10	1.0	>180 & <1000	80
B8	5	5	40	10	1.0	>180 & <1000	100
C1	5	5	40	10	0.5	-	180
C2	5	5	40	10	0.5	-	130
C3	5	5	40	10	1.0	-	70
C4	5	5	40	10	1.0	-	100

As resulted from **Table 7**, recovered KCl quantity ranges from 60 mg to 200 mg with one single experiment providing 360 mg solid. According to the table, increasing the volume of the added flotation agent increases the recovered solid (**Fig. 5**) as more froth is collected [26].

Fig. 5. Recovered KCl crystals

3 Results and discussion

3.1 Feedstock characterization

Table 8 shows the concentration of main anions and cations contained in the three brine samples treated in this work and in seawater.

Table 8. Ions concentration in seawater and brine

Ions concentration (mg/L)	Brine (1st sample)	Brine 2nd sample	Brine 3rd sample	Seawater
K^+	813	874	906	380
Na	19674	17781	18230	8026
Ca^{2+}	1552	1472	1523	450
Mg^{2+}	2736	2225	2200	1314
Cl^-	35400	44000	43800	27000
SO_4^{2-}	3820	5700	4730	4400
HCO_3^-	238	107	221	140
PO_4^3	0.08	0.42	0.23	-
NO_3^-	0.01	1.10	0.80	-
TDS	6.85 g/100ml	7.43 g/100ml	7.48 g/ 100ml	3.45 g/ 100ml
Electrical conductivity	64.2 mS/cm^2	64.2 mS/cm^2	64.2 mS/cm^2	50.000 uS/cm
pH	7.77	7.70	7.80	7.50-8.40

3.2 Results from the factorial design

3.2.1 Mg^{2+} recovery with NaOH (2M) addition

According to **Table 9**, the maximum Mg^{2+} removal and minimum Ca^{2+} removal have occurred on experiments 5 and 6. In these cases, 90% of reagent's stoichiometric quantity is mixed with brine sample for 45 min.

Table 9. $Mg(OH)_2$ recovery through brine reaction with NaOH (2M)

N/N	Experiments A/A	Quantity NaOH (2M) (ml)	Mixing time (min)	$\%Mg^{2+}$ removal	$\%Ca^{2+}$ removal	Mg^{2+}/Ca^{2+}	Recovered $Mg(OH)_2$ mass (g)
N1	1	20.25	15	86.50	67.20	1.49	0.76
	2	20.25	15	86.70	59.10	1.69	0.87
N2	3	24.75	45	99.00	82.30	1.22	0.90
	4	24.75	45	99.90	70.80	1.41	1.10
N3	5	20.25	45	89.90	48.80	2.05	0.60
	6	20.25	45	89.70	53.60	1.89	1.07
N4	7	24.75	15	98.80	69.20	1.43	0.97
	8	24.75	15	100.00	65.90	1.52	0.83
Centre							
Centre	9	22.25	30	92.00	54.60	1.68	0.84
	10	22.25	30	96.50	49.70	1.74	0.93
	11	22.25	30	95.50	50.50	1.79	0.85
	12	22.25	30	94.70	51.20	1.75	0.87
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0.00	100.00	1.276

Fig. 6 shows that experiments with maximum amount of reagent and maximum stirring time (N2) result in largest amount of salts recovery.

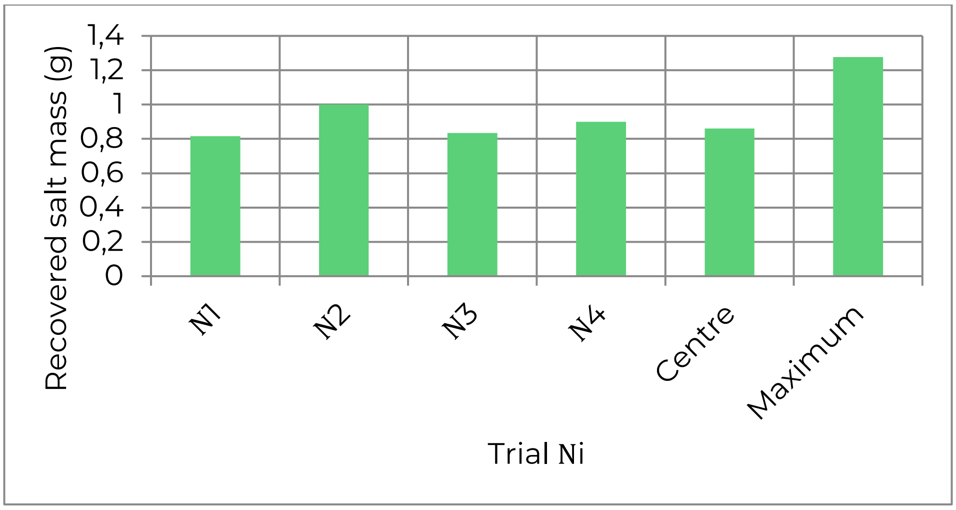

Fig. 6. Mass of recovered $Mg(OH)_2$ for every trial

Table 10. $Mg(OH)_2$ recovery through brine reaction with NaOH (2M)

A/A	Quantity of NaOH (2M) (ml)	Stirring time (min)
N1	20.25	15
N2	24.75	45
N3	20.25	45
N4	24.75	15
Centre	22.25	30
Maximum	Stoichiometry	

After processing the factorial experimental results (**Table 10**) [24, 27], the following model is developed, correlating the $Mg(OH)_2$ recovery from brine (Y, %) with the selected controlling parameters:

Y = -2.228 + 0.102 * (NaOH (2M) addition) + 0.077 * (stirring time) – 0.003 * (NaOH (2M) addition) * (stirring time) (4)

Equation 4 shows that all parameters are statistically important including their interaction. Furthermore, both mathematical models proved to be adequate according to the Fisher criterion [25, 28, 29, 30, 31].

3.2.2 Mg^{2+} recovery with $Ca(OH)_2$ addition

According to **Table 11**, maximum Mg removal has occurred with higher reagent dosage.

Table 11. $Mg(OH)_2$ recovery through brine reaction with $Ca(OH)_2$

N/N	Experiments No	Quantity $Ca(OH)_2$ (g)	Mixing time (min)	%Mg removal	Recovered $Mg(OH)_2$ mass (g)
N1	1	1.220	15	86.88	0.936
	2	1.220	15	87.46	0.881
N2	3	1.492	45	99.98	1.652
	4	1.492	45	99.62	1.716
N3	5	1.220	45	86.91	1.145
	6	1.220	45	86.64	1.195
N4	7	1.492	15	99.98	1.030
	8	1.492	15	99.18	0.940
			Centre		
Centre	9	1.356	30	94.39	1.390
	10	1.356	30	94.48	1.444
	11	1.356	30	95.30	1.368
	12	1.356	30	96.67	1.240
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	1.067

Fig. 7 shows that experiments of N_2 trials provide the highest amount of salts recovery.

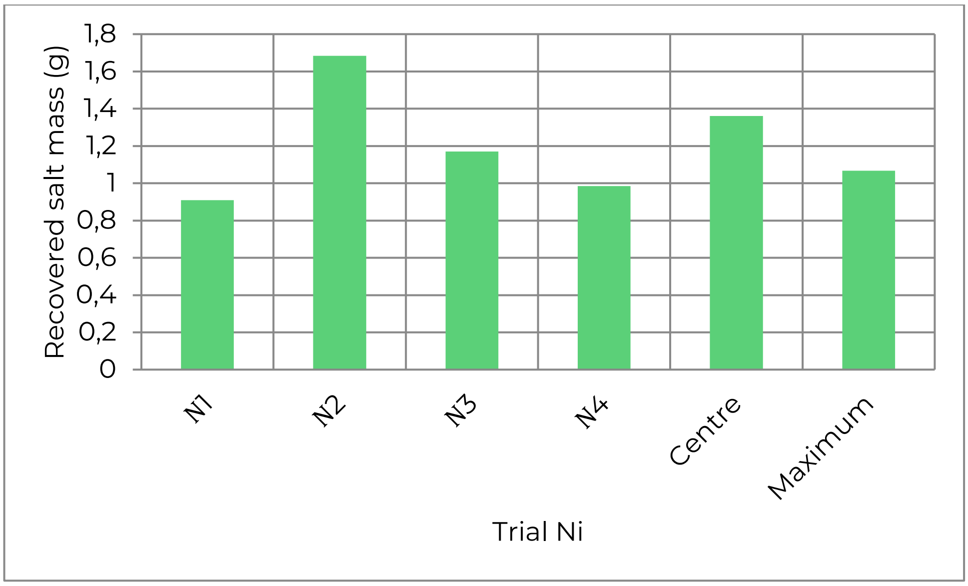

Fig. 7. Mass of recovered $CaCO_3$ for every trial

First degree equation 5 shows that the most important parameter for Mg^{2+} recovery through $Ca(OH)_2$ addition is reagent's quantity, whereas reaction time is not considered as a factor that can affect the results.

$Y = 0.295 + 0.47 * (Ca(OH)_2 \text{ addition})$ (5)

3.2.3 Ca^{2+} recovery with Na_2CO_3 addition

Table 12 shows that all different experiments result in an average class rate of 99% $CaCO_3$ recovery.

Table 12. $CaCO_3$ recovery through brine reaction with Na_2CO_3

N/N	Experiment No	Quantity Na_2CO_3 (g)	Mixing time (min)	%Ca removal	Recovered $CaCO_3$ mass (g)
N1	1	0.432	15	97.00	0.33
	2	0.432	15	98.00	0.35
N2	3	0.528	45	99.00	0.39
	4	0.528	45	98.00	0.34
N3	5	0.432	45	99.00	0.37
	6	0.432	45	99.00	0.38
N4	7	0.528	15	99.00	0.33
	8	0.528	15	99.00	0.37
		Centre			
Centre	9	0.48	30	98.00	0.32
	10	0.48	30	99.00	0.35
	11	0.48	30	98.00	0.33
	12	0.48	30	99.00	0.37
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0.45

Equation (6) shows that Ca^{2+} removal increases both with Na_2CO_3 addition and stirring time. However, reagent's addition has a greater effect on Ca^{2+} removal because of its greater coefficient.

$Y = 0.9372 + 0.0081 * (Na_2CO_3 \text{ addition}) + 0.0002 * (\text{stirring time})$ (6)

3.3 Nanofiltration simulation model

According to the experimental process flow diagram (**Fig. 1**) the brine after Mg^{2+} and Ca^{2+} removal will enter the NF unit. The occupation of the NF unit is necessary for the removal of SO_4^{2-}ions from the seawater desalination brine. Regarding the NF process unit the separation efficiency was set as the main optimization parameter. Since only small volumes of brine (200ml and 50 L) have been treated during the lab-scale experiments, it was not possible to implement NF step. Thus, it was decided to run a simulation model for the treatment of 0.5 m^3/day of brine (raw feed composition is presented in **Table 13**) using the water application value engine (WAVE) software.

Table 13. Concentrations of brine ions and TDS before and after NF process

	Raw Feed (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
K	912.60	1,588	729.80
Na	21,974	37,701	17,718
Mg	11.60	30.57	6.46
Ca	17.40	45.98	9.66
SO_4^{2-}	3,416	15,046	271.30
TDS	58,688	103,304	46,616

After many runs with different types of NF membranes the most appropriate seems to be the membrane NF270-2540 in terms of SO_4^{-2} removal. This membrane seems to be more appropriate (large pore diameter: 270 μm) because the stream is very dense and would create fouling and scaling issues [32]. The removal efficiency results in the brine salts & TDS removal percentages are described in **Table 14**. The simulation was performed under pH=7. For this type of membrane and aforementioned conditions no special comments were derived from the wave simulation model regarding fouling or scaling issues.

Table 14. NF % removal of brine ions & TDS

	% removal of major ions
K	20
Na	19
Mg	44
Ca	44
SO_4^{2-}	92
TDS	21

To conclude with, the simulation of the NF process using membrane NF270-2540 implied a 92% removal (Table 14) of SO42- from the brine inlet. The resulting effluent streams will be used for the optimisation of the downstream processes.

4 Conclusions

Summing up, in the first part of the experimental process, the salts are recovered by precipitation as $Mg(OH)_2$ and $CaCO_3$ after the addition of NaOH or $Ca(OH)_2$ and Na_2CO_3. Then, the divalent SO_4^2 are separated from the brine using nanofiltration (NF). The next part of the process targets brine concentration and the recovery of a mixed salt of NaCl and KCl applying thermal crystallization. In the final stage, KCl is collected from the mixed salt by flotation.

The main achievement of this work is the proof that macro and micronutrients can be recovered from the brine produced by an RO desalination plant. The acquisition of such end-products adds high value to the existing desalination plants, contributing to the alignment with EU Water Framework Directive, Circular Economy Package and sustainability in the agricultural sector. Furthermore, this work contributes to the definition of the main design of a system parameters and their values.

To achieve the recovery of water and salts from RO desalination brine next steps should be followed:

- $Mg(OH)_2$ recovery (precipitation)
- $CaCO_3$ recovery (precipitation)
- Separation of the divalent SO_4^2 from the brine (nanofiltration).
- Brine concentration (water evaporation)
- Recovery of a mixed salt of NaCl and KCl
- Separation of KCl from the mixed NaCl-KCl salt (flotation).

A sustainable brine treatment leads to avoidance of its disposal in the sea and decreases its impact on the environment and aquatic life. Also, recovery of nutrients from brine could reduce the CO_2 emissions in comparison with the conventional methods of nutrients production. Moreover, this technology facilitates compliance with proposed regional/EU-27 regulations towards replacing the production of fossil-based fertilizers. The introduced seawater brine technology framework outlines a sustainable, competitive zero liquid discharge approach to completely convert brine into reclaimed water and salts of commercial value. Last but not least, the results of this preliminary work justify the feasibility of the process upscaling.

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