Design of a Zero Liquid Discharge system for the recovery of $Mg(OH)_2$, $CaCO_3$ and KCl from seawater desalination brine to be used as Bio-Based Fertilizers

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Introduction

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 high concentration of minerals and metals. 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 (J. Le Dirach Simon Nisan, C. Poletiko, 2005). 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 reclaimed water. Brine treatment can contribute to the minimization of the environmental footprint of desalination plant (Ogunbiyi, et al., 2021).

This study summarizes a preliminary investigation to achieve recovery from desalination brine of KCl, $Mg(OH)_2$, and $CaCO_3$, as valuable macro and micronutrients. Samples are taken from a desalination plant at south-east Athens. Factorial experiments are conducted to optimize the purity and quantity of the recovered minerals that will be obtained as marketable ingredients of Biobased Fertilizers (BBFs). The samples are collected and stored at ambient conditions. Analysis is performed according to Standard Methods (APHA).

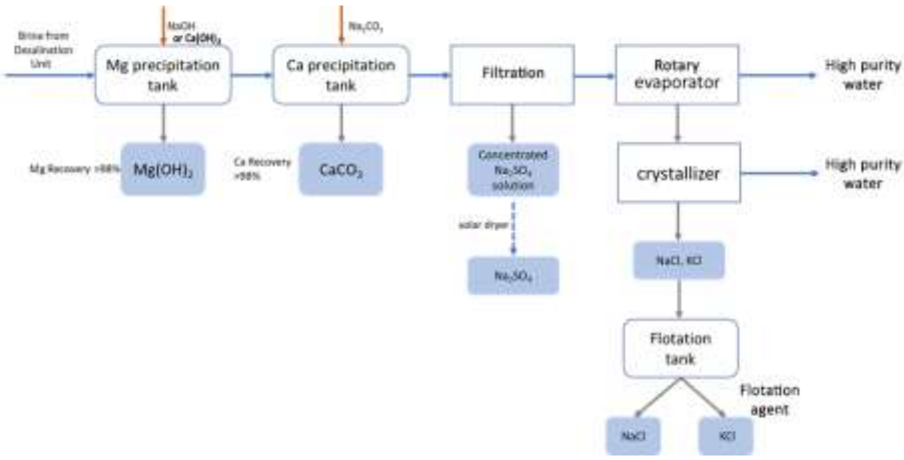

Figure 1: Process flow diagram of the proposed seawater brine treatment

Materials and Methods

Figure 1 describes the bench-scale experiments conducted for the proposed seawater brine treatment. Lab-scale experiments were designed and conducted to treat 200 ml and 50 L samples of seawater RO desalination brine. The first step of the brine treatment train is the precipitation of Mg^{2+} in the form of $Mg(OH)_2$. The addition of NaOH and Ca(OH)2 reagents for Mg^{2+} recovery is studied. Two series of experiments are carried out under different values of stirring time and quantity of reagent to define 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 series of the former experiments, 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+}) will be led to filtration for Na_2SO_4 separation from NaCl - KCl rich stream. The monovalent salt stream 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.

For the recovery of Mg^{2+} and Ca^{2+} a 2^2 factorial experiment was designed for statistical evaluation of the tests and results. The design parameters for assessment and optimization include mixing time and the quantity of reagent added, which are examined under various parameter values.

Results

Below are presented the equations that resulted from the factorial experiments.

*Y = -2.228 + 0.102 * (NaOH (2M) addition) + 0.077 * (stirring time) – 0.003 * (NaOH (2M) addition) * (stirring time) (1)*

Equation 1 shows that when NaOH is used as a reagent for Mg^{2+} recovery, its quantity is the most important factor. However, besides reagent's addition also stirring time is statistically important including its interaction with the reagent.

*Y = 0.295 + 0.47 * (Ca(OH)2 addition) (2)* *Y = 0.9372 + 0.0081 * (Na2CO3 addition) + 0.0002 * (stirring time) (3)*

First degree equation (2) 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.
Equation (3) 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.

The optimum results in terms of the purity of the recovered salts, using sodium hydroxide (NaOH) as a reagent yields higher purity (~93%) for magnesium recovery when the stirring time of the mixture is longer (45 min). Conversely, when calcium hydroxide (Ca(OH)2) is used, shorter mixing times result in higher purity (~86%) for the recovered salts. However, the purity of the recovered calcium carbonate (CaCO3) salts remains unaffected by the conditions, with all trials exhibiting high performance (~99%).
The important parameters for the recovery of potassium chloride (KCl), which affect the recovery ratio and salts' purity, are the type of flotation agent added its volume and the particle size of the recovered solid. Two different flotation agents, sodium dodecyl sulfate and hexadecyl trimethyl ammonium bromide, were utilized.
Hexadecyl Trimethyl Ammonium Bromide showed better performance at an even smaller amount of 0.03% and reached a recovery of 90% with similar purity of 60% of recovered KCl.
To sum up, recovered salts of $Mg(OH)_2$, $CaCO_3$ and KCl from this task are of such purity as to be used as nutrients for Bio-based Fertilizers. The main achievement of this work is proof that macro and micronutrients can be recovered from the brine produced by an RO desalination plant. Furthermore, this work contributes to the definition of the main designing of the pilot system parameters and their values. The acquisition of end-products that add high value to the existing desalination plants, thus the alignment with the Circular Economy Package. 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 reduces 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.

References

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