Nutrient recovery from seawater brine - a circular economy approach for Bio-Based Fertilizers production

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Water is a one of the most important natural resources and a key to the survival of living organisms. Due to its importance, it needs to be managed in a sustainable way. As it is unequally distributed around the world it is usually a reason of geopolitical, geostrategic, and geo-economic issues. A commonly used method to produce fresh water in areas that face scarcity problems is seawater desalination by reverse-osmosis. This method produces 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. Extraction of materials (like Magnesium, Calcium, and Potassium salts) and fresh water recovery would contribute to the minimization of environmental footprint of integrated desalination plants (J. Le Dirach Simon Nisan, C. Poletiko, 2005). Given its limited geological sources, Mg^{2+} has been qualified as a Critical Raw Material by the EU COM(2017)490 (Billing, A.E. and Dold, P.L., 1988). In addition, to achieving a sustainable circular economy, recovery and reuse of potassium are necessary since its current consumption rate will lead to the depletion of its reserves by 2111 (United States Geological Survey, 2018).

This study summarizes preliminary investigation to achieve recovery from desalination brine of KCl, $Mg(OH)_2$, and $CaCO_3$, as valuable macro and micro nutrients. Samples are taken from a desalination plant at south-east Athens. Factorial experiments under various conditions are carried out 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).

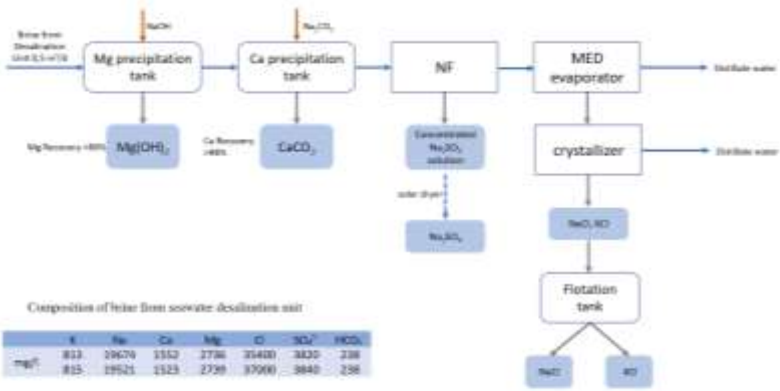

Figure 1 Process flow diagram of the proposed seawater brine treatment

The bench-scale experiments of the proposed seawater brine treatment are described in Figure 1. The first step is the precipitation of Mg^{2+} of the seawater desalination brine into $Mg(OH)_2$ after adding NaOH. A series of experiments was carried out with different values of the parameters (stirring time and quantity of NaOH) to recover the highest quantity of Mg^{2+}. Na_2CO_3 was added in the brine after Mg removal for $CaCO_3$ precipitation. As in the former operation, stirring time and quantity of the reactant were two parameters examined under different conditions in order to achieve the maximum recovery of $CaCO_3$. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) will be led to NF unit for Na_2SO_4 separation from NaCl-KCl rich stream. Monovalent salt stream is further concentrated by MED evaporator and crystallizer and KCl was separated from NaCl by flotation. Sodium Dodecyl Sulfate is used as floating agent. The KCL crystals were collected and washed with ethanol.

For the recovery of Mg^{2+} and Ca^{2+} a 2^2 factorial experiment was designed with two parameters that affect the experiments; reactant's quantity and the stirring time. A series of experiments is carried out under different conditions and combinations of the two parameters. X_1 refers to reactant's quantity and X_2 to stirring time; b_0, b_1, b_{12} are the importance factors that reveal the weight of each parameter. Stoichiometric quantity of the reactant is used as center 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) a 110% of reactant's quantity is added with a stirring time of 45 min while at the lower (-1), a 90% of the stoichiometric quantity is added with 15 min stirring time. Below are presented the equations that resulted from the analysis. Equation 1 shows that the most important parameters for the Mg^{2+} recovery were parameter X_1 (reactant quantity) and also the interaction of X_1 and X_2 (reaction time). Concerning the recovery of Ca^{2+} the extreme values where arithmetically close to the stoichiometric ones, therefore the factorial design in this case could not be applied.

$$Y = b_0 + b_1*X_1 + b_{12}*X_1X_2 = 1.549 - 0.156*X1 - 0.098*X1X2$$

***Equation 1** First degree equation for* Mg^{2+} *recovery*

$$Y = b_0 = 0.999$$

***Equation 2** Zero degree equation for* Ca^{2+} *recovery*

The optimum results for the Mg recovery were obtained by adding 90 % of the stoichiometric quantity of NaOH in the brine sample and stirring the mixture for 45 min. Under these conditions, a 99.7 % recovery of $Mg(OH)_2$ was achieved. As for the precipitation of $CaCO_3$ it was proved that a 100 % recovery performed by adding the stoichiometric quantity of Na_2CO_3 and stirring for 30 min. The resulted diagrams from the X-Ray Diffraction analysis are presented below and confirm that the recovered crystals are composed of $Mg(OH)_2$, $CaCO_3$ and KCl. Figure 2 shows the presence of Brucite and Magnesite and some $CaCO_3$ impurities in precipitated $Mg(OH)_2$. Figure 3 proves the precipitation of Calcite and Portlandite after soda addition. Finally, Figure 4 shows the presence of potassium; Sylvite and traces of Potassium sulfate. Recovered crystals of KCl are shown in Image 1.

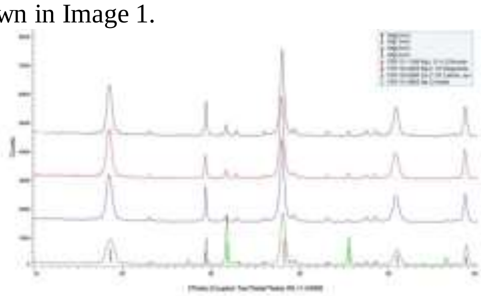

Figure 2. Graphic representation of the presence of **$Mg(OH)_2$**

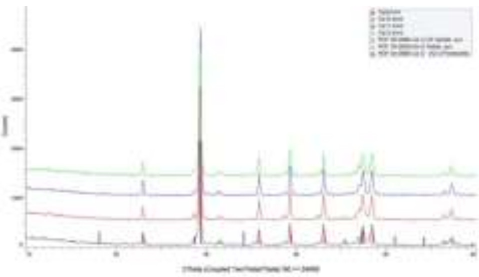

Figure 3. Graphic representation of the presence of **$CaCO_3$**

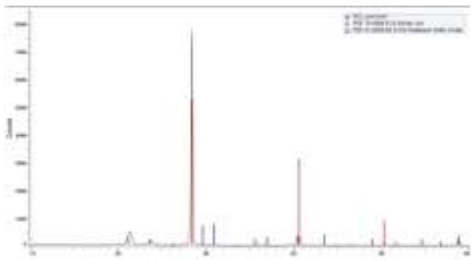

Figure 4 Graphic representation of the presence of **KCl** crystals

Image 1. KCl crystals

The main contribution of this work is the acquisition of end-products that add high value in the existing desalination plants, thus the alignment with Circular Economy Package. Avoidance of brine disposal in the sea decreases its impact on the environment and the aquatic life. In addition, recovery of nutrients from brine reduces 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 SB technology framework outlines a sustainable, competitive Zero Liquid Discharge approach to completely convert SB into reclaimed water and salts of commerce.

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