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Selective separation of seawater Mg^{2+} ions for use in downstream water treatment processes

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ABSTRACT

A nanofiltration-based method is presented for selectively separating soluble Mg(II) species from seawater, with the aim of using the Mg-loaded brine for either enriching desalinated water with magnesium ions or for enhancing precipitation of struvite from wastewater steams. Two 2.4″ commercial NF membranes were tested under varying operational conditions. The membrane that was chosen for further investigation (DS-5 DL, Osmonics) showed lower Cl:Mg and Na:Mg concentration ratios in the brine, and improved performance (with respect to the investigated process) at high recovery values. Since the addition of antiscalants was perceived detrimental to the downstream uses of the brine, the aquatic chemistry program PHREEQC was used to simulate the critical (highest) recovery values at which no $CaSO_4$ would precipitate, assuming two concentration polarization factors. To prevent $CaCO_3$ precipitation at the critical recovery values a theoretical calculation was performed (PHREEQC) to determine the required strong acid dosages to the raw seawater. Using the DS-5 DL membrane at 64% recovery, the attained Mg(II) concentration in the brine was 3500 mg/l. Therefore, for attaining 12.15 mg Mg/l of desalinated water the brine should be dosed to the water at a 1:288 ratio, resulting in additional concentrations of 32.5 mg SO_4^{-2}/l, 89.3 mg Cl^-/l, 39.4 mg Na^+/l, 3.3 mg Ca^{+2}/l, and 0.01 mg B/l. The overall cost of the proposed process was estimated at 0.00098 \$/m^3 product water, i.e. approximately five times lower than two assessed alternative processes and more than one order of magnitude cheaper than implementing direct dissolution of chemicals, using either $MgCl_2$ or $MgSO_4$.

1. Introduction

Seawater is characterized by a high Mg^{2+} concentration (~1430 mg/l in the Mediterranean Sea; 1280 mg/l on average in the oceans) and a relatively high Ca^{2+} concentration (400–500 mg/l). Mg^{2+} ions, if separated selectively from seawater (i.e. if the counter anions are made up predominantly from the relatively non-problematic species SO_4^{2-} rather than Cl^-) can be used in a cost effective fashion within a variety of water/wastewater treatment processes. Two of these applications, i.e. Mg^{2+} addition to post treated desalinated water; and removal of orthophosphate species from wastewater via precipitation of struvite ($MgNH_4PO_4$), a potentially reusable product, are discussed below. However, efficient and low cost separation of Mg^{2+} ions from a solution (seawater) which contains a very high concentration of Cl^- ions (~20,000 mg/l) and Na^+ ions (~11,000 mg/l), constitutes a challenge. The presence of these two monovalent ions (along with other seawater constituents, e.g. boron) should be minimized since they are unwanted in the context of both desalinated water and wastewater operations. This work presents a nanofiltration-based method for the separation of Mg^{2+} ions from seawater. Before a detailed description of the process is presented, the main potential uses of Mg-rich solutions from seawater origin are discussed.

1.1. *Possible uses for cheap Mg^{2+}-containing solutions within water treatment processes*

1.1.1. *Addition of magnesium ions to the product water within the post treatment step of desalination plants*

The World Health Organization (WHO) has recommended in its recent publications the inclusion of Mg^{2+} and Ca^{2+} ions in desalinated and naturally soft waters [1,2] because of their acknowledged public health beneficial effects. Both ions are welcome not only in drinking water but also in desalinated water designated for irrigation [3] and in treated wastewater from desalinated water origin [4]. From the human health perspective, magnesium ions are recommended by the WHO at a concentration higher than 10 mg Mg/l and calcium ions at a concentration higher than 20–30 mg/l [1,2]. Following this recommendation, the Israeli Ministry of Health is currently promoting a new regulation to add a minimum of 10 mg/l

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of Mg^{2+} to desalinated water. In all desalination plants in Israel, Ca^{2+} ions are added as part of the treatment since calcium (and bicarbonate) ions are also required for "chemical stability" purposes, i.e. to reduce the aggressiveness of soft waters to the water distribution systems. Calcium and bicarbonate ions are added to desalinated waters in the "post treatment" step, through the dissolution of solid $CaCO_3$ (quarry limestone), which releases to the water both Ca^{2+} ions and carbonate alkalinity. However, to date, Mg^{2+} ions are not added.

Hitherto, the addition of Mg^{2+} ions to desalinated water could potentially be carried out using one of the following processes: (1) Direct dosage of magnesium salts, such as $MgCl_2$ or $MgSO_4$, to the water, as practiced in Cyprus, for example [5]; (2) dissolution of quarry dolomite ($MgCa(CO_3)_2$) rocks [6]; or (3) a process based on extraction of Mg^{2+} ions from seawater by a cation exchange resin and subsequent release of the Mg^{2+} to the desalinated water in exchange for Ca^{2+} ions, which originate from $CaCO_3$ dissolution [7]. Another option that is sometimes proposed in seawater desalination plants is to blend the desalinated water with ~1% seawater (volume to volume basis) to attain Mg^{2+} concentration of ~13 mg/l. This option suffers from a major disadvantage that in addition to Mg^{2+}other unwanted seawater species, namely Na^+, Br^- and Cl^- ions are added to the water at high concentrations.

1.1.2. Use of Mg^{2+} salts for recovery and reuse of a phosphorus fertilizer product from wastewater streams

A cheap Mg-rich solution separated from the sea may be also used for intentional precipitation of the crystal struvite ($MgNH_4PO_4{\cdot}6H_2O$) as part of the operation of domestic wastewater treatment plants located near the shore. Struvite, a white crystalline compound, consisting of magnesium (Mg^{2+}), ammonium ($NH_4{}^+$) and phosphate ($PO_4{}^{3-}$) at equal molar concentrations, is known to precipitate in wastewater treatment plants (WWTP) around the world. Such precipitation is normally unwanted since it gives rise to clogging of pipes and pumps, causing both operational difficulties and increased maintenance costs. However, whereas in WWTP struvite is a recognized operational problem, in agricultural applications it may be considered a desirable product: struvite may be employed as a cheap replacement to slow-release fertilizers or as a component in other commercial fertilizers [8–10], due to its low (but not very low) solubility in neutral pH solutions [11].

In addition, since it has been shown that a significant percentage of the dissolved phosphate in wastewater can be recovered through struvite crystallization if controlled precipitation is applied [10,12,13,14,15], using the recovered phosphorous makes struvite a sustainable product. This is significant as natural phosphorus resources are dwindling worldwide and according to current assessments stocks will reach a critically low point by the end of the century [16]. Struvite precipitation occurs only when at least two of the three species, Mg^{2+}, $NH_4{}^+$ and $PO_4{}^{3-}$ are present at relatively high concentrations. Such combination of concentrations is encountered in WWTP only in the anaerobic sludge treatment line. Thus, deliberate precipitation of struvite is typically located on the pipe which delivers the anaerobic digester supernatants back to the treatment plant. At this point the Mg^{2+} concentration is typically roughly one order of magnitude smaller than that of the total ammonia and phosphate weak acid systems, hence the dosage of external magnesium salts (namely $MgCl_2$ and $MgSO_4$) is required for precipitation of a significant mass of struvite solids [12,17–21]. To date, the high cost of magnesium salts limits the application of this process. Notwithstanding, recovery of phosphate from wastewater streams will become, in the foreseeable future, essential for maintaining appropriate phosphorus supply for food production, all over the world.

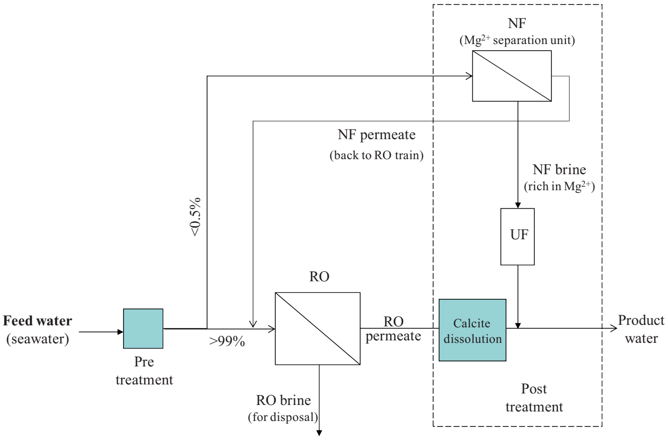

Fig. 1. Schematic of the proposed Mg^{2+} separation process and re-injection of the NF brine to the effluent of the calcite dissolution reactor as part of the desalination post treatment process (indicated by a dashed line).

With respect to this option (similarly to the desalinated water option, described previously) it is noted that addition of unwanted components (Cl^-, Na^+, etc.) to wastewater should also be minimized, particularly in places where treated effluents are reused for agricultural irrigation (e.g. Spain, Australia, Israel, etc.). Another point worth mentioning is that if the Mg^{2+} separation method that is used results also in a high Ca^{2+} concentration, the dosage of Ca^{2+} along with the Mg^{2+} may interfere with the precipitation of a pure struvite product, due to possible competition between struvite and calcium phosphate precipitants. This point, which is not addressed in this paper, requires further investigation.

1.2. The proposed process

This paper introduces a new method for separating Mg^{2+} ions from seawater in a fashion that maximizes the Mg^{2+} concentration in the target solution while at the same time minimizes the addition of the unwelcome species (Cl^-, Na^+, B, Br^-) to the receiving water. The Mg^{2+} separation method is based on passing seawater through a specific NF membrane in a way that (1) enhances separation between divalent and monovalent ions; (2) generates brine with the highest Mg^{2+} concentration possible without using antiscalants which are unwelcome in the receiving water in both discussed alternatives, i.e. desalinated water and struvite precipitation reactors; (3) minimizes the ratio between the unwanted Cl^- and Na^+ ions and the wanted Mg^{2+} ions in the brine. The final NF Mg^{2+}-rich brine can be ultimately used as the solution which supplies Mg^{2+} ions either as part of the post treatment stage in the desalination plant or dosed for enhancing struvite precipitation within the operation of wastewater treatment plants. The proposed process is depicted schematically in Figs. 1 and 2 for the two suggested uses of the brine.

NF membranes are characterized by an intermediate molecular weight cut-off between 150 and 1000 dalton, i.e. in between RO and UF membranes. Due to a charged surface (typically negative, rarely positive) they can be used for separation of electrolytes according to ionic valences. Many works have attempted to model the rejection of uncharged and charged species by NF membranes (e.g., [22–25]. Negatively charged NF membranes typically reject $SO_4{}^{2-}$ ions at >99% [23] while positively charged membranes can reject Ca^{2+} and Mg^{2+} at a similar efficiency [26]. A few models have been developed to predict the rejection of ions through NF membranes in the context of multi-component feeding solutions (e.g., [22,25,27,28]). However, with the current knowledge it seems that accurate predictive calculations, which involve combined effects of