

Wastewater Reuse: Treatment of Membrane Concentrates by induced precipitation

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Abstract

The widespread application of nanofiltration (NF) and reverse osmosis (RO) membranes in wastewater reuse inevitably generates a concentrate stream. Due to high concentrations of phosphate and salts, disposal of membrane concentrates is a problem which seriously constrains the application of this technology, especially in inland applications. There is a need for technologies which facilitate an affordable and environmentally-safe disposal of membrane concentrates. The objectives of this study are to investigate appropriate treatment techniques to 1) increase the recovery of the membrane filtration to minimize the volume of the concentrate stream, and 2) decrease the nutrient load of the concentrate to enable discharge into surface water bodies. The results show that chemical precipitation by dosing of sodium hydroxide solution is rapid and removes more than 90 % of phosphate and calcium ions. By the removal of calcium ions, chemical precipitation can significantly reduce the scaling potential of NF and RO concentrates. This may allow for higher recoveries in the NF/RO process.

Keywords: membrane concentrate; precipitation; scaling potential, wastewater reuse

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1 Introduction

The reuse of treated municipal wastewater is already practiced in many parts of the world and continues to gain importance. The necessary advanced wastewater treatment for reclamation includes membrane filtration processes, which can provide an excellent barrier for pathogens and contaminants. However, high pressure membrane processes will inevitably generate a concentrate stream of 5 – 25 % of the feed volume. Management and disposal of membrane concentrates is a problem which might seriously constrain the application of this technology in inland communities (Nederlof et al. 2005), and also the widely practiced discharge into seawater has caused environmental concerns (Tularam and Ilahee 2007). For inland applications, treatment options for membrane concentrates include discharge into surface water bodies, discharge into wastewater treatment plants, and deep-well injection. Due to the rejection of polyvalent anions by nanofiltration (NF) and reverse osmosis (RO) membranes, high concentrations of phosphate occur in membrane concentrates. Since even small phosphate concentrations can cause eutrophication, phosphorus-rich concentrate streams cannot be discharged into small to medium-sized surface water bodies. Consequently, both discharge into surface water and deep-well injection are difficult due to severe restrictions by water authorities. From a resource perspective, a potential recovery of nutrients from the concentrate stream might also be an interesting option. Discharge into the sewer system is not always possible and results in high costs. There is a need for technologies which facilitate an affordable and environmentally safe concentrate disposal. Where the above disposal options are not feasible, the alternative is zero liquid discharge (ZLD). In ZLD desalination, the concentrate is treated to produce desalinated water and essentially dry salts, which can be achieved by thermal desalination or evaporation ponds. This results in high energy or large land area demands (Bond 2006).

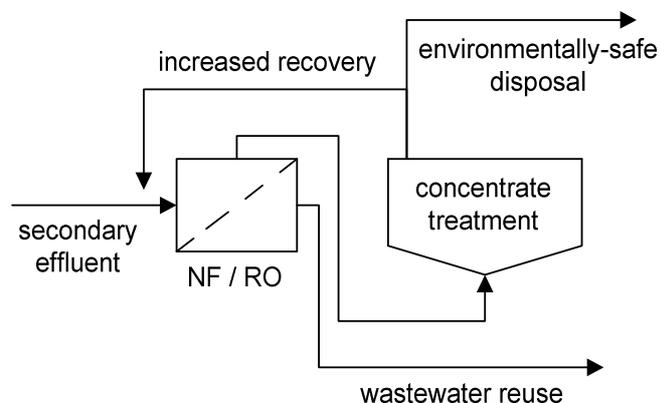


Figure 1: Investigated treatment scheme

The objectives of this study are to investigate appropriate treatment techniques to 1) increase the recovery of the membrane filtration to more than 98 % and minimize the volume of the concentrate stream, and 2) increase the concentrate quality to enable discharge in surface water bodies (Figure 1). Volume minimization requires the removal of scaling components, e.g. calcium ions. Chemical precipitation / softening has been reported to be a potential treatment option for this purpose (Heijman et al. 2007). Since most concentrate brines are supersaturated with respect to calcium phosphate compounds, induced crystallization of calcium phosphates using an appropriate seed material such as calcite (Donnert and Salecker 1999) or tobermorite (Berg et al. 2006) might be another treatment option.

2 Methods

Materials and model solutions

Membrane concentrate was produced from filtered secondary effluent and Berlin tap water using a nanofiltration pilot plant. A DOW NF270 membrane was operated in cross-flow mode with a water conversion factor (WCF) of 0.7 – 0.8. NF concentrate of filtered secondary effluent and tap water concentrate was produced discontinuously in a 200 L feed tank. NF concentrate was recycled to the feed tank, NF permeate was discarded.

To study the effect of concentrate water quality, RO concentrate from a full-scale RO application (the Torreele facility in Wulpen, Belgium) was also used. Reverse osmosis of ultra-filtered secondary effluent is used as a pre-treatment for infiltration and reclamation (Van Houtte and Verbauwheide 2008). The RO plant is operated using DOW Filmtec 30LE membranes at a WCF of approx. 0.75. Table 1 shows water quality data for the used concentrate solutions. RO concentrate data are in agreement with recently reported discharge water data (Van Houtte and Verbauwheide 2008).

Batch precipitation experiments

In 2 L batches, different amounts of sodium hydroxide solution (3.1 – 22.5 mM NaOH) and calcite seeds were added to 1.6 L of NF and RO concentrates. After addition of NaOH, the solution was stirred for 2 h at 250 rpm. Samples were taken regularly, filtered (0.45 µm) and analyzed for phosphate and other ions.

Fixed-bed calcite column

Three laboratory-scale columns were operated in series using NF concentrate of tertiary effluent. The columns had a diameter of 25 mm and 40 mm, respectively, and used a total dry mass of 600 g calcite as filter material. The total empty-bed contact time (EBCT) was adjusted to 25 minutes. The columns were operated for 165 h using a total volume of 200 L NF concentrate.

Analyses

Orthophosphate was determined using a flow injection analyzer (FIAstar 5000, Foss Tecator) according to ISO 15681-1. The standard deviation was determined to be 4.8 % at a mean concentration of 0.016 mg/L $\text{PO}_4^{3-}\text{-P}$ and 0.77 % at 3.8 mg/L $\text{PO}_4^{3-}\text{-P}$ with a detection limit of 3 µg/L. The concentrations of dissolved ions were analyzed using Ion Chromatography (Dionex IonPac AS 11/14). DOC was analyzed by thermal-catalytic oxidation using a highTOC analyzer (elementar Analysensysteme, Germany).

3 Results and Discussions

Figure 2 shows the removal of phosphate and other water constituents by induced precipitation by addition of NaOH. For the NF concentrate, a phosphate removal of 70 % is reached using 3.1 mM NaOH, corresponding to approx. pH 9.2. Higher dosages of NaOH increase the removal to close to 100 % at a NaOH dosage of 9.4 and 15.6 mM, corresponding to pH 10.2 and pH 11.4, respectively. For RO concentrate, a complete phosphate removal can already be achieved using 6.3 mM, corresponding to pH 9.2. Besides the removal of phosphate, chemical softening reduces the concentration of Ca^{2+} (removal of 50-90 %) effectively. At pH values higher than 10.5, the removal of

Mg^{2+} is possible. This is due to the precipitation of $Mg(OH)_2$, which is known to occur at these pH values. The removal of K^+ , Cl^- , SO_4^{2-} is negligible (lower than 10%). The addition of NaOH to increase the pH and precipitate calcium carbonate and calcium phosphate, leads to an increased Na^+ concentration and therefore no reduction of TDS is achieved.

Figure 3 shows the calculated solubility index (SI) for calcium carbonate of the membrane concentrate solutions prior and after batch precipitation as a function of pH. The calculation is based on the water quality data shown in table 1, chemical speciation calculations were done using the software MINEQL+. Obviously, both membrane concentrate solutions have a similar scaling potential as expressed in the SI_{CaCO_3} . Chemical precipitation using NaOH can significantly reduce the scaling potential and may facilitate higher recoveries in the membrane filtration step.

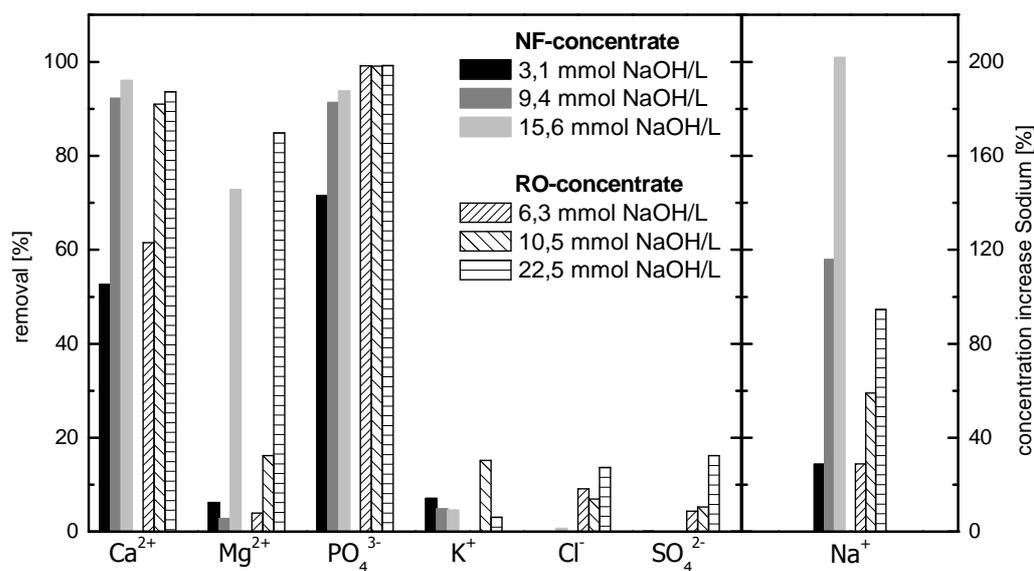


Figure 2: Removal of dissolved ions by chemical precipitation using different amounts of NaOH

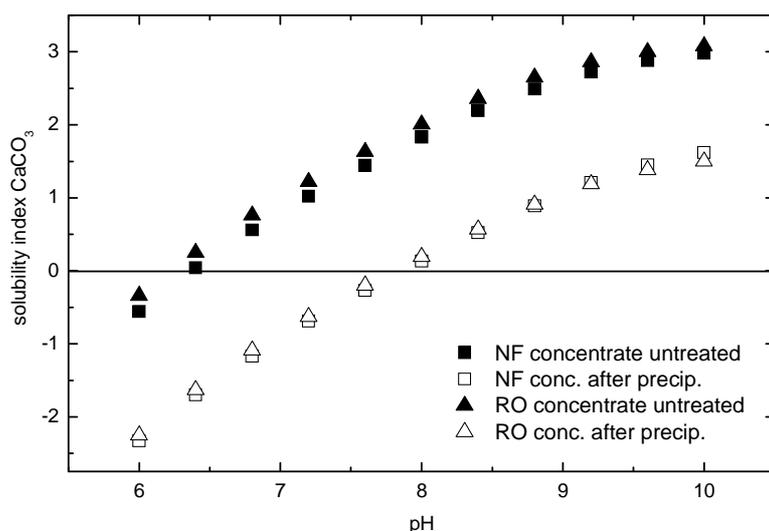


Figure 3: Calculated solubility index for calcium carbonate for membrane concentrate prior and after treatment

Figure 4 shows the kinetics of the precipitation reaction. Phosphate and calcium removal is rapid, more than 90 % removal are reached within 0.5 minutes. The lowest dosage of 3.1 mM NaOH corresponding to pH 9.2 is not sufficient to achieve a comparable removal of phosphate and calcium. After an initial concentration decrease, a slight increase is observed after 5 to 10 minutes, before a slow concentration decrease can be observed until the end of the experiment. This might be explained by the kinetics of the precipitation reaction, which result in pH changes.

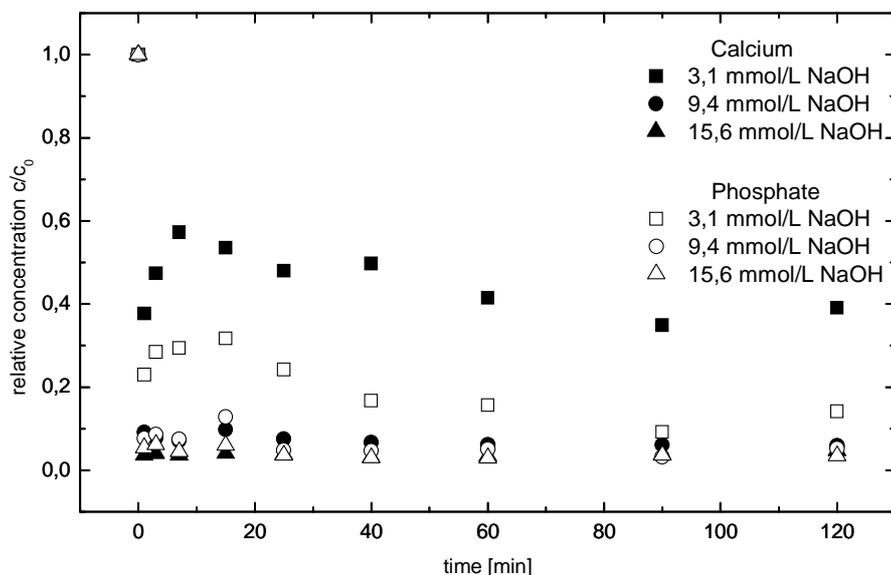


Figure 4: Precipitation kinetics; calcium and phosphate concentration decrease after addition of NaOH

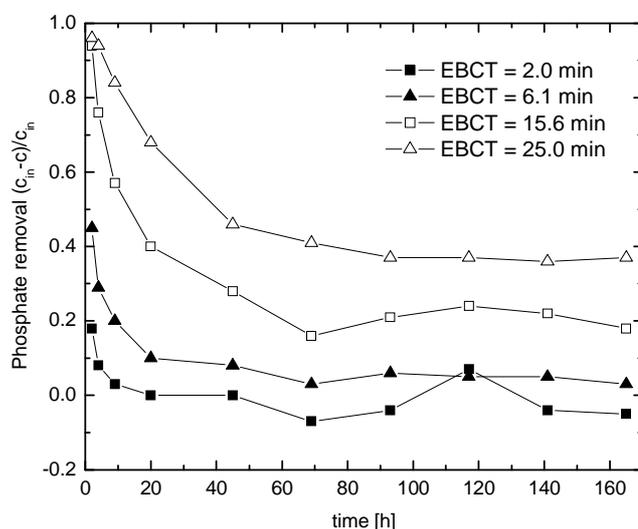


Figure 5: Phosphate removal in a calcite fixed-bed column crystallizer for different empty bed contact times ($c_0 = 0.587 \text{ mg/L PO}_4^{3-}\text{-P}$, pH 8.0 – 8.6)

Calcite can provide a condensation surface for the precipitation of hydroxyl apatite. If calcite seeding material is added without addition of NaOH, phosphate and calcium removal can also be observed, but the precipitation is kinetically inhibited. After 30 h batch operation, only 40 % removal were observed

(data not shown). These observations were confirmed by results from operation of a calcite fixed-bed column. Figure 5 shows an initially increased removal of phosphate, probably due to adsorption onto the calcite surface. After 70 h of operation, a steady state is reached. For an EBCT of 25 minutes the influent phosphate concentration of 600 $\mu\text{g/L PO}_4^{3-}\text{-P}$ was reduced to 350 $\mu\text{g/L PO}_4^{3-}\text{-P}$, corresponding to a $\text{PO}_4^{3-}\text{-P}$ removal of around 40 %. A higher EBCT can most likely improve phosphate removal.

4 Conclusions

- Chemical precipitation using NaOH is rapid and removes more than 90 % of phosphate and calcium.
- Induced crystallization by addition of calcite seeds shows a good removal of phosphate (up to 40%) and a partial removal of calcium, but the required contact times are high due to slow kinetics.
- Chemical precipitation significantly reduces the scaling potential and may therefore allow for higher recoveries in high-pressure membrane filtration.
- High removal of phosphate may permit environmentally-safe discharge into surface water bodies.

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References

- Berg, U., Donnert, D., Weidler, P. G., Kaschka, E., Knoll, G., and Nueesch, R. (2006). "Phosphorus removal and recovery from wastewater by tobermorite-seeded crystallisation of calcium phosphate." *Water Science and Technology*, 53(3), 131-138.
- Bond, R. "Desalination with Zero Liquid Discharge." *AWWA Water Quality Technology Conference*, Denver.
- Donnert, D., and Salecker, M. (1999). "Elimination of phosphorus from municipal and industrial waste water." *Water Science And Technology*, 40(4-5), 195-202.
- Heijman, S. G. J., Guo, H., Li, S., and van Dijk, J. C. "Zero liquid discharge: 99% recovery is possible." *7. Aachener Tagung Wasser und Membranen (AWM)*, Aachen.
- Nederlof, M. M., van Paassen, J. A. M., and Jong, R. (2005). "Nanofiltration concentrate disposal: experiences in The Netherlands." *Desalination*, 178(1-3), 303.
- Tularam, G. A., and Ilahee, M. (2007). "Environmental concerns of desalinating seawater using reverse osmosis." *Journal Of Environmental Monitoring*, 9(8), 805-813.
- Van Houtte, E., and Verbauwhe, J. (2008). "Operational experience with indirect potable reuse at the Flemish Coast." *Desalination*, 218(1-3), 198-207.