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# Separation of antiscalants from reverse osmosis concentrates using nanofiltration

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ABSTRACT

One of the serious problems found in desalination using reverse osmosis (RO) is concentrate or brine management. This concentrate can actually be used as a raw material for salt production. However, antiscalants added during RO process should be removed before salt crystallization. This paper presents the separation of antiscalants from RO concentrate solution using nanofiltration (NF) membrane. Sodium hexametaphosphate (SHMP) and disodium ethylenediaminetetraacetate ($Na_2EDTA$) were used as models of antiscalants. The effect of antiscalants concentration and addition of natural organic matters on both flux behavior and rejection were investigated. The results showed that the permeate flux behavior was influenced by the sodium chloride solution itself as a solution background, antiscalant type and antiscalant concentration. Osmotic pressure, concentration polarization and fouling or scaling contributed to flux decline during nanofiltration of antiscalants. NF membrane demonstrated very high rejection for both SHMP and $Na_2EDTA$.

## 1. Introduction

Reverse osmosis (RO) as today's leading process for producing fresh water from seawater and brackish water has replaced the conventional desalination process. This technology has successfully been utilized to solve desalination problems due to its ability to produce superior and stable quality of water in a relatively little energy demand. However, this process results in concentrated saline water, also known as RO concentrate waste, which contains high concentration of dissolved salts [1,2]. This RO brine waste usually contains concentrations of total dissolved solids (TDS) 68,130 mg/L, $Ca^{2+}$ 961 mg/L, $Mg^{2+}$ 2940 mg/L, $Cl^{-}$ 42,500 mg/L, $Na^{+}$ 17,000 mg/L, $HCO^{3-}$ 267 mg/L, $SO_4^{2-}$ 6420 mg/L and chemical residues from pre-treatment process of RO [3]. The management of the concentrated waste stream is one of the remaining obstacles for the implementation of desalination using RO membranes, since the concentrate is usually unusable and has to be discharged or further treated. Normally, brines resulted from desalination plants in coastal area are directly discharged to the sea, posing adverse environmental effects on the receiving marine environment [4]. In addition, treating concentrate of RO is very costly.

Currently, brine utilization is getting more and more attention from both researchers and industries. In principle, brine utilization is directed to either increasing water or obtaining valuable components from seawater [5–11]. Among them, salt production by evaporating ~~of~~ RO concentrate is very interesting from practical point of view. Membrane distillation and membrane crystallizer have been proposed to increase water recovery and to obtain salt crystals [6,8,11]. However, these processes did not separate antiscalants from the salt crystals. It is important to note that antiscalants are present in RO brine as a consequence of control of scaling formation on RO membrane surface during desalination [12]. Therefore, separation of antiscalants from RO brine is very important when salt production will be performed.

Common antiscalants used for desalination using RO are polyacrylic acid, carboxylic acids, polyphosphates, phosphonate (threshold agents), anion polymer, sodium hexametaphosphate (SHMP), trisodium phosphate, crystal modifiers, sequestering agent (disodium ethylenediaminetetraacetate/$Na_2EDTA$), and dispersant [13–15]. Among several types of antiscalants, SHMP and $Na_2EDTA$ are the most frequently used due to their effective ways to prevent scaling in the desalination process [16–18]. The existence of antiscalants in the RO concentrates waste has negative impact on the environment and health. SHMP is toxic, causing heat to the water body, damaging the reef, eutrophication and heavy metal accumulation. In addition, SHMP causes irritation of the mucous membranes if inhaled, intestinal damage if ingested, gastrointestinal irritation, nausea, diarrhea, affect the nervous system in high doses, heart disorders, and decreased blood pressure. $Na_2EDTA$ leads to eutrophication and if it enters into the human body in excessive amounts causes body deficiencies of Ca and other minerals. This is because of

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$Na_2EDTA$ has an effective binding metal ions such as calcium ions [19,20]. Therefore, the proper method is needed to eliminate antiscalant from reverse osmosis concentrate.

Several techniques have been proposed for separation of antiscalants. Boels et al. [21] and McCool et al. [13] reported that iron coated waste filtration sand and intermediate concentrate demineralization can eliminate antiscalant from the RO concentrate. However, this method requires chemicals addition, generates sludge, low permeate quality, high operating costs, and the antiscalant in the RO concentrate is still not completely separated. In this study, separation of antiscalant from waste concentrates RO using nanofiltration membranes was investigated. Nanofiltration was selected because it requires lower operating pressures and temperatures, high rejection of organic molecules, low operation and maintenance costs [22]. SHMP and $Na_2EDTA$ were used as models of antiscalants dissolved in RO concentrate waste. Furthermore, sodium alginate was used as a model of organic matters in the waste concentrates. It should be noted that concentrate wastes, as byproducts of desalination using RO membrane, contain organic substances [23].

## 2. Materials and methods

### 2.1. Materials

In this study, SHMP and $Na_2EDTA$ were used as models of antiscalants, while sodium alginate (SA) was used as a model of natural organic matters. SHMP and SA were purchased from local company, Semarang, Indonesia. $Na_2EDTA$ was purchased from Merck, Germany. NaCl (technical grade) was purchased from PT. Unichem Candi Industri, Indonesia. $KH_2PO_4$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $NH_4VO_3$, HCl, $H_2SO_4$ and NaOH were purchased from Merck, Germany. NaCl (p.a. grade) was purchased from Sigma Aldrich Germany. Nanofiltration membrane (NF 270) was obtained from Dow Filmtec Membranes, USA.

### 2.2. Methods

The filtration experiments were performed by using a home-made laboratory scale for cross flow filtration [24].The set-up consisted of a feed tank (3 L volume), a pump, a pressure indicator connected to feed side of membrane to determine the trans-membrane pressure and a flat-sheet membrane cell. Fig. 1 shows the simplified diagram of experimental set-up. A new circular membrane disk was used in each experiment. The membrane was firstly compacted by filtering pure water for at least 0.5 h at a pressure of 600 kPa. The volume of feed was much larger than the volume taken as a sample for the analysis. In addition, the retentate and permeate were returned to the feed tank. All experiments were performed at room temperature (28 ± 2 °C) and at a constant trans-membrane pressure (500 kPa).

Synthetically prepared RO concentrate solution was used in this study. The RO concentrate solution was prepared by dissolving sodium chloride (technical grade) in pure water to obtain 60,000 ppm solution. A certain concentration of either SHMP or $Na_2EDTA$ with and without addition of sodium alginate was dissolved in this synthetic concentrate solution. The concentration of SHMP was varied, i.e. 2, 4, and 6 ppm, while the concentration of $Na_2EDTA$ was varied, i.e. 2, 3, and 4 mM. The selection of antiscalants concentration was based on the concentration when they are used in RO process.

The flux profile was expressed in term of normalized flux ($J/J_o$). The initial flux ($J_o$) was measured by passing pure water after the compaction was conducted, while the permeate flux (J) was gravimetrically measured every 10 min during the filtration was performed. The concentrations of SHMP and $Na_2EDTA$ were analyzed using spectrophotometer UV–Vis (Genesys 10S UV–Vis, USA) at wavelength of 400 nm and 263 nm, respectively. The membrane surface was visualized by using a Scanning Electron Microscope (JEOL JSM-6510LA SEM, Japan). The outer surface of the sample was coated with gold/palladium and sputtered for 0.5 min before analysis.

## 3. Results and discussion

### 3.1. Flux behavior during nanofiltration of antiscalants

The nanofiltration behavior of antiscalant was investigated by filtering the feed solutions containing different concentration of SHMP and $Na_2EDTA$. In addition, the feed solution containing NaCl only (0 ppm of antiscalant) was also filtered. The experiments were performed at constant trans-membrane pressure. The results are expressed in term of flux (normalized flux) as a function of filtration time and presented in Figs. 2 and 3.

It is shown that both antiscalants solution displayed rapid flux decline in the early stage of filtration. Thereafter, relatively constant permeate after 30 min of filtration was demonstrated by SHMP, whereas gradual decrease was shown by $Na_2EDTA$. The flux decline during nanofiltration can basically be attributed to concentration polarization, osmotic pressure and fouling or scaling. The presence of concentration polarization on the membrane surface can increase the level of flux decline due to osmotic pressure. Furthermore, concentration polarization can also facilitate fouling by altering interactions

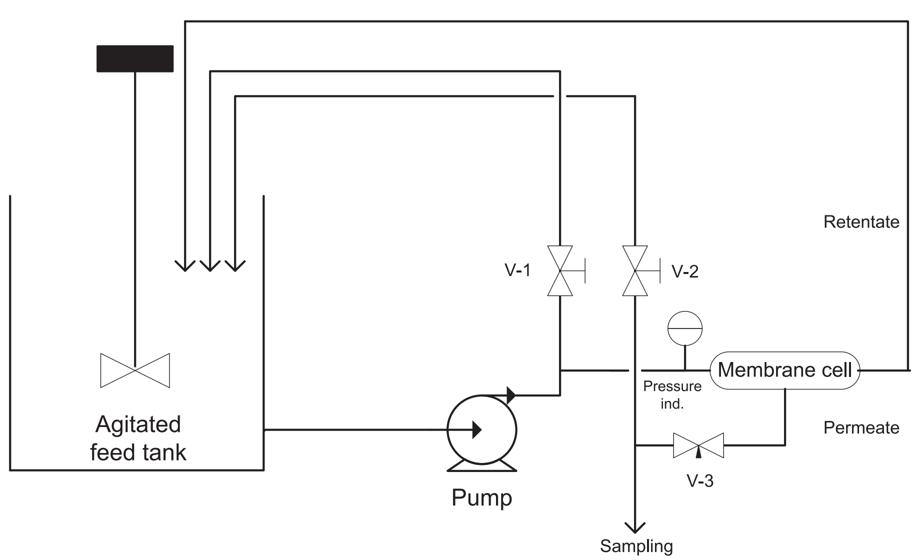


**Fig. 1.** The simplified diagram of nanofiltration experimental set-up [24].