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Freeze concentration for membrane concentrate treatment and volume reduction

Wa Gao

Department of Civil Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1 Canada
Email: wagao@lakeheadu.ca

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ABSTRACT

Application of membrane technologies has increased dramatically in recent years due to limited unpolluted source water available. Membrane filtration, especially reverse osmosis and nanofiltration, has been used to desalinate seawater, brackish groundwater, and reclaim wastewater for both potable and nonpotable uses. With continued installation of membrane plants, concentrate disposal is becoming a major factor affecting the viability of many membrane projects. Preliminary experimental results indicated that significant reduction in solids, conductivity, and TOC causing materials could be achieved in the ice formed from freezing of membrane concentrate. Freeze concentration could be an effective treatment and volume reduction method for membrane concentrate.

Keywords: Membrane concentrate treatment; Freeze concentration; Waste volume reduction; Impurity rejection; Wastewater treatment; Desalination; Membrane filtration

1. Introduction

Due to the limited unpolluted source water available, desalination of seawater or brackish water is becoming increasingly an important method for the production of potable water and the reuse of treated municipal wastewater is now practiced in many parts of the world [1]. Membrane technologies play an important role in seawater/brackish water desalination and wastewater reuse. Membrane filtration plants, especially reverse osmosis and nanofiltration plants, have increased dramatically in recent years. With continuing installation of membrane plants, disposal of the concentrate is becoming a major factor affecting the viability of many membrane projects [2]. Membrane filtration plants generate a large volume of liquid waste (concentrate) that includes the reject-brine, backwash water, and chemical solutions used for cleaning of membranes. The product water recovery was only 30–40% for some membrane-based desalination plants [3–5]. In most cases, the concentrate was discharged into surface water or sanitary sewers without any treatment (except some type of pH adjustment for cleaning wastes) although deep well injection or evaporation ponds were also used [1,3–5]. Risk implications associated with membrane concentrate disposal are to date not adequately understood [2]. Discharging the concentrate of desalination plants into seawater has been considered a safe option, but recent studies showed that dilution of the concentrate may be lower than the usually accepted and it may significantly affect extensions of marine communities [5,6]. The concentrate composition could adversely influence the sewage treatment processes and increase dissolved solids content in the final effluent (which could affect its reuse) when discharging

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a large volume of the concentrate into sanitary sewers [4]. Salts, metals, and organic contaminants contained in the feed water become concentrated with the process, along with chemicals and reaction byproducts from pretreatment. High concentrations of pharmaceutical drug residues and endocrine disrupters were found in membrane concentrate as it could serve as a large reservoir for drug residues [2]. With the current membrane concentrate disposal practice, contaminants such as arsenic, mercury, or pharmaceutical drug residues that already removed from feed water were released back into the environment at higher concentrations. Meanwhile, concentrate disposal procedures have the highest degree of complexity and are subjected to increasingly stringent discharge regulations that are limiting the use of sanitary sewers and receiving streams for disposal [1]. Treatment of membrane concentrate is becoming necessary and volume minimization, even zero-liquid discharge may be soon required for some operations [3,1]. So far, limited efforts have been made to develop practical treatment technologies for environmentally sound management of membrane concentrate. The objective of this preliminary study was to investigate the potential of freeze concentration as a treatment method for membrane concentrate.

2. Freezing treatment of water, wastewater, or liquid wastes

Freezing technology has been used successfully in food and chemical industries for years, however, its application in water/wastewater treatment has been limited. Some researchers have examined the potential of freezing as a cost-effective water, wastewater, or liquid waste treatment method in recent years. Treatment of various industrial effluents or liquid wastes using freezing has been reported [7–12]. Freezing as a desalination method was investigated intensively in the past, and there are renewed interests in application of freeze technology in seawater or brackish water desalination, recently by Attia [13] and Rich et al. [14]. Freezing has long been recognized as an effective sludge conditioning technique and is becoming increasingly popular due to the improvements in the design and efficiency of the facilities [15]. For the regions where natural freezing is available, freezing is a simple and cost-effective alternative for wastewater and sludge treatment [16,10,17]. Facey and Smith [18] studied freeze-thaw technique for removal of color-causing materials in the concentrate of an ultrafiltration membrane plant used for treatment of kraft pulp mill effluent. Randall et al. [19] attempted using eutectic freeze crystallization (EFC) method to treat reverse osmosis brine and reported 97% conversion of the liquid waste from the reverse osmosis plant as pure water, pure calcium sulfate (98.0% purity), and pure sodium sulfate (96.4% purity). The overall estimated conversion of the waste stream generated from the reverse osmosis plant to viable products was calculated to be 99.9%. The advantages of using freezing as a treatment method include no addition of chemicals, high treatment efficiency, high capacity of waste volume reduction, recovery of a pure water stream that may be reused, and low corrosion of the treatment facility.

Freeze concentration is a physical process that involves the fractional crystallization of water and subsequent removal of ice. When freeze concentration is used to purify water or liquid waste, impurities are separated from water during the formation of ice crystals and concentrated in the liquid phase. Without any pretreatments and addition of chemicals, effective removal of dissolved organic and inorganic contaminants (nearly 100% in some cases), toxicity reduction, and waste volume minimization was achieved [8,11,12]. Recent study also indicated that freeze concentration could effectively remove pharmaceutically active compounds in water [20]. Freeze concentration of impurities can be accomplished using two techniques: suspension crystallization and progressive freezing. The conventional suspension crystallization method involves ice nucleation, ice crystal growth, and ice separation processes. The entire system is complex and requires expensive initial capital investment; therefore, its practical application has been limited. Instead of forming many small ice crystals, only a large single ice crystal is formed and grown on the cooling surface during progressive freeze concentration. The separation of ice crystals from the feed solution is much easier in progressive free concentration; thus, the operation system could be simplified to substantially reduce the process cost [21].

3. Materials and methods

3.1. Membrane concentrate samples

The membrane concentrate samples used in this preliminary study were collected from a municipal drinking water treatment plant that uses ultrafiltration process. The plant is an inland freshwater treatment plant and gets its source water from Lake Superior. The treatment capacity of the plant is about 114 ML/d. The membrane filters are cleaned with 100 mg/L chlorine solution three times per week and then 500 mg/L of chlorine solution once every month. The membrane concentrate samples used in this preliminary study were a mixture of the backwash (80%) and the cleaning

Table 1
Characteristics of the membrane concentrate samples used in this study

Parameter	Concentration
pH	7.95
Conductivity	211 μm/cm
Total solids (TS)	173 mg/L
Turbidity	3.65 (NTU)
Total organic carbon (TOC)	77 mg/L

solution (20%). The backwash solution was collected from the backwash equalization tank, and the cleaning solution was collected from the clean-in-place tank. The characteristics of the collected membrane concentrate samples are summarized in Table 1.

3.2. Freezing tests of the membrane concentrate

The progressive unidirectional downward freezing method used in the previous studies [20,8] was used in this preliminary research. The progressive unidirectional downward freezing technique was used because the freezing process is similar to the natural freezing occurring in a storage pond during winter and therefore might be modified as a natural freezing method for the treatment of membrane concentrate for those filtration plants located in the regions where natural freezing is available. The ice samples collected from this study was thus not washed. The source concentrate (feed water) was placed in 1000-mL beakers and frozen in an environmentally controlled test room (a walk-in freezer) (Climatic Testing Systems Incorporated, Warminster, PA, USA) at −7 ℃. The temperature fluctuation of the freezer was at ±0.5 ℃. Samples were precooled to near 0 ℃ before the freezing test. The beakers were insulated and freezing took place from top to bottom. The samples were stirred with magnetic bars during the freezing by placing the beakers on magnetic stirrers. The samples were taken out of the freezer after approximately 80% or 90% of the original volume was frozen. The degree of freezing (80% or 90%) was examined to evaluate the trade-off between volume reduction and the ice (water) quality. The unfrozen liquid was then separated from the ice. The ice samples were melted at room temperature.

3.3. Sample analysis

pH, conductivity, total organic carbon (TOC), total solids (TS), and turbidity of the source membrane concentrate (the feed water for the freezing tests), ice and unfrozen liquid samples collected were analyzed. *Standard Methods for the Examination of Water and Wastewater* [22] were followed for the parameters measured.

4. Results and discussion

Fig. 1 shows the pH ratios of the ice and unfrozen liquid samples to that of the feed water (C/C_o, where C_o is the concentration of the feed water and C is the concentration in an ice or liquid sample). The pH of the ice samples was slightly lower than that of the feed water while the pH of the unfrozen liquid samples was slight higher. The difference of pH between the ice and the liquid samples after freezing indicated the change in the distribution of ionic impurities in the ice (solid) and liquid phases. Similar observations were reported previously by other researchers, such as Workman and Reynolds [23] and Gross [24]. Ion transfer or the preferential incorporation of cationic impurities and their replacement by hydrogen ions in the ice during freezing was affected by many factors such as freezing rates, chemical nature, and concentrations of the impurities. The concentration of hydrogen ions in the ice phase was attributed to the competing processes of ion incorporation, rejection, and separation [24].

Fig. 2 compares impurity concentration ratios of the ice samples to those of the feed water. As shown in the figure, obvious reduction of conductivity, TOC, and total solids concentration were observed in all ice samples (all concentration ratios of the ice samples were <1.0). The removal efficiencies for ionic impurities, TOC causing materials, and solids were at the similar levels, about 70–80% reduction in the ice samples when

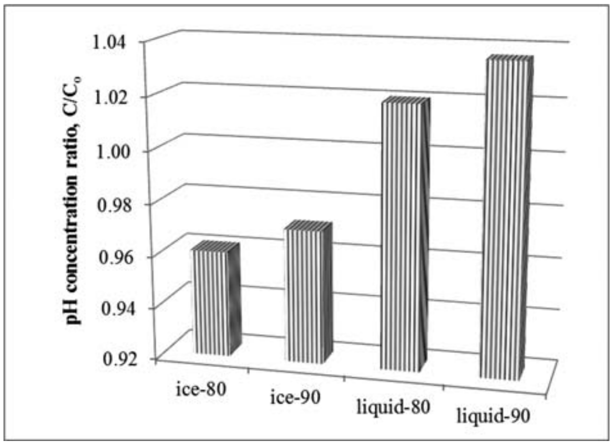

Fig. 1. Comparison of pH concentration ratios of ice and liquid samples (ice-80 and ice-90 are the ice samples obtained with freezing of 80% or 90% of the original feed water volume. Liquid-80 and liquid-90 are unfrozen liquid samples collected from 80% or 90% freezing).

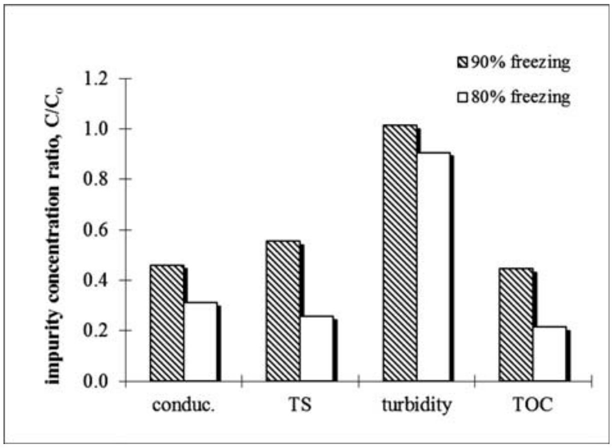

Fig. 2. Comparison of impurity concentration ratios of ice samples obtained from 80% or 90% freezing of the original feed water.

80% of the feed concentrate was frozen and 40–60% reduction when 90% of the feed water was frozen. The unfrozen liquid contained high concentrations of impurities rejected during formation of ice. The conductivity, TOC, and TS concentration ratios of the unfrozen liquid samples to those of the feed water were in the range of 2–6. The impurity removal level in the ice samples collected from 80% freezing was obviously higher than those from 90% freezing. This is primarily caused by contamination of ice samples because the ice samples were not washed when they were separated from the unfrozen liquid that contained high concentration of impurities. There were more impurities attached to the ice surface when 90% of the original liquid (volume) was frozen as compared to those ice samples with 80% freezing. A simple ice washing step would greatly improve the quality of the ice. Attachment of high concentration of impurities may also explain the poor reduction in turbidity level observed in the ice samples. The membrane concentrate from microfiltration or ultrafiltration operations usually contains higher concentrations of suspended and colloidal particles as compare with the concentrate from reverse osmosis or nanofiltration plants. Membrane concentrate of reverse osmosis or nanofiltration operations is consisted of mostly dissolved solids. The characteristics of membrane concentrate are also depending on the feed water characteristics and the pretreatment processes in addition to the membrane processes used. The characteristics of membrane concentrate have a profound impact on the possible treatment options.

TOC removal level observed in this study was lower than those seen in the previous studies where the same freezing technique was used to separate pharmaceutically active compounds from water [20] or dissolved organics contaminants in pulp mill effluent or petroleum refinery wastewater [9]. Greater than 80% reduction of TOC was achieved in the ice samples made from water that contained pharmaceutical drugs (single drug or mixture of four drugs) in the single-stage freezing and more than 99% reduction of TOC in the ice samples with two-stage freezing. The TOC removal levels were about 90–96% for petroleum refinery effluent and pulp mill wastewater with freezing only 70% of the original feed water volume. Freeze concentration is known for effective separation of dissolved solids, both organic and inorganics in a liquid. The lower TOC removal efficiency observed from this study was probably related to the sample handling when the ice samples were separated from the unfrozen liquid as well as the higher colloidal particle concentrations in the ultrafiltration membrane concentrate used as the feed water for the freezing process. More research will be carried out in the future to evaluate freeze concentration of membrane concentrate and the factors that influence impurity removal efficiency such as freezing rates and membrane concentrate characteristics. The capacity of freeze concentration on liquid volume reduction was obvious. The original concentrate (feed water) volume was reduced by 80% when 80% of the concentrate was turned into ice. If necessary, two or more stages of freezing could be used to recover the water and reduce the volume of the residue (or concentrate) to minimum. The cost of handling/disposal would be reduced with a smaller volume of residue.

5. Summary and conclusions

Without any pretreatment processes and washing of ice samples, obvious reduction of organic and inorganic impurities and volume of the concentrate of an ultrafiltration plant were achieved using a simple downward unidirectional freezing method. The degree of freezing and sample handling during separation of ice and liquid affected ice (water) quality. Freeze concentration could be an effective method that not only remove impurities from membrane concentrate but also reduce concentrate volume. Depending on the site conditions, municipal or industrial membrane filtration plants may use natural or mechanical freeze concentration to treat the concentrate generated from their operations, and the pure water recovered from freeze concentration may be used as product water or other purposes based on the requirement on water quality. For those plants where salts (e.g. for some desalination plants) or other products are recovered from the concentrate using evaporation techniques, freeze concentration could be used as a pretreatment option to reduce operating cost as freezing processes usually use less energy than evaporation.

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