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Brine pre-treatment technologies for zero liquid discharge systems

Galilee Uy Semblante, Jonathan Zhiqiang Lee, Lai Yoke Lee, Say Leong Ong, How Yong Ng*

Sembcorp-NUS Corporate Laboratory, National University of Singapore, Faculty of Engineering, Block E1A, #04-01, 1 Engineering Drive 2, Singapore 117576, Singapore
Centre for Water Research, Department of Civil & Environmental Engineering, Faculty of Engineering, National University of Singapore, Singapore, Block E1A, #07-01, 1 Engineering Drive 2, Singapore 117576, Singapore

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ABSTRACT

The management of brine produced by the reverse osmosis process is challenging due to its high salt and organic content. Limitations in brine disposal options sometimes necessitate the use of zero liquid discharge (ZLD) approach. ZLD systems may include a membrane process – which is used to recover water and to further concentrate brine – followed by thermal treatment. In such systems, a high-water recovery rate is difficult to achieve due to the early onset of membrane scaling and fouling. Brine pre-treatment is therefore necessary to protect the membrane and facilitate ZLD. Literature shows that the most common brine pre-treatment process, chemical precipitation, is generally costly because of high chemical consumption and hazardous sludge production. Moreover, its performance may be hindered by the temporal fluctuations in brine chemistry and the occurrence of residual antiscalants in the brine. A critical evaluation of alternative pre-treatment options was performed. It was found that electrocoagulation and nanofiltration processes have promising performance in terms of hardness and organic removals. Meanwhile, coagulation and adsorption processes show potential for organic removal. Further studies should be performed on process optimization and cost analysis to determine the feasibility of applying these technologies in ZLD systems.

1. Introduction

Brine is a highly concentrated reject stream produced by the reverse osmosis (RO) process in water purification applications such as desalination or water reuse. The management of brine is traditionally performed through ocean outfall, sewer discharge, evaporation ponds and deep well injection. Recently, these practices have become untenable due to environmental risks, constriction of discharge standards and increase in efforts to recover resources from brine [1–4]. To eliminate the need for disposal, brine can be treated using the zero liquid discharge (ZLD) approach. ZLD completely avoids the emission of liquid waste and allows the recovery of water and salts [5]. Sometimes, due to stringent discharge standards, ZLD is the only way to ensure compliance with regulations [4]. ZLD can be realized through thermal processes such as concentrators and crystallizers, which are mature technologies that have been applied in full-scale plants for many years [4,6]. However, thermal processes are not economical because they have high capital investment and consume huge amounts of energy.

The cost of ZLD can be reduced by using a membrane process to further concentrate brine prior to thermal treatment [4,7] as illustrated in Fig. 1. Several membrane technologies have been proposed such as RO, electrodialysis (ED)/electodialysis reversal (EDR), membrane distillation (MD) and forward osmosis (FO) [4,7]. RO is a well-established process but it can only concentrate brine to salinity of around 70,000 mg/L due to hydraulic pressure limitations [4]. Non-pressure driven membranes have higher salinity limit than RO and therefore they can attain higher brine concentration. It has been demonstrated in pilot-scale studies that MD can reach a brine salinity of 86,000 mg/L [8], while EDR can reach 100,000–200,000 mg/L [8,9]. Meanwhile, a recently built ZLD plant has used FO to concentrate industrial brine to a salinity of 220,000 mg/L [4]. In addition to their high performance, EDR, MD and FO present opportunities for resource recovery [10], and therefore they could be attractive options for ZLD. However, the main challenge that limits membrane efficiency is membrane fouling from inorganic (also termed "scaling") and organic matters [11–13]. Scaling and organic fouling decrease the maximum possible water recovery, necessitate time and chemicals for membrane cleaning and increase the frequency of membrane replacement. Scaling can be alleviated through the addition of acid and antiscalants to the feed [11,12]. Due to the highly concentrated nature of brine, these approaches are only effective when the membrane is operated at low water recoveries [14]. Meanwhile, organic fouling is challenging to predict and is dependent on

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* Corresponding author at: Sembcorp-NUS Corporate Laboratory, National University of Singapore, Faculty of Engineering, Block E1A, #04-01, 1 Engineering Drive 2, Singapore 117576, Singapore.
E-mail address: ceenghy@nus.edu.sg (H.Y. Ng).

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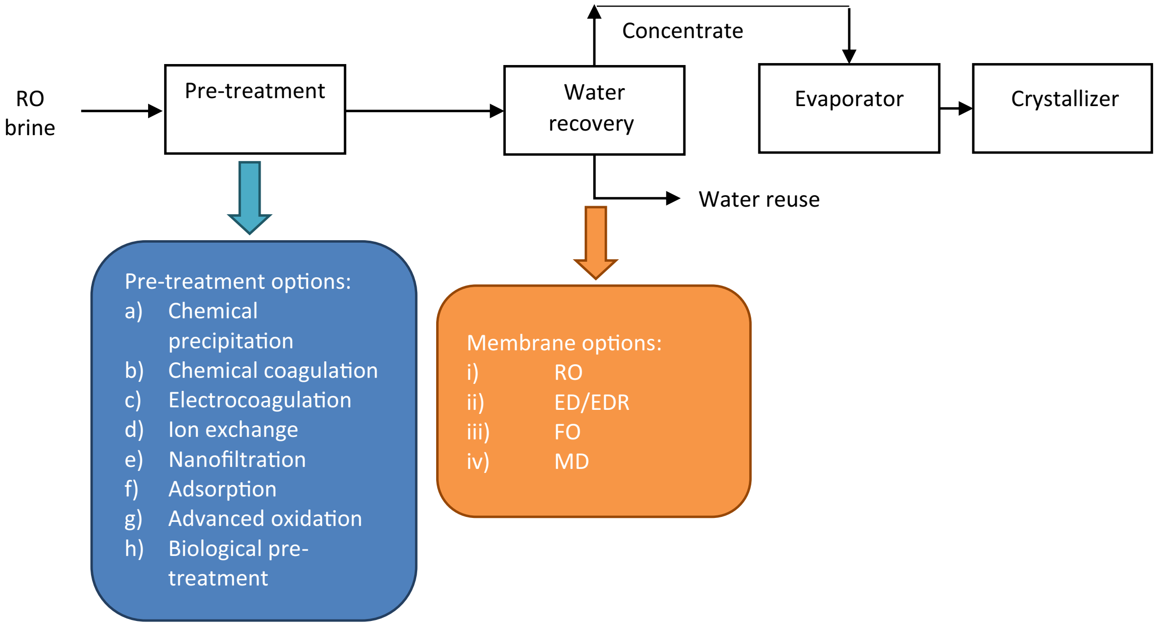

Fig. 1. The process flow of a ZLD system with membrane and thermal treatment.

factors such as organic composition and membrane surface characteristics [15].

To enhance membrane performance in ZLD, a pre-treatment step is necessary (Fig. 1). The goal of pre-treatment is to remove precursor ions and potential organic foulants from brine to protect the downstream membrane processes [16]. By eliminating these compounds, pre-treatment also helps to minimize downstream treatment requirements. Currently, chemical precipitation is the most common pre-treatment process in the industry [17]. Although this technique readily reduces hardness ions (Mg^{2+} and Ca^{2+}), it is challenging to manage operation at optimum chemical dosage especially during temporal variation in brine characteristics. Furthermore, the solid byproduct (chemical sludge) is considered hazardous and therefore difficult to handle and dispose [18]. Consequently, there is an ongoing effort to improve the precipitation process (e.g., through addition of seed material to accelerate crystal growth) or to find alternative approaches, which may include combinations of various technologies.

This review critically analyses the brine pre-treatment technologies that can be used to achieve ZLD. The performance, cost and limitations of technologies currently in use are discussed. Other technologies that might be able to handle the extreme characteristics of brine (e.g., relatively high salt and organic concentration) are identified. The potential technologies proposed here are not new; some have been used in wastewater treatment or as membrane pre-treatment. However, they are hardly applied specifically for ZLD systems. Successful brine pre-treatment could enhance the water recovery of membrane processes and reduce the operating cost of the ZLD process.

2. Challenges in brine management

To determine the removal requirements and to conceptualize an appropriate pre-treatment strategy, brine analysis must be performed (Table 1). Brines from brackish or seawater desalination are characterized with relatively high total dissolved solids (TDS), e.g., 20,000 mg/L [19], and low total organic carbon (TOC), e.g., 2 mg/L [20]. In comparison, municipal brines have relatively low TDS and high TOC, e.g., 1000 mg/L and 20 mg/L, respectively [21]. Industrial brines have a wide range of characteristics based on the source (Table 1). For example, remarkably high TOC of 200 mg/L has been reported for brine produced by the tanning industry [22].

2.1. *Potential targets for removal*

The key targets for removal during brine pre-treatment are scaling precursors in the form of divalent ions and organic compounds. The commonly observed scale-forming compounds include calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) and silica (SiO_2) [11,13], given the abundance of precursor ions in many types of source waters (Table 1). The precipitation of $CaCO_3$ can be prevented by removing alkalinity through acid addition. However, the cost can be significant especially if the alkalinity is high. Also, this approach is unable to manage non-carbonate precipitates that can lead to severe scaling issues. For example, at $pH < 7$, silica occurs as silicic acid $(H_2SO_3)_n$ that can aggregate and deposit on the membrane surface [13]. Mono-silicic acid can also bind on the membrane surface and polymerise to form an amorphous fouling layer [13]. At $pH > 7$, silica occurs as silicate ion $(SiO_3{}^{2-})_n$ and reacts with Al^{3+} and Fe^{3+} to form metal silicate scale [13,30,31]. Therefore the relevant precursor ions must be addressed during the pre-treatment process [32].

The scope of treatment for organic compounds depends on the type of membrane in the ZLD system. Certain membrane processes are highly susceptible to membrane fouling. For example, for EDR, Vermaas et al. [33] reported that 10–20 mg/L of TOC in the feed can result in fouling and 40% decrease in power density (caused by increase in pressure drop between inlet and outlet of feed). Nonetheless, using TOC or dissolved organic carbon (DOC) values is insufficient to predict fouling potential in membranes since the organic composition may vary significantly. Brines may contain natural organic matter (NOM), which consists of humic and fulvic acids and their byproducts [34]. Municipal and industrial brines originating from biological treatment processes may also have microbes and microbial byproducts in the form of proteins and carbohydrates [35]. They may further contain refractory compounds such as pesticides, pharmaceuticals and steroid hormones, which are ubiquitous in municipal and certain industrial wastewaters, e.g., agricultural waste [15,35]. Specific types of compounds can be relevant to fouling. For instance, humic acids would deposit on polyamide membrane surface [36]. To date, there is limited information on the organic composition of brines, especially those produced in industrial processes, and its impact on membrane fouling in ZLD systems.