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A study of membrane distillation and crystallization for lithium recovery from high-concentrated aqueous solutions

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ABSTRACT

Membrane distillation is emerging as an interesting solution to address the difficulties and limits of conventional pressure driven membrane processes to treat highly concentrated solutions. Mineral depletion, new environmental regulations and emerging opportunities emphasize the treatment of waste streams with extraordinary high concentrations. In this current study, comparative analysis of membrane crystallization in direct-contact, osmotic and vacuum configurations have been carried out with the aim to recover lithium chloride from aqueous solutions. To precipitate LiCl from single salt solutions, a concentration above 14 M is required. The osmotic pressure associated with this concentrated solution is very high and its treatment is challenging for direct-contact membrane distillation and osmotic membrane distillation. The phenomena of osmotic pressure has been avoided by using vacuum membrane distillation. Only the application of vacuum membrane distillation, among the studied configurations, ensures the achievement of supersaturation required for crystallization. Moreover, studies on crystal morphology has been performed. Crystals can be recovered in cubic or orthorhombic polymorphic structures depending on the operative conditions. In general, this study provides an interesting comparative analysis of various membrane distillation configurations to treat highly concentrated solutions, which can contribute to the future integrated membrane desalination systems for simultaneously water, energy and minerals production.

1. Introduction

Conventional resources of raw materials are depleting rapidly due to increasing population and improved living standards [1], thus the development of future society is strongly related with continuous and adequate supply of raw materials. The speed of mineral extraction is higher than ever for their rapidly growing demand. However, the resources of raw materials are finite and require sustainability in terms of production, manufacturing, use and recovery. As mineral and metals depletion are becoming a reality, the primary production is getting more difficult, expensive [2] and requires more energy [3]. The problem of water availability in mining and energy production creates a new and recent realized problem to mineral extraction. Stressed nexus of raw materials resources, fresh water and energy raise the question on how long time mineral production can be carried out at the speed of the required quantities/qualities at reasonable costs [3].

An example of a future possible scarce element is lithium, which is interesting, in particular, for its increasing use in lithium-ion batteries for replacing the fuel dependent transportation system with electrical or hybrid electrical vehicles. Different studies discuss the availability of lithium sources in relation to whether the available lithium in future is able to meet the demand [4–7]. Lithium compounds are mainly being produced from brines and hard-rock mining [8]. Several drawbacks are attributed to the state-of-the-art lithium recovery such as low lithium grades, low-recovery factors, complications in making new production sites or enlarging existing areas for salt lake brines [6]. Furthermore the mining industry is harsh for the environment and associated with high-level of pollution [6]. Some drawbacks are also associated with the recovery of lithium from salt-lake brine such as contaminants and separation from compounds such as magnesium [9].

Recovery of components of interest from waste streams and

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exploitation of nontraditional sustainable resources are the fundamental keys to realize the objective of sustainable development. For instance, seawater contains all the elements present in periodic table, providing the opportunity to recover rare or expensive elements. Extraction of lithium from seawater could be an interesting pathway to bridge the gap between demand and supply of this material in perspective. Research on recovery of lithium from seawater has mainly been focused towards manganese oxide based adsorbents [10–13]. Publications from Umeno et al. [10] and Chung et al. [11] are membrane based adsorption which is centered on Li+/H+ exchange [10,11]. Supported liquid membranes might also be a potential lithium extractor from seawater [14]. However, the main issue for these technologies is the extraction at the low concentration contained in seawater at efficient rate and reasonable economic expenses. Another limitation of lithium recovery from seawater but also from brine is the magnesium to lithium ratio, i.e. 7000:1 in seawater. The magnesium content reduces the evaporation rate and the similar chemistries makes the recovery more difficult [15]. From economical point of view, the lithium production cost is as high as 80$/kg, which is not compatible with recovery from spodume (6–8$/kg) or from salt lake brines (2–3$/kg) [6]. Application of innovative processes (standalone or integrated with conventional processes) and more rational use of conventional separation and purification processes may be necessary to recover valuable components from non-conventional sources.

Crystallization might also be a potential technology for lithium recovery from nonconventional resources including brine. Crystallization is one of the fundamental unit operations applied for simultaneous separation and purification of chemical species from solution. The process has been extensively applied in food, pharmaceutical, chemical and environmental divisions of process industry [16]. In order to cope the new challenges of better process control, low-energy consumption, small footprint and excellent control on selection of polymorph [17], a relatively new crystallization technique known as Membrane Crystallization (MCr) has been proposed recently [18–20]. The technique relies upon the evaporation of solvent from solution in contact with a hydrophobic membrane to form super-saturated solution. The operational principle of MCr is essentially the same as that of membrane distillation which is based on the vapor pressure gradient created across a microporous hydrophobic membrane [21,22]. Principally, MCr can be operated in all modes of MD including direct contact, vacuum, sweep gas, air gap and osmotic shown in Fig. 1. In direct contact membrane distillation (DCMD), a cold stream in direct contact with the membrane condenses the vapors while the vapors are collected and condensed externally in vacuum and sweep gas configurations. In osmotic membrane distillation (OMD), a draw solution is used to concentrate the feed solution. All these configurations have their own merits and demerits [21]. Technical feasibility of MCr process for recovery of salts from seawater brine is well acknowledged in the literature [23–26]. Due to its established capability to concentrate the solutions to their saturation level, MCr can be an interesting candidate for lithium recovery. MCr also possesses the potential to realize the objective of zero liquid discharge in industry. However, recovery of highly soluble components such as lithium and reaching the objective of zero liquid discharge requires the treatment of extraordinary concentrated solutions. Solubility of LiCl in aqueous solution is 15.6 mol/kg H_2O (~14 M) at 20 °C [27]. At such high concentrations, the osmotic pressure of the solution can limit the migration of solvent from solution to the permeate side making the application of some MD configurations less interesting for further recovery. In current study, an experimental and theoretical comparative analysis of DCMD–MCr, OMD–MCr and VMD–MCr for treatment of highly concentrated solutions has been performed to recover crystals from single LiCl salt solutions.

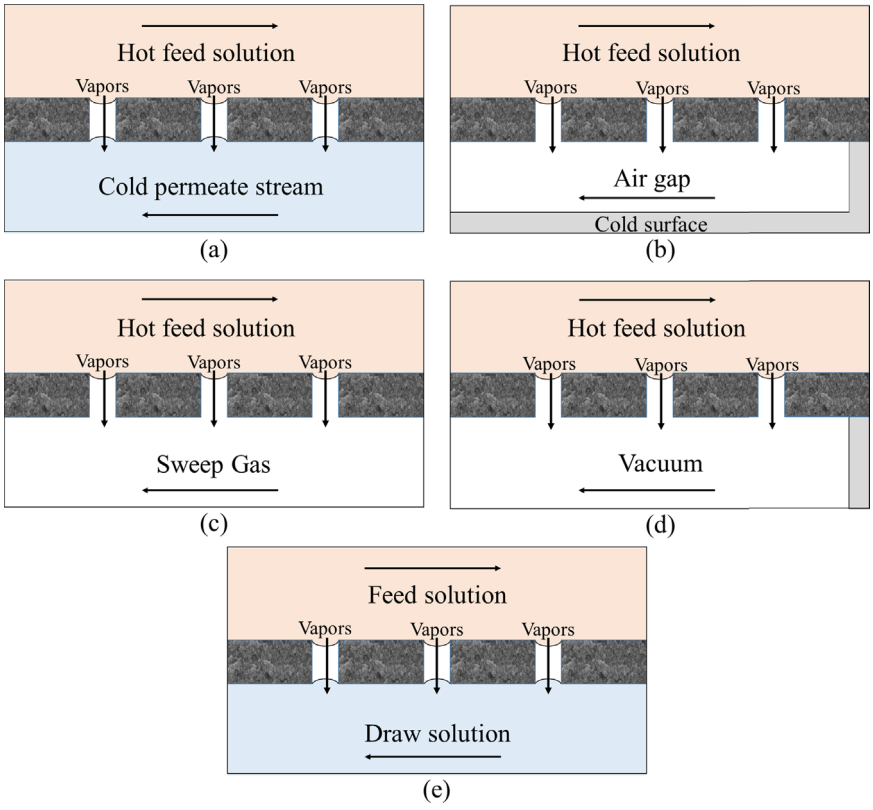

Fig. 1. Basic configurations of membrane distillation, (a) direct contact membrane distillation (b) air gap membrane distillation (c) sweep gas membrane distillation (d) vacuum membrane distillation (e) osmotic membrane distillation.