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Integration of reverse osmosis and membrane crystallization for sodium sulphate recovery

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ABSTRACT

Reverse osmosis and membrane crystallization are evaluated in this work as stand-alone and integrated technologies for the recovery of Na_2SO_4 from aqueous solutions. When SO_2 is removed from flue gases by absorption in an aqueous solution and reacts with NaOH, a reusable product (*i.e.*, Na_2SO_4) of industrial interest can be obtained.

For stand-alone reverse osmosis, the effect of the concentration of the feed solution and pressure is studied. For membrane crystallization, the influence of the concentration and flow rate of the feed and osmotic solutions on the process performance has been determined. The characterization of the obtained crystals shows that $Na_2SO_4 \cdot 10H_2O$ is obtained. From the experimental results, the potential for integration of reverse osmosis and membrane crystallization is simulated. It was concluded that using a reverse osmosis unit prior to the membrane crystallization unit minimizes the total membrane area in comparison with the stand-alone processes.

1. Introduction

Removal of SO_2 from industrial flue gas is a key issue in air pollution control since SO_2 emissions are the major factor in acidic deposition, which damages lakes, streams, plants and forest growth [1]. SO_2 is mainly generated by combustion of fossil fuels or by industrial processes, such as the manufacture of ZnO from ZnS, and emitted to the atmosphere as byproduct. Different strategies for SO_2 emission control and gas desulphurization have been studied [2–4]. One of the common approaches is the use of sorbents in contact with the flue gas stream in order to eliminate SO_2.

Dimethyl aniline (DMA) is a typical organic solvent used for SO_2 removal by absorption, due to its affinity with SO_2 [5,6]. The industrial process involves absorption and desorption stages in which DMA can be released to the atmosphere due to evaporation and drag-out of droplets [7]. This is a point of concern since DMA is an aromatic toxic amine that has severe effects on human health when inhaled [8,9]. In addition, SO_2 stripping is an energy intensive operation. Thus, other more efficient solutions are proposed in the recent research as alternative for SO_2 removal. Examples include the use of water enriched with DMA, trying to minimize the use of DMA while improving the rate of absorption of SO_2 in water [6], and application of inorganic solutions, such as alkaline slurries of $Ca(OH)_2/Mg(OH)_2$ [10,11]. However, the chemical reaction between $Ca(OH)_2/Mg(OH)_2$ and SO_2 results in large quantities of solid waste as $CaSO_3/MgSO_3$. Sodium citrate (Na_3Ci)/citric acid buffer solutions have been also investigated for absorbing SO_2; in this approach, SO_2 can be recovered from the Na_3Ci solution by forming Na_2SO_3 [12]. Na_3Ci is a non-toxic reagent and the process is characterized by the absence of fouling problems and low oxidation losses of SO_2 but the recovery of dissolved SO_2 involves stripping by steam or further reaction of the absorbed solution with H_2S to produce sulfur [13]. This requires additional energy for the production of steam or H_2S. NaOH in aqueous solution has been also proposed as an efficient way to remove acid gases, such as CO_2 and SO_2 from flue gas [14–16]. When an aqueous NaOH solution is used as absorbent for SO_2 gas, the following reactions take place:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + 0.5O_2 \rightarrow Na_2SO_4$$

Na_2SO_4 is a compound with a large number of applications, such as soaps and detergents, glass, paper pulp, *etc.* NaOH is a cost-effective absorbent, with high absorption efficiency (>92%) [14]. However, the sludge that is formed when NaOH reacts with SO_2

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makes the recovery of this compound uninteresting from an economic point of view.

The main focus of this work is to develop a process that allows the production of Na_2SO_4 as a reusable compound for further industrial application as raw material. Membrane crystallization and reverse osmosis are employed to fulfill this objective.

Membrane crystallization (MC) is an innovative technology that makes use of the mass transfer of solvents through microporous membranes in order to concentrate solutions above the saturation limit. A supersaturated solution is then obtained and crystals may nucleate and grow under these conditions. The membrane acts as a barrier that separates the feed solution and the osmotic solution. Membrane crystallization has been studied for the recovery of salts from concentrates [17–19] and recently, this technique has been investigated for the recovery of Na_2CO_3 from aqueous streams as a method for CO_2 sequestration [20]. An interesting advantage of membrane crystallization is that it uses less energy to achieve supersaturation in comparison with solvent evaporation. Furthermore, the purity of the crystals can be controlled. For example, in the study of membrane crystallization performed by Ye et al. to produce Na_2CO_3, the purity of Na_2CO_3 crystals reached up to 99.5% [21].

On the other hand, reverse osmosis (RO) separates dissolved salts or organic compounds with relatively low molar mass from an aqueous solution. RO requires an applied pressure larger than the osmotic pressure, in order to force water to pass through the membrane in the reverse direction of osmosis. The mechanism of transport of solutes and water through a RO membrane does not occur only by sieving, but through interactions with the membrane [22]. Compared with thermal processes, RO is operated at room temperature, without using a heat source. RO is a reference process for seawater desalination [23–25] and is also used in industrial wastewater treatment as a method of pollution abatement and to obtain cost savings through reuse [26]. RO has been shown to be an efficient and cost-effective process step in large scale desalination and for treatment of complex industrial waste [27]. The RO process requires only 5–7 kWh/m^3 of product water compared to 15–16 kWh/m^3 required by the most efficient distillation process [28]. In addition, RO can also be employed for crystallizing salts and it shows a better control over product quality and reduction of energy conversion [29–31].

Integration of membrane-based systems has shown clear benefits in desalination [32,33], concentration of protein solutions [34], waste water treatment [35], and NaCl crystallization [18,36]. In this work, membrane crystallization is used to crystallize Na_2SO_4 from an aqueous solution and the possibility of combining this technology with an RO unit is investigated. The separation efficiency in RO depends on the solute concentration and the applied pressure. Therefore, the influence of operational pressure under fixed solute concentration, and the influence of the concentration of the feed solution under fixed operational pressure are studied. The crystallization of Na_2SO_4 using membrane crystallization is studied as a function of the concentration of Na_2SO_4 in the feed solution, the concentration of NaCl in the stripping solution, and the flow rate of feed and stripping solutions. Finally, the performance of the integrated membrane crystallization – reverse osmosis process is simulated.

2. Materials and methods

2.1. Chemicals

Na_2SO_4 (Anhydrous, Sigma–Aldrich, purity ≥99.0%) is used to prepare the feed solution in membrane crystallization and reverse osmosis experiments. NaCl (VWR, PROLABO, purity >99.9%) is used as osmotic solution in membrane crystallization.

Table 1
Specification of reverse osmosis membrane dow BW 30.

Membrane type	Polyamide thin-film composite
Maximum operating temperature	45 °C
Maximum operating pressure	41 bar
Maximum pressure drop	1.0 bar
pH Range, continuous operation	2–11
pH Range, short-term cleaning (30 min)	1–13
Maximum feed flow	19 m^3/h
Maximum feed salt density index	SDI 5
Free chlorine tolerance	<0.1 ppm
Active surface area	37 m^2

2.2. Experimental setup and operation

2.2.1. Reverse osmosis

A Na_2SO_4 solution with concentration ranging from 30 g/L to 150 g/L was used for RO experiments. Na_2SO_4 was dissolved in ultra pure water (18.2 MΩ cm^{-1}) and stirred until a homogeneous solution was obtained. The experimental set-up of RO presents a cross-flow configuration. A BW 30 commercial membrane (Dow FilmTec, USA) was used. The specifications of the membrane are given in Table 1. Different concentrations of the feed solution and different pressures were studied according to the following approach:

Constant Pressure: the operation pressure is kept constant at 30 bar and the concentration of the feed solution varies from 30 g/L to 150 g/L. The effect of the concentration of feed solution is thus investigated.

Constant Concentration: the concentration of feed solution is kept at 60 g/L and different pressures ranging from 16 bar to 24 bar are studied.

In both sets of experiments, the permeate is recycled in order to keep the concentration of the feed solution constant.

The water flux through the membrane J_w was estimated by the following equation:

$$J_w = K \cdot (\Delta P - \Delta \Pi) \quad (1)$$

where J_w is the water flux, K is the permeability, ΔP is the pressure difference across the membrane, and $\Delta\prod$ is the osmotic pressure.

The performance in terms of rejection of an RO system can be determined by using the solution-diffusion model [22]:

$$R_i = 1 - \frac{C_{p,i}}{C_{f,i}} = \left[1 - \frac{\rho_w \cdot B}{K \cdot (\Delta P - \Pi)}\right] \quad (2)$$

where R_i is the salt rejection of component i, and $C_{p,i}$ and $C_{f,i}$ are the concentrations of component i in the permeate and in the feed, respectively. ρ_w is the density of water, B is the solute permeability constant. The permeability of pure water K through the RO membrane was calculated with the following equation:

$$K = \frac{\Delta V}{\Delta t \cdot A \cdot P} \quad (3)$$

where ΔV is the volume of collected permeate, Δt is the time between two measurements, A is the effective area of membrane and P is the applied pressure.

2.3. Membrane crystallization

The detailed experimental setup is shown in Fig. 1. A hollow fiber membrane contactor (Liqui-cel, MiniModule membrane contactor, Germany) is used as the membrane crystallization device. The specifications of the membrane are given in Table 2. Solutions