Separation and Purification Technology 166 (2016) 135–141

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Selective separation of chloride and sulfate by nanofiltration for high saline wastewater recycling

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ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form 7 April 2016
Accepted 8 April 2016
Available online 9 April 2016

Keywords:
Chloride and sulfate
Separation
Nanofiltration
Saline wastewater
Recycling

ABSTRACT

In order to effectively separate chloride (such as NaCl) and sulfate (such as Na_2SO_4) for high saline wastewater recycling, one commercial NF membrane (named Desal-DL) was employed in the permeation of the single and binary salt solutions of NaCl and Na_2SO_4 with a lab-scale cross-flow batch module, where the salt concentration ranged from 4 to 96 g L^{-1} and the operating pressures varied from 0.6 to 2.4 MPa as well as the temperature was kept under room temperature. The experimental results showed that the Desal-DL NF membrane had a low rejection to NaCl and a high rejection to Na_2SO_4 for single salt solutions. While for binary salt solutions, the membrane presented a bit higher rejection to SO_4^{2-} and much lower rejection to Cl^-, even special negative rejection to Cl^- was observed when the concentration of Na_2SO_4 was high. This implies that NF is suitable to be used for the separation of Na_2SO_4 and NaCl from their binary solution, where Na_2SO_4 could be retained by the NF membrane and concentrated to high concentration while NaCl could pass through the membrane and might be diluted to low concentration with a diafiltration operation mode. Finally the selective separation of Na_2SO_4 and NaCl by NF diafiltration was simulated for the binary salt solution containing 23.4 g L^{-1} NaCl and 8.76 g L^{-1} Na_2SO_4. A highly concentrated solution of Na_2SO_4 (71.74 g L^{-1}) and a relatively pure solution of NaCl (20.79 g L^{-1}) were obtained, which favored the post-treatment of high saline wastewater for inorganic salts recycling.

1. Introduction

High saline wastewaters are generated in large amounts in many factories, such as petroleum, tannery, paper mills and pharmaceutical industries [1,2]. They usually contain high concentrations of chlorides and sulfates (e.g., the average values of 8.20–16.4 and 14.7–21.1 g L^{-1} for chromium tannery wastewater [3], 14.2 and 5.92 g L^{-1} for drilling water concentrates from Skhira [4]). If the discharge of such wastewater is without prior treatment, it would lead to severe damage on soil, surface and groundwater, aquatic life, etc. [2,5]. Concerning the sustainability of the environment, the treatment of the saline effluent has been becoming a major concern for researchers and regulators. Some traditional methods have been applied to the treatment of such wastewaters, such as chemical precipitation, physical-chemical and biological technologies [2,5,6]. Among them, membrane processes are regarded as one of the most cost-effective and sustainable methods.

In order to reduce the harmful discharge and achieve the salt resource recycling, a sequential process based on the appropriate combination of membrane technologies can be applied for the treatment of high saline wastewater. During the process, chloride and sulfate will be separated first, and electrodialysis (ED) process or reverse osmosis (RO) will be used then to concentrate the salt solution. The concentrated NaCl or Na_2SO_4 solution can be utilized to produce HCl or H_2SO_4 and NaOH via bipolar membrane electrodialysis (BMED) or salt crystals via crystallization [7]. Within this process, the separation of chloride and sulfate is the initial step and of great significance for the successful recycling.

It has been reported that nanofiltration (NF) has the potential to treat wastewater and reuse water, especially to separate monovalent and multivalent ions [8–13]. NF membranes have a porous structure with pore size close to the nanometer and are usually charged at natural pH. As a consequence, the selectivity of NF membranes for ions of different sizes and charge densities is significantly different, which makes NF suitable for fractionation of salts [9,14–16]. There are numerous studies on the application of NF membranes in separation of mixed salt solutions, especially for the dilute sodium chloride and sodium sulfate ($NaCl/Na_2SO_4$) system. It has been found the membrane type, permeate flux, total salt

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http://dx.doi.org/10.1016/j.seppur.2016.04.009
1383-5866/

concentration and salt concentration ratio affected the NF separation efficiency of Cl^-/SO_4^{2-} [7,15–23]. A significant decrease in Cl^- rejection was found when SO_4^{2-} was added to the feed solution [17,18]. The increase of total ion concentration generally decreased NaCl retentions whereas the increase of permeate flux increased ion retention [16]. In addition, negative rejection to Cl^- was often observed in the nanofiltration of mixed salt solution [16–18,21,22]. As SO_4^{2-} was almost totally rejected by the membranes, the selective separation of chloride and sulfate is possible.

However, many authors have worked on modeling the transport of ions through NF membranes [15,17–21], the studies testing real applications related with high concentration of chloride and sulfate are few. On the other hand, some high salt concentrations have also been studied but the change of the Na_2SO_4 concentration with the filtration process on the separation performance has not been considered [7,23]. As the NF process goes, the feed solution will be concentrated and the salt retention may change. Furthermore, there are few reports on treating the highly concentrated solutions using Desal-DL NF membrane. The commonly used membrane for the separation is the NF270 membrane provided by Dow Filmtec. However, the membrane retention for sulfate is low when the chloride concentration is high, which decreases the separation efficiency [7,23].

The aim of this work was to determine the feasibility of separating chloride and sulfate (specifically the binary salt solution of NaCl and Na_2SO_4) with high concentration using Desal-DL NF membrane. Single and binary salt solutions were applied under different operating pressures and different salt concentrations. Diafiltration process was also simply simulated for separating the binary salt solution aiming at recovering the inorganic salt resource. Analysis of obtained results allows for offering the new approach to the treatment and recycling of the high saline wastewater by nanofiltration.

2. Materials and methods

2.1. Membrane and solutes

Desal-DL membrane (GE Osmonics, USA) was chosen in this study. According to the manufacturer's data, the membrane is a thin-film composite membrane and made from aromatic polyamide/polysulfone. It has a MWCO between 150 and 300, a maximum temperature of 45 °C, a maximum pressure of 4.1 MPa and pH ranges of 3–9.

The solutes used were sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) (reagent grade; Beijing Modern Eastern Fine Chemical Corporation).

2.2. Permeation experiment

A lab-scale cross-flow NF equipment with an effective membrane area of 35.3 cm^2 was operated in batch mode. Both the retentate and permeate were recycled back to the feed vessel in order to keep the concentration of feed solution constant. Prior to the experiments, the membrane was pre-compacted using ultra-pure water at the operating pressure of 1.5 MPa for at least 2 h to avoid any compression effects and to establish leak tightness [23]. The permeation experiments were performed under the conditions of the room temperature of 25 °C, the cycling flow rate of feed solution through the membrane of 340 L h^{-1} and the operating pressure of 0.6–2.4 MPa.

The chromium tannery wastewater and drilling water mentioned in introduction section were taken as reference to set the salt concentration of model solutions used in the permeation experiments. Both single salt solutions of NaCl or Na_2SO_4 and their binary mixtures over the concentration range of 4–96 g L^{-1} were applied. The binary salt solutions at various total salt concentrations and Na_2SO_4 concentrations were intended to model the possible wastewaters. The detailed information about the concentrations of salt solutions has been summarized in Table 1.

The concentrations of single salt solution were measured with an electrical conductivity meter (DDSJ-308A, China), and the binary salt solutions were analyzed by ion chromatography (IC-A3, Japan).

In the permeation experiment, the volumetric flux can be calculated as

$$J_v = \frac{V}{t \cdot A_m} \quad (1)$$

where V is the volume of the permeate, t is the nanofiltration time, and A_m is the membrane area.

The observed rejection to component i can be expressed as

$$R_{obs,i} = 1 - \frac{C_{p,i}}{C_{f,i}} \quad (2)$$

where $c_{p,i}$ and $c_{f,i}$ are concentrations of component i in the permeate and the feed solution, respectively. In order to assure the steady and reasonable results, volumetric flux and solute concentration were tested at least two consecutive samples (obtained at a given set of experimental conditions), with the average deviation below 2%.

2.3. Diafiltration simulation

Diafiltration is a process of washing dissolved components through the membrane in order to improve the recovery of the component in the permeate, or to achieve high purity of the retained component [24–27]. The typical diafiltration process may involve three steps: pre-concentration, diafiltration, and post-concentration. The process by using NF membranes is proved to be efficient in separating varied mixtures. Applications can be found in separation of saccharides from a NaCl solution [24], purification and enrichment of XOs from XOs syrup [25], desalination and concentration of liquid dyes [26], recovery of laccase from fermentation broths [27] and many other fields.

According to the mass balance for component i in the feed solution, the following equations for concentration and diafiltration steps can be obtained [24]:

$$\frac{C_{f,i}}{C_{f,i0}} = \left(\frac{V_{f0}}{V_f}\right)^{R_{obs,i}} \text{ (pre- and post-concentration)} \quad (3)$$

$$\frac{C_{f,i}}{C_{f,i0}} = exp\left[-\frac{V_w}{V_{f0}}(1 - R_{obs,i})\right] \text{ (diafiltration)} \quad (4)$$

Table 1
The concentrations of the feed solution.

Run no.	Feed concentration (g L^{-1})	
	NaCl	Na_2SO_4
1	4	–
2	8	–
3	16	–
4	32	–
5	–	4
6	–	8
7	–	16
8	–	32
9	4	4
10	8	8
11	16	16
12	32	32
13	32	6.4
14	32	16
15	32	64