



Research article

Selective recovery of salt from coal gasification brine by nanofiltration membranes



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ABSTRACT

The selective extraction and concentration of salt from coal gasification brine (CGB) by nanofiltration membranes is a promising technology to achieve near-zero liquid discharge of coal gasification wastewater. To investigate the feasibility of recovery of salts and the interaction of organic compounds, multivalent ions and monovalent ions on the rejection ratio, three nanofiltration membranes (OWNF1, NF270 and Desal-5 DK) with an 1812 spiral-wound module were used in crossflow filtration. The rejection mechanism was analyzed by comparing the rejection performance as a function of the operation pressure (increasing from 1.0 MPa to 2.5 MPa), the concentration (increasing from 10,000 mg/L to 25,000 mg/L) and pH values (increasing from 3.0 to 10.0). The concentrations of anions and cations were determined using an ion chromatographic analyzer and an inductively coupled plasma emission spectrometer, respectively. The results show that the rejection of sulfate and the chemical oxygen demand were higher than 92.12% and 78.84%, respectively, at appropriate operation, while negative rejection of chloride was observed in the CGB. The decreasing rejection of organic compounds was due to swelling of the membrane pore in high-concentration solutions. Meanwhile, the organic compounds weakened the negative charge of the membrane active layer, consequently decreasing the ion rejection. More than 85% of the sodium chloride could be recovered, indicating that this technology is suitable for resource recovery from CGB and near-zero liquid discharge of coal gasification industry.

1. Introduction

Near-zero liquid discharge (ZLD) of coal gasification wastewater (CGW) is crucial for environmental protection and the sustainable development of the coal gasification industry in China (Jia et al., 2015). Coal gasification brine (CGB) is the reverse osmosis concentrate generated in the reuse CGW. The properties of CGB are complex because contains both a high concentration of salts (the total dissolved solids (TDS) reaches 35,000 mg/L) and several organic compounds (the chemical oxygen demand (COD) is greater than 1000 mg/L) (Fang and Han, 2018). The salts come from coal, groundwater and lakes, together with chemical addition in the production process. The organic pollutants in CGB are the degradation products of organic compounds produced during biological treatment and the advanced oxidation process of CGW (Hou et al., 2016; Zhuang et al., 2014) and mainly consist of esters, alkanes, alcohols, ketones, olefins and amides (Fang et al., 2013; Xu et al., 2015).

Currently, the conventional technology for treating CGB integrates the processes of reverse osmosis, evaporation and crystallization (Jia et al., 2016). Nevertheless, the deficiencies of serious membrane fouling and the production of huge quantities of unusable salt-mixtures constrains the application of this process. Considering that ZLD and the reuse of brine from CGW remarkably reduces the expenditure of salts, the brine should be regarded as a resource rather than a waste. Therefore, economic and efficient technologies which exhibit both excellent rejection of multivalent ions and organic compounds and recovery of available salts from CGB are highly desired.

Nanofiltration (NF) membranes are applied to treat wastewater and reuse water, specifically to separate monovalent ions and multivalent ions from mixed solutions (Thamaraiselvan and Oren, 2017). The ion rejection of a mixed salt solution is difficult to predict from the ion rejection of a single-salt solution. Nielsen and Jonsson (1994) applied NF membranes to separate NaNO₃ from a NaNO₃ + Na₂SO₄ solution and showed that a change in NaNO₃ rejection was induced by adding

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Na_2SO_4 . The multivalent anions (e.g., $\text{Cr}_2\text{O}_4^{2-}$, SO_4^{2-}) of the mixed solution were excellently rejected by the negatively charged NF membranes (Cho et al., 2015). By contrast, low rejection of monovalent anions is frequently obtained (e.g., Cl^-). The concentration of monovalent anions did not even change when the concentration of multivalent ions in the permeate decreased in the NF membrane separation process (Ren et al., 2017; Turek and Gonet, 1997). It is noteworthy that negative rejection of monovalent anions could have been obtained from a mixed solution with high salinity. In addition, increased solution pH significantly decreases monovalent ion rejection in a mixed solution (Sabaté et al., 2008; Szoke et al., 2003). From this, we concluded that the selectivity of NF membranes is significantly different for ions with different sizes and charges, which makes NF membranes suitable for the separation of salts (Yan et al., 2016).

Membrane rejection of organic compounds has been extensively studied in recent years. There are three aspects that can influence the rejection of organic compounds: a) membrane pore size, membrane material and charge—an NF membrane with the strongest charge among three NF membranes has shown excellent rejection of charged organic compounds (Zhao et al., 2017); b) solute characteristics including molecular size, charge and polarity; c) feed solution chemistry including the pH value, concentrations and constituents (Košutić and Kunst, 2002), the effects of which were exemplified by the increasing rejection of biogenic amines from 5% in a neutral solution to 40% at alkaline conditions (Sabaté et al., 2008) and the higher estrone rejection at alkaline conditions because of the greater solubility of estrone molecules under these conditions (Hu et al., 2007). In addition, organic compounds largely affect ion rejection because of the changed conditions of the membrane-solution (Bargeman et al., 2005; Sadrzadeh et al., 2015).

The study of the separation of organic and mixed salts by NF membranes is less reported. Hydrophilicity was found to be the primary factor in the separation of natively charged sugar and salt mixtures (Mänttari et al., 2006). A salt-organic separation factor was introduced and membrane surface properties were assessed to compare different membrane performances (Negares et al., 2012). Furthermore, studies of the removal of organic compounds from CGB by NF membranes have not been reported.

This work applied three NF membranes (OWNF1, NF270 and Desal-5 DK) to recover salt from CGB containing highly concentrated sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and organic compounds at the laboratory scale. The principal objective of this research is to expound the feasibility of salt recovery from CGB and to analyze the interaction of organic compounds with salts and the relationship of membrane-solute on rejection in the NF membrane process. This work should be useful for understanding the NF process in highly concentrated salt and organic compound solutions and achieving resource utilization from CGB.

2. Materials and methods

2.1. Characteristics of the experimental membranes

An NF laboratory-scale experiment was conducted with three NF membranes. Both the NF-270 (Dow/Filmtec, US) and Desal-5 DK (GE Osmonics, US) membranes are widely applied as commercial membranes, with similar membrane pore sizes and different charges. OWNF1 (Originwater, China) is a loose NF membrane with a larger membrane pore size among the three NF membranes. The specific characteristics used for membranes were based on information from previous literature and given by the membrane manufacturers, as shown in Table S1 of the Supporting Material.

2.2. Properties of the experimental solution

The laboratory experiment was carried out using two feedwaters,

which were divided into two parts. The CGB discharged from a coal gasification plant of the Inner Mongolia Province, China and the synthetic solution in the experiment was synthesized from NaCl and Na_2SO_4 based on the characterization of CGB in terms of ion concentrations. All salts were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. The concentrations of the synthetic solution ranged from 10,000 mg/L to 25,000 mg/L, in which the NaCl increased from 5000 mg/L to 20,000 mg/L and the Na_2SO_4 remained at 5000 mg/L. The properties of the CGB can be found in Table S2 of the Supporting Material. The molecular weights, diffusivities and solute radius values used for the ions are listed in Table S3 of the Supporting Material.

2.3. Experimental set-up and protocol

The laboratory experiment was carried out in a recycle mode with both permeate and concentrate recycling back into the feedtank, and the schematic diagram of the laboratory-scale set-up is shown in Fig. S1 of the Supporting Material. The CGB or synthetic solution was collected in the 1.0 m³ water tank to adjust to a consistent quality and was transferred by a feed water pump to the feedwater tank, then delivered to the NF membrane module by a high-pressure pump. This device was fitted with an 1812 spiral-wound module providing a filtration area of 0.36 m², and the cross-flow velocity at 0.30 m/s.

New NF membranes were immersed in deionized water for 24 h, then were flushed with deionized water for 1 h at 20 bar (NF270 and Desal-5 DK) or 4 bar (OWNF1) to eliminate compression effects before the rejection experiment (Oatley-Radcliffe et al., 2014). To exclude the influence of temperature, we designed a temperature controller (Yinchuan instrument XMT, China) to keep the temperature of the feedwater consistently at 20 °C.

The rejection of ions and organic compounds was determined based on the difference between the concentration of the ions and organic compounds in the permeate and the rejection was calculated using Eq. (1). The flux was calculated using Eq. (2).

$$R = (1 - C_f/C_p) \times 100\% \quad (1)$$

$$J_v = Q/A \quad (2)$$

where C_f and C_p are the average concentrations in feedwater and permeate, respectively, R is the rejection rate, Q is the flow rate of the permeate, A is the effective membrane area of the membrane modules, and J_v is the flux.

The solute distribution coefficients Γ_i were related to each other by the condition of local electric neutrality according to the standard fixed charge model:

$$\sum_i Z_i c_i \Gamma_i = -Z_\chi c_\chi \quad (3)$$

where Z_χ and c_χ are the sign and the concentration of the fixed electric charges, respectively. In dimensionless form, Eq. (3) can be rewritten this way:

$$\Gamma_i \equiv \exp(-Z_i \psi) \quad (4)$$

The distribution coefficients can be expressed through the Donnan potential at given virtual concentrations of ions and the concentrations of fixed charges.

2.4. Analytical methods

The experiment analyzed the quality of the CGB, and each stream of NF included measurements of the conductivity, pH, COD, and concentration of ions (sodium ion, chloride ion and sulfate ion). The conductivity was measured with a conductivity meter (DDS-307A/Precision & Scientific Instrument, China). The pH was measured with a pH meter (HQ30D/Hach, USA). The concentration of organic compounds was analyzed in terms of COD by potassium dichromate

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