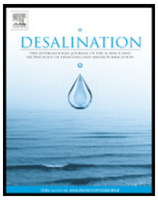
Desalination 268 (2011) 233–237

Contents lists available at ScienceDirect

Desalination

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



Separation of ammonium salts from coking wastewater with nanofiltration combined with diafiltration

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ARTICLE INFO

Article history:
Received 26 June 2010
Received in revised form 13 October 2010
Accepted 13 October 2010
Available online 9 November 2010

Keywords:
Coking wastewater
Ammonium salt
Nanofiltration
Diafiltration

ABSTRACT

It is rather difficult to separate high concentration of ammonium thiosulfate from ammonium thiocyanate in coking wastewater which results in resources waste and environment pollution. In this work, a membrane process of nanofiltration (NF) was applied to solve the problem. The experimental results showed that the NF membrane selectively retained $(NH_4)_2S_2O_3$ with a rejection of 95.0% at a concentration of more than 60 g L^{-1}. Meanwhile, the permeation of NH_4SCN was 120.0% at a concentration of nearly 120 g L^{-1}. Diafiltration was optimized to ensure a high average salt rejection of 93.4% for $(NH_4)_2S_2O_3$. In addition, salt concentrations and yields can be predicted by theoretical calculation. The results reveal that the NF membranes are successful in separating high concentration of bi-component ammonium salt solutions into mono-component ones.

1. Introduction

High concentration of mixed ammonium salts (total salt concentrations < 350 g L^{-1} while $(NH_4)_2S_2O_3 > 60$ g L^{-1} and $NH_4SCN > 100$ g L^{-1}) in coking desulfurization wastewater remains a critical problem and represents an important waste source as well as environmental pollution. The salts are considerably difficult to be separated from each other owing to their similar high solubility and close salt molecule size [1]. Consequently, they are generally discharged with the wastewater directly after being diluted despite of their significant economic values since $(NH_4)_2S_2O_3$ is the most common component of photographic fixing agent while NH_4SCN has many uses in the manufacture of chemicals, pharmaceuticals and pesticides.

Related attempts have been made to solve the problem. Direct decomposition wastes salt resources and consumes a large amount of energy. Takahax–Hirohax technique has a high cost in reclaiming the salts in terms of ammonium sulfate on account of high pressure and specific catalysts [2]. Reported crystallization method retrieved NH_4SCN with a maximum yield of 60% after decomposing $(NH_4)_2S_2O_3$ in a complicated way [3]. Recovery of salt in terms of sodium and potassium thiocyanate consumes a substantial number of chemicals [4]. New method of separating the ammonium salt of $(NH_4)_2SO_4$ in supercritical water was with a quite low separation efficiency, about 49% at high temperature of 470 and 500 °C [5]. Carbon nanotube (CNT) sheets were also used for the desalination of sodium chloride with an adsorption uptake of about 600 mg·g^{-1} in a rather long time of 25 h, when the initial salt concentration was 40 g L^{-1}[6]. All the above-mentioned attempts suffer from high costs, complex processes or low yields. Therefore, a new method is highly demanded to separate and recover the ammonium salts from the wastewater directly and individually for the sake of economic and environmental concerns.

Nanofiltration (NF) developed in recent years is a cost-effective and energy-saving membrane separation process [7], which has been found a wide range of applications in many industries, even in treating wastewater from the coking gas purification process. It was revealed that the NF membranes generally showed superior salt rejections (higher than 94.4%), but no other report further addressed the treatment of the desulfurization wastewater [8].

Awadalla et al. [9] studied the retention of ammonium salts by NF membrane process with the result that 98% of ammonium iron sulphate and only 55% of ammonium sulphate were removed. Similar retention of ammonium by NF membrane was 56.2% reported by reference [10]. One thing has to be mentioned, their salt concentrations were less than 1 g L^{-1}. As referred to the capacities of NF membrane to separate high salt concentration water solutions, Karelin et al. [11] found that NF membranes retained bivalent ions at electrolyte concentrations up to 200 g L^{-1}, but the ions rejection was very low (<70%) at the bivalent salt concentration of 50 g L^{-1}. One successful exception was reported in a patent for treating high concentration (nearly 300 g L^{-1}) of salt solutions, but its bivalent salt concentration was less than 20 g L^{-1} [12]. It is concluded there is a new possibility of increasing the separation efficiency of monovalent ions from a multicomponent system with the aid of NF membranes [13]. So it is very challenging for the effective removal of bivalent ammonium with a concentration > 60 g L^{-1} which will be exploited in detail in this work.

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doi:10.1016/j.desal.2010.10.034

Diafiltration is a method to obtain high quality product. Continuous flux of liquid across the membrane brings away the micro-solute and collects the macro-solute with high quality as the product [14]. It was reported that diafiltration was not suitable for use in the removal of Cr (VI) due to the great amount of water consumption [15]. On the contrary, NF with diafiltration has been successfully used in removing monovalent organic salts from a simulated fermentation broth with a rejection of about 80% at a sodium succinate concentration of 42 g L^{-1} [16]. Inorganic salt of potassium chloride at 75 g L^{-1} was eliminated from an ion-exchanged solution effectively by NF in a diafiltration mode with a rejection of 80%, while the rejection of potassium clavulanate was constant over 99% [17]. The desalination of soy sauce by NF and diafiltration obtained an amino nitrogen rejection of 70% and a salt removal ratio of only 50% at a high concentration of NaCl up to 177 g L^{-1}[18]. The degree of demineralization with NF membranes significantly decreased with increasing salt concentrations even in combination with diafiltration. Therefore, it is rather difficult to separate $(NH_4)_2S_2O_3$ (>60 g L^{-1}) from NH_4SCN (>100 g L^{-1}) when the total salt concentration was about 200 g L^{-1} by NF with diafiltration.

In this work, an NF process consisting of pre-concentration, diafiltration and post-concentration step was developed for the separation of $(NH_4)_2S_2O_3$ from NH_4SCN at high concentrations in the coking wastewater for the purpose of recovering both single salts.

2. Materials and methods

2.1. Water characteristics

The NF feed was the actual wastewater of desulfurization process from a coking plant in China. After being prefiltrated by a nineteen-channel zirconia ceramic membrane with an average pore size of 50 nm to eliminate suspended solids, it had a high salinity, i.e. $(NH_4)_2S_2O_3$ of 60–90 g L^{-1} and NH_4SCN of 100–120 g L^{-1}.

2.2. Membranes and methods

NF membrane (DK1812, GE Corp., U.S.), was tested in the apparatus shown in Fig. 1. The membrane was first characterized by deionized water, then run under a pressure of 1.0–2.0 MPa at a recirculation flow rate of 780 L h^{-1} in the NF processes. Concentrations of $(NH_4)_2S_2O_3$ and NH_4SCN were measured by an iodometric method and a ferric thiocyanate colorimetric method, respectively and the detailed procedures can be found elsewhere [19].

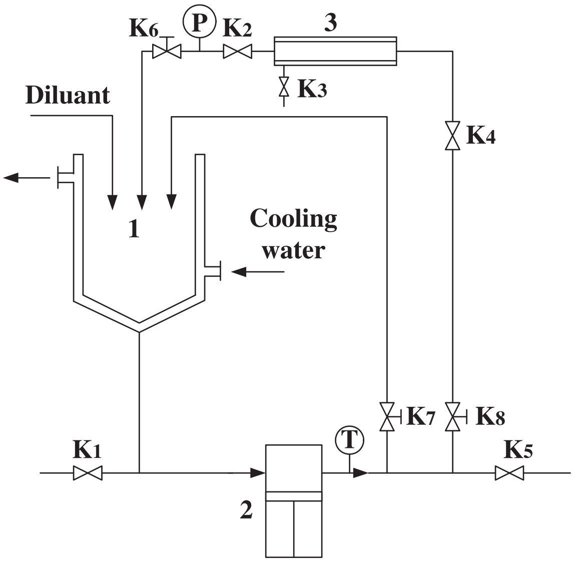

Fig. 1. Schematic diagram of the NF setup. 1. Feed tank, 2. Plunger pump, 3. NF membrane module, K_1–K_8 – valves, T – temperature gauge, P – pressure gauge.

The experiments on the pressure effect were performed in recycling mode (recycling the permeate stream and the retentate to the feed tank). The NF separation process consisted of three operations: pre-concentration, diafiltration and post-concentration. All of them were operated in continuous mode (collecting the permeate stream separately and recycling the retentate to the feed tank). In addition, the diafiltration experiment was performed in a constant volume mode: fresh deionized water was added to the feed tank as a diluant to wash out NH_4SCN at a rate which balanced the permeate flow rate. After each run, the membrane was cleaned with deionized water until the flux was regenerated.

3. The model of pre-concentration, diafiltration and post-concentration

According to the work of Wang et al. [20], the variation of solute concentration can be modeled by following Eq. (1) for pre- and post-concentration and Eq. (2) for diafiltration process, respectively.

$$\frac{C_{F,i}}{C_{F,i0}} = \left(\frac{V_0}{V_F}\right)^{R_i} \tag{1}$$

$$\frac{C_{F,i}}{C_{F,i0}} = \exp\left[-\frac{V_w}{V_0}(1-R_i)\right] \tag{2}$$

Where $C_{F,\,i}$, is the concentration of component i in the feed solution during the process, g L^{-1}; $C_{F,\,i0}$, the initial concentration; V_F, the feed bulk left in the tank during concentration process; V_0, the initial volume in feed tank before filtration process; V_w, the volume of added deionized water in the diafiltration process. R stands for the observed rejection (hereinafter referred to as rejection), equal to $1-P$. Subscript $i=1$ for $(NH_4)_2S_2O_3$ and 2 for NH_4SCN.

The rejection of $(NH_4)_2S_2O_3$ and the permeation of NH_4SCN were calculated according to following Eqs. (3) and (4):

$$R_1 = \left(1-\frac{C_{P1}}{C_{F1}}\right) \times 100\% \tag{3}$$

$$P_2 = \frac{C_{P2}}{C_{F2}} \times 100\% \tag{4}$$

where the subscript P denotes permeate and F feed.

4. Results and discussion

The operating pressure varied from 1.0 MPa to 2.0 MPa to demonstrate the role of NF membrane in separating the salts from the wastewater. Fig. 2(a) shows that high operating pressure resulted in high permeate flux, which was common since high pressure pushed more solvent through the membrane [21]. As shown in Fig. 2(b), the rejection of $(NH_4)_2S_2O_3$ and permeation of NH_4SCN grew remarkably when pressure increased from 1.0 MPa to 1.5 MPa. The highest rejection of $(NH_4)_2S_2O_3$ (95.0%) and permeation of NH_4SCN (120.0%) were observed both at 1.5 MPa. But when the pressure was further increased to 2.0 MPa, the salt rejection or permeation came down. This phenomenon can be explained by the dissolution–diffusion model [22]. On one side, as pressure increased, the volume of permeated water increased, but permeated salt flux remained constant, therefore, a high salt rejection/permeation was observed. On the other side, low salt content in permeate induced a large concentration difference between the retentate and permeate, which led to a low salt rejection. Therefore, the rejection and permeation first increased and then decreased with increasing pressure. There is