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Journal of Membrane Science 301 (2007) 200–209

journal of
MEMBRANE
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Application of vacuum membrane distillation for ammonia removal

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Received 25 May 2006; received in revised form 26 May 2007; accepted 12 June 2007
Available online 16 June 2007

Abstract

This study aims to investigate the applicability of membrane distillation for ammonia removal from its aqueous solutions. Among the different recognized membrane distillation configurations, vacuum membrane distillation is applied in the present work for ammonia removal. The effects of different operating parameters on ammonia removal from aqueous solutions of different concentrations have been investigated. Experimental results showed that high feed temperatures, low downstream pressures and high initial feed concentrations and pH levels enhance ammonia removal efficiency. The pH is found to be the most dominant factor. Temperature and concentration polarizations within feed boundary layer proved to have a significant influence on mass transport. High feed flow velocity is an important tool diminishing temperature and concentration polarizations effects. The resistance to mass transfer is found to switch from being predominantly located in the feed side at low feed temperatures and flow velocities to be nearly located within the membrane pores at 55.7 °C and reasonably higher feed flow velocity of 0.84 m/s. Although high feed temperatures and low downstream pressures increase remarkably the total transmembrane flux and the ammonia removal rate, the corresponding ammonia separation factors were decreased. Ammonia removal efficiencies higher than 90% with separation factors of more than 8 were achieved in this study.

Keywords: Membrane distillation; Ammonia removal; VMD experiments

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1. Introduction

The increased pollution levels both in atmosphere and in water cause seriousness environmental problems [1,2]. When excessive amount of ammonia (NH_3) is being emitted to the atmosphere or discharged with wastewater effluent streams, it is considered as one of those harmful pollutant constituents that damage seriously the environment. The main source for ammonia emission to the atmosphere comes from agriculture (i.e. from livestock urine and manures and from some nitrogen fertilizers and crops) [2]. The main source for wastewater contaminations by ammonia or nitrogen compounds comes from municipal wastewater and to much more extent comes from industrial wastewater effluent streams (i.e. fertilizer manufacture, ceramics and cement works, petroleum refining and combustion processes). The concentration of ammonia in the contaminated effluent streams may vary widely in accordance to their sources [1]. Moreover, due to its high solubility in water and to its chemical reactivity, NH_3 is considered cause for eutrophication of surface water (i.e. the enrichment of water by nutrients causing an accelerated growth of algae for example) and also for the depletion of oxygen in receiving water lakes and rivers [2]. As active chemical species, ammonia in atmosphere oxidizes and when it is washed out by rains, it forms nitric acid. As a consequence, acidic rains increase acidification problem in soil and ground water. Worldwide regulatory authorities recognize the seriousness of the problem and standards have been globally implemented in order to preserve and protect our natural environment ammonia/nitrogen discharges.

There are several well-established technologies dealing with ammonia/nitrogen removal from wastewater effluents. Each one has its advantages and disadvantages. Applicability of ammonia removal technologies generally depends upon several factors such as: contamination level of wastewater to be treated, plant safety and regulatory considerations, boundary conditions of wastewater itself and plant site (pH level, wastewater composition, availability of cheap heating source and the

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0376-7388/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.memsci.2007.06.021

chemicals required to perform separation process), etc. Conventional methods of ammonia removal by lime treatment and aeration or stripping may be in some situations costly and inefficient [3,4]. The problem is that the used air cannot be discharged before another treatment stage (i.e. post-treatment) to prevent air pollution problems. Realizing the amount of air required for the stripping process and the need for its purification, the capital cost for any ammonia treatment plant is of concern. However, advancements in plant design and advantaging from the available boundary conditions can make the liming and air stripping technology more efficient and a cost-effective technology than other ammonia removal technologies [5]. On the other hand, biologically based ammonia removal methods require large tanks, long retention times, tightly controlled operating conditions and long recovery times to regenerate the specialized bacteria in the set-up. The operating cost of any biologically based system is also of concern since large quantities of chemicals are required. Once again, for some particular applications and based on certain boundary conditions, the biological ammonia removal technology may be the best choice. Nevertheless, membrane based gas absorption/stripping processes have been widely explored since 1980s because of their attractive advantages compared to the traditional methods [6,7]. These include larger interfacial area per unit volume and more controllable gas and liquid flow rates. It must be pointed out here that continuously there is a need for alternative and effective separation techniques exhibiting higher efficiency. In this case, an alternative process leading to higher performance, reducing or even eliminating the excessive amounts of acid solutions required to perform the ammonia removal is needed. Membrane distillation (MD) may be the adequate alternative.

MD process refers to the physical separation of a mixture across a hydrophobic microporous membrane by means of a thermal driven process. The membrane acts as a barrier to separate a warm solution (usually feed side) from a cooler chamber (permeate side) which contains either a liquid or a gas phase [8]. The hydrophobic nature of the microporous membrane prevents liquid solutions from entering its pores due to the surface tension forces. As a result, a fixed interface is formed at the pores entrances. The concentration and temperature difference at the pores entrances produces a vapor pressure gradient, which is the driving force for vapor molecules of more volatile compounds to migrate from the feed to the permeate side of the membrane. At the permeate side, migrated molecules (depending on the configuration used) are either condensed or removed in vapor phase out of the membrane module [9,10]. Within MD literature, there are four well-recognized MD configurations. These MD configurations are classified in accordance to the way by which the migrated molecules are condensed at the permeate side or removed out of the module in vapor phase. When the condensation process takes place at the cold membrane surface of the permeate side by means of a direct circulation of a cold liquid, frequently distilled water, the process is termed direct contact membrane distillation (DCMD). When the condensation process takes place inside the membrane module over a cold surface (that is been separated from the membrane surface by a stagnant air gap) the process is known by air gap membrane distillation (AGMD). In other two configurations, migrated molecules are removed out of the membrane module for condensation. In such situations, migrated molecules can be removed either by a vacuum giving rise to the known vacuum membrane distillation (VMD), or swept away by a sweeping gas leading to the MD configuration: sweeping gas membrane distillation (SGMD). MD process is therefore, a combination of membrane separation and evaporation/condensation process. The potential advantages of MD process in comparison to the conventional separation processes rely on the low operating temperature and pressure (i.e. atmospheric pressure can be applied) [9,10].

This work was conducted to study the application of VMD for ammonia removal from its aqueous solutions. In order to achieve the optimum operating conditions for ammonia removal by VMD, the effects of feed flow velocity, feed temperature, permeate pressure, initial feed ammonia concentration and pH on permeate flux and ammonia removal rate efficiency as well as on separation factor were investigated.

2. Theory

The ammonia in wastewater effluents exists in two forms, as volatile ammonia and ammonium ions. Ammonia treatment processes seek to maximize the volatile ammonia component. However, the amount of ammonia that can be removed from aqueous solutions depends to a great extent on two factors, namely the temperature and the pH value of the aqueous solution. It is worth quoting that solubility of ammonia in water is a declining function of temperature. For instance, one volume of water can dissolve 1200 vol. of ammonia at 0 °C and atmospheric pressure; whereas at 20 °C this solubility decreases to 700 vol. of ammonia per 1 vol. of water [11]. However, increasing temperature only, cannot release all the dissolved ammonia due to the fact that much of its quantity dissociates instantly in water to form unstable $NH_4{}^+$ solutions, according to the following chemical reaction:

$$NH_3 + H_2O \overset{K_1}{\longleftrightarrow} NH_4^+ + OH^- \tag{1}$$

At a temperature of 25 °C, the equilibrium constants for this reaction are, $K_1 = 1.8 \times 10^{-5}$ towards $NH_4{}^+$ formation and $K_2 = 5.6 \times 10^{-10}$ towards ammonia formation [12]. Thus, the equilibrium of the reaction to the right side is almost 3.2×10^4 times higher than that towards the left side. It must be pointed out that increasing pH value of the aqueous solution favors the presence of ammonia and, therefore, the aqueous solution turned to be enriched with ammonia molecules rather than with the ammonium ions, which results in better ammonia removal efficiencies. It must be stated that the vapor pressure of aqueous solutions containing ammonia is higher than that of water. Increasing the ammonia concentration in water, would remarkably increase the vapor pressure of the solution.

As stated previously, attempts are made in the present study to conduct VMD for ammonia removal from its aqueous solutions. The ammonia removal efficiency (R) is determined as follows