



Supported-gas-membrane process for removal and recovery of aliphatic amines from aqueous streams

Jie He^a, Huaqun Liu^a, Pengfei Shan^a, Kunming Zhang^a, Yingjie Qin^{a,b,*}, Liqiang Liu^b

^a School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China

^b Chembrane Research & Engineering, Inc., Bridgewater, NJ 08807, USA

HIGHLIGHTS

- Supported-gas-membrane process firstly to remove and recover aliphatic amines from aqueous solution.
- A mathematical model was established and solved numerically.
- Overall mass transfer coefficient was a strong function of polarity of amine.
- Amine could be enriched for > 20 times while > 95% of amine was recovered.
- A long-term operation stability was performed and tested well for > 30 days.

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ABSTRACT

The removal and enrichment of aliphatic amines with low molecular weights from their individual aqueous solutions was investigated theoretically and experimentally via a hollow-fiber supported-gas-membrane (SGM) process. Aqueous solutions containing 200–5000 mg L⁻¹ amine were tested as feed, and an aqueous solution of 10 wt% sulfuric acid was used as an absorbing solution. Amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine, as well as ammonia, were tested in the SGM process. The experimental data demonstrated that the overall mass transfer coefficient was a strong function of the polarity of the amine or amine/water volatility and was not a simple function of the molecular weight or boiling point of amines; the order was determined to be trimethylamine > ammonia > triethylamine > diethylamine > ethylamine > dimethylamine > methylamine. The influences on mass transfer coefficients of the feed-in temperature, feed-in concentration, feed flow rate, and the concentration of NaOH pre-added to the feed were also investigated. Among these operating factors, the feed-in temperature and NaOH concentration were crucial; increasing the feed-in temperature and the NaOH concentration led to a significant increase in the mass transfer coefficient, especially when the amine concentration in the feed was low. Mathematical models incorporating laminar flow, ion and molecular diffusion, dissociation equilibrium and vapor–liquid equilibrium were established and solved numerically. When the surface tension of the feed solution was > 45 mN m⁻¹, the SGM process demonstrated good stability during a test period of at least 30 days. Greater than 95% of the amine was recovered, and the amine could be enriched by > 20 times in the absorbing solution. Thus, this SGM-based separation process is suitable to remove, recover, and concentrate amines from their aqueous solutions.

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1. Introduction

Aliphatic amines of low molecular weight are widely used in a variety of industries (Meng et al., 2010; Chang et al., 2010; Wang et

* Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel./fax: +86 22 27890430.

E-mail address: yjqin@tju.edu.cn (Y. Qin).

al., 2011). For instance, methylamine is mainly used in the production of medicines (hormone or caffeine), agricultural chemicals (carbaryl, rogor, and so on) and explosives; dimethylamine is used for synthesis of dimethylformamide, agricultural chemicals, and medicines and is used in tanneries; trimethylamine is used in the production of feed additives, weedicides, and ion exchange resins; ethylamine is used in synthesizing dyes, extraction, emulsification, rubber vulcanizing, medicine production and petroleum refining; diethylamine is used in organic synthesis and as a curing agent for

epoxy; triethylamine is mainly used as an organic solvent, inhibitor, catalyst, and preservative, and it is also used for synthesizing dyes. Amine-containing wastewater streams are produced during the operation of amine-related processes; for instance, dimethylamine-containing wastewater is produced from the hydrolysis of dimethylformamide in the artificial leather industry (Chang et al., 2010). With the extensive application of amines and amine derivatives, the environmental impact of amine emission cannot be ignored, especially when increasing amounts of amine-containing wastewater from chemical plants, refineries and pharmaceutical plants are discharged into surface water and underground water in China.

Aliphatic amines of low molecular weight are volatile, more basic than ammonia, more toxic than ammonia, and less biodegradable than ammonia. Several conventional methods (Meng et al., 2010; Zhang et al., 2010; Wang et al., 2011; Chen et al., 2008; Chang et al., 2010; Qu and Chen, 2009) such as ion exchange, chemical precipitation, oxidation, biodegradation, distillation and air stripping have been applied to the treatment of amine-containing wastewaters. Among these methods, air or steam stripping is the most widely used in the chemical industry; however, it still has problems such as high cost of equipment, high power or steam consumption, and secondary pollution.

The supported-gas-membrane (SGM) separation process may provide an alternative technology for amine removal and recovery. The SGM process (or trans-membrane stripping/absorption process) is a technology that combines membrane separation with a conventional absorption and stripping (desorption) process, in which a hydrophobic microporous membrane is placed between a feed, which is an aqueous solution containing a volatile species, and an absorbing solution, which is an aqueous solution usually containing a reactive absorbing agent (Qin and Cabral, 1997; Qin et al., 1996). In such a membrane-based separation process, volatile species evaporate from the aqueous feed at the interface between the feed and the filled gas within the micropores in the membrane wall, diffuse through the gas-filled micropores, and then dissolve into the absorbing solution at the interface between the gas-filled micropores and the absorbing solution. The driving force of this membrane process lies in the difference of the partial pressure of the volatile species over the feed and that over the absorbing solution (Yang and Cussler, 1986). However, the partial pressure of the volatile species over the absorbing solution is usually thought to be zero when the volatile species is acidic and the absorbing agent is basic, the volatile species is basic and the absorbing agent is acidic, or the volatile species is an oxidant and the absorbing agent is a reductant. The membrane used in the SGM process is commonly in the form of microporous hydrophobic hollow fibers, and such types of hollow fibers are usually made from polytetrafluoroethylene, polypropylene (PP) and polyvinylidene fluoride. When a hollow-fiber membrane module—which is usually called a membrane contactor—is used, the feed solution usually flows through the lumen of the hollow fibers while the reactive absorption solution flows through the shell side of the membrane modules; such an operation mode usually leads to a higher overall mass transfer coefficient (Qin et al., 1990; Qin and Cabral, 1997).

Currently, research on the applications of membrane-based absorption, membrane-based stripping or the SGM process is quite extensively studied for the removal of volatile and reactive species such as O₂, CO₂, NH₃, H₂S, SO₂, HCN, NO, Cl₂, Br₂, and I₂ from gaseous or aqueous feed streams to another aqueous solution (Yang and Cussler, 1986; Imai et al., 1982; Yang and Cussler, 1986; Kenfield et al., 1988; Semmens et al., 1989, 1990; Qin et al., 1990, 1996; Qin and Cabral, 1997; Wang et al., 1993; Mackenzie and King, 1985; Titmas and Fluto, 1993). Some of those processes have been commercialized, such as the stripping of O₂ or CO₂ from ultrapure water. However, until now, there has been no report on

the application of membrane-based absorption, membrane-based air stripping or the SGM process to remove amine from a gaseous stream or an aqueous solution. Compared to the above-mentioned conventional methods for removing amine from aqueous solutions, the SGM process using modules made from a porous hydrophobic membrane has several prominent features and benefits (Meng et al., 2010; Zhang et al., 2010; Wang et al., 2011; Chen et al., 2008; Chang et al., 2010; Qu and Chen, 2009). First, the stripping of amine from the aqueous solution and the subsequent absorption of amine in another aqueous solution, which is usually an acidic absorbent solution, occur simultaneously in a single-membrane contactor by replacing both a stripping (desorption) column and an absorption column; thus, this membrane-based process provides a maximum driving force for amine removal (Meng et al., 2010; Chen et al., 2008). Second, the feed and stripping streams are located in each side of the microporous hydrophobic membrane and cannot influence each other; thus, the flexibility is greatly improved relative to the conventional column (Chang et al., 2010; Qu and Chen, 2009). Third, the membrane module has a high packing density, and the hollow-fiber membrane has a small diameter; therefore, the membrane contactor can supply a much higher surface area per volume compared to conventional columns (Wang et al., 2011; Chen et al., 2008). Fourth, compared to conventional separation contactors, a commercialized membrane contactor with excellent shell-side structure design encounters no back-mixing, wall flow, by pass flow, dead angle, flooding, foaming entrainment, and so on; thus, the overall transfer coefficient of this membrane-based separation process is much higher (Zhang et al., 2010; Wang et al., 2011). Finally, compared to air stripping or steam stripping, the operational cost of the SGM process is much lower because it almost eliminates the consumption of steam and consumes much less electricity to drive the wastewater and absorbing solution to pass through the membrane module (Meng et al., 2010; Chen et al., 2008).

In this study, the SGM process for removing, recovering, purifying and concentrating various amines from their respective aqueous solutions was investigated experimentally and theoretically. The effects of operation parameters such as the feed-in temperature, feed-in concentration, and feed-in flow rate as well as membrane properties on the performance of amine removal were examined and discussed in detail. The mass transfer coefficient, removal/recovery percentage, and enrichment ratio were used to characterize the efficiency of the SGM-based separation process for amine removal. The long-term operational stability of the SGM process was tested for dimethylamine. This work is a significant contribution to the treatment of wastewater streams containing amines.

2. Experimental

Ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, trimethylamine, hydrochloric acid (HCl), and sulfuric acid (H₂SO₄) were all purchased from Jiangtian Chemical Corporation (Tianjin, China). All chemicals used in the experiment were of reagent grade and were employed without further purification. Aqueous amine solutions were prepared by adding a certain quantity of amine to deionized water. The exact concentration of amine was determined by titration with a HCl solution using a titrator (DL28, Mettler Toledo, Columbus, OH, USA) with an error of less than 0.5%. The surface tension of the aqueous feed solution containing different amines at various concentrations was measured by using surface tensiometer (NDJ-8S, Fangrui Instrument, Inc., Shanghai, China). The feed liquid entry pressure (LEP) of the polypropylene (PP)

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