

Influence of osmotic distillation on membrane absorption for the treatment of high strength ammonia wastewater

WANG Guan-ping¹, SHI Han-chang¹, SHEN Zhi-song²

(1. Environment Simulation and Pollution Control State Key Joint Laboratory, Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China. E-mail: wgp00@mails.tsinghua.edu.cn; 2. Jiangsu Institute of Microbiology, Wuxi 214063, China)

Abstract: Osmotic distillation (OD) was found to be a coupled process in membrane absorption (MA) for the treatment of high strength ammonia wastewater. As a result, ammonia could not be concentrated in absorption solution (AS) as expected. The inhibition of the coupled OD in MA process was investigated as well as various factors affecting the inhibition. The results indicated that the coupled OD can be effectively inhibited by heating concentrated solution and cooling dilute solution. It was also found that experimental minimum inhibition temperature difference (MITD) between concentrated and dilute solutions was different when using polyvinylidene fluoride (PVDF) and polypropylene (PP) membranes respectively, which could be ascribed to material properties, such as OD and membrane distillation (MD) coefficients of the membranes. Experimental MITDs were found to be higher than theoretical MITDs which were calculated using a simplified method.

Keywords: membrane absorption; osmotic distillation; high strength ammonia wastewater

Introduction

Ammonia is a major pollutant in water pollution in China, and the treatment of high strength ammonia wastewater is still a difficult problem in wastewater treatment. A novel technique, membrane absorption (MA), has been introduced by some researchers (Rajalo, 1994; Qin, 1996) to treat high strength ammonia wastewater. MA is also known as gas-filled membrane absorption, gas membrane or membrane absorption-desorption, which is a membrane process combining desorption and absorption process together (Winston, 1992). The pivotal part of the process is the hydrophobic microporous membrane that consists of a gas layer separating two aqueous solutions (Fig. 1). The two solutions can not be mixed together unless the pressure difference across the membrane is higher than the expel pressure. Volatile solute like ammonia can pass across the membrane pores, but liquid and nonvolatile solutes are completely retained.

A pilot scale study was conducted in laboratory for the treatment of high strength ammonia wastewater by using MA process (Wang, 2002). We used equipments as those shown in Fig. 2, and (1) was a H_2SO_4 solution reservoir and (7) was an ammonia wastewater reservoir. High efficiency of ammonia removal was achieved in the study: the ammonia concentration in wastewater could be reduced from 2000 mg/L to less than 15 mg/L with ammonia transfer flux of $8 \text{ g}/(\text{m}^2 \cdot \text{h})$, and more than 99% of ammonia could be recovered in the absorption solution (AS).

It was found that the volume of the AS expanded continuously in the process, which led to impossibility of

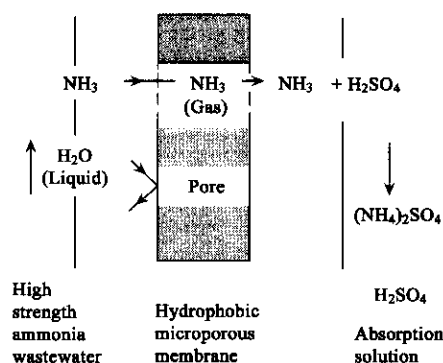


Fig. 1 Mechanism of MA

ammonia condensation in the AS. The measure flux of water permeation was $150 \text{ g}/(\text{m}^2 \cdot \text{h})$ and it was caused by osmotic distillation (OD). OD, also known as isothermal membrane distillation (MD), was investigated widely among researchers (Werner, 1996). The driving force of OD was vapor pressure difference, and it was originated from a concentration difference (ΔC) of solutions between the two sides of membrane. In the MA process, 2 g NH_3 -N/L ammonia solution was circulated on the feed side, and 10% (w/w) H_2SO_4 solution on the absorption side. Therefore, the water vapor pressure on the feed side was higher than that on the AS side, which led to the transfer of water vapor from the feed to the AS, and it was an unwanted process in MA for ammonia recovery.

If the volume of AS tank was 300 ml and the initial volume of 10% H_2SO_4 was 250 ml, H_2SO_4 could be reacted completely within 13.5 h but the tank would be fully filled by "leaked" water after 4 h. As shown in Table 1, theoretically we can get 13.14% $(\text{NH}_4)_2\text{SO}_4$ solution without OD after

13.5 h and there would be no residual H_2SO_4 in the final solution. But with the coupled OD process, the AS tank was filled up after 4 h and we could only get 3.31 % $(\text{NH}_4)_2\text{SO}_4$ solution with 5.89% residual H_2SO_4 .

Table 1 Influence of OD on MA

Time, h	AS volume		$(\text{NH}_4)_2\text{SO}_4$ in AS, %		H_2SO_4 in AS, %	
	Without OD	With OD	Without OD	With OD	Without OD	With OD
0	250	250	0	0	10	10
4	251	299	3.94	3.31	7.02	5.89
13.5	255	417*	13.14	8.03	0	0

Notes: * AS tank was assumed to be big enough

It was clear that the coupled OD leads to two disastrous results in MA process for the treatment of high strength ammonia wastewater. Firstly, the ammonia removed from wastewater could not be concentrated in the AS. Theoretically, ammonia could be concentrated from 2 g NH_3 -N/L to 12 % $(\text{NH}_4)_2\text{SO}_4$ when the AS is 10% H_2SO_4 . But

actually, $(\text{NH}_4)_2\text{SO}_4$ concentration was less than 4% when the AS tank was filled up by “leaked” water. Secondly, the system might be forced to stop running if such a dilute $(\text{NH}_4)_2\text{SO}_4$ solution with residual H_2SO_4 could not be easily reused in industry.

In this paper, inhibition of OD was investigated by means of heating the AS and cooling the feed. The water vapor pressure difference across the membrane was raised by a temperature difference(ΔT). Pure water(de-ionized water) and NaCl solution were used to simulate the feed and the AS respectively(Fig.4). Two kinds of membranes were used in the study to get a comprehensive conclusion.

1 Experimental

Polypropylene (PP) hollow fiber membrane and polyvinylidene fluoride (PVDF) flat sheet membrane (Table 2) were used in the experiments.

Table 2 Features of membranes

Material	Inside diameters, μm	Wall thickness, μm	Pore size, μm	Porosity, %	Expel pressure, MPa	Manufacturer
Hollow fiber PP	400	50	0.03	35	0.25	Tianjin, China
Flat sheet PVDF	—	70	0.22	75	0.05	Hangzhou, China

As shown in Fig.2, the osmotic agent(NaCl solution of varied concentration) and the feed agent(pure water) were circulated co-currently along two sides of the membrane. In this paper, the inside of the PP hollow fiber membrane is called lumen side, and the outside of the fibers is called shell side. HFMC was made by potting 75 pieces of fibers into a glass shell. The packing method of fibers was random and membrane area was 141 cm^2 .

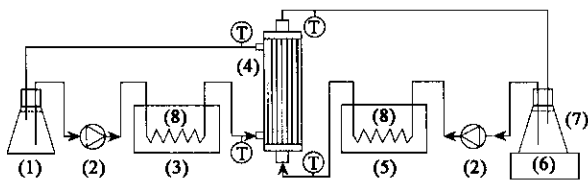


Fig.2 Schematic diagram of OD inhibition experiment
1. NaCl/ H_2SO_4 solution reservoir; 2. peristaltic pump; 3. thermostat; 4. HFMC; 5. low temperature thermostat; 6. electronic balance; 7. pure water/ammonia wastewater reservoir; 8. heat exchange tube; T. electrothermometer

A part of the experiments was conducted using the PVDF flat sheet membrane contactor(FSMC) instead of the PP HFMC. The structure of the FSMC is shown in Fig.3 and it had a membrane area of 40 cm^2 .

After the experiments with agents (NaCl solution and pure water) were finished, the experiments with H_2SO_4 as the AS and ammonia wastewater (NH_4Cl solution) as the feed were conducted to investigate the inhibition of OD by ΔT in MA process.

The mean temperature of pure water in cold side was

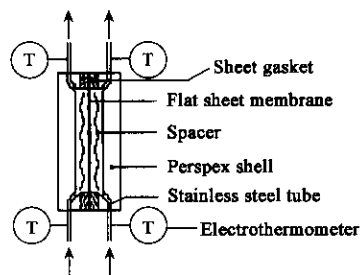


Fig.3 Structure of FSMC

kept at 19.7 $^{\circ}\text{C}$ by using the low temperature thermostat, and that of NaCl solution was the same or higher. The circulation velocity(V) of the fluids was 0.04 m/s in FSMC and 0.2 m/s in HFMC. Pure water permeated across the membrane with the help of a ΔC of NaCl solution or a ΔT between two sides of the membrane. The weight variation of pure water receiver was measured by the electronic balance, so that the water flux could be calculated from the weight difference at an interval of 30 or 60 min.

2 Results and discussion

2.1 Experiments with NaCl solution and pure water

The effects of inhibition of coupled OD process by ΔT across the membrane are shown in Fig.4 and 5. The minus flux in the figures means that water transfers from pure water to NaCl solution; the plus flux means that water transfers from NaCl solution to pure water. ΔT_m means log mean temperature difference across the membrane. The temperature of the intersecting points of tie lines and axial line of zero flux

is minimal inhibition temperature difference (MITD) of OD (Table 3). When ΔT_m is equal to MITD, the water vapor of NaCl solution is the same as that of pure water, so that the flux of water is zero.

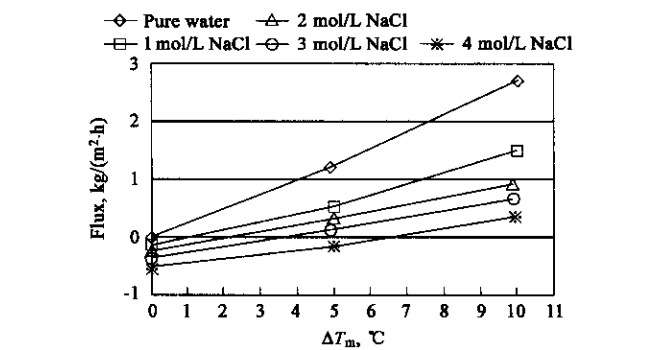


Fig.4 Inhibition of OD using PVDF FSMC, brine circulated in hot side and pure water in cold side

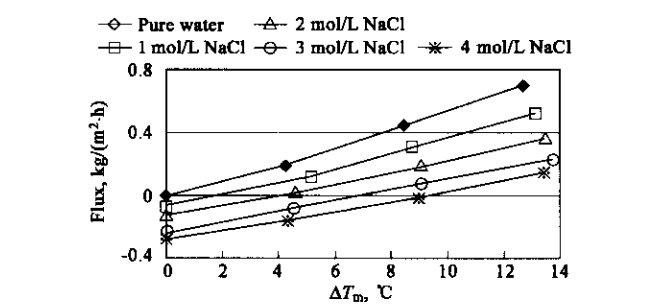


Fig.5 Inhibition of OD using PP HFMC, brine circulated in hot/shell side and pure water in cold/lumen side

Table 3 MITD of two kinds of membranes, °C					
Concentration of NaCl, mol/L		1	2	3	4
Experimental	PVDF	1	2.1	3.7	6.6
	PP	1.8	4.1	6.9	9.4
Calculated	PVDF	0.49	1.10	1.84	2.73
	PP				

The results indicated that the inhibition of OD can be realized by ΔT across the membrane. The flux is zero or minus when ΔT_m is zero, and it gradually turns to plus when ΔT_m increases even the hot side is NaCl solution. The higher the concentration of NaCl solution is, the bigger the MITD is. The absolute value of the flux of PVDF membrane is bigger than that of PP membrane under the same conditions.

The experimental results of MITD are shown on the 2nd and 3rd lines in Table 3. In the experiments with PVDF FSMC, MITD of 3.7°C can cancel out OD flux with a ΔC of 3 mol/L NaCl solution, which is close to what Godino had reported (Godino, 1995). However, our results from PP HFMC showed big difference to Godino's. In our experiment, MITD of 6.9°C for PP membrane, which is nearly twice of that for PVDF membrane, can only cancel out OD flux with a ΔC of 3 mol/L NaCl solution. The differences are caused by various membrane material properties, such as MD/OD coefficients.

As illustrated in Fig.6, two membrane processes exist at the same time if there are both ΔT and ΔC across the membrane. The driving force of MD (vapor transfers from right to left) originates from ΔT , while that of OD (vapor transfers from left to right) originates from ΔC . The comprehensive direction of vapor transfer depends on the competitive result of two membrane processes. The purpose of heating the NaCl solution and cooling the pure water is to increase MD flux. If MD flux is bigger than OD flux, OD process will be inhibited.

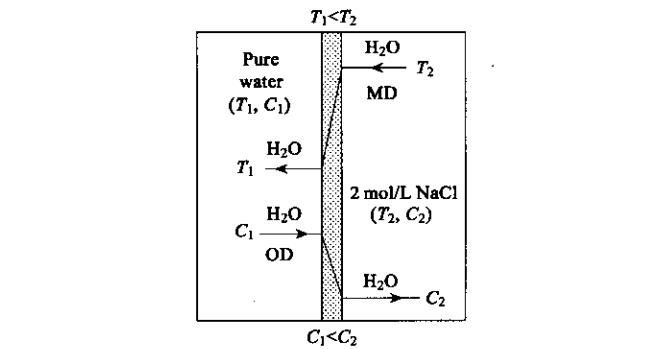


Fig.6 Inhibition of OD by MD

Other researches (Lawson, 1997) indicated that MD flux was proportional to membrane pore size and porosity, but was inversely proportional to membrane thickness and tortuosity. As shown in Table 2, the thickness of two membranes are virtually the same, but pore size and porosity of PVDF membrane are much larger. As a result, theoretical flux including MD and OD of PVDF membrane should be higher than that of PP membrane. And the experimental results (Fig.7 and 8) accord with it.

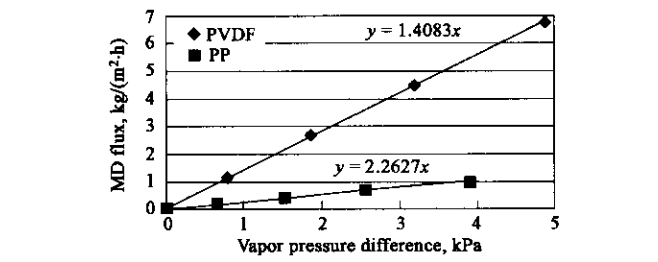


Fig.7 MD flux of pure water
Temperature in cold side is kept at 19.7°C, and in hot side is the same or higher

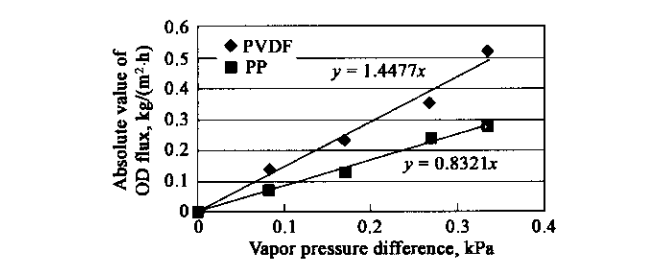


Fig.8 OD flux without ΔT
Temperatures in two side are the same, from 9.7°C to 49.7°C with a step of 10°C

In some cases, the mass flux of MD and OD may be written as a linear function of the vapor pressure difference across the membrane, given by,

$$N = k_{MD} \Delta P = k_{MD} (P_{b1} - P_{b2}), \tag{1}$$

$$J = k_{OD} \Delta P = k_{OD} (P_{b1} - P_{b2}). \tag{2}$$

Where N is the MD flux(kg/(m²·h)); J is the OD flux(kg/(m²·h)); k_{MD} is the MD coefficient; k_{OD} is the OD coefficient; ΔP is the water vapor pressure difference across the membrane (kPa), and P_{b1} and P_{b2} are the vapor pressures in the hot side(NaCl solution) and cold side(pure water) (kPa).

As shown in Table 4, k_{MD} and k_{OD} of PVDF membrane are 5.36 and 1.74 times as that of PP membrane, so the MD and OD fluxes of PVDF membrane are higher. k_{MD}/k_{OD} of PVDF membrane is 3.03 times as that of PP membrane, therefore when temperature of hot side is increased, the flux difference between MD and OD of PVDF membrane increases faster than that of PP membrane. As a result, we need less ΔT to inhibit OD through MD when using PVDF membrane other than PP membrane.

Table 4 MD and OD coefficient of membranes

		k_{MD}	k_{OD}	k_{MD}/k_{OD}
Membrane material	PVDF	1.4083	1.4477	0.97
	PP	0.2627	0.8321	0.32
Ratio of PVDF/PP		5.36	1.74	3.03

The 4th and 5th lines in Table 3 can be calculated through Equation (3) (Shi, 1996) and Equation (4) (Lawson, 1995).

$$\lg P_0 = 7.07406 - \frac{1657.46}{227.02 + t}, \tag{3}$$

where P_0 is the vapor pressure of pure water(kPa), and t is the temperature(°C).

$$P = P_0 (1 - x)(1 - 0.5x - 10x^2). \tag{4}$$

Where P is the vapor pressure of NaCl solution(kPa), and x is the mole fraction of NaCl in the solution.

Equation (3) may be rewritten in the form:

$$P_0 = 10^{\left(7.07406 - \frac{1657.46}{227.02 + t}\right)}. \tag{5}$$

Substituting Equation (5) in Equation (4) yields

$$P = 10^{\left(7.07406 - \frac{1657.46}{227.02 + t}\right)} (1 - x)(1 - 0.5x - 10x^2). \tag{6}$$

The vapor pressure of pure water and NaCl solution with a certain concentration can be worked out by Equation (6). For pure water in the experiments, t_0 is always kept at 19.7°C, so P_0 is 2.27 kPa. For NaCl solution, when MITD is reached, P is equal to P_0 . Hence

$$10^{\left(7.07406 - \frac{1657.46}{227.02 + t}\right)} (1 - x)(1 - 0.5x - 10x^2) = 2.27. \tag{7}$$

That is

$$t = \frac{1657.46}{7.07406 - \lg\left(\frac{2.27}{(1 - x)(1 - 0.5x - 10x^2)}\right)} - 227.02. \tag{8}$$

So t can be worked out through Equation (8). Values of calculated MITDs, which are t minus t_0 , are shown in Table 3.

Table 3 shows that experimental MITDs are much higher than calculated values. For PVDF membrane, experimental MITDs are about twice as that of calculated values; for PP membrane that is about 4 times. The discrepancy between experimental and theoretical MITDs is caused by two main reasons.

Firstly, temperature polarization caused the difference between experimental and calculated MITDs. The heat transferred in MD includes two parts: one for heat conduction through membranes, and the other for vapor evaporation and condensation through membrane pores. As shown in Fig. 9, the calculated MITD is nearly equal to T_{1m} minus T_{2m} , but not T_1 minus T_2 . There are still some deviations in our calculation because T_{1m} and T_{2m} are considered as T_1 and T_2 approximately.

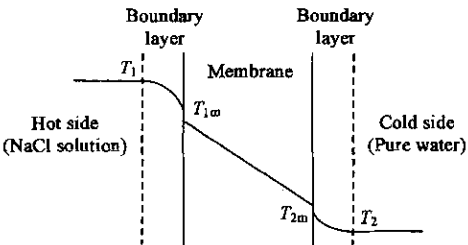


Fig.9 Temperature profile in membrane distillation

Secondly, the OD flux is influenced by temperature obviously. Vapor pressure difference in OD process without ΔT can be got with the help of Equation (4),

$$\Delta P = P_0 - P = P_0 [1 - (1 - x)(1 - 0.5x - 10x^2)]. \tag{9}$$

For a NaCl solution with a certain concentration, x is a constant. From Equation (5), P_0 gets bigger when t gets higher. So ΔP increases when t gets higher. As a result, extra temperature difference is needed to raise MD flux, so as to cancel out the extra increase of OD flux caused by temperature increase.

The deviation of PP membrane is higher than PVDF membrane because gas permeability of PP membrane is smaller than that of PVDF membrane, and it has been discussed in the previous part. Furthermore, influence of temperature on OD and MD processes is very complex. Physical properties of pure water and NaCl solution, including viscosity, heat capacity and etc., change with temperature's variation(Schofield, 1990). In this paper, we used a simplified method to calculate MITDs, and the results were acceptable. A more accurate model can be established in the future to work out more accurate MITD values.

2.2 Experiments with H₂SO₄ solution and ammonia wastewater

Under the same conditions, MA experiments with 2 mol/

L H_2SO_4 solution as the AS and ammonia wastewater (2.5 g/L NH_4Cl solution) as the feed, using HFMC, were conducted. Mass transfer coefficient (λ) was used to describe the ammonia removal effect (Semmens, 1990). The initial pH value of ammonia wastewater was adjusted to 11.25 so that ammonia would be volatile. At the same time, inhibition of OD was also investigated in the MA process and the experiments of inhibition were conducted before the initial pH value was adjusted. The temperature of ammonia wastewater was kept at 19.7°C, and the temperatures of the AS were 19.7, 24.7, 29.7 and 34.7°C.

The results are shown in Fig. 10. The OD fluxes turn from minus to plus gradually when ΔT is increased. When ΔT reaches 5°C, vapor pressures across the membrane are about the same, and the coupled OD in MA process are completely inhibited. λ remains virtually unchanged even though the temperature of the AS is increased.

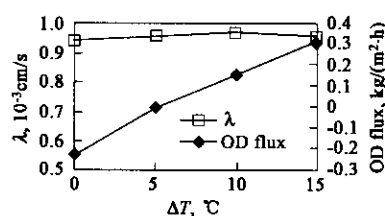


Fig. 10 Influence of ΔT on ammonia mass transfer coefficient and OD flux

3 Conclusions

The research has indicated that the coupled OD process in MA process could be inhibited effectively by heating the concentrated solution and cooling the dilute solution, therefore MA process can be widely applied in industry even though there is a concentration difference between the feed and the AS.

OD and MD flux are affected significantly by material properties of the membranes. The OD coefficient, MD coefficient and ratio of MD coefficient to OD coefficient of

PVDF membrane are bigger than that of PP membrane accordingly. It is more difficult to inhibit OD through MD using PVDF membrane than using PP membrane.

Theoretical MITDs are worked out in the paper by a simplified method. The calculated MITDs are much lower than experimental ones because temperature polarization and influence of temperature on OD flux.

MA experiments with ΔT indicated that the coupled OD in MA process can be completely inhibited by increasing ΔT , and ammonia transfer coefficient is unchanged even though the temperature of the AS is increased.

References:

- Godino M P, Pena L, Ortiz-Zarate J M *et al.*, 1995. Coupled phenomena membrane distillation and osmotic distillation through a porous hydrophobic membrane[J]. *Separation Science and Technology*, 30(6): 993—1011.
- Lawson K W, 1995. Membrane distillation[D]. Austin: University of Texas at Austin.
- Lawson K W, Lloyd D R, 1997. Membrane distillation[J]. *J Membrane Sci*, 124 (1): 1—25.
- Qin Y, Joaquim M S C, Wang S, 1996. Hollow fiber gas-membrane process for removal of NH_3 from solution and CO_2 [J]. *AIChE J*, 42 (7): 1945—1956.
- Rajalo G, Tereping O, Petrovskaya T, 1994. Thermally forced membrane desorption-absorption of ammonia[J]. *J Membrane Sci*, 89: 93—99.
- Schofield R W, Fane A G, Felland C J D *et al.*, 1990. Factors affecting flux in membrane distillation[J]. *J Membrane Sci*, 77: 279—294.
- Semmens M J, Foster D M, Cussler E L, 1990. Ammonia removal from water using microporous hollow fibers[J]. *J Membrane Sci*, 51: 127—140.
- Shi J, 1996. Chemical engineering handbook (Chinese)[M]. Beijing: Chemical Engineering Press.
- Wang G P, Fang X L, Shi H C *et al.*, 2002. Study of membrane absorption-desorption process for the treatment of high strength ammonia wastewater[J]. *Techniques and Equipment for Environmental Pollution Control*, 3 (7): 56—60.
- Werner K, Ali B, Roger B, 1996. Osmotic evaporation through macroporous hydrophobic membranes: a survey of current research and applications[J]. *J Membrane Sci*, 121: 25—36.
- Winston H W S, Kamalesh K S, 1992. Membrane handbook[M]. Van Nostr and Reinhold.

(Received for review August 12, 2003. Accepted September 27, 2003)