Membrane materials contribution to mass transfer of ammonia in membrane contactors

Agata Zarebska[1*], May-Britt Hägg[2], Birgir Norddahl[1], Knud Villy Christensen[1]
1 Dept. of Chemical Eng., Biotechnology and Environmental Tech., SDU, Niels Bohrs Allé 1, DK-5230 Odense M, Denmark, agz@kbm.sdu.dk
2 Dept. of Chemical Engineering, NTNU, Sem Saelandsvei 4, 7491 Trondheim, Norway
*Corresponding author: agz@kbm.sdu.dk

Abstract
Membrane contactors performance depends on membrane characteristics and operating conditions. This study discusses the importance of material selection, pore sizes and porosity on overall mass transfer through hydrophobic microporous membranes. To demonstrate how membrane material contributes to overall mass transfer (K_m), flat sheet symmetric membranes: polypropylene, polytetrafluoroethylene, and asymmetric membrane: polysulfone, have been tested during ammonia removal from a model manure solution with particle size 125 µm. Obtained K_m values for PTFE ($64 \pm 15 \cdot 10^{-3}$ m/h) is marginally higher compared to value obtained for PP ($55 \pm 13 \cdot 10^{-3}$ m/h). Further the fouling tendency was higher for the PTFE membrane, as the contact angle decreased, suggesting a hydrophilic character of the foulants. The overall mass transfer coefficient decreased by nearly 60% in case of PTFE due to particle adhesion while no particle influence was seen for PP.

1. Introduction

Membrane contactors (MC) works by evaporation of volatiles through a porous gas filled membrane. They have been applied successfully for removing volatile ammonia from water and wastewater or as a post treatment of biogas plant effluents. MC presents a possible technology for ammonia fertilizer production from animal wastes *[1, 2*]. In most membrane processes, the membrane acts as a sieve allowing passage of some components while rejecting others *[3, 4]*. Contrary to pressure driven membrane processes, membrane contactors act as an interface to “keep in contact” two phases without dispersing one phase into the other *[3, 5]*. However, a diffusive transport of components from one phase to the other is possible. This process is a function of feed conditions and membrane properties and depends on raw materials and preparation methods *[2, 4]*. Depending on the microstructure of the membrane, one distinguish between symmetric and asymmetric membranes *[4]*. Symmetric membranes can be dense or have sponge structure or straight pores, while asymmetric membranes are composed of two layers: one thin dense layer with or without pores and a second highly porous layer *[4]*. The aim of this work is to add knowledge on how membrane structure and particle fouling can limit the mass transfer of ammonia as expressed by the mass transfer coefficient K_m. In order to demonstrate how the membrane material contributes to mass transfer, flat sheet symmetric membranes: polypropylene (PP), polytetrafluoroethylene (PTFE), and an asymmetric membrane polysulfone (PSF) were tested during ammonia removal from a model manure solution with and without particles smaller than 125 µm.

The membrane pore size (r_p), porosity (ε), thickness (δ) and hydrophobicity as expressed by the contact angle (θ) were analyzed with the following methods:

- Scanning electron microscope (SEM) to observe the morphology and study membrane thickness
- Brunauer-Emmett-Teller (BET) adsorption to characterize average pore size of membrane
- Contact angle to obtain information about the hydrophilicity/hydrophobicity of the membrane surface
- Gas permeation test to study membrane effective surface porosity

2. Materials and methods

2.1. MaterialsAll chemicals used for preparing the model manure solution were analytical grade reagents, except commercial pig fat (lard) and straw. The chemical composition of the model manure solution used is presented in Table 1. Straw, which represents particles present in manure was milled and sieved with aperture size 125 µm. Sulfuric acid 0.5 M (VWR A/S Herlev, Denmark) was used to adsorb ammonia.

Table 1 Chemical composition of model manure solution

Compound	Concentration [g/L]
NH_4HCO_3	17
CH_3COOH	10
Straw	5
Gelatine	3.75
Lard	2.30
Benzoic acid	0.02
$Mg_3(PO_4)_2$	1.80
$Ca_3(PO_4)_2$	1.25
Na_2S	3

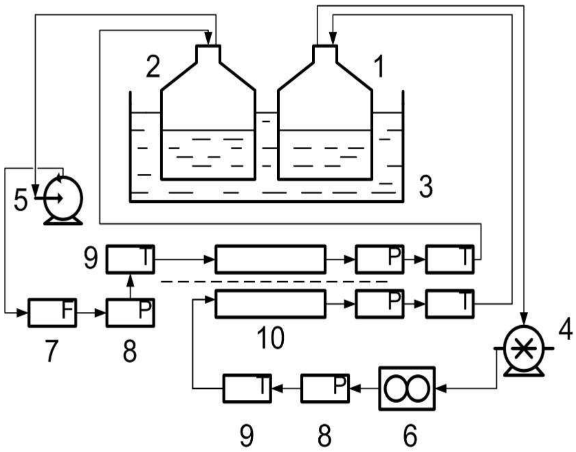

Fig. 1 The MC experimental set-up: 1: feed reservoir; 2: acid reservoir; 3: water bath; 4: magnetic drive turbine pump; 5: centrifugal pump; 6: IFC 100 Krohne Mag flowmeter; 7: Platon Bobbin flowmeter, 8: pressure gauges; 9: thermometers; 10: flat sheet membrane

2.2. Experimental setup

A schematic representation of the experimental setup used in this study for ammonia removal is depicted in Figure 1. The membranes used were a hydrophobic polypropylene membrane (PP, Accurel ® PP 2E HF (R/P)) from Membrana GmbH, polytetrafluoroethylene (PTFE Membrane Filters, Type 118) from Sartorius and polysulfone (GRM0.2PP) from Alfa Lavel. The model manure solution was passed through one side of the membrane, while the stripping solution containing sulfuric acid was pumped across the other. The pH of the model solution was adjusted to 11 using 5 M NaOH to ensure ammonia evaporation. Both feed and acid solutions were recycled to their respective tanks placed in a water bath to maintain the temperature at 35°C. The feed flow velocity was 0.03cm/s and the acid flow velocity 0.03 cm/s.

2.3. Analysis method

The ammonia concentration on the feed side was measured using a standard Kjeldahl distillation unit (Kjeltec TM2100, Höganäs, Sweden) and back titration (APHA Standard Method 2005). On the acid side ammonia was determined by Dr. Lange ammonium kits and a digital spectrophotometer.

2.4. Characterization techniques

Scanning electron microscope (SEM) (SEM Hitachi S-3400N, Japan) was used to observe the morphology and measure membrane thickness of the MC membranes. The membranes were fractured in liquid nitrogen to obtain a smooth cross section. Then the samples were dried and gold coated. The SEM pictures were taken at various magnifications at an accelerating voltage of 15 kV. Gas permeation tests were performed on flat sheet membranes, with an area of 5.3 cm^2 placed in a test module. As feed gas ammonia was introduced to the module at a pressure of 1.4 bar with flow rate of 100 ml/s. The equations used for calculating mean pore size and effective surface porosity assumes that membrane pores are straight and cylindrical in shape and is a combination of Poiseuille flow and Knudsen diffusion [6] per default the porosity therefore includes a correction for constrictions and tortuosity. Static contact angle measurements were performed using Theta Life Optical Tensiometer TL 100. The average of at least ten readings, when the water drop stabilized on membrane surface was used for contact angle measurement. Average pore size was determined using BET (Tristar II 3020). Before analysis, the membrane samples were prepared by degassing under vacuum at a 150 °C overnight (Vac Prep 061 Sample Degas System).

2.5. Mass transfer

To determine the overall mass transfer coefficient (K_m), the change of ammonia concentration with time was used (6).

$$\ln\left(\frac{C_0}{C_t}\right) = \frac{K_m \cdot A_m}{V} \cdot t \qquad \textbf{Eq. 1}$$

Table 2 Overall mass transfer of ammonia

K_m [m/h] x 10^3			
PTFE	**PTFE with particles <125 µm**	**PP**	**PP with particles <125 µm**
64 ±15	26 ± 11	55 ± 13	44 ± 11

Table 3 Membrane characterization

Parameter, unit	Value		
Membrane material	**PTFE**	**PP**	**PSF**
Average pore size [µm]	0.03	0.04	0.02
Thickness [µm]	62	177	58
Contact angle clean	126	143	99
Contact angle +model soln.	119	135	49
Effective porosity	308501	234832	3272

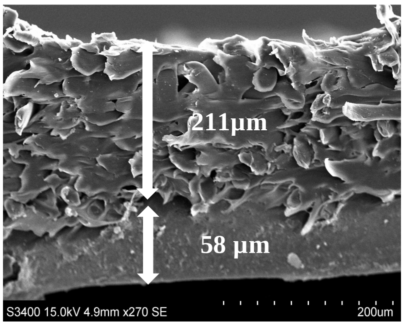

Fig. 2a SEM of the PSF membrane

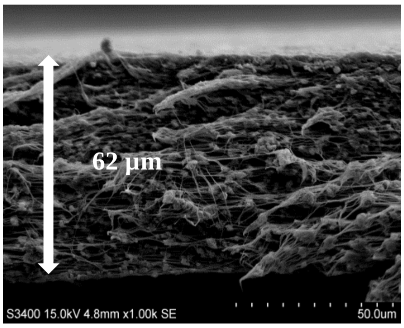

Fig. 2b SEM of the PTFE membrane

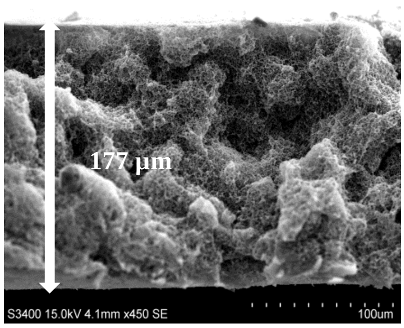

Fig. 2c SEM of the PP membrane

3. Results and discussion

The measured mass transfer coefficients are presented in Table 2. PTFE reveals higher mass transfer coefficient due to smaller membrane thickness (Fig. 2b) and higher effective porosity (Table 2) and therefore smaller membrane resistance. On the other hand PTFE membranes are more prone to particulate fouling, as shown by the decrease of the overall mass transfer coefficient (Table 2). It might be due to the lower surface energy of PTFE that influences membrane particle adsorption and causesfouling; as supported by the thorough work of Tu et al. *[7]*. From contact angle measurements, after immersing membranes for a week in model solution, it was found that the fouling is ofa hydrophilic character (Table 2). Hydrophilization of the PTFE membrane indicates adsorption of foulants such as polysaccharides and protein, which tend to accumulate on membrane surfaces and are rejected by hydrophobic membranes *[8-11]*. Tests with PSF membranes, turned out to be unsuccessful due to membrane wetting that hinders ammonia removal by MC. The obtained K_m values for the model manure solution without particles are similar to results of du Preez et al. for PP hollow fibers, who reported mass transfer coefficients of

$24.9 \cdot 10^{-3}$ m/h at 25 °C and $62.1 \cdot 10^{-3}$ m/h at 55 °C *[1]*. However, with particle addition, reduction of the value of mass transfer coefficient was for PTFE. This is in agreement with Ahn et al. *[12]* and could explain, why ultrafiltered manure yielded higher mass transport efficiency opposed to sieved manure as investigated in a previous study *[13]*.

4. Conclusion

The tested PTFE membrane show higher overall mass transfer of ammonia due to higher effective porosity and thinner membrane wall compared to the tested PP membrane. For the model manure solution without particles K_m was found to be $64 \pm 15 \cdot 10^{-3}$ m/h and for PP $55 \pm 13 \cdot 10^{-3}$ m/h. Particle adhesion has an adverse effect on PTFE membranes as the overall mass transfer of ammonia decreasing with 60%. In case of the PP membrane obtained K_m values were not significantly different, for solutions with or without 125 µm particles. Fouling in case of PTFE membrane has a hydrophilic character probably due to presents of polysaccharides and proteins. It was further found, that PSF cannot be used for ammonia removal in MC process as the membrane is wetted immediately by the model solution.

References

[1] du Preez, J.; Norddahl, B.; Christensen, K. The BIOREK((R)) concept: a hybrid membrane bioreactor concept for very strong wastewater. Desalination 2005, 183 (1-3), 407-415.

[2] Semmens, M. J.; Foster, D. M.; Cussler, E. L. Ammonia Removal from Water Using Microporous Hollow Fibers. Journal of Membrane Science 1990, 51 (1-2), 127-140.

[3] R.W.Baker Membrane technology and applications; Second edition ed.; Wiley: Membrane Technology and Research, Inc.Menlo Park, California, 2004.

[4] E.Drioli, A. C. &. E. C. Membrane contactors: fundamentals, applications and potentialities; First edition ed.; Elsevier: Amsterdam, 2006.

[5] F.Wiesler Membrane contactors: an introduction to the technology. Ultrapure Water May/June,1996.

[6] Li, K.; Kong, J. F.; Wang, D.; Teo, W. K. Tailor-made asymmetric PVDF hollow fibers for soluble gas removal. AIChE Journal 1999, 45 (6), 1211-1219.

[7] Tu, S. C.; Ravindran, V.; Den, W.; Pirbazari, M. Predictive membrane transport model for nanofiltration processes in water treatment. AIChE Journal 2001, 47 (6), 1346-1362.

[8] Maximous, N.; Nakhla, G.; Wan, W. Comparative assessment of hydrophobic and hydrophilic membrane fouling in wastewater applications. Journal of Membrane Science 2009, 339 (1-2), 93-99.

[9] Shon, H. K.; Vigneswaran, S.; Kim, I. S.; Cho, J.; Ngo, H. H. Effect of pretreatment on the fouling of membranes: Application in biologically treated sewage effluent. Journal of Membrane Science 2004, 234 (1-2), 111-120.

[10] Susanto, H.; Franzka, S.; Ulbricht, M. Dextran fouling of polyethersulfone ultrafiltration membranes-Causes, extent and consequences. Journal of Membrane Science 2007, 296 (1-2), 147-155.

[11] Zarebska, A.; Norddahl, B.; Christensen, K. V. Fouling characterization of membrane contactors used for the recovery and concentration of ammonia from undigested pig slurry. 11th World Filtration Congress & Exhibition Abstract Book W.Höflinger , G.Mauschitz, Eds.; Filtech: Graz, Austria, 2012; p 209.

[12] Ahn, Y. T.; Hwang, Y. H.; Shin, H. S. Application of PTFE membrane for ammonia removal in a membrane contactor. Water Science and Technology 2011, 63 (12), 2944-2948.

[13] Zarebska, A.; Christensen, K. V.; Norddahl, B. The Application of Membrane Contactors for Ammonia Recovery from Pig Slurry. Procedia Engineering, 44, 2012; pp 1642-1645.