Characterization of fouling of membrane contactors

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Ammonia stripping, Fouling, Membrane contactors

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Characterization of fouling of membrane contactors

In this study liquid-liquid membrane contactors have been tested for ammonia removal from model manure solution and undigested pig manure. The aim of this work is to compare the efficiency of ammonia removal by different hydrophobic membranes including the material's influence on mass transfer of ammonia and membrane fouling tendency. The surface morphology of both clean and fouled membranes by model manure solution and undigested pig manure has been studied by: Optical and Atomic Force Microscopy and contact angle measurements. Based on the experimental results, it is concluded that real manure achieved higher ammonia removal than the synthetic model manure solution. This might be due to the larger particle size of the milled straw in the model solution compared to the size of suspended solids present in real manure. From the fouling autopsy, it was found that PTFE membranes are more prone to fouling than PP membranes. In both membranes the hydrophobicity decreased after running the process for 30 h, especially when undigested pig manure was used.

1. INTRODUCTION

As livestock and agricultural farms grow in size there is a need for proper manure management. Animal slurry (manure) can be used as valuable fertilizers as it contains a large amount of nutrients: N, P, K, or it can be used as a substrate for biogas plants. Another reason why manure management is important is manure's negative influence on the environment. Excess of manure might lead to air and water pollution, eutrophication or even acid rains or greenhouse effect [3]. Therefore manure management is important both to avoid negative environmental impact, but also to optimize fertilizer usage and biogas production.

One method for obtaining a fertilizer fraction rich in ammonia (N-fertilizer) is to separate ammonia from the liquid fraction of animal manure. For this purpose membrane contactors have been used. In membrane contactors the membrane acts as a porous gas filled barrier between two phases (in this study both phases are liquids) and prevents them from mixing. As the ammonia molecules are transferred from the feed phase only by diffusion through the gas filled pores, the membrane material does not

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influence the relative rate of permeation and thus does not influence the separation. The process is thus more related to common ammonia stripping in packed columns than to most membrane processes.

Removal of ammonia using membrane contactor stripping has advantages compared to traditional stripping methods: larger surface area per volume, elimination of channeling and flooding as often occur in traditional column stripping operations. On the other hand, there are also problems with membrane contactors especially wetting and fouling. Wetting occurs when the feed penetrate to the stripping phase as a liquid instead of evaporating as a gas. When this happens no increase in ammonia concentration occurs. Fouling is a consequence of an accumulation of deposit on the membrane surface or within the membrane's pores and decreases the ammonia transport through the membrane.

Since fouling is a complex phenomenon and manure is a mixture of faeces and urine, when investigating fouling and comparing different membrane materials resistance to fouling, it is useful, if a standard model manure solution that mimic undigested manure can be used. In this way experiments will not be influenced by daily fluctuations in manure composition.

In this study, comparative experiments using a model manure solution and undigested pig manure have been carried out in order to study the efficiency of ammonia removal by membranes including the membrane material's influence on mass transfer of ammonia and the fouling tendency.

2. MATERIALS AND METHODS

Two types of feed have been used: Model manure solution and undigested pig manure. The chemical composition of the model manure solution and the experimental setup are described in [7]. To simulate particulate matter in manure, straw was milled and sieved through analytical sieves with a pore size of 0.125 mm and added to the model solution. Before undigested pig manure was used, it was separated by a decanter centrifuge and then sieved (analytical sieves Retsch 5657- W. Germany DIN 4188, pores size of 0.355 mm and 0.125mm). Further preparation involved addition of 5M NaOH solution to increase pH to 11 in order to ensure that all ammonia and ammonium in the feed is present as ammonia. Two types of membranes were used: polytetrafluoroethylene (PTFE Membrane Filters, Type 118, Sartorius) and polypropylene (PP, Accurel ® PP 2E HF (R/P), Membrane GmbH) both with an average pore size of 0.2 µm and membrane area of 32 cm^2.

The Undigested manure/model manure solution was fed with a flow equal to 1.8 $^{l}/_{min}$ at pH 11 and 40 °C. As the stripping solution for absorbing ammonia, sulfuric acid (0.5M) was used. The sulfuric acid was kept at the same temperature, and circulating with flow rate of 1 $^{l}/_{min}$.

During the first 4 hours of each experiment the ammonia concentration on both sides of the membrane was measured every hour. As the concentration change with time decreased thereafter, the measurements were done less frequent. The ammonia concentration in the manure was determined by Kjeldahl distillation (Kjeltec TM2100, Hoganas, Sweden) and back titration (APHA Standard Method 2005). The concentration of ammonia in the sulfuric acid was analyzed directly using a Hach Dr. Lange spectrophotometer and Dr. Lange kits (LCK 303).

Surface morphology was characterized by Atomic Force Microscopy and optical microscopy while hydrophilicity/hydrophobicity of the membranes was studied by contact angle measurements. Images of water drops on the membrane surface (PP and PTFE clean and fouled) were obtained by an Olympus camera (E-3) and contact angles were determined using MR ruler software (5.1). Membranes were also analyzed with respect to their surface roughness. This parameter was obtained by Atomic Force Microscopy DME (Dual Scope DS 95-50-E). AFM images were done in tapping mode using an AC probe and DME scan tool software

The flux of ammonia is expressed by Eq 1.

$$J = k_m \cdot \left(C_{NH_3,feed} - C_{NH_3,acid}\right) \qquad \text{(eq1)}$$

The ammonia flux is related to the difference between the ammonia concentration in the feed and the stripping acid and to the overall mass transfer coefficient (k_m).

3. RESULTS AND DISCUSSION

As seen on figures 1 the initial ammonia flux is high but decreases exponentially. For the PTFE membrane the ammonia fluxes are higher than for the PP membrane especially during the first few hours of the experiments. This is most likely due to the membrane thickness as the PTFE membrane is 62 µm thick while the PP is 177 µm [5]. The thinner the membrane the faster the transport through the gas filled pores. For both membranes fluxes for undigested pig manure are higher than for the model solution. It might be due to the larger particle size of milled straw compared to the size of suspended solids present in manure as this influence fouling.

Both PP and PTFE membranes are hydrophobic. However, based on the contact angles measurements, after running the process continuously for 30h, the hydrophobicity of the membrane surface decreases. Further the contact angle decreased more when running with undigested pig manure. As the contact angle decrease is a direct result of hydrophilicity of the fouled membrane surface, this difference must be explained by the greater complexity of the undigested pig manure compared to the model solution. As proteins and polysaccharides are the major foulants responsible for hydrophilization of the membrane surface the composition of proteins and polysaccharides is important when mimicking membrane fouling and wetting [6].

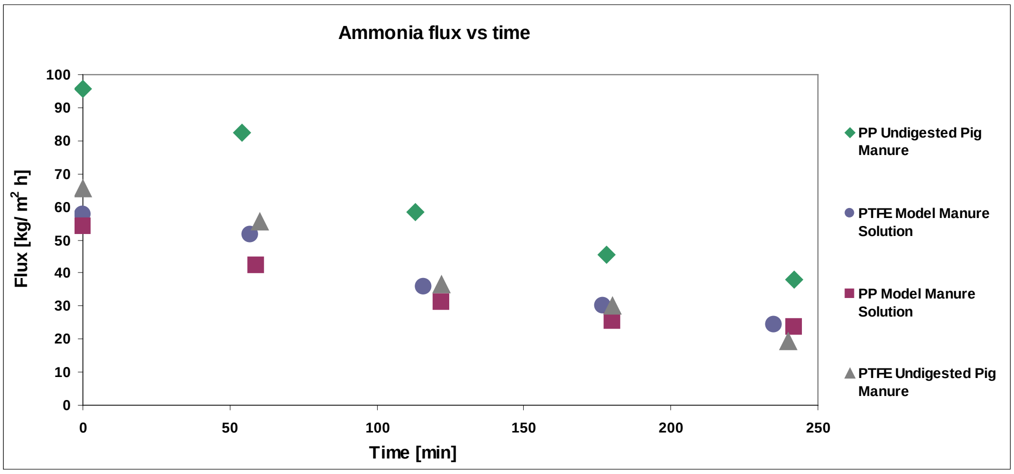

Figure 1. Ammonia flux through membrane

Table 1. Contact angle measurements

PTFE clean	PTFE fouled by synthetic manure	PTFE fouled by undigested pig manure	PP clean	PP fouled by synthetic manure	PP fouled by undigested pig manure
$113^{o} \pm 4$	$90^{o} \pm 3$	$79^{o} \pm 2$	$135^{o} \pm 4$	$90^{o} \pm 6$	$79^{o} \pm 2$

Fouling is highly dependent on the membrane surface roughness [4]. As seen from Fig 2d and 2f PTFE has a higher tendency to fouling compared to the PP membrane (Fig. 2b & 2e). This is due to a combination of the lesser hydrophobicity and higher roughness of the PTFE membrane which has more elongated pores where particulate deposit can easier accumulate (Fig. 2c).

Further, pictures (not shown) obtained by optical microscope suggests inhomogeneous crystal growth on the membrane surface.

These findings are in accordance with Zarebska at el. [8] who reported the presence of inorganic elements incorporated into the organic deposit together with some bacteria on PP tubular membranes used for stripping ammonia from undigested pig slurry. It is highly probable that the observed morphological changes are due to the same reasons, though further analysis is required.

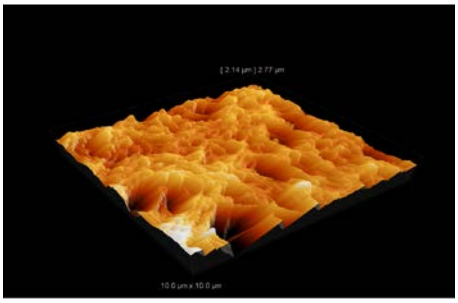

Fig. 2a PP clean

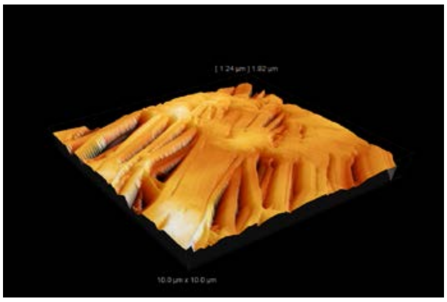

Fig. 2c PTFE clean

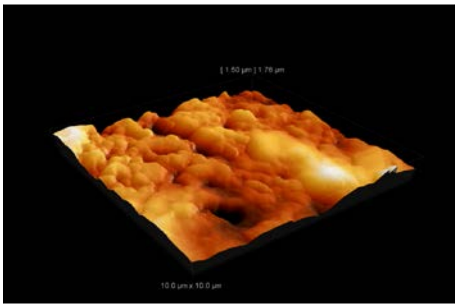

Fig. 2b PP fouled by synthetic manure

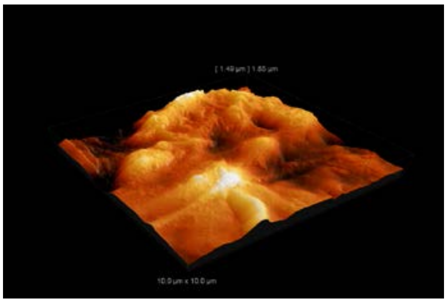

Fig. 2d PTFE fouled by synthetic manure

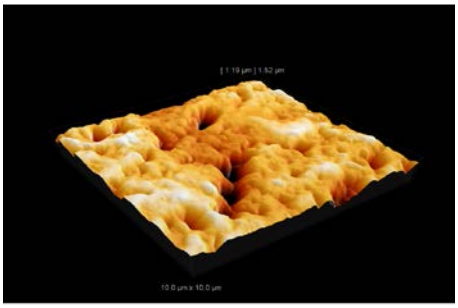

Fig. 2e PP fouled by undigested pig manure

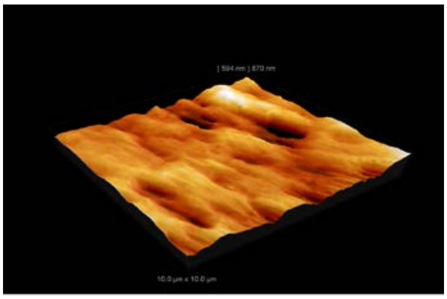

Fig. 2f PTFE fouled by undigested pig manure

3. CONCLUSION

In this study a PTFE and a PP membrane were compared for ammonia removal from a model manure solution and undigested pig manure. The PTFE membrane gave higher initial ammonia fluxes, though the fouling was more severe than for the PP membrane. Further it was found that the initial ammonia fluxes were lower and fouling more severe when running with undigested pig manure. Based on the measured contact angles the hydrophilicity was higher for the fouling layer formed by undigested pig manure though both fouling layers were hydrophilic. Additionally from AFM observations, it was found that the membrane surface becomes smoother when fouled by undigested pig manure. The fouling experiments thus show that not all important foulants have been included in the model manure solution and further work therefore is needed.

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PODSUMOWANIE

Doświadczenie zostało przeprowadzone dla dwóch różnych faz zasilających, mianowicie gnojowicy syntetycznej i naturalnej Porównane również zostały efekty procesu dla innych typów membran, PP oraz PTFE. Wyższy przepływ amoniaku zauważono dla membrany PTFE, czego powodem mogło być jej mniejsze zanieczyszczenie w stosunku do PP. Dalsze badania wykazały, że wyższy przepływ amoniaku występuje dla gnojowicy naturalnej. Przypuszczalnie jest to rezultat budowy cząsteczek zawartych w słomie dodanej do modelowej gnojowicy. Ze zdjęcia uzyskanych mikroskopem AFM wynika, że powierzchnia membran staje się bardziej płaska na skutek działania gnojowicy naturalnej. Za przeprowadzonych eksperymentów można wnioskować, że model syntetycznej gnojowicy powinien zostać dopracowany.