Journal of Membrane Science 484 (2015) 119–132

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fouling mitigation in membrane distillation processes during ammonia stripping from pig manure

Agata Zarebska [a,*], Ángel Cid Amor [a], Klaudia Ciurkot [a], Henrik Karring [a], Ole Thygesen [a], Thomas Prangsgaard Andersen [a], May-Britt Hägg [b], Knud Villy Christensen [a], Birgir Norddahl [a]

[a] Department of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Niels Bohrs Allé 1, DK-5230 Odense M, Denmark

[b] Department of Chemical Engineering, Norwegian University of Science and Technology, Sem Saelandsvei 6, 7491 Trondheim, Norway

ARTICLE INFO

Article history:
Received 23 September 2014
Received in revised form
5 February 2015
Accepted 4 March 2015
Available online 12 March 2015

Keywords:
Membrane distillation
Fouling
Membrane autopsy
Cleaning
Feed pretreatment

ABSTRACT

Over time fouling leads to membrane wetting. This is the biggest obstacle to widespread use of membrane distillation (MD) for ammonia removal from animal slurry. Feed pretreatment and cleaning strategies of membrane surfaces are the most common methods to prevent or diminish fouling phenomena. This study investigates preliminary fouling of polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes. A model manure solution was used as feed. In addition cleaning efficiencies with deionized water, NaOH/citric acid, and Novadan agents were studied. Further microfiltration and ultrafiltration were examined as manure pretreatment to diminish fouling. To this end polyvinylidene fluoride membranes (PVDF 0.2 μm and 150 kDa respectively) were used. Organic fouling was shown to be dominant. For the model manure solution the fouling comprised lipids, carbohydrates and proteins. For pig slurry the fouling additionally contained carboxylates, free fatty acids and lignin. Among the tested cleaning strategies, Novadan agents were the most successful in removing proteins and carbohydrates from the PTFE membrane while it only removed proteins from the PP membrane. Using microfiltration or ultrafiltration as a pretreatment prior to MD doubled the ammonia mass transfer coefficient for the PTFE membrane, while for the PP membrane, the ammonia mass transfer coefficient was increased 4-fold.

1. Introduction

Animal waste management is challenging in areas with a dense livestock population. This is mainly due to the hazard of releasing ammonia to air, water, and soil leading to pollution of ecosystems [1,2].

Membrane distillation (MD) can remove volatile ammonia particularly from wastewater and biogas plant effluents [3–5]. Moreover MD can produce ammonia fertilizer from the liquid fraction of animal slurry by separating ammonia from a feed solution into an acidic strip solution [3,6]. Taking the increasing prices of mineral fertilizers into consideration, production of ammonia fertilizers based on animal waste could also be profitable and at the same time the negative impact of local over fertilization would be reduced [3,7]. However, membrane wetting due to adsorption of organic matter and deposition of inorganic elements on the membrane surface is a major obstacle for the use of MD for ammonia stripping of animal wastes [8]. Furthermore the MD process requires prior removal of suspended solids present in manure in order to reduce the risk of pump damage and clogging the membrane inlet/outlet when using tubular modules in

Abbreviations: AFM, atomic force microscopy; CA, contact angle; E1, unsieved pig manure; E1*, pig manure sieved with 355 μm aperture; E1**, pig manure sieved with 125 μm aperture; FT-IR, Fourier Transform-Infrared; MD, membrane distillation; MF, microfiltration; MS, model manure solution; PP, polypropylene; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; SDS-PAGE, sodium dodecyl sulfate-polyacrylamide gel electrophoresis; SEM, scanning electron microscope; UF, ultrafiltration; A_m, membrane area (m^2); C_0, total ammoniacal nitrogen concentration in MD feed at time zero ($g\,l^{-1}$); CA, contact angle; C_t, total ammoniacal nitrogen concentration in MD feed at time t ($g\,l^{-1}$); K_m, the overall mass transfer coefficient ($m\,s^{-1}$); L_p, effective pore length (m); M_w, molecular weight of gas (g/mol); p_{av}, mean pressure (Pa); P_d, downstream pressure (Pa); P_k, gas permeance under Knudsen flow regime ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$); P_p, gas permeance under Poiseuille flow regime ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$); P_t, total gas permeance (Eq. (A.3): m^3/m^2 h bar, Eq. (A.4): $mol\,m^{-2}\,Pa^{-1}\,s^{-1}$); P_u, upstream pressure (Pa); R, universal gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$); Ra, mean membrane roughness (nm); $r_{p,m}$, mean pore size (m); TAN, total ammoniacal nitrogen ($g\,l^{-1}$); TKN, total Kjeldahl nitrogen ($g\,l^{-1}$); V, volume of the feed (m^3); μ, viscosity of gas (Pa s); ψ, surface porosity

* Corresponding author.
E-mail address: agata.agnieszka.zarebska@gmail.com (A. Zarebska).

http://dx.doi.org/10.1016/j.memsci.2015.03.010
0376-7388/

inside-out configuration. This also diminishes the suspended solids inhibitory effect on ammonia mass transfer through the membrane [6,9].

Fouling is a function of physical and chemical properties of feed (pH, ionic strength, concentration, temperature), foulants characteristics, hydrodynamic conditions, and membrane properties (pore size and shape, surface charge, hydrophobicity, roughness) [10]. Among these factors, the most important are foulants characteristics and membrane properties, since when kept within practical limits the feed velocity has a negligible effect on the overall ammonia mass transfer [5].

Among the many compounds present in slurry such as carbohydrates, humic substances, inorganics, and lipids, the most recalcitrant foulants for membrane distillation performance are proteins, which cause the loss of membrane hydrophobicity [8].

Protein–membrane interactions are influenced by feed solution pH and ionic strength resulting in adsorption or aggregation of proteins and further plugging of membrane pores or formation of a cake layer on the membrane surface. For instance the presence of divalent cations such as calcium might lead to complex formation between calcium and some organic compounds and thus exacerbation of a fouling layer on the membrane surface [11,12]. Additionally interactions between amphoteric charged proteins and negatively charged membranes are pronounced due to amino acid rearrangements [13,14].

Opposed to pressure-driven membrane processes, the membrane in MD acts as a physical support for the vapor–liquid interface at each pore entrance. The membrane keeps the two phases "in contact" without dispersing one phase into the other. This allows only volatile components to diffuse across the membrane [15,16]. To avoid liquid penetration membrane materials to be used in MD have to meet specific requirements such as high hydrophobicity, small pore size with a narrow pore size distribution, high porosity, good thermal stability and chemical resistance to feed streams [17]. These properties depend on raw materials and preparation methods [5,18].

A number of polymers such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) fulfill the necessary requirement of hydrophobicity. The MD membranes produced from these materials though are originally fabricated for microfiltration [19]. Their hydrophobic surfaces are more prone to fouling than hydrophilic surfaces. This might be due to their lower surface energy which influences membrane particle adsorption and causes fouling as reported by Alhadidi et al. and Tu et al. [20,21]. Moreover morphological structures on membranes like large pores and rough surfaces will intensify fouling [20].

The main technique to mitigate fouling phenomena are feed pretreatment and membrane cleaning [22]. Feed pretreatment might be a combination of other membrane processes for instance microfiltration (MF) or ultrafiltration (UF). This results in removal of suspended particles while small colloidal matter is not removed [23]. However advanced pretreatment with UF will significantly increase the cost of running a MD process, with operating costs being similar to air stripping [24].

Cleaning methods are dependent upon the character of the fouling layer and restricted by the chemical resistance of the membrane material. Since fouling is dominated by organic fouling together with deposited inorganic elements [8], dissociation of proteins and release of salts in the organic matrix of the fouling layer is highly desired. The disintegration of the fouling layer can be achieved by using alkaline or acidic solutions, metal chelating agents, surfactants and enzymatic solutions [13]. However due to the risk of surface hydrophilization only base and acid cleaners can be used for effective removal of organic foulants and inorganic salts [25].

To date, investigations of different feed pretreatments and their effects on foulants' characteristics are scarce. Gryta et al. [26] suggested boiling of waste water for 30 min followed by filtration prior to the MD process in order to remove proteins from the feed. However, that method cannot be used for slurry before ammonia stripping due to the loss of ammonia upon boiling. du Preez et al. [3] and Waeger-Baumann and Fuchs [6] have ultrafiltered anaerobically digested effluents separated by decanter centrifuge or screw press and used those fractions as feed to MD. However, they did not investigate fouling in the reported studies [3,6]. In a study [8] undigested pig manure separated by screw press and drained by sieving with aperture 125 μm was continuously introduced to MD for one week until membrane wetting occurred. This was most likely due to proteins adsorption as revealed by a fouling autopsy. To our knowledge, all previously reported studies dealing with animal wastes have used tubular/capillary polypropylene (PP) membranes. Furthermore no attempts of evaluating chemical cleaning efficiencies on MD processes have been reported. In addition very few comparative studies using PTFE and PP membranes in MD processes are available.

In this study the effects of different feed pretreatments and cleaning procedures on fouling were investigated during ammonia stripping from the liquid fraction of pig manure using flat sheet membranes made of PP and PTFE. Since fouling is a complex phenomenon and manure is a complex biological mixture composed of feces and urine, primarily a standard model manure solution that mimics undigested manure was used to gain knowledge about major foulants and cleaning efficiencies. In this way experiments were not influenced by daily fluctuations in manure composition due to e.g. microbial activity. However, the experiments were also performed using the liquid fraction from real pig manure. The pig manure was separated by a decanter centrifuge into a slurry rich in solids and a liquid fraction low in solids. This liquid fraction was then sieved and micro- or ultrafiltrated to study the effects of the different pretreatments on the protein properties and subsequent fouling propensity on MD. By characterizing both the proteins present in the liquid fraction of manure and membrane properties, insight into the fouling mechanism and material contribution may be obtained.

2. Materials and methods

2.1. Feed solutions

2.1.1. Model manure solution

All chemicals used for preparing the model manure solution were analytical grade reagents, except commercial lard (Dragsbaek, Denmark) and straw. The chemical composition of the model manure solution was selected based on thorough studies of literature related to pig manure [27,28] and is presented in Table 1. Lard was chosen as lipid source since it is dominated by the same fatty acids present in pig manure [29,30]. Straw (winter wheat), which represents organic particles present in manure and at the same time is a source of carbohydrates was milled (Retsch Ultracentifugal mill type ZM1) and sieved through an aperture size 125 μm (Retsch 5657-W. Germany DIN 4188). To mimic the protein in manure the model manure solution was supplemented with gelatin. Benzoic acid was added to prevent microbial growth, while sodium sulfide was included to remove oxygen to resemble the anaerobic environment in the manure.

2.1.2. Manure

Raw swine manure was collected from a controlled pig house at the Danish Pig Research Centre located in Grønhøj, Denmark and separated by decanter centrifugation (GEA UCD 305-00-02 Westfalia). To avoid larger particles blocking the membrane module inlet/outlet liquid effluent was further sieved through analytical