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Performance of a polypropylene membrane contactor for the recovery of dissolved methane from anaerobic effluents: Mass transfer evaluation, long-term operation and cleaning strategies

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ABSTRACT

A polypropylene membrane contactor was used for the recovery of dissolved methane from an anaerobic reactor effluent. Effect of operational parameters, operation mode and fouling on long-term operation was studied using vacuum pressure or N_2 as sweep gas. Results were analyzed based on the mass transfer estimations. Lower performance was observed in the shell-side mode due to the lower liquid velocity and the probable channeling. Membrane pore wetting was observed with the increase in Q_L in the vacuum-pressure mode. This was confirmed with mass transfer resistance analysis, resulting in an estimated wetted pore fraction of between 0.25 and 0.53. The highest removal efficiencies were obtained with the liquid flowing in the lumen side and sweep-gas operation (between 98% and 67% for Q_L between 4.1 and 27.2 $L\,h^{-1}$), with negligible effect of the N_2 flow rate. In the long-term operation, the impact of membrane fouling was less intense in the lumen side, with longer operation time and more reversible fouling. A complete characterization of the fouling based on water sample analysis concluded that both inorganic and organic foulants were present, probably with higher biofouling presence. A combination of water and chemical cleanings resulted in a recommended protocol based on daily water cleaning.

1. Introduction

Anaerobic reactors for the wastewater treatments generate a methane-rich biogas, which can be used in combustion for the production of heat and/or electricity. Even though the low solubility of methane in water, residual dissolved methane (D-CH_4) is often present in the final water effluent, especially in anaerobic treatments at sub-*meso*philic and psychrophilic temperatures ($< 25\,^{\circ}C$) due to the increase in gas solubility at low temperatures [1]. Increase in greenhouse gas diffuse emissions, loss of energy source and generation of potential explosive atmospheres when discharged into closed vessels or sewers are the main problems when managing these effluents. Thus, its recovery/removal is necessary for economic, environmental and security reasons. The treatment technologies for gas desorption from anaerobic waters include spray aeration, packed towers, tray aerators, diffuse aeration, and membrane contactors [2]. The use of membrane contactors is a commercially available mature technology for applications such as O_2 or CO_2 removal, among others [3]. However, its application for the removal D-CH_4 from anaerobic effluents is still at research/pilot level. From the first promising results [4–8], the number of published papers has grown in recent years [9–14], demonstrating the interest of scientific community in this technology. However, some practical implications, such as the long-term stability of membrane contactors and the optimum driving force (vacuum/sweep gas) are still scarcely studied, and further research is needed.

Membrane contactors offer many advantages over conventional technologies [2]; however, the presence of the membrane introduces an additional mass transfer resistance. Depending on membrane material, the nature of the liquid phase and transmembrane pressure, the membrane pores may be occupied by liquid, corresponding to the so-called wetted operation, which strongly decreases the permeate flux. Measures to prevent the wetting problem may include the increase in the hydrophobicity of the membrane by increasing the contact angle between the liquid and the membrane [14]. The surface tension of the liquid phase also plays an important role. The presence of organic compounds may decrease the surface tension of solutions, which decreases the breakthrough pressure, leading to a rapid increase in membrane wetting. The wetting phenomenon is an effect widely studied in the CO_2 absorption using organic absorbents [15,16], and water-based absorbents [17–19]. In the application of membrane

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contactors for degassing water solutions, the wetting phenomenon is also reported to be associated with the increase in liquid flow rate [10,20].

The driving force for D-CH_4 removal can be obtained by applying vacuum or using a sweep gas on the gas side. For the recovery and reuse of the downstream gas phase, methane concentration in the recovered gas for commercial microturbines should be higher than 35% [21]. To achieve such a concentration, sweep-gas mode at low gas-to-liquid flow-rate ratio (G/L) was proposed [11]; however, this induced an increase in gas phase mass transfer resistance, and so a reduction in the D-CH_4 recovery efficiency. Vacuum operation overcomes this problem and some authors recommend it [12,22]. However, vacuum operation is less energetically favorable than use of sweep gas, and higher pressure difference between gas and liquid phase could induce pore wetting [10].

Loss of performance due to membrane fouling is one of the main problems encountered when coupling biological reactors and membrane technologies. In this regard, natural organic matter related to microbial and extracellular polymer substances has been described as the major type of foulant in biological wastewater treatment units [23]. Fortunately, membrane contactors are less sensitive to fouling, since there is no convective flow through the membrane pores causing concentration polarization, as in the pressure-driven membrane process of membrane bioreactors. Clogging due to suspended particles coming from the regular discharge of surplus biomass particles may be a major concern in membrane contactors, and prefiltration is necessary. Suspended solid concentration in anaerobic effluents usually are in the range 100–300 mg L^{-1}. The particle size analysis of the effluent of a laboratory-scale anaerobic reactor operated under similar conditions than the one of this study revealed that 60–85% of solids were higher than 300 µm, so susceptible of generate rapid clogging of the hollow fiber membrane contactors, especially when liquid flows inside the fibers [24]. Also, protein adsorption (organic fouling) and salt precipitation (inorganic fouling) onto the membrane surface can be involved as causes of fouling [25,26]. For the industrial application of the technology, operational and cleaning strategies optimization are of crucial interest for the prevention of the use of cleaning chemicals to ensure an economically feasible operation with a long stable life of the system.

Few studies can be found in the literature that evaluate the long-term operation of membrane contactors for methane degassing. Bandara et al. [5,6] indicated that membrane fouling of the contactor was insignificant for their long-term experiments with a lab-scale UASB reactor (> 30days). Sethunga et al. [14] operated a modified PVDF hollow fiber membrane contactor with synthetic water containing dissolved biogas for 10 days to investigate the resistance to pore wetting, and concluded that the fluctuation of the methane flux was less than 10%. In our previous work [12] with a PDMS membrane contactor, long-term experiments in lumen-side and shell-side mode treating an anaerobic effluent included both intermediate water and chemical cleaning and the characterization of organic and inorganic foulants. Results highlighted the importance of implementing a prevention strategy of membrane fouling, based preferably on the use of water cleaning. The polypropylene membrane contactor of this study showed higher removal efficiency than the PDMS in short-term experiments when pore wetting phenomenon was not observed [10]. For the industrial application of the technology, it is crucial not only the short-term efficiency but also the performance in long-term and continuous operation, so the present work extend and complement our previous studies and allow comparison of response of membrane materials from the fouling perspective.

In this context, the aim of this work is to assess the performance of a polypropylene membrane contactor for the removal of dissolved methane from the effluent of a laboratory-scale expanded granular sludge-bed anaerobic reactor. Influence of the operational parameters (liquid flow rate, vacuum pressure and sweep gas flow rate) on the methane removal efficiency was studied in short-term experiments. An analysis of the results based on mass transfer evaluation is also presented. In the present work, our previous study [10] is broadened, with a greater range of operation conditions, including an estimation of the mass transfer resistances with literature correlations. As a special novelty, to study the impact of the fouling on removal efficiency, long-term experiments in the lumen side and shell side were performed. Research efforts were aimed at characterizing the fouling and optimizing the cleaning strategies, focusing on the application of the technology.

2. Materials and methods

2.1. Experimental set-up and operation

The anaerobic effluent used in the degassing experiments came from a laboratory-scale expanded granular sludge-bed (EGSB) anaerobic reactor operated at 25 °C. Granular anaerobic sludge (4 L) from the wastewater treatment plant of a local brewery (Font Salem, El Puig) was used for inoculation. The reactor treated 8 L d^{-1} of synthetic wastewater polluted with ethanol with an organic load rate of 30 kg chemical oxygen demand (COD) m^{-3} d^{-1}. The sludge bed was kept expanded with a recirculation up-flow velocity of 10.7 m h^{-1}. A liquid–gas separator device was placed at the top of the reactor. The gas outlet was connected to a gas wash bottle containing sodium hydroxide solution to remove carbon dioxide and hydrogen sulfide from the biogas. Biogas composition of the headspace of the bioreactor was measured from samples taken prior to the gas wash bottle. The methane flow rate was monitored periodically with a gas flowmeter (MGC-10 PMMA, Ritter, Germany) and the pH and conductivity with a multiparameter sensor (pH/Cond 340i WTW, Germany). Alkalinity, volatile fatty acids (VFA), COD, and nutrient concentration in the inlet and outlet of the reactor were analyzed according to standard methods [27]. A detailed description of the system and procedure can be found elsewhere [28,29].

A commercial hollow-fiber membrane contactor with polypropylene (PP) fibers was used for D-CH_4 removal (1 × 5.5 MiniModule, Liqui-Cel, Membrana GmbH, Germany), connected to the recirculation stream of the bioreactor, with similar composition to the final effluent. The main characteristics of the membrane contactor are presented in Table 1. The anaerobic stream was pumped through the contactor using a peristaltic pump (Watson-Marlow, USA). A 40 µm prefilter was placed prior to the contactor, in order to prevent the membrane contactor clogging with particulate matter from the bioreactor. Liquid pressures at the inlet and outlet of the membrane contactor were measured using a portable manometer MP112 (Kimo, Spain). A complete scheme of the EGSB reactor and the membrane contactor is presented in Fig. 1.

Table 1
Polypropylene membrane contactor specifications and operational conditions.

Module inner diameter, m	0.025
Module length, m	0.176
Number of fibers	2300
Effective fiber length, L, m	0.1397
Inner diameter, µm	220
Outer diameter, µm	300
Fiber wall thickness, l, µm	40
Inner area, A_i, m^2	0.180
Outer area, A_o, m^2	0.303
Pore radius, r_p, µm	0.02
Shell inner diameter, m	0.025
Packing fraction, ϕ	0.33
Porosity, ε	0.4
Tortuosity, τ	1.4
Lumen side volume, m^3	16×10^{-6}
Shell side volume, m^3	25×10^{-6}
Max. liquid flow-rate, Q_L, L h^{-1}	30
Typical sweep gas flow-rate, Q_{N2}, L h^{-1}	26.0–800