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Demethanization of aqueous anaerobic effluents using a polydimethylsiloxane membrane module: Mass transfer, fouling and energy analysis

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A B S T R A C T

The performance, fouling and feasibility of a polydimethylsiloxane hollow fibre membrane module for in situ methane degasification from the effluent of an Expanded Granular Sludge Bed anaerobic reactor has been investigated. Experiments at different operational conditions were carried out (liquid flow, sweep gas flow and vacuum pressure) with maximum removal efficiency (77%) at lowest flow-rate ($0.4\ L\ h^{-1}$), highest vacuum gauge pressure (−800 mbar) and liquid flowing in lumen side. Mass transport analysis denoted a considerably higher methane transfer than that predicted (attributed to liquid oversaturation). An enhancement factor for liquid phase has been proposed to correlate the experimental results. Long-term experiments were also performed in order to determine the possible influence of fouling on the module performance, and it showed that relatively frequent cleaning with water might be carried out to ensure preservation of the membrane efficiency. Characterization of water quality before and after membrane module was carried out to elucidate fouling causes. Energy balance analysis evidenced that energy production exceeded the system energy requirements. A substantial reduction of CO_2 equivalent emissions showed the positive environmental impact of this technology.

1. Introduction

The minimization of the loss of residual methane from aqueous effluents of anaerobically treated wastewater systems has recently attracted growing interest, with an increasing number of studies about it in the last years [1–4]. This interest is based on the fact that the recovery of this residual dissolved methane (or at least its removal) in these effluents presents several potential benefits of a diverse nature: environmental (avoiding the emission of a powerful greenhouse gas), economic (recovering a power source) and safety (reducing the possibility of creating an explosive atmosphere) [1,5,6]. In addition, it has been frequently described [4–8] that dissolved methane can be found in these effluents in concentrations above the saturation level, which would suggest that the impact of the discharge of this residual methane may be even higher than expected, especially taking into account that more sustainable anaerobic processes should be carried out at relatively low-temperature [8], ambient or psychrophilic conditions (<20 °C), which favours the solubility of methane in water.

The removal of dissolved gases from liquids is conventionally achieved with some type of vacuum or forced draft packed towers [9,10]. These towers are filled with packing that creates a large surface area for the contact of liquid and gas phases. Nevertheless, in these systems, the direct contact of liquid and gas phases can frequently lead to problems such as foaming, flooding, and emulsions [9,11]. Moreover, these systems have large footprints, height requirements, require a second pump for repressurization and usually demand greater attention during times of system start-up and flow adjustment [12,13]. The development and implementation of a technology to economically recover dissolved methane from process effluents could improve the viability and sustainability of anaerobic wastewater treatment [1,4]. In this sense, the membrane hollow fibre contactor has emerged recently as a promising technology that seems able to demethanize aqueous streams, with benefits with respect to conventional separation technologies. Among such benefits are higher volumetric mass transfer coefficients that lead to compact and smaller systems [14] and avoiding the direct contact of liquid and gas phases. So, Bandara et al. [15–17] demonstrated that degasification using a multi-layered composite hollow fibre degassing module (with porous and non-porous materials) is a promising technology for improving methane recovery from the effluent of a bench-scale Upflow Anaerobic Sludge Blanket (UASB)

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process for treating low-strength wastewater at low temperature. In a preliminary work, Cookney et al. [6] showed the potential for recovering dissolved methane from low-temperature UASB treating domestic wastewater using a polydimethylsiloxane (PDMS) membrane contactor. This work was continued later by including a polypropylene microporous membrane contactor, and both synthetic and real anaerobic effluents form the UASB and membrane bioreactor [10]. The authors also showed that this application could both be economically practicable and avoid net CO_2 emissions. Luo et al. [18] demonstrated that a degassing membrane coupled UASB reactor was able to achieve in situ biogas upgrading and decrease the dissolved CH_4 concentration in the anaerobic effluent. Unfortunately, studies on the removal of residual dissolved methane from anaerobic effluents are still very scarce, and further research in this field is needed to improve and deepen the knowledge and performance of this technology, especially in that related to membrane fouling and long-term experiments.

In this context, research for in situ removal/recovery of methane from the effluent of an Expanded Granular Sludge Bed (EGSB) anaerobic reactor is being carried out in our research group. A comparative study of two different degassing membrane contactors [19], microporous (polypropylene) and non-porous (PDMS), showed that the performance of both contactors was not very unequal, but wetting phenomena were observed for the microporous module, which is one of the major potential bottlenecks of this type of microporous material. In this sense, dense (or non-porous) membrane materials can offer a solution to prevent wetting and may simultaneously offer acceptable mass transfer performances [20].

In the first part of the present work we have extended our previous study [19] with different operating conditions on the performance of the PDMS module for methane degassing. An analysis of the experimental results based on a resistance to mass transfer study is presented. In addition, and as especial novelty, the incidence of membrane fouling in long-term experiments has been determined. To the best of our knowledge, this is the first attempt in the literature to study the membrane fouling in long term experiments in methane degassing of anaerobic effluents. Finally, a feasibility study considering energy recovery and demand has been carried out for a given application of a degassing process using a contactor of nonporous membrane of PDMS.

Table 1
Geometric and operational characteristics of the non-porous polydimethylsiloxane (PDMS) contactor module.

Geometric characteristics	
Module inner diameter, m	0.016
Module length, m	0.14
Number of fibres	320
Effective fibre length, m	0.083
Inner diameter, μm	190
Outer diameter, μm	300
Fibre wall thickness, μm	55
Inner area (A_i), m^2	0.0159
Outer area (A_o), m^2	0.0250
Shell tube inner diameter, m	0.016
Packing fraction	0.113
Lumen side volume, m^3	$7.53 \cdot 10^{-7}$
Shell side volume, m^3	$1.48 \cdot 10^{-5}$
Operational characteristics	
Max. liquid flow rate $L\,h^{-1}$	12
Typical sweep gas flow rate, $L\,h^{-1}$	2.7–27.0
Max. shell to lumen TMP[a], mbar	1050
Max. lumen to shell TMP[a], mbar	3100

[a] TMP: Transmembrane pressure.

2. Materials and methods

2.1. Experimental set-up

A commercial hollow fibre membrane contactor module (PDMSXA-250, supplied by PermSelect®, MedArray Inc., USA) was selected as usual in water degassing industrial applications. The main properties of the degassing module (DM) are summarized in Table 1.

A laboratory scale EGSB anaerobic reactor was operated at 25 °C for almost 3 years. The EGSB reactor was initially inoculated with 4 L of granular anaerobic sludge from the wastewater treatment plant of a local brewery. The bioreactor treated 8 L $d^{-1}$of a synthetic wastewater polluted with ethanol with an organic load rate of 32 kg chemical oxygen demand (COD) $m^{-3}\,d^{-1}$, being a relatively high strength wastewater comparing with most of conventional anaerobic treatments [4]. A high recirculation flow was maintained to expand the sludge bed with an up-flow velocity of 10.7 m h^{-1}. A liquid–gas separator device was placed at the top of the reactor, and the biogas was collected through a sodium hydroxide solution. The methane flow rate and biogas composition were monitored with a flow meter (MGC-10 PMMA, Ritter, Germany) and a biogas analyser (Combimass GA-m, Binder, Germany), respectively. Water characteristics based on pH, conductivity, alkalinity, volatile fatty acids, COD, solids and nutrients concentrations were periodically checked. A detailed description of the biological system and procedure can be found elsewhere [21].

A diagram of the EGSB reactor and the DM contactor is shown in Fig. 1. The membrane module was coupled to the EGSB reactor and fed with a fraction of flow from the recirculation stream, in which the concentration of the dissolved methane (D-CH_4) was similar to that in the effluent stream. The stream was flowed through the contactor, using a peristaltic pump (Watson-Marlow, USA), resulting in flow rates from 0.4 to 10.8 L h^{-1}. A stainless-steel filter of 40 μm was set-up prior to membrane module to avoid DM contactor clogging by the solid particulates from the anaerobic reactor. This filter was periodically cleaned and no biofilm development was observed on it. The liquid pressure drop at the inlet and outlet of the membrane was measured using a portable manometer MP 112 (Kimo, Spain). For vacuum pressure experiments, a vacuum pump N026.3.AT.18 (KNF Neuberger, Germany) was used for vacuum operation, getting vacuum gauge pressures (P_{vac}) of −140, −500 and −800 mbar. For countercurrent sweep gas experiments, nitrogen gas with a high purity (>99.8%) supplied by Carburos Metálicos S.A. (Spain) was introduced into the contactor with flow rates ranging between 2.7 and 27.0 L h^{-1} (STP) using a mass flow controller (Bronkhorst Hi-Tec, The Netherlands).

The DM contactor was operated both in lumen side mode (LS), where experiments were carried out with the liquid flowing in the lumen side and vacuum pressure or sweep gas applied in the shell side, and in shell side mode (SS) where the fluids were swapped.

The selection between vacuum or sweep gas mode operations depends basically on the aim of the process. Vacuum operation is the most feasible solution when the recovery of degassing components is desired, since sweep gas operation would involve subsequent costly separation/purification operations. If the process is carried out only for liquid degassing, sweep gas mode can be selected since it usually needs low energy consumption [22]. A combination mode (modest sweep with moderate vacuum) could be used to enhance the degassing performance by increasing the gas transfer driving force [23], but this intermediate situation induces an increase in energetic costs [22].

Cleaning of the DM module with deionised water at countercurrent flow during 30 min was done every day after experiments. A control experiment was repeated every month to ensure that the