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Dissolved methane recovery from anaerobic effluents using hollow fibre membrane contactors

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ABSTRACT

Hollow fibre membrane contactor (HFMC) systems have been studied for the desorption of dissolved methane from both analogue and real anaerobic effluents to ascertain process boundary conditions for separation. When using analogue effluents to establish baseline conditions, up to 98.9% methane removal was demonstrated. Elevated organic concentrations have been previously shown to promote micropore wetting. Consequently, for anaerobic effluent from an upflow anaerobic sludge blanket reactor, which was characterised by a high organic concentration, a nonporous HFMC was selected. Interestingly, mass transfer data from real effluent exceeded that produced with the analogue effluent and was ostensibly due to methane supersaturation of the anaerobic effluent which increased the concentration gradient yielding enhanced mass transfer. However, at high liquid velocities a palpable decline in removal efficiency was noted for the nonporous HFMC which was ascribed to the low permeability of the nonporous polymer provoking membrane controlled mass transfer. For anaerobic effluent from an anaerobic membrane bioreactor (MBR), a microporous HFMC was used as the permeate comprised only a low organic solute concentration. Mass transfer data compared similarly to that of an analogue which suggests that the low organic concentration in anaerobic MBR permeate does not promote pore wetting in microporous HFMC. Importantly, scale-up modelling of the mass transfer data evidenced that whilst dissolved methane is in dilute form, the revenue generated from the recovered methane is sufficient to offset operational and investment costs of a single stage recovery process, however, the economic return is diminished if discharge is to a closed conduit as this requires a multi-stage array to achieve the required dissolved methane consent of 0.14 mg l^{-1}.

1. Introduction

In engineered anaerobic environments such as landfills or anaerobic wastewater treatment processes, the process effluent produced is generally at equilibrium with the gas phase, a significant fraction of which is methane (CH_4, 50% to 80% v/v in gas phase) [1]. Consequently, anaerobic effluents commonly comprise between 10 and 25 mg l^{-1} of dissolved methane dependent upon the partial pressure of methane in the process atmosphere [2,3]. Several authors have also reported on anaerobic effluents that are 'supersaturated' with dissolved methane, which demonstrates that dissolved methane concentrations can be higher than those predicted based on Henry's law, ostensibly due to the formation of microbubbles [4,5]. Hartley and Lant [5] recorded an average supersaturation index of 1.6 (C_e/C^*, measured concentration in water/expected equilibrium concentration) from an ambient temperature high rate anaerobic migrating bed reactor treating crude domestic wastewater. The authors latterly estimated supersaturation indices of between 1.9 and 6.9 for previously published studies. Cookney et al. [3] also recorded an effluent supersaturation index of 1.6 when operating an upflow anaerobic sludge blanket reactor (UASB) for domestic wastewater treatment and importantly noted that dissolved methane accounted for over 50% of the methane produced, which constrains the opportunity for energy generation from full flow anaerobic treatment and will inevitably broaden carbon footprint [6].

Dissolved methane must be removed from anaerobic effluents that are to be discharged to sewer or other enclosed conduits to avoid generating potentially explosive atmospheres. The lower explosive limit (LEL) for methane in the gas phase is 5% v/v which at equilibrium corresponds to a dissolved methane concentration of 1.4 mg l^{-1} at 15 °C and 101.325 kPa [7]. Consequently, a factor of safety of ten has been applied in industry to ensure that explosive conditions are avoided, leading to a dissolved methane discharge consent of 0.14 mgCH_4 l^{-1} often being enforced [2]. Multi-stage

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bubble column cross-flow cascades or forced draft aerators are generally used to provide contact between the methane saturated liquid phase and a dilute gas phase (air or nitrogen) which introduces a concentration gradient at the gas–liquid interface to create the driving force for stripping. Both processes yield a compliant effluent, however, considerable process scale is demanded to enable sufficient contact time [8]. Furthermore, significant air flows are required which produce a dilute gas phase below the LEL for methane (around 0.03%CH_4 v/v in the stripped gas) [2,8].

Micro-porous hollow-fibre membrane contactors enable the same desorption mechanism to conventional bubble columns through mediating contact between the gas and liquid phases. However, the hydrophobic micro-porous membrane supports non-dispersive contact between the liquid and gas phases where the dissolved gas is free to diffuse through the gas filled pores [9]. Furthermore, the hollow-fibre geometry yields higher packing densities leading to large specific surface areas which enable reduced process scale and lower gas-to-liquid ratios to be employed. For example, O'Haver et al. [10] demonstrated superior removal efficiencies with a HFMC compared to an aerated bubble column for desorption of volatile organic compounds (VOCs) from a contaminated surface stream requiring a unit volume only 7.5% of the column [10]. Hydrophobic micro-porous HFMC have also seen wide commercial deployment for oxygen (O_2) desorption from high quality industrial process waters [11]. However, their application to wastewater is more limited since wastewater comprised of concentrated organic solutes have been shown to induce membrane wetting of the micro-pores, a process whereby water penetrates the gas filled pore (either partially or fully) impeding gas transport [12,13].

To obviate the wetting phenomenon, nonporous membranes have instead been used as the boundary between the liquid and gas phase [9]. Both Bandara et al. [14] and Cookney et al. [3] have employed nonporous membranes (composite with polyethylene as the nonporous substrate [14]; symmetric polydimethylsiloxane, PDMS [3]) for dissolved methane recovery from the anaerobic effluent of UASB reactors which are noted to comprise both particulate and soluble organics. In their study, Bandara et al. [14] were able to successfully demonstrate that the methane recovered was of a viable concentration for reuse in energy generation. However, the authors did not seek to optimise the hydrodynamic environment and as such residence times within the membrane vessel were between 2.8 and 9.2 h which are practically unsustainable at full scale. Cookney et al. [3] undertook preliminary investigation of the hydrodynamic environment and determined that maximum dissolved methane removal efficiency (72%) was achieved at the lowest liquid velocity trialled but the authors did not explicitly investigate rate limiting phenomena thus the boundary conditions for methane recovery were not clearly identified. Both nonporous HFMC studies applied wastewater to the shell-side of the membrane to avoid the risk of clogging the fibre lumen with particulate matter. It is encouraging that the adoption of wide bore fibres by Cookney et al. [3] generated sufficient interstitial spacing (packing fraction of 0.43) to avoid the onset of fouling or clogging of the surrounding channel.

However, in nonporous membranes, it has been established that the membrane wall can present a significant resistance to mass transfer as the gases have to diffuse through the dynamic free volume network of the polymer [9]. Thus whilst both nonporous HFMC studies importantly identified the potential for dissolved methane recovery from UASB effluents, micro-porous hollow-fibre membranes would be preferentially selected for dissolved methane removal where anaerobic effluents are sufficiently low in organic solutes to limit wetting phenomena as this will enhance mass transfer and limit process scale. Several authors have now proposed the use of anaerobic membrane bioreactors (AnMBR) as an alternative reactor configuration to UASB reactors since the micro or ultrafiltration membrane that is integrated into the process can produce permeate that is free of particulate matter (suspended solids) and is low in organic solutes [15]. As a consequence of the low organic solute concentration, microporous HFMC could be considered appropriate for application to AnMBR permeate for dissolved methane recovery. Furthermore, the anaerobic permeate can be applied to the lumen-side of the microporous membrane due to the absence of particles, which has been noted to provide preferential mass transport in microporous HFMC at pilot scale [19].

From a review of the literature, very different attributes (membrane material and fibre packing density) are required when applying hollow fibre membrane contactor technology to the two principle anaerobic reactor configurations (AnMBR or UASB) considered for anaerobic wastewater treatment. Specifically, for effluent comprised of high organics and high solids concentration (typical of UASB reactors), hollow-fibres comprised of nonporous material are advantageous as they limit wetting phenomena; loose fibre packing is also advantageous as this limits clogging of the interstitial fibre spacing [3]. In contrast, the high permeate quality produced from an AnMBR (no solids, low organics) suggests HFMC comprised of microporous material and higher packing density can be used, which would advantage mass transfer, as the risks of wetting and clogging are obviated. The aim of this study is therefore not to provide a direct comparison of porous and nonporous HFMC for dissolved methane recovery but is instead to examine application of HFMC technology to the recovery of dissolved methane from the two principle anaerobic reactor configurations considered for full scale wastewater treatment. Specific objectives are to: (i) to establish baseline mass transfer data for two selected HFMC designs within a controlled environment using an analogue effluent; (ii) examine dissolved methane recovery from UASB reactor effluent using nonporous HFMC, with liquid flow on the shell-side, to avoid the risk of wetting and lumen blockage by particulate and soluble organics; (iii) examine dissolved methane recovery from AnMBR reactor permeate using microporous HFMC, with liquid flow on the lumen-side to maximise mass transfer in anaerobic permeate comprised of no particulates and only a low organic solute concentration; and (iv) use baseline mass transfer data generated from analogue effluents to benchmark and diagnose HFMC performance on real effluent.

2. Materials and methods

2.1. Experimental set-up

The PDMS HF membrane contactor comprised 13 dense polydimethylsiloxane fibres with a 250 μm wall and 3.2 mm lumen diameter (Sterilin Limited, Newport, UK) (Table 1). The fibre ends were pre-treated with sealant to enhance adhesion (Dow Corning, Seneffe, Belgium) and potted into a PVC shell (23 mm internal diameter) using a mixture of epoxy resin/polyolefin primer (FredAldous, Manchester, UK; Loctite, Henkel, Germany). The PDMS membrane yielded a 0.62 m fibre length with total contact area 0.094 m^2 and packing fraction (ø) 0.34. The packing fraction and fibre outer diameter were specified similar to a previous HFMC study which evidenced limited fouling/clogging in HFMC applied to real wastewater comprising particulate matter [3]. The PDMS membrane was operated counter-currently with water flowing parallel to the fibres on the shell-side to avoid the risk of lumen clogging. Nitrogen enriched air was produced from compressed air (8 barg) using a nitrogen selective HF membrane (5-M, N_2 Gen. Ltd., London, UK) and introduced into the HF lumen. Nitrogen gas