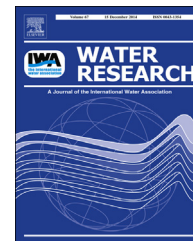




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Biogas upgrading by chemical absorption using ammonia rich absorbents derived from wastewater

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ABSTRACT

The use of ammonia (NH₃) rich wastewaters as an ecological chemical absorption solvent for the selective extraction of carbon dioxide (CO₂) during biogas upgrading to 'biomethane' has been studied. Aqueous ammonia absorbents of up to 10,000 gNH₃ m⁻³ demonstrated CO₂ absorption rates higher than recorded in the literature for packed columns using 20,000–80,000 g NH₃ m⁻³ which can be ascribed to the process intensification provided by the hollow fibre membrane contactor used in this study to support absorption. Centrifuge return liquors (2325 g m⁻³ ionised ammonium, NH₄⁺) and a regenerant (477 gNH₄⁺ m⁻³) produced from a cationic ion exchanger used to harvest NH₄⁺ from crude wastewater were also tested. Carbon dioxide fluxes measured for both wastewaters compared reasonably with analogue ammonia absorption solvents of equivalent NH₃ concentration. Importantly, this demonstrates that ammonia rich wastewaters can facilitate chemically enhanced CO₂ separation which eliminates the need for costly exogenic chemicals or complex chemical handling which are critical barriers to implementation of chemical absorption. When testing NH₃ analogues, the potential to recover the reaction product ammonium bicarbonate (NH₄HCO₃) in crystalline form was also illustrated. This is significant as it suggests a new pathway for ammonia separation which avoids biological nitrification and produces ammonia stabilised into a commercially viable fertiliser (NH₄HCO₃). However, in real ammonia rich wastewaters, sodium bicarbonate and calcium carbonate were preferentially formed over NH₄HCO₃ although it is proposed that NH₄HCO₃ can be preferentially formed by manipulating both ion exchange and absorbent chemistry.

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1. Introduction

Biogas produced through the anaerobic digestion of sewage sludge can be exploited either through co-generation for electricity and heat production (CHP) or it can be upgraded to natural gas standards (biomethane). Due to recently introduced financial incentives the revenue from biomethane can be up to 70% higher than for electricity production (Read and Hofmann, 2011). Whilst trace biogas impurities, such as

hydrogen sulfide H₂S and particulates, are routinely removed (e.g. by activated carbon) prior to further biogas utilisation (Rautenbach and Welsch, 1994); upgrading to produce biomethane requires additional removal of the bulk CO₂ fraction to increase methane content to the equivalent of natural gas and is most commonly undertaken by absorption (Persson et al., 2007). This represents a new unit process operation to the water industry, although the same separation technology has seen extensive investigation for deployment into carbon capture and storage (CCS). In CCS, chemical absorption is

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applied in a packed column which mediates contact between the CO₂ rich gas and a highly reactive chemical solvent such as monoethanolamine (MEA) that is selective for CO₂ and offers high absorption capacities of around 0.55 kg CO₂ kgMEA⁻¹ (Mani et al., 2006). However, a high specific energy demand for solvent regeneration, in addition to chemical losses due to persistent solvent degradation, and associated costs have largely hindered uptake of chemical absorption by water utilities implementing biogas upgrading. Instead, physical absorption using a water solvent is favoured, despite requiring larger absorption columns and higher liquid consumption due to a lower overall mass transfer coefficient (Patterson et al., 2011).

Aqueous free ammonia (NH₃) has been identified as an alternate chemical absorbent pathway to organic chemicals (e.g. MEA) for CCS as it does not degrade, it is not corrosive and it requires up to 75% less energy than MEA for regeneration due to weaker bonding of CO₂ to ammonia (Budzianowski, 2011a). Furthermore, aqueous ammonia provides an absorption capacity of 1.76 kgCO₂ kgNH₃⁻¹ which is around three times higher than the capacity (by mass) of MEA and is only one sixth of the cost (Mani et al., 2006; Makhloufi et al., 2014). Aqueous ammonia therefore presents analogous opportunities for biogas upgrading where the gas phase is characterised by a higher CO₂ mole fraction than in CCS. Budzianowski (2011b) suggested that ecological solvents rich in ammonium offered potential for exploitation in biogas upgrading. At wastewater treatment works, sludge liquors comprise ammonium concentrations ranging 500 to 2000 mg NH₄⁺ L⁻¹ (0.2% wt.) (Thornton et al., 2007) although ammonium concentrations up to 10,000 mgNH₄⁺ L⁻¹ (1% wt.) have been achieved using zeolites to harvest and concentrate ammonium from dilute wastewaters (Mackinnon et al., 2003). Whilst this is an attractive route to chemical cost reduction for water utilities undertaking biogas upgrading, this concentration range is below the 8–10% wt. range commonly applied to aqueous ammonia CO₂ absorption in packed columns (Puxty et al., 2010; Shuangchen et al., 2013; Budzianowski, 2011b) which suggests that ecological solvents may offer less favourable enhancement of absorption.

The key disadvantage of aqueous ammonia solvents is that the high saturated vapour pressure introduces NH₃ slip into the gas phase, where outlet flue gas concentrations of up to 2000 ppmv NH₃ have been reported (Kozak et al., 2009). This requires ammonia washing abatement equipment at the outlet of the absorption column which will influence both capital cost and energy demand (Shuangchen et al., 2013). Budzianowski (2011b) proposed that NH₃ slip could be diminished through the introduction of hollow fibre membrane contactor (HFMC) technology as an alternative absorption process to conventional packed columns. Rather than enabling direct contact between the gas and liquid phase as with conventional columns, the hydrophobic membrane in the HFMC supports non-dispersive contact between gas and liquid phase with gases free to diffuse through the micropores. Porous membranes are resilient to common biogas impurities (i.e. H₂S) and may even combine removal with upgrading if necessary since the acid gas does not permeate through the polymer (Rongwong et al., 2012). HFMC therefore present an opportunity to exploit the key advantages of

aqueous ammonia absorption for biogas upgrading whilst also diminishing NH₃ slip. The high specific surface area (around 3000 m² m⁻³) in HFMCs also provides greater process intensification when compared to packed columns (around 300 m² m⁻³) reducing both process scale and absorption solvent consumption (Makhloufi et al., 2014). For instance, Nii and Takeuchi (1992) compared HFMC technology with packed columns for chemical absorption and noted an order of magnitude reduction in absorbent solvent flow rate required to achieve analogous CO₂ separation from flue gas. It is therefore proposed that the enhanced absorbent utilisation afforded by HFMC technology could enable the practicable use of lower concentration ecological solvents for chemical cost reduction.

Absorption and reaction of CO₂ into aqueous ammonia is complex with both NH₃ and CO₂ undergoing multiple liquid phase reactions (Mani et al., 2006; Budzianowski, 2011a). However, several authors have cited the potential of this process for the production and recovery of the key reaction product ammonium bicarbonate (NH₄HCO₃) which has a commercial value of around €111 tonne⁻¹ (Budzianowski, 2011b; Hernandez and Torero, 2013). This is particularly attractive for biogas upgrading using ammonia rich wastewater as the chemical solvent since stabilisation of ammonium into the reaction product circumvents the need for direct biological treatment of ammonium in the wastewater. The following investigation therefore aims to establish the suitability of ammonia rich wastewater as a chemical solvent for biogas upgrading using HFMC technology as the underpinning absorption process. Specifically, this study seeks to: (i) quantify the chemical absorption potential of low concentration (environmentally relevant) aqueous ammonia solvents for CO₂ separation; (ii) determine the reactivity of real ammonia rich wastewaters compared to exogenic ammonia absorbents of equal concentration; (iii) measure the volatility of NH₃ into the gas phase within appropriate absorbent and process boundary conditions; and (iv) establish the feasibility of recovering the favoured reactant product NH₄HCO₃.

2. Materials and methods

2.1. Equipment setup and operation

Synthetic biogas was prepared using mass flow controllers (0.01–1.0 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK) to mix methane (99.995%) and carbon dioxide (99.7%) (BOC gases, Ipswich, UK) in-line at a typical flow rate 750 mL min⁻¹ (2.5 s HFMC residence time) to provide a 60:40/CH₄:CO₂ gas which was supplied into the hollow fibre membrane lumen. The HFMC comprised 7400 polypropylene fibres each with an outer diameter and length of 300 μm and 0.113 m respectively (total surface area 0.79 m², Membrana GmbH, Wuppertal, Germany). The fibres comprised a 0.03 μm nominal pore size and 40% porosity with a packing density of 0.369 (Fig. 1a). Absorbent was stored in a 10 L PVC tank, maintained at 19–21 °C by a thermostatic water bath (GD120, Grant Instruments Cambridge Ltd., Shepreth, UK) and was passed through the HFMC shell, in counter-current mode using a centrifugal pump (max. 6 L min⁻¹, 50010 series, Jabsco GmbH,

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