Water Research, 2014, Vol. 67, pp. 175-186

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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 (NH_3) rich wastewaters as an ecological chemical absorption solvent for the selective extraction of carbon dioxide (CO_2) during biogas upgrading to 'biomethane' has been studied. Aqueous ammonia absorbents of up to 10000 $gNH_3\ m^{-3}$ demonstrated CO_2 absorption rates higher than recorded in the literature for packed columns using 20000-80000 $gNH_3\ m^{-3}$ 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, NH_4^+) and a regenerant (477 $gNH_4^+\ m^{-3}$) produced from a cationic ion exchanger used to harvest NH_4^+ from crude wastewater were also tested. Carbon dioxide fluxes measured for both wastewaters compared reasonably with analogue ammonia absorption solvents of equivalent NH_3 concentration. Importantly, this demonstrates that ammonia rich wastewaters can facilitate chemically enhanced CO_2 separation which eliminates the need for costly exogenic chemicals or complex chemical handling which are critical barriers to implementation of chemical absorption. When testing NH_3 analogues, the potential to recover the reaction product ammonium bicarbonate (NH_4HCO_3) 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 (NH_4HCO_3). However, in real ammonia rich wastewaters, sodium bicarbonate and calcium carbonate were preferentially formed over NH_4HCO_3 although it is proposed that NH_4HCO_3 can be preferentially formed by manipulating both ion exchange and absorbent chemistry.

Keywords: carbon dioxide sequestration; crystallisation; gas/liquid contactor; chemical scrubbing

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 H_2S 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 CO_2 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 applied in a packed column which mediates contact between the CO_2 rich gas and a highly reactive chemical solvent such as monoethanolamine (MEA) that is selective for CO_2 and offers high absorption capacities of around 0.55 kg CO_2 $kgMEA^{-1}$ (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 (NH_3) 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 CO_2 to ammonia (Budzianowski, 2011a). Furthermore, aqueous ammonia provides an absorption capacity of 1.76 $kgCO_2$ $kgNH_3^{-1}$ 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 CO_2 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 mgNH_4^+ L^{-1} (0.2% wt.) (Thornton et al., 2007) although ammonium concentrations up to 10000 mgNH_4^+ 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 to 10% wt. range commonly applied to aqueous ammonia CO_2 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 NH_3 slip into the gas phase, where outlet flue gas concentrations of up to 2000 ppmv NH_3 have been reported (Kozak, 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 NH_3 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. H_2S) 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 NH_3 slip. The high specific surface area (around 3000 m^2 m^{-3}) in HFMCs also provides greater process intensification when compared to packed columns (around 300 m^2 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 CO_2 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 CO_2 into aqueous ammonia is complex with both NH_3 and CO_2 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 (NH_4HCO_3) which has a commercial value of around €111 $tonne^{-1}$ (Budzianowski, 2011b; Hernandez et al., 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 CO_2 separation; (ii) determine the reactivity of real ammonia rich wastewaters compared to exogenic ammonia absorbents of equal concentration; (iii) measure the volatility of NH_3 into the gas phase within appropriate absorbent and process boundary conditions; and (iv) establish the feasibility of recovering the favoured reactant product NH_4HCO_3.

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 / CH_4:CO_2 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 m^2, 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, Norderstedt, Germany) at a typical flow rate of 100 mL min^{-1} (60 s hydraulic residence time). Ammonia slip in to the gas phase was determined by the method described by Kuntke *et al*. (2012). The out-gas was bubbled through diffusers in two 1 L capacity gas tight aspirator bottles (Schott Duran, VWR, The Netherlands) in series, containing 500 mL of 0.4 mol L^{-1} sulphuric acid; the second bottle enabling verification of breakthrough from the first.

The ion exchanger comprised a 10 L column containing 4 l of clinoptilolite resin (RS Minerals, Guisborough, UK) and was prepared by passing a 50 g_{NaCl} L^{-1} (99%, Fisher Chemicals, Loughborough, UK) regenerant through the column at 5 bed volumes per hour (Bv h^{-1}) for 30 minutes followed by a DI rinse at 5 Bv h^{-1} for 60 minutes (McAdam *et al.*, 2010) (Fig. 1b). The column was operated in down-flow using crude sewage (10-20 gNH_4^+ m^{-3}) at 4.2 Bv h^{-1} (Aiyuk *et al.*, 2004) until breakthrough which was noted at 166 Bv. The column was regenerated using 20 L of 50 g_{NaCl} L^{-1} at 1 BV h^{-1}. The IEX regenerant was filtered through a 1.2 µm filter (GF/C 15 mm, Fisher Scientific, Loughborough, UK) prior to use. Return liquor was collected from a digestate dewatering centrifuge at a local WWTW and was filtered through a 6-12 µm filter before centrifugation (Sorvall Legend RT+, Thermo Fisher Scientific, Hemel Hempstead, UK) at 5000 rpm for 10 minutes with the decant filtered through a 1.2 µm filter.

2.2 Chemical preparation, sampling and analysis

Analogue absorbents were freshly prepared by adding saturated aqueous ammonia solution (35 %, 2.5 L, Fisher Chemicals) to DI water. Ammonia concentration was confirmed by ammonium cell test. The pH of real and synthetic absorbents was fixed at pH 11 (excluding variable pH experiments). Aqueous ammonia analysis was undertaken using cell tests (VWR International Ltd., Poole, UK) with photometric determination using a Spectroquant Nova 60 (Merck-Millipore, Darnstadt, Germany). Gas composition after the HFMC was determined using an infrared biogas analyser (Yieldmaster, accuracy <0.2% full-scale, Bluesens gas sensor GmbH, Herten, Germany). Gas flow rate was measured using a bubble flow meter (50 mL, Restek, Bellefonte, USA). Flux (J_{CO2}, mol m^{-2} s^{-1}) was calculated using:

$$J_{CO2} = \frac{\left[\left(Q_{G,in} x C_{G,in}\right) - \left(Q_{G,out} x C_{G,out}\right)\right] x 273.15 x 1000}{\left(22.4 x A_m x T_c\right)} \quad \text{(Equation 1)}$$

where $Q_{G,\,in}$ and $Q_{G,\,out}$ are gas flow rate before and after HFMC respectively (m^3 s^{-1}), $c_{G,\,in}$ and $c_{G,\,out}$ are the CO_2 content before and after HFMC respectively (mol mol^{-1}), A_m refers to the membrane surface area for absorption (m^2) and T_G is the gas temperature (K) (Atchariyawut et al., 2007). The enhancement in flux provided by the chemical reactivity of the absorbent was characterised using the 'enhancement factor' (*E*) which can be applied providing an identical driving force for mass transfer is assumed (Dindore et al., 2005):

$$E = \frac{CO_2\, flux(chemical)}{CO_2\, flux(physical)} \quad \text{(Equation 2)}$$

Microscopy of membrane fibres and crystals was performed by scanning electron microscope (SEM, XL30, FEI, Hillsboro, Oregon, USA)), energy dispersive x-ray spectroscopy (EDX, Oxford Instruments NTS, Abingdon, UK) and x-ray diffraction (XRD, D5005, Siemens, Munich, Germany).

2.3 Liquid phase chemical reactions of CO_2 and aqueous ammonia

The following chemical reactions are known to take place during chemical absorption of CO_2 into aqueous ammonia (Puxty et al., 2012; Niu et al., 2012):

$$CO_2 + H_2O \leftrightarrow HCO_3^- \quad \text{(Equation 3)}$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \quad \text{(Equation 4)}$$

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad \text{(Equation 5)}$$

$$CO_2 + NH_3 \leftrightarrow NH_2COO^- + H^+ \quad \text{(Equation 6)}$$

$$NH_2COO^- + H_2O \leftrightarrow NH_3 + HCO_3^- \quad \text{(Equation 7)}$$

$$NH_4HCO_3(s) \leftrightarrow NH_4^+ + HCO_3^- \quad \text{(Equation 8)}$$

The ammonium-ammonia equilibrium can be driven toward free ammonia (NH_3, Equation 5) by increasing absorbent pH (SM 1). Carbon dioxide reacts with either water to form bicarbonate (Equation 3) or free ammonia to form carbamate (NH_2COO^-) (Equation 6).

3. Results

3.1 Assessment of CO_2 absorption using analogue ammonia absorbents

An increase in solvent pH under fixed hydrodynamic conditions notably increased J_{CO2} at higher free ammonia concentrations (Fig. 2). For example, J_{CO2} increased from 0.14×10^{-4} mol m^{-2} s^{-1} at pH 8 (20 °C) to 0.26×10^{-4} mol m^{-2} s^{-1} at pH 11 (20 °C). An increase in pH drives the ammoniacal nitrogen ($[NH_4^+]$ + $[NH_3]$, NH_4-N) equilibrium toward free ammonia with around 15%, 90% and 99% present as free ammonia at pH 8, 10 and 11 respectively at 20°C (SM 1, Equation 5). Initial aqueous ammonia concentration also positively increased J_{CO2} with a flux of 0.7×10^{-4} mol m^{-2} s^{-1} recorded in 10 g m^{-3} NH_3 solution compared to 0.38×10^{-4} mol m^{-2} s^{-1} in 10000 g m^{-3} NH_3 solution operated under identical boundary conditions (pH 11, 20 °C). However, absorbent temperature did not markedly change J_{CO2} except for the most concentrated solvent tested (10000 gNH_3 m^{-3}).

At a G/L of 0.075, the CH_4 composition of the outlet gas phase was between 98 % and 99 % for the 5000 gNH_3 m^{-3} and 10000 gNH_3 m^{-3} absorbents (Fig. 3a). Upon increasing Q_G (with a fixed Q_L, 6.7×10^{-6} m^3 s^{-1}), biogas CH_4 composition decreased which was more evident for the higher concentration ammonia absorbents. However, J_{CO2} increased as Q_G and with higher fluxes noted

when using the more concentrated NH_3 absorbents (Fig. 3b). At the maximum hydrodynamic conditions tested (G/L 4.2), J_{CO2} were $0.94x10^{-4}$ mol m^{-2} s^{-1} for the 10 and 100 gNH_3 m^{-3} absorbents and $1.7x10^{-4}$ mol m^{-2} s^{-1} and $2.3x10^{-4}$ mol m^{-2} s^{-1} for the 5000 and 10000 gNH_3 m^{-3} ammonia absorbents respectively.

3.2 Measurement of ammonia volatility within process boundary conditions

The loss of ammonia into the gas phase (or NH_3 slip) was ostensibly a function of initial aqueous ammonia concentration when Q_L and Q_G were fixed at $1.67x10^{-6}$ m^3 s^{-1} and $1.25x10^{-5}$ m^3 s^{-1} respectively at constant pH (11) and solvent temperature (20 °C) (Fig. 4). At an aqueous NH_3 absorbent concentration of 10000 g m^{-3}, which has been achieved in ecological absorbents through concentrating ammonia using ion exchange (Mackinnon et al., 2003), an NH_3 concentration of only 0.002 gNH_3 m^{-3} was measured in the treated gas phase. This is below the proposed UK standard for gas phase ammonia in gas to grid applications (dashed line) (Environment Agency, 2013). Niu et al. (2012) also noted NH_3 slip was dependent on initial NH_3 concentration when testing ammonia absorbents within the same concentration range for CO_2 separation from a packed column. However, the observed losses were considerably higher than noted in this study.

3.3 Efficacy of real ammonia rich wastewaters to deliver enhanced CO_2 absorption

Return liquor and IEX regenerant were prepared and characterised (Table 2). For both of the real absorbents tested, chemical enhancement was maximised at the highest G/L ratio imposed (Fig. 5). A maximum *E* of 14.9 and 2.9 were determined for the return liquor (2325 gNH_3 m^{-3}) and IEX regenerant (447 gNH_3 m^{-3}) respectively at a G/L of 37.5. However, *E* reduced sharply following a decrease in G/L ratio toward an E of 1 which is comparable to the J_{CO2} measured with DI water as the physical absorption solvent. Enhancement factors produced from the real wastewaters were compared to those measured with analogue ammonia absorbents using the same boundary conditions (Fig. 6a and 6b). The enhancement factor for the return liquor was broadly in agreement

with that determined for the analogue. The chemical enhancement of the IEX regenerant was characterised by a gradient similar to the parity line (where E_{real}/E_{syn} = 1) but was below that predicted based on the analogue.

3.4 Identifying the reaction products formed in real absorbents

In a preliminary assessment, synthetic biogas was bubbled through an 85000 g_{NH3} m^{-3} analogue NH_3 solution and within a short time frame a solid NH_4HCO_3 product was produced in situ which displayed regularly shaped crystals when examined by SEM (Fig. 7). The crystals comprised only carbon (C), oxygen (O) and nitrogen (N) peaks (EDX spectra) with an O:N ratio of 3:1 which is indicative of the NH_4HCO_3 salt and was confirmed by XRD. In a subsequent assessment, an 85000 gNH_3 m^{-3} analogue absorbent was then run through a single fibre microporous HFMC (a PTFE fibre was used for easy potting) for approximately 5 minutes. Whilst no solid was visible within the absorbent reservoir, SEM analysis of the fibre revealed that NH_4HCO_3 crystals had grown in situ on the membrane surface. Ion exchange regenerant was tested in the PP HFMC and resulted in in situ crystal formation which exited the HFMC in the absorbent and was collected in a coarse filter (6-12 µm retention) for analysis (Fig. 7). The crystals were fine and amorphous in structure and were principally calcium carbonate ($CaCO_3$) although other cationic impurities including sodium, potassium and aluminium were also noted. In situ precipitation did not occur during return liquor assessment under identical hydrodynamic conditions to the IEX regenerant. Consequently, to enhance the likelihood for precipitation, the return liquor was recirculated in the HFMC until complete exhaustion of the absorbent. The crystalline solid was finally obtained through mild evaporation of the saturated return liquor. The EDX spectrum analysis suggested the crystal to be reasonably pure, comprising C, O and Na in a ratio indicative of sodium bicarbonate ($NaHCO_3$).

4. Discussion

A key finding from this study was that the low aqueous ammonia concentration present within environmental absorbents do enable chemical enhancement of CO_2 flux. The limiting aqueous NH_3 concentration needed to enhance CO_2 flux over water was between 100 $gNH_3\ m^{-3}$ and 447 $gNH_3\ m^{-3}$ with the upper value being indicative of the ammonium concentration reached in the IEX concentrate. This is above the ammonium concentration found in treated final effluent (around 10 g $NH_4^+\ m^{-3}$) which is commonly employed as the absorbent in water scrubbers for biogas upgrading at wastewater treatment works (Persson et al., 2007). An increase in pH of the 10 and 100 g m^{-3} ammonium/ammonia absorbents did not increase CO_2 flux (Fig. 2). When pH is increased from neutrality (pH 7) to pH 11, shifting the NH_4-N equilibrium towards ca.100% free ammonia (Equation 5, SM 1). It is therefore asserted that since the increase in available reactant (ammonia) did not increase CO_2 flux, absorption within aqueous ammonia solvents below 100 $gNH_3\ m^{-3}$ is primarily governed by physical absorption. At aqueous ammoniacal nitrogen concentrations greater than 1000 g m^{-3}, a linear increase in CO_2 flux was demonstrated with an increase in pH (Fig. 2b) and is indicative of the chemical enhancement provided by the increase in available free ammonia (Esquiroz-Molina et al., 2013). Significantly, for the highest aqueous NH_4-N absorbent concentration evaluated (10000 g m^{-3}), no further increase in CO_2 flux was noted as pH increased from pH10 to pH11 (Fig. 2a). This is analogous to the work of Esquiroz-Molina et al. (2013) and can be ascribed to the presence of an excess of free ammonia present in the reaction zone at the gas-absorbent interface at pH10, where the enhanced reactivity offsets the lower gaseous solubility constant thereby minimising liquid side resistance. Interestingly, in commercial aqueous ammonia packed column processes, pH is between 8.8 and 9.6 (Yeh et al., 2005) where the lower fraction of free ammonia available within this pH range can be tolerated through higher absolute NH_4-N concentrations, which are typically in the range of 50000 to 100000 g m^{-3} (Puxty et al., 2010; Budzianowski, 2011a; Niu et al., 2012). Therefore within environmental absorbents, the reduced reactivity imposed by lower absolute NH_4-N concentration can be offset by shifting the equilibrium toward free ammonia using mild pH correction.

An increase in absorbent temperature did not markedly enhance CO_2 flux within the environmental ammonia concentration range tested (Fig. 2). Zeng et al. (2011) also investigated the role of temperature (range 20-50 °C) in controlling NH_3-CO_2 reaction kinetics in 2-8% wt. aqueous ammonia and similarly noted only slight enhancement of the overall mass transfer coefficient between 20 and 40°C (293-313 K), which is within the range where forward reactions are favoured (Bai et al., 1997). The low temperature dependency potentially explains why the chilled aqueous ammonia process (temp. 1.7 °C) is commercially viable; the low temperature being favoured to limit ammonia slip (Valenti et al., 2009). In this study, an NH_3 concentration of 0.002 $gNH_3\ m^{-3}$ was measured in the gas phase for the 10000 $g_{NH3}\ m^{-3}$ absorbent at a temperature of 20°C which is an order of magnitude below the proposed gas phase ammonia concentration limit (0.02 $gNH_3\ m^{-3}$) for biomethane as a vehicle fuel or natural gas substitute (Persson et al., 2007; Environment Agency, 2013). Ammonia slip was demonstrated to be concentration dependent (Fig. 4) thus the low NH_3 slip recorded in this study can be explained by the lower environmentally relevant ammonia concentration range studied. However, NH_3 slip was also two orders of magnitude below that observed in a packed column using aqueous ammonia within a similar concentration range (Fig. 4, Niu et al., 2012). Budzianowski (2011a) postulated that the difference in NH_3 slip was due to the hydraulic characteristics of each technology where the transport of NH_3 to the gas-liquid interface in packed columns was reasonably turbulent whereas the preferential laminar flow regime in HFMC (*Re* = 57 - 570 in this study) minimises the transport of NH_3 to the gas-liquid interface as NH_3 transport is limited to radial diffusion from the absorbent bulk to the boundary layer. Further, stagnant NH_3 within the gas-filled membrane pores, absent in column-based systems, will likely resist NH_3 mass transfer from the liquid phase, which could conceivably also play a role. Therefore, HFMCs appear practically advantageous to limit ammonia slip, and when coupled with the relatively low NH_3 concentration range used, enable a sufficiently clean produced gas for use.

At low gas flows, methane content in the gas outlet exceeded 98% (Fig. 3) which meets standards for biomethane (Persson et al., 2007). An increase in gas flow rate decreased methane

content in the outlet gas but increased CO_2 flux into the receiving ammonia absorbent. In chemically reactive absorption systems, an increased gas flow often mediates solute flux (Esquiroz-Molina et al., 2013) as this permits replenishment of CO_2 at the solvent-membrane interface and sustains a high bulk gas CO_2 partial pressure (Zeng et al., 2013). At full scale, the balance between higher flux to reduce scale and maintenance of the outlet gas quality can be achieved through extension of reactor length (Noble and Stern, 1995). At the highest flux recorded using 10000 g_{NH3} m^{-3} aqueous ammonia absorbent, an overall absorption rate of 8.4 kmol m^{-3} h^{-1} was recorded. For comparison, Zeng et al. (2013) reported an overall absorption rate of 2.37 kmol m^{-3} h^{-1} from a 15% CO_2 v/v flue gas using 7.7% wt. aqueous ammonia in a packed column. This process comparison illustrates that analogous CO_2 fluxes can be achieved with lower concentration environmental aqueous ammonia absorbents through the process intensification provided by the HFMC. Chemical enhancement within the real matrices reached a plateau at a gas-liquid ratio of 15-19 (Fig. 5). The absorbent flow regime is characteristically laminar. Consequently the CO_2 loading applied at the high G/L ratio depletes the reactant within the immediate vicinity of the gas-liquid interface and absorption rate then becomes limited by the radial diffusion of the reactant to the reactant plane (Dindore et al., 2005). Importantly, this demonstrates real environmental absorbents provide considerable enhancement of CO_2 flux versus water which is the absorbent currently favoured by water utilities (Persson et al., 2007). Chemical enhancement provided by the return liquor was equivalent to that of the analogue indicating that enhancement was ostensibly a function of initial ammonia concentration. However, the IEX regenerant provided lower enhancement than an analogue of equivalent concentration which can be ascribed to the salt concentration (50 g L^{-1}) which is known to reduce the physical solubility of CO_2 into the absorbent (Mcleod et al., 2013). Higher chemical reactivity can be engineered into the IEX regenerant through increasing ammonia concentration which is dependent upon the zeolites cation exchange capacity (CEC), and ammonium loading (Mackinnon et al., 2003). For example, Mackinnon et al. (2003) used a higher CEC zeolite (MesoLite) to provide a regenerant

concentration of up to 10000 gNH_4-N m^{-3}, which in this study has been shown sufficient to provide high CO_2 fluxes (Fig. 3).

A CO_2/NH_3 absorbent loading of 0.046 mol mol^{-1} resulted from the maximum CO_2 flux achieved (Fig. 3). For these absorbent loading conditions (i.e. low loading and high pH) there is general agreement that the reaction product ammonium carbamate is favoured which is three times more soluble than ammonium bicarbonate and so does not readily precipitate (Mani et al., 2006; Budzianowski, 2011a). Data from Jänecke (1929) indicates that at a CO_2 loading of around 0.5 $molCO_2$ $molNH_3^{-1}$ the equilibria shifts to favour bicarbonate (Equation 4) and ammonium ions (Equation 5) (Mani et al., 2006; Puxty et al., 2010) leading to preferential formation of ammonium bicarbonate (Equation 6). In this study, this NH_4HCO_3 precipitation route was demonstrated under high CO_2 loading by bubbling CO_2 directly into the analogue ammonia absorbent (Fig. 7). Importantly, sequestration of both ammonia and CO_2 into precipitated NH_4HCO_3 eliminates the cost and complexity of solvent regeneration which represents a key barrier to uptake of chemical absorption (Mani et al., 2006). Following absorbent recirculation within the HFMC, ammonium bicarbonate crystals were also shown to preferentially form at the membrane surface. This is similar to the mechanism introduced by Di Profio et al. (2010) in the membrane crystallisation reactor which has been applied specifically for the enhancement of crystallisation kinetics. The authors proposed that the porous membrane surface provided cavities where solute molecules become trapped leading to localised supersaturated zones. Consequently, the use of the membrane for ammonia CO_2 absorption can enable ammonium bicarbonate crystallisation at lower CO_2 loadings than previously proposed in packed column investigation. The membrane's high controllability in favour of crystal growth versus nucleation can allow sufficiently sized crystals to detach due to the sheer of liquid flow and avoid scaling (Di Profio et al., 2010). However, pore wetting during operation can cause crystal formation within the fibre bore (McLeod et al., in press). This can be avoided by selection of suitably hydrophobic membranes possessing small (<0.2 μm), circular pores in addition to solvents possessing high surface tension (such as highly electrolytic wastewaters).

In the IEX regenerant $CaCO_3$ was preferentially formed over NH_4HCO_3 due to its lower solubility (Table 1). The cations Na^+, K^+ and Al^{3+} were also present within the precipitate due to co-separation by the cationic zeolite used. Ciambelli et al. (1985) fractionated a cationic IEX regenerant from an IEX column used for ammonium separation and identified that the Ca^{2+} rich (and ammonia poor) regenerant fraction was first eluted from the IEX column ahead of ammonium. It is therefore proposed that further selectivity toward NH_4HCO_3 can be imparted when using IEX by more strict regulation of the regenerant cycle to favour ammonium. However, in the return liquor, sodium bicarbonate ($NaHCO_3$) was preferentially precipitated due to its lower solubility constant and high $[Na^+]$ gradient. The high availability of $[Na^+]$ ions can be ascribed to the considerable sodium hydroxide addition needed to overcome the liquors buffering capacity to reach pH11. Interestingly, Hecht et al. (1990) demonstrated that equilibrium between NH_3 and NH_4^+ (Equation 1) can be successively re-established at low pH (i.e. pH7.8) following consumption of the free NH_3 by solvent recirculation. Consequently, operation at lower pH will potentially provide more favourable conditions for ammonium bicarbonate precipitation due to the lower $[Na^+]$ gradient albeit at lower CO_2 fluxes.

To establish key financial benefits from this study, revenue generation from biomethane is compared to a conventional WWTW where biogas is used in CHP to produce electricity and NH_4-N is treated by nitrification. The illustrative WWTW treats 500000 m^3 d^{-1} total flow, 25000 kgNH_4-N d^{-1} (50 gNH_4-N m^{-3}) and produces 3400 m^3 h^{-1} raw biogas (60:40 / CH_4:CO_2) which generates an annual revenue of £2.8M y^{-1} following subtraction of aeration costs (£2.9M y^{-1}) which are assumed entirely attributable to nitrification (Table 3). The removal of trace H_2S and particulate impurities is assumed to be a uniform requirement for each scenario and therefore can be neglected for simplicity. However, if 100 ppmv H_2S in the biogas and a capacity of 0.3 kg sulfur kg^{-1} carbon are assumed (Rautenbach and Welsch, 1994), then approximately 1 t of carbon media y^{-1} would be required for a 3400 m^3 h^{-1} biogas flow. Based on an ammonium mass balance from return liquors (Jaffer et al., 2001), 22% of the biogas flow can be upgraded with ammonia (78% to CHP), which yields an

increased revenue of £1.3 M y^{-1}. A further £0.9M y^{-1} in revenue can be achieved through including NH_4HCO_3 recovery (total £5 M y^{-1}). Smaller illustrative WWTWs (15000 m^3 d^{-1}), typically receiving lower strength raw influent (25 gNH_4-N m^{-3}) and generating a 50% lower biogas flow per m^3 influent, will have a reduced nitrification demand upon the ASP and possess a lower return liquor flow (assuming no imported sludge); therefore a 41 K£ y^{-1} baseline revenue via CHP is assumed. Based upon the stoichiometry of the NH_4HCO_3 product, 33% of the biogas flow may be directed towards upgrading, yielding an increased revenue of 33 K£ y^{-1} (74 K£ y^{-1} total). Combined use of both CHP and upgrading is considered to be most feasible at full scale as some CHP capacity is needed to deliver heat for the AD. However, it is worth noting that up to 40% of the ammonium load can be attributed to the return liquors (Johnson, 2011) hence the projected revenue (based on 22%) can be considered conservative. Importantly, this added value could not be realised if exogenic chemicals (i.e. MEA) were used for biogas upgrading due to the high cost of chemical regeneration (-2.2 M£ y^{-1}) (Knudsen *et al.*, 2009).

The capital cost of the membrane installation can be determined by using the overall mass transfer coefficient (K_L, m s^{-1}) to calculate the membrane length needed to achieve a given CO_2 removal from the gas phase:

$$ln\left(\frac{c_1}{c_0}\right) = \frac{-K_L a L}{V_L} \quad \text{(Equation 9)}$$

where L is the active membrane length (m), a is the specific surface area for the HFMC (m^2 m^{-3}), V_L is the superficial liquid velocity (m s^{-1}), and c_0 and c_1 are the inlet and outlet dissolved CO_2 concentrations in the liquid respectively (Noble and Stern, 1995). A K_L of $1.53x10^{-4}$ m s^{-1} was observed in the present study using a return liquor chemical solvent. Therefore, for a 95% CH_4 biomethane output, a membrane cost of £90000 is estimated; assuming full-scale HFMCs (Liqui-cel, 14x40 extra flow) at 40 £ m^{-2} membrane area (Prasad and Sirkar, 1989). A payback time for a single module of just 15 d has negligible impact upon the economic benefit for the large WWTW, even when conservative module lifetimes of 0.5-3 y are considered (Prasad and Sirkar, 1989). The reduced return liquor flow of the smaller WWTW requires only a single full-scale HFMC (£15000). Although

lower revenues result in a longer time (6 months), this may be acceptable if a feasible lifetime of ca.10 y can be realised (Prasad and Sirkar, 1989).

Full upgrading, where 100% of the gas load is used for biomethane production, increases revenue to £9.5 M y^{-1} due to the higher incentivisation levy for biomethane (Read and Hofmann, 2011). Based on using IEX for harvesting NH_4^+ from primary effluent then 100% upgrading is theoretically achievable as mass balancing indicates the full ammonium load provides a mole ratio of 1.2:1 NH_4-N:CO_2 which is within range of the stoichiometric conversion (1:1 NH_4^+/CO_2 into NH_4HCO_3). With the inclusion of NH_4HCO_3 recovery to 100% upgrading, revenue is estimated to increase by £10.7 M y^{-1} versus the base case (115 K£ y^{-1} in excess of the 41 K£ y^{-1} baseline for small works). Interestingly, the added value provided by selling NH_4HCO_3 as a fertilizer and the reduction in aeration costs (for nitrification) could reduce the financial risk in investing in biomethane, where uncertainty over the future value of biomethane incentives is currently impeding implementation of biogas upgrading facilities within the UK.

For the large example WWTW an IEX bed size of approximately 6000 t (1 M£) was estimated based upon literature values for clinoptilolite media CEC and cost (Aiyuk et al., 2004), with an annual media attrition of 3% demonstrated for full-scale IEX of municipal wastewater (Svetich, 1993). Based upon the operational IEX conditions in the present study and the maximum K_L observed for the IEX regenerant solvent ($1.4x10^{-4}$ m s^{-1}); a membrane installation totalling £525000 is estimated for a 95% CH_4 biomethane. As a result a total payback time of 0.14 y is anticipated for the combined IEX and membrane technologies. However, optimised operation of the IEX exchanger could reduce the regenerant flow and associated membrane capital cost in real scenarios. At a smaller scale WWTW the IEX bed capital cost approaches parity with the single full-scale HFMC required, incurring a combined capital cost of £30,000 with a payback time of 0.25 y.

5. Conclusions

Aqueous ammonia absorbents in the concentration range identified in ammonia rich wastewaters have been shown to enable chemically enhanced CO_2 separation. Implementation of ecological solvents obviates the perceived challenges of chemical absorption where concerns regarding chemical handling and chemical cost can be precluded. The IEX regenerant provided less chemical reactivity than the return liquor due principally to the lower free ammonia concentration. The CO_2 absorption rate recorded using the high concentration NH_3 analogue (10000 g m^{-3}) demonstrated the potential of an optimised IEX process for ecological solvent production and were superior to those identified for packed columns in the literature where higher aqueous ammonia concentrations (2-8% wt.) are used. The enhanced absorption rate and low ammonia slip presented in this study can be attributed to the process intensification and specific hydrodynamic profile developed in HFMC technology. However, ecological solvents could still be of interest for retrofit to existing water scrubbers provided low ammonia slip can be achieved. The recovery of ammonium bicarbonate was illustrated but proved complex in real wastewater. Reaction product recovery can eliminate solvent regeneration, reduce wastewater treatment costs and provide a new revenue stream. Consequently, further investigation into more controlled methods of NH_4HCO_3 crystallisation in complex wastewaters is economically warranted and several possible options have been proposed.

Acknowledgments

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC, V/N: 08001923), Anglian Water, Northumbrian Water, Severn Trent Water and Yorkshire Water for their financial support.

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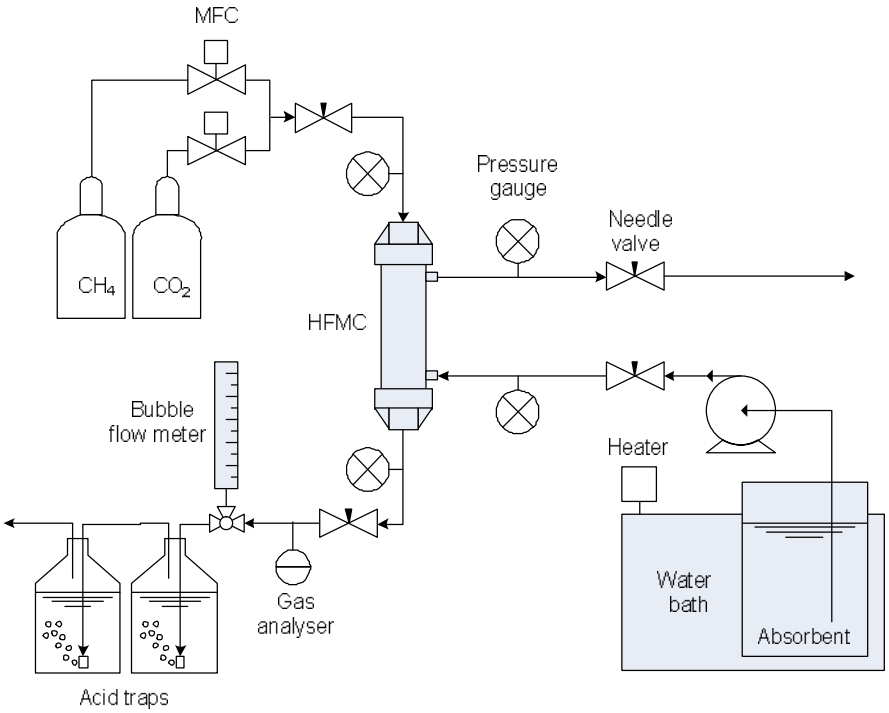
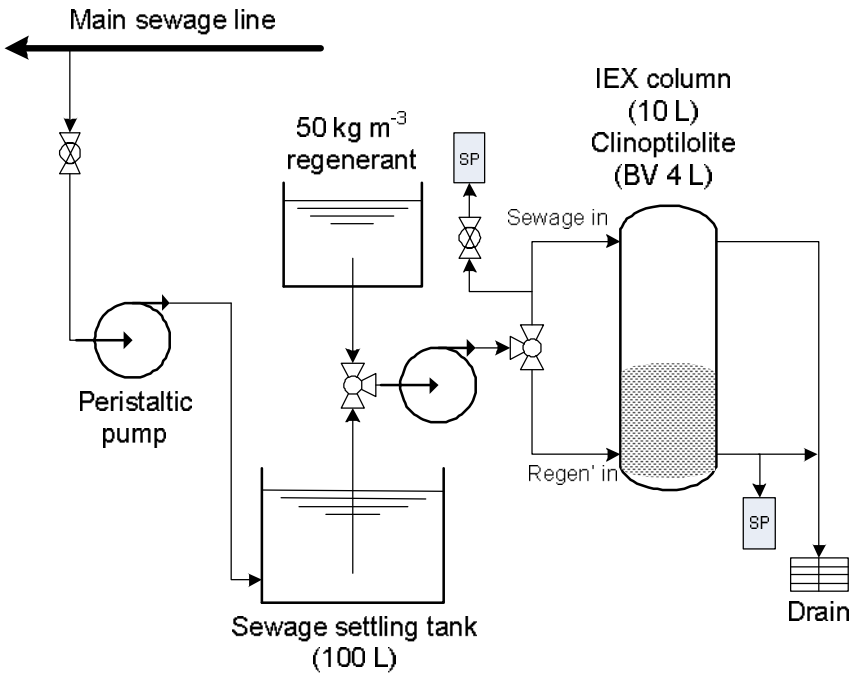


(a)



(b)

Fig. 1. (a) Set-up used for gas absorption in a polypropylene micro-porous hollow fibre membrane contactor; (b) ion exchange (IEX) column for removal of ammoniacal nitrogen (NH_4-N) from raw sewage by clinoptilolite and subsequent production of NH_4-N rich IEX regenerant. SP indicates sampling point.

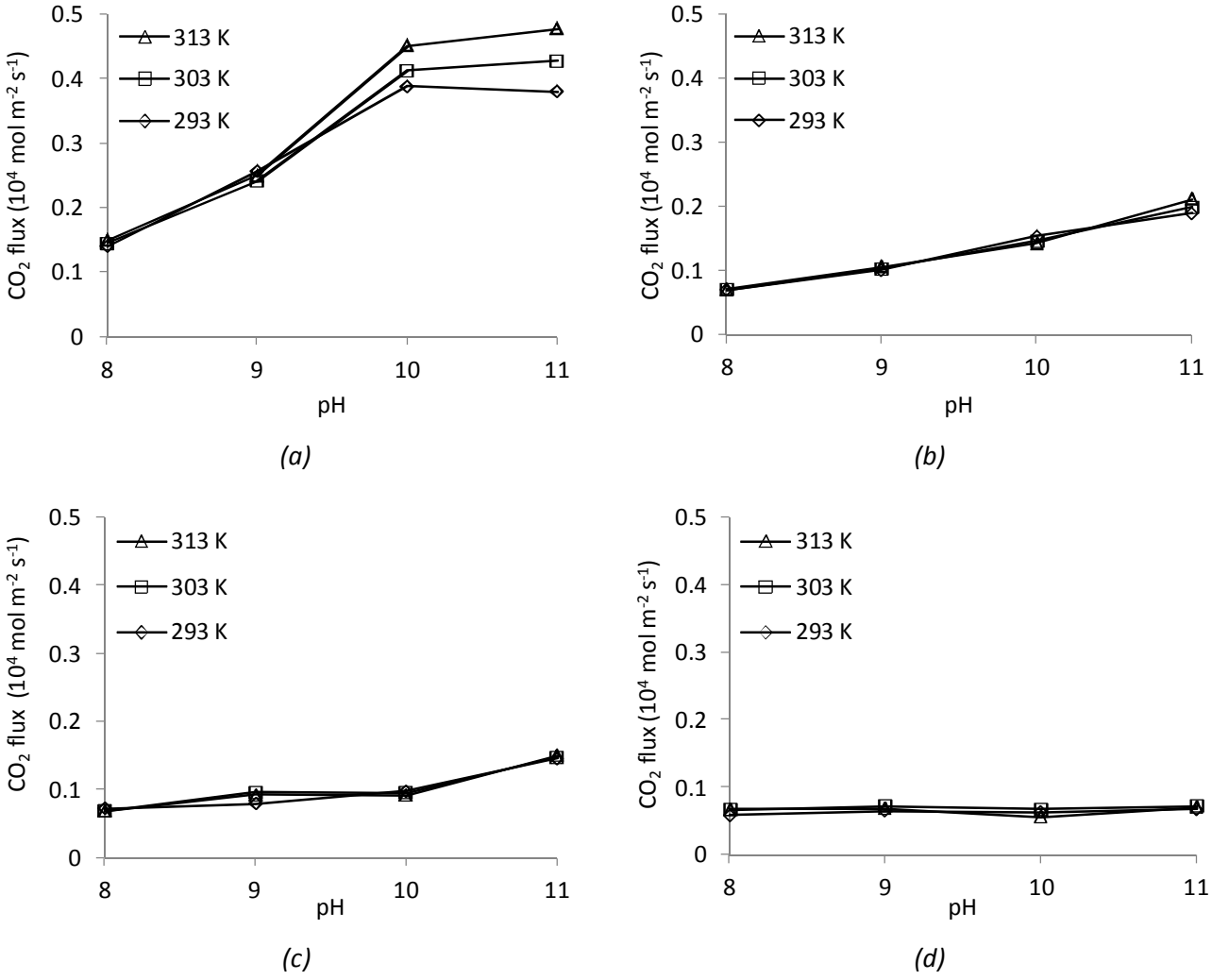
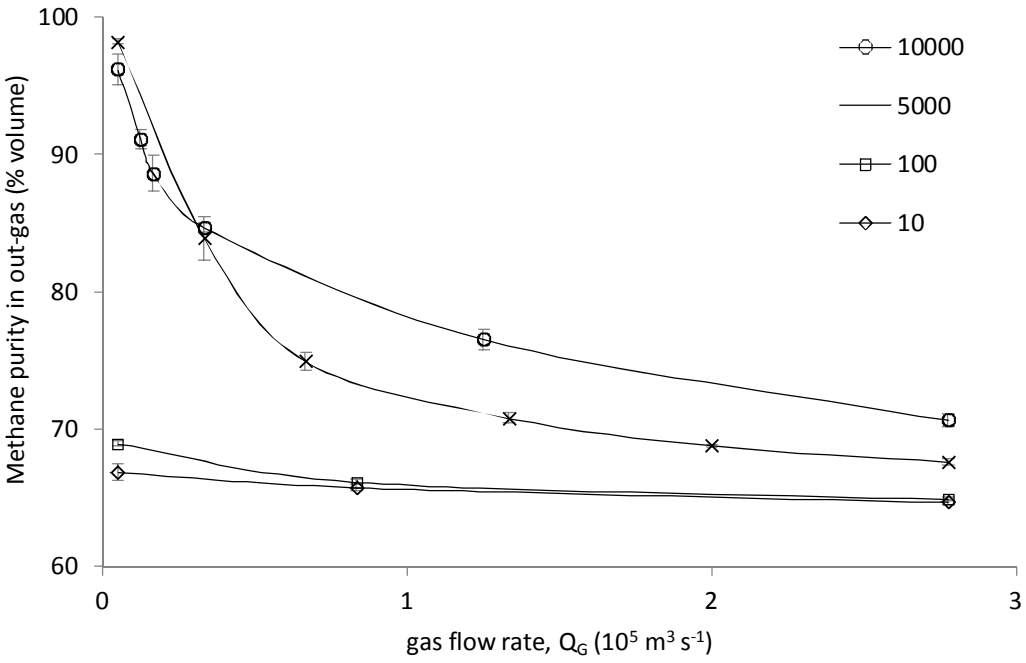


Fig. 2. Influence of pH and temperature upon CO_2 flux (J_{CO2}) in analogue NH_3 absorbents with concentrations of: (a) 10000 g_{NH3} m^{-3}; (b) 1000 g_{NH3} m^{-3}; (c) 100 g_{NH3} m^{-3}; and (d) 10 g_{NH3} m^{-3} under fixed liquid and gas flow rates ($1.67x10^{-6}$ m^3 s^{-1} and $1.25x10^{-5}$ m^3 s^{-1} respectively).



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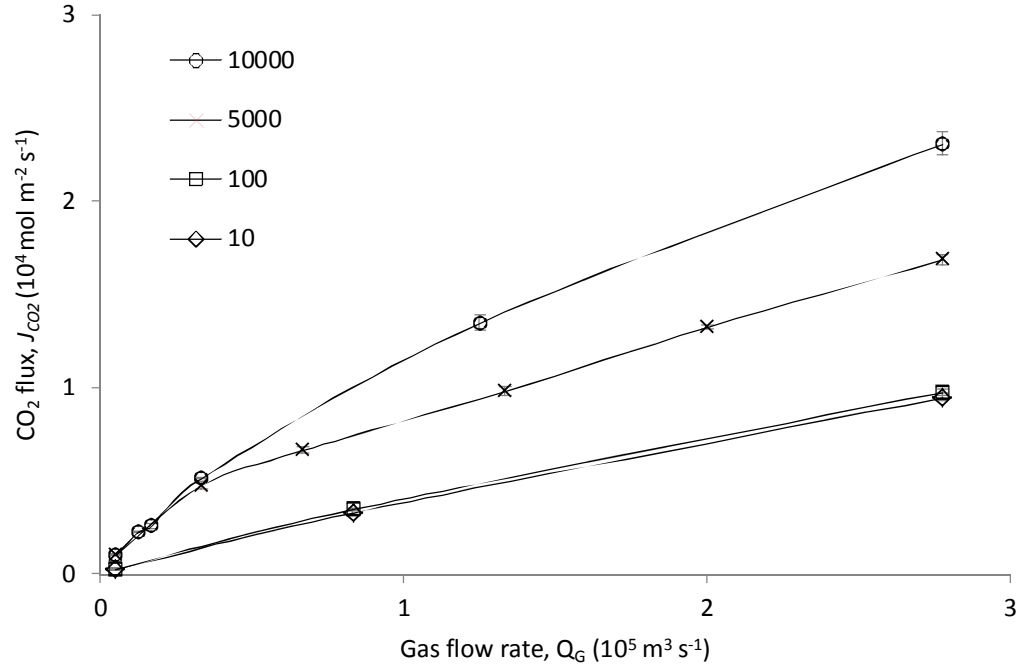


(b)

Fig. 3. Effect of variable gas flow rate (Q_G , 0.05 x 10^{-5}-2.8 x 10^{-5} m^3 s^{-1}) upon: (a) methane purity in the gas exiting the HFMC; and (b) CO_2 flux. Fixed liquid flow rate (Q_L) 6.7 x 10^{-6} m^3 s^{-1}. Analogue absorbent NH_3 concentrations ranging 10 to 10000 g_{NH3} m^{-3}.

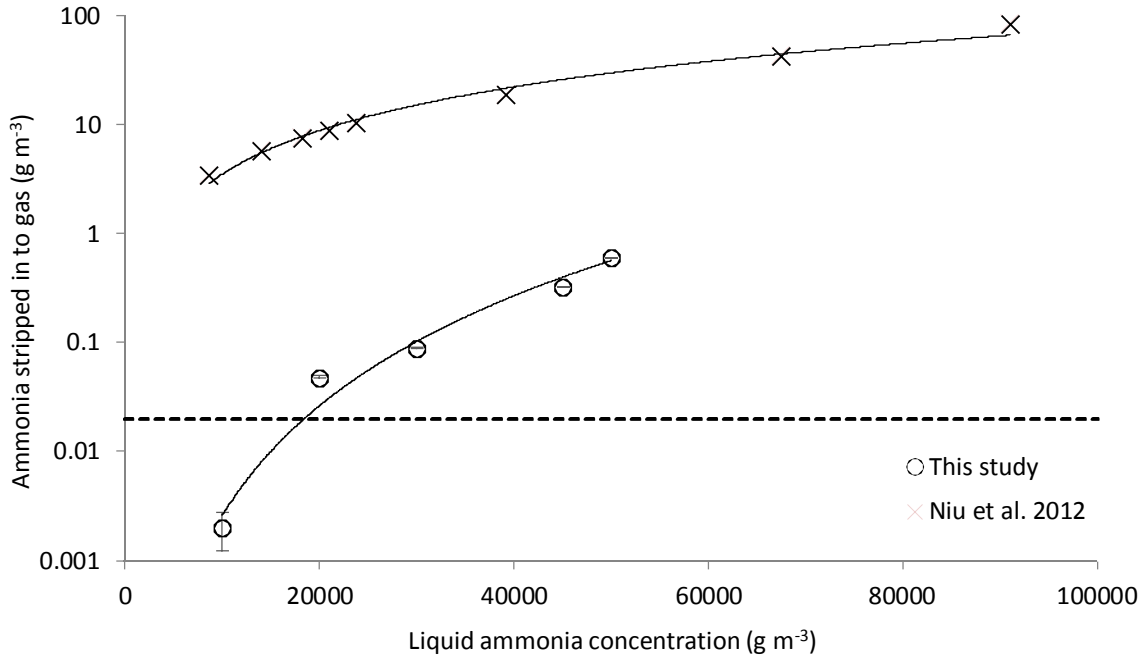


Fig. 4. Effect of increasing NH_3 concentration on NH_3 slip into the gas phase. Fixed liquid and initial gas flow rates (Q_L , 1.67 x 10^{-6} m^3 s^{-1}; Q_G , 1.25 x 10^{-5} m^3 s^{-1}). The dotted line represents the concentration limit for NH_3 in biomethane for gas-to-grid and vehicular use (0.02 g m^{-3}).

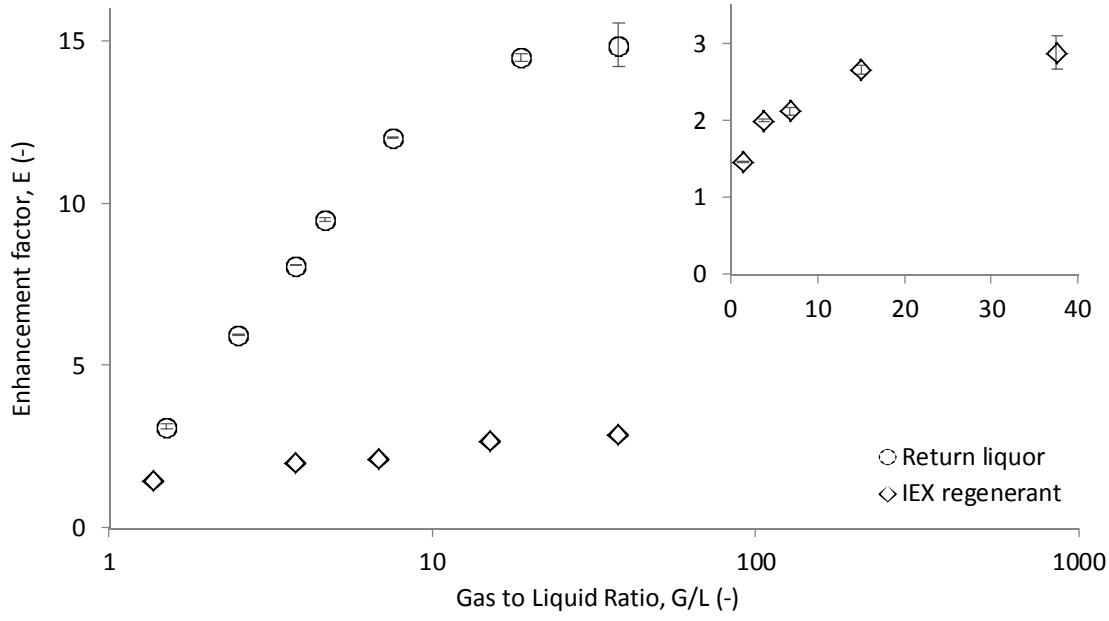
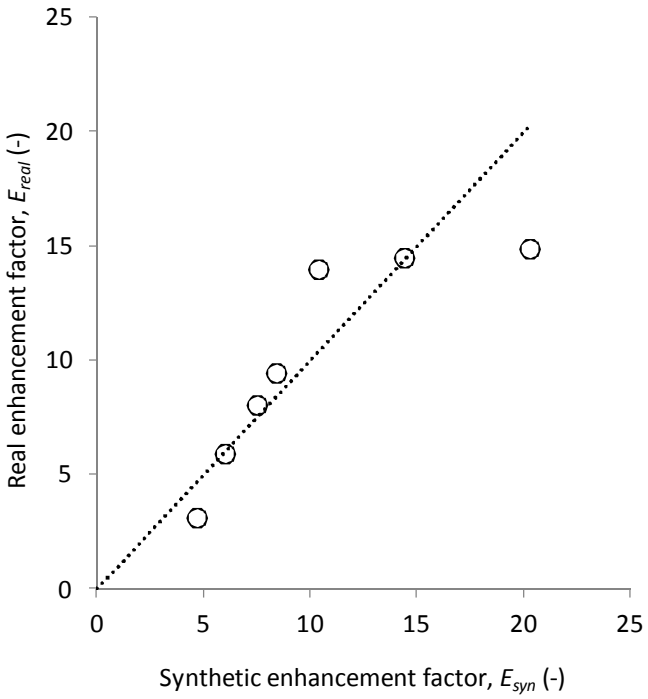


Fig. 5. Effect of variable gas-to-liquid ratio upon enhancement factor (E, dimensionless), determined by ratio of CO_2 flux for return liquor or IEX regenerant (2325 g m^{-3} and 447 g m^{-3} respectively) against CO_2 flux in DI water.



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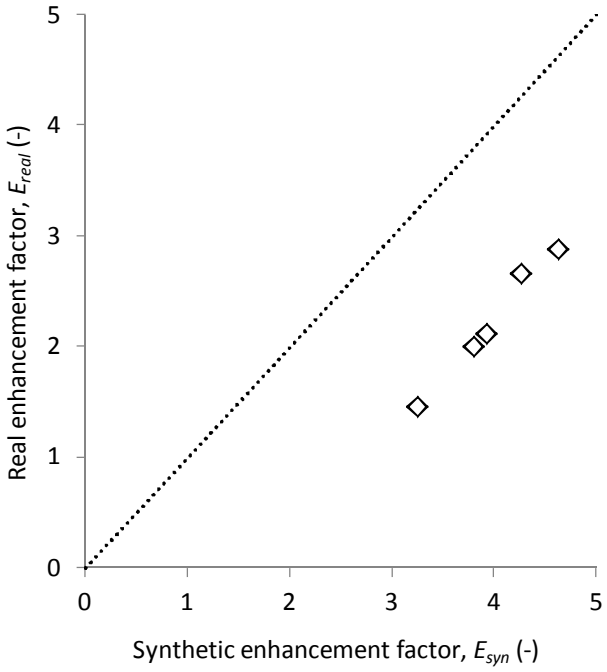

(b)

Fig. 6. Effect of variable liquid flow rate (Q_L, 0.17 x 10^{-5}-1.7 x 10^{-5} m^3 s^{-1}) upon enhancement factor (E, dimensionless) determined by ratio of CO_2 flux for (a) return liquor or (b) IEX regenerant against CO_2 flux in DI water. Parity line plotted for reference (dotted line).

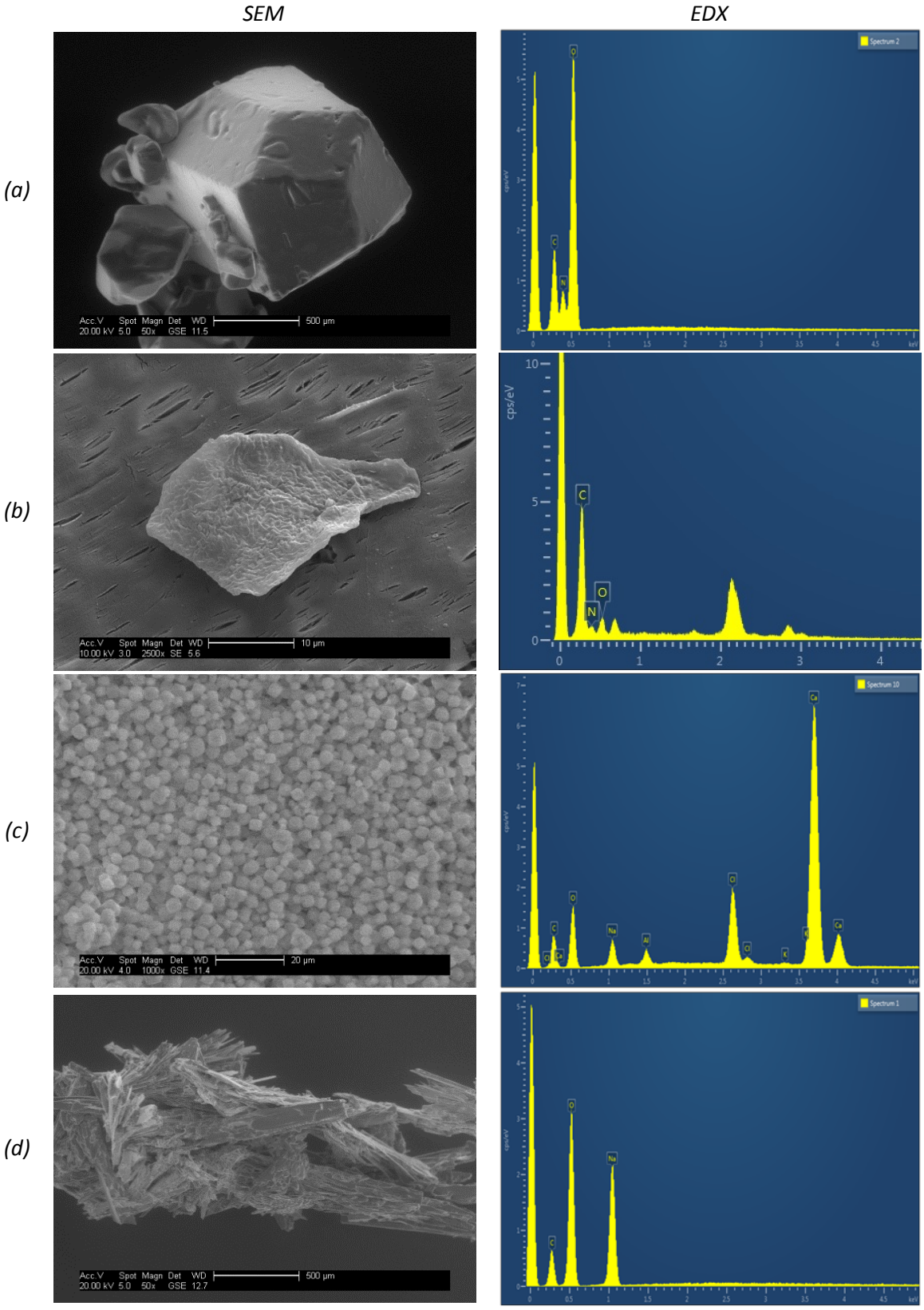

Fig. 7. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectra of ammonium bicarbonate formed in situ by bubbling gas through bulk solvent and by nucleation on the membrane surface (a & b respectively), in situ calcium carbonate from IEX regenerant (c), and sodium bicarbonate from dehydration of return liquor saturated by CO_2 (d).

Table 1. Molecular masses and pure water solubilities of several binary carbonate and bicarbonate salts.

Name	Formula	Molecular mass g mol^{-1}	Water solubility mol L^{-1} (20 °C)	Solubility product pK_{sp}	Ref.
Ammonium bicarbonate	NH_4HCO_3	79.06	2.24	-0.70	Trypuć *et al.*, (1998)
Sodium bicarbonate	$NaHCO_3$	84.01	0.67	0.35	Trypuć *et al.*, (1998)
Calcium carbonate	$CaCO_3$	100.09	$5.8x10^{-5}$	8.47	Haynes, (2012)

Table 2. Characterisation of raw wastewater matrices and subsequently derived absorbents

Wastewater matrix	pH -	NH_4-N g m^{-3}	Conductivity mS cm^{-1}	COD g m^{-3}	TSS kg m^{-3}
Raw return liquor	8.3	2460	4.9	8400	5.6
Raw IEX regenerant	7.2	477	76.6	1060	
Filtered return liquor	11	2325	5.1	7900	4.6
Filtered IEX regenerant	11	477	76.6	1060	

Table 3. Characterisation of raw wastewater matrices and subsequently derived absorbents

Scenario	Biogas utilisation	CHP[c]	Upgrade[c]	NH_4HCO_3[d]	Aeration[a]	Total	Net gain[e]
Baseline	100% CHP 0% Upgrade	5.7	N/a	N/a	-2.9	2.8	N/a
Partial upgrading[g]	78% CHP 22% Upgrade[b]	4.4	2.1	N/a	-2.4	4.1	+1.3
Partial upgrading and recovering NH_4HCO_3[g]	78% CHP 22% upgrade[b]	4.4	2.1	0.9	-2.4	5.0	+2.2
Full upgrading[h]	0% CHP 100% Upgrade	N/a	9.5	N/a	N/a[f]	9.5	+6.7
Full upgrading and recovering NH_4HCO_3[h]	0% CHP 100% Upgrade	N/a	9.5	4.0	N/a[f]	13.5	+10.7

N/a - Not applicable to the specific scenario. CHP - Combined heat and power. [a]Aeration cost based solely on nitrification demand using: 4.34 kgO_2 kgN^{-1}, oxygen transfer efficiency 15%, water depth 5 m. [b]Biogas split based on ammonia availability in return liquor using concentration and flow from Jaffer et al. (2001). [c]Biogas costs based on Read and Hofmann (2011). [d]Ammonium bicarbonate wholesale value based on Hernandez et al. (2013). [e]Financial gain over baseline scenario (100% CHP plus nitrification). [f]Assumes 100% NH_4 utilisation for biogas upgrading, where mass balance across the example works demonstrates a mole ratio of 1.2:1 NH_4^+-N: CO_2 which indicates an excess of NH_4^+-N given the stoichiometric conversion of NH_4^+ into NH_4HCO_3 is 1:1. [g]Using return liquors. [h]Using IEX regenerant following wastewater treatment.

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

McLeod, Andrew J.; Jefferson, Bruce; McAdam, Ewan J.

2014-09-18
IWA Publishing
http://dx.doi.org/10.1016/j.watres.2014.09.010
Andrew McLeod, Bruce Jefferson, Ewan J. McAdam, Biogas upgrading by chemical absorption using ammonia rich absorbents derived from wastewater, Water Research, Volume 67, 15 December 2014, Pages 175-186

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