

CRANFIELD UNIVERSITY

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CHEMICALLY REACTIVE MEMBRANE CRYSTALLISATION
REACTOR FOR CO₂ SEPARATION AND AMMONIA RECOVERY

SCHOOL OF ENERGY, ENVIRONMENT AND AGRIFOOD
Cranfield Water Science Institute

PhD

Academic Year: 2014 - 2018

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October 2018

Abstract

This thesis introduces an integrated system comprised of a thermal stripper and a hollow fibre membrane contactor (HFMC) for concentration of ammonia (NH_3) from wastewater and control of chemically mediated membrane crystallisation of ammonium bicarbonate (NH_4HCO_3) to enable simultaneous ammonia removal, biogas upgrading (through carbon dioxide, CO_2 , separation), fertilizer production and harvesting within a single and economical process. In particular, recirculation of a refrigerated aqueous ammonia absorbent within the chemically reactive membrane crystallisation reactor (CR-MCr), demonstrated to reduce free ammonia introduction into the gas phase and convert NH_3 into non-volatile ammonium (NH_4^+), thus preventing gas side crystallisation, which leads to process blockage, and promoting liquid side crystallisation of NH_4HCO_3 . The thermodynamic and kinetics of the CO_2 - NH_3 - H_2O system have also been investigated to facilitate shell-side (liquid side) crystallisation of the ammonium salt within the CR-MCr. A transition from large (PTFE) to tight (PP) membrane pore size material obviated wetting and enabled consistent and reproducible NH_4HCO_3 crystallisation on the membrane-liquid interface. The X-ray diffraction analysis of the crystals produced with the absorbent recovered from return liquor, indicated the products to be reasonably pure ammonium bicarbonate, which evidenced the reduction in cationic competition through application of pre-treatment. A comparison between batch and membrane crystallisation kinetics demonstrated the hydrophobic fibre to underpin primary heterogeneous nucleation in an unseeded supersaturated solution and laminar regime, decoupled from secondary nucleation and growth, which mainly occur in the bulk downstream, contrarily to batch crystallisation where primary and secondary homogeneous nucleation are followed by growth and agglomeration, promoted by enhanced mixing and CO_2 bubbling, within the same environment. As a result, an increasing population density at raising levels of supersaturation has been observed in the first case, against a declining population density vs. supersaturation in the latter. A slower pH transient in membrane crystallisation, compared with conventional batch operation, could be balanced by raising the membrane-liquid interfacial surface area, which would increase the nucleation rate, whilst the yield of ammonia removal could be maximised up to 99% (ammonium bicarbonate solubility limit) through an increase in absorbent pH, which would eliminate the partial conversion of solute (bicarbonate) into carbonic acid, caused by a dynamic reaction zone, therefore closing the gap to control nucleation and growth in membrane crystallisation of ammonium bicarbonate.

Acknowledgements

Firstly sincere thanks to my supervisor Ewan McAdam for his guidance and encouragement in developing this project over the past 4 years.

I must extend my gratitude to EPSRC and to my sponsors at Anglian Water, Northumbrian Water and Severn Trent Water for their financial support and in particular to their representatives at my regular meetings: Adam Brookes, Andrew Moore, and Peter Vale for their enthusiasm toward the project. I would like to thank all my friends in Cranfield Water Science Institute, particularly Olivier, Farhad, Joana, Judith, Edwina, Kanming, Sonia and Matthew, and all the Italian friends in Bedford for their support and good humour. Thanks also to my STREAM friends, in particular those at cohort VI.

Thanks to my family, particularly mum and grandparents for their relentless aid and thank to my psychotherapist Francesco Tortono, I would have never been so motivated without your help and encouragement. Thanks to my girlfriend's family, in particular Dawn for her enthusiasm and encouragement. Finally, Jessie, thanks for always supporting me, since I met you this project has gone from the bottom to the top.

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Abbreviations

C/C*	Supersaturation ratio
CCS	Carbon capture and storage
CHP	Combined heat and power
CR-MCr	Chemically reactive membrane crystallisation reactor
CSA	Cross sectional area
DI	De-ionised
EDX	Energy dispersive spectroscopy
FITs	Feed-In Tariffs
G/L	Gas to liquid ratio
HFMC	Hollow fibre membrane contactor
ID	Inner diameter
kWh	Kilowatt hour
mol	Moles
OD	Outer diameter
PE	Population equivalent
PP	Polypropylene
PSA	Pressure swing absorption
PTFE	Polytetrafluoroethylene
Re	Reynolds number
RH	Relative humidity
RHI	Renewable heat incentive
ROC	Renewables Obligation Certificate
RTFO	Renewable Transport Fuel Obligation
SBBR	Semi-batch bubble reactor
SCBR	Semi-continuous bubble reactor
SEM	Scanning electron microscopy
SP	Single pass
SVP	Saturated vapour pressure
wt.	Weight
WWTW	Wastewater treatment works
XRD	X-Ray diffraction

Chemical formulae

NH_4HCO_3	Ammonium bicarbonate
$\text{NH}_2\text{COONH}_3$	Ammonium carbamate
$(\text{NH}_4)_2\text{CO}_3$	Ammonium carbonate
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulphate
CaCO_3	Calcium carbonate
NH_2COOH	Carbamic acid
H_2CO_3	Carbonic acid
HCl	Hydrochloric acid
NaHCO_3	Sodium bicarbonate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
H_2SO_4	Sulfuric acid
H_2O	Water

Cations

H^+	Hydron
Na^+	Sodium
Ca^{2+}	Calcium
NH_4^+	Ammonium

Anions

HCO_3^-	Bicarbonate
NH_2COO^-	Carbamate
CO_3^{2-}	Carbonate
Cl^-	Chlorine
OH^-	Hydroxide

Gases

H ₂	Hydrogen
H ₂ O	Water
CH ₄	Methane
N ₂	Nitrogen
O ₂	Oxygen
NH ₃	Ammonia
CO ₂	Carbon dioxide
H ₂ S	Hydrogen sulfide

Solvents

NH ₃ (aq)	Aqueous ammonia
MEA	Monoethanolamine

Greek symbols

α	Relative fraction	-
γ	Surface tension	mN m ⁻¹
ε	Porosity	%
θ	Contact angle	°
μ	Dynamic viscosity	mPa s ⁻¹
ρ	Mass density	g cm ³
Ω	Electrical resistance	Volts per amp

Notations

a	Specific surface area	$\text{m}^2 \text{ m}^{-3}$
A_m	Membrane surface area	m^2
C	Celsius	
C^*	Concentration at supersaturation	$\text{mol} / \text{g L}^{-1}$
d_h	Characteristic length	m
E	Enhancement factor	-
G	Gibb's free energy	kJ mol^{-1}
J	Joules	
J	Flux	$\text{mol m}^2 \text{ s}^{-1}$
K_G	Gas mass transfer coefficient	m s^{-1}
K_a	Acid dissociation constant	-
K_L	Liquid mass transfer coefficient	m s^{-1}
K_m	Membrane mass transfer coefficient	m s^{-1}
K	Kelvin	
L	Litre / contactor length	
M_r	Relative molecular mass	g mol^{-1}
N	Newton	
P	Pressure	Bar
Q_G	Gas flow rate	$\text{m}^3 \text{ s}^{-1}$
Q_L	Liquid flow rate	$\text{m}^3 \text{ s}^{-1}$
R	Molar gas constant	$\text{m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1} / \text{cal K}^{-1} \text{ mol}^{-1}$
T	Temperature	$^{\circ}\text{C} / \text{K}$
V_G	Gas velocity	m s^{-1}
V_L	Liquid velocity	m s^{-1}

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Chapter 1

Introduction

1.1 Waste water treatment power consumption and renewable energy incentives

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Energy efficiency improvement can be achieved through:

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- (c) Integral Energy Management, including use of biogas from anaerobic digestion (AD) for combined heat and power production (CHP), heat recovery for sludge drying or incineration, adoption of renewable energies (such as wind and solar energy).

To promote the usage of renewable energy in the UK and meet the target of 15% of the total energy generation from renewable sources by 2020, the UK Government introduced a number of financial incentive mechanisms, including (Gover et al., 2012):

- (1) The Renewables Obligation Certificates (ROCs): one of the major supports for large-scale renewable electricity projects in the UK. They were introduced in 2002 in England, Wales and Scotland, and consisted in obligation certificates issued for renewable electricity produced in order to stimulate increasing electricity supply from renewable sources. The ROCs closed on 31st March 2017 (Gray et al., 2018).
- (2) Renewable Transport Fuel Obligation (RTFO): commenced on 15th April 2008 to reduce CO₂ emissions from fuel used for transport purposes by incentivisation of renewable fuels (Norman et al., 2018).
- (3) Feed-In Tariffs (FITs): a scheme introduced on 1st April 2010 that offers payments to small-scale electricity projects such as households and utilities that produce renewable electricity up to 5MW.
- (4) Renewable Heat Incentives (RHI): a UK Government scheme launched on 9th April 2014, which encourages the uptake of renewable heat technologies among householders, communities and businesses through financial incentives.

Biogas produced from the decomposition of organic waste in AD is a type of biofuel primarily formed by carbon dioxide (~40%) and methane (~60%), and can be adopted through cogeneration in combined heat and power for electricity and heat production or for biogas upgrading into biomethane for injection in the gas grid as a natural gas substitute. Originally, water utilities adopted the whole biogas produced for CHP, but with the end of ROCs incentives and the introduction of RTFO and RHI, the revenues expected from refinement of biogas into biomethane exceeded those for electricity production by 70%, inducing a significant transition towards biogas upgrading operations within the UK (Read and Hofmann, 2011).

1.2 Biogas upgrading technologies

Among the several established biogas upgrading technologies, the most widely implemented are:

- (1) Absorption systems: they include both physical and chemical absorption methods. The first introduces a physical absorbent (such as water or polyethylene glycol), which selectively removes carbon dioxide (CO₂) from the biogas due to its greater solubility into the solution compared with methane (CH₄) (Kapoor et al., 2017, Hoyer K., 2016).

Due to the ready availability of water and relative simplicity of the technology, water scrubbers cover 36% of global biogas upgrading plants (corresponding to 179 units) and process a total volumetric flow of biogas of $190,500 \text{ m}^3 \text{ h}^{-1}$, against only $52,000 \text{ m}^3 \text{ h}^{-1}$ with organic physical scrubbers (IEA, 2016). On the other hand, chemical absorption provides process intensification through the adoption of amine solutions, such as monoethanolamine (MEA), typically used as absorbent (McLeod et al., 2014). However, MEA's high regeneration energy demand ($4 \text{ GJ tonCO}_2\text{removed}^{-1}$) and MEA losses ($6.5 \text{ kgMEA tonCO}_2\text{removed}^{-1}$) due to its oxidative degradation, limited large scale deployment of chemical absorption technology (Steeneveldt et al., 2006; Yang et al., 2013). For this reason chemical absorption uptake is approximately half that for water scrubbing, with 91 plants and $90,600 \text{ m}^3 \text{ h}^{-1}$ of biogas refined (IEA, 2016).

(2) Permeable membrane: the process involves the penetration of permeate (biogas) through the membrane, which is typically polymeric (Scholz et al., 2012). Differently from hydrophobic membrane operations, where chemical absorption enhances CO_2 separation (Makhloufi et al., 2014), in this case the separation principle is based on various solubility and particle size of the gaseous species within the biogas into the membrane material (Miltner et al., 2017). The biogas is fed to a membrane module at pressures between 5 and 30 atm. Small size molecules in the biogas such as H_2S , CO_2 and H_2O preferentially pass through the membrane into the permeate side (at low pressure), while bigger molecules such as CH_4 leave the membrane module as the retentate with a purity up to 99.5% (Miltner et al., 2012). The advantages of this technology include compact systems, low maintenance, and less skilled labour compared with chemical absorption process. However key drawbacks are high cost of the membrane and its degradation with time, which currently limits its deployment to small scale installations (Sahota et al., 2018).

(3) Pressure swing adsorption processes (PSA): based on selective adsorption of gas molecules at high pressure (3-8 atm) on solid surfaces (usually activated carbon or zeolites) according to their molecular size, it is then followed by adsorbent regeneration, where pressure is reduced to atmospheric level (Sahota et al., 2018). Main advantages of this technology are the compactness of the equipment, low capital cost and energy demand. Nevertheless, low methane recovery penalises this method when compared with previous processes (Augelletti et al., 2017). Globally, 84 PSA plants are in operation, with approximately $85,600 \text{ m}^3 \text{ h}^{-1}$ of biogas treated (IEA, 2016).

Even though water scrubbing is currently the most implemented biogas upgrading method at WWTWs, the identification of ammonia as a valid substitute of MEA for chemical absorption in packed columns stimulated the interest for both water utilities and carbon capture and storage applications (CCS). In particular, NH_3 does not degrade, it requires 75% less energy

than MEA for regeneration and provides three times higher absorption capacity (Makhloufi et al., 2014). Nevertheless, aqueous ammonia high saturated vapour pressure introduces NH_3 slip in the atmosphere (Kozak et al., 2009), thus requiring a washing section at the outlet of the absorption column to meet ammonia emission limits, which would raise both capital cost and energy demand (Shuangchen et al., 2013). Investigation in alternative gas-liquid contacting technology to facilitate absorption led to the recognition of hollow fibre membrane contactors (HFMCs) as one of the most promising strategies for process intensification and ammonia slip reduction (Drioli et al., 2001).

1.3 Project development

The hollow fibre membrane contactors technology has been tested for the first time for CCS applications by Qui and Cussler in the 1980s (Qi and Cussler, 1985 a and b). Zhao et al., (2016) reviewed and summarized advantages and disadvantages of membrane contactors compared with conventional absorption columns (Figure 1.2).

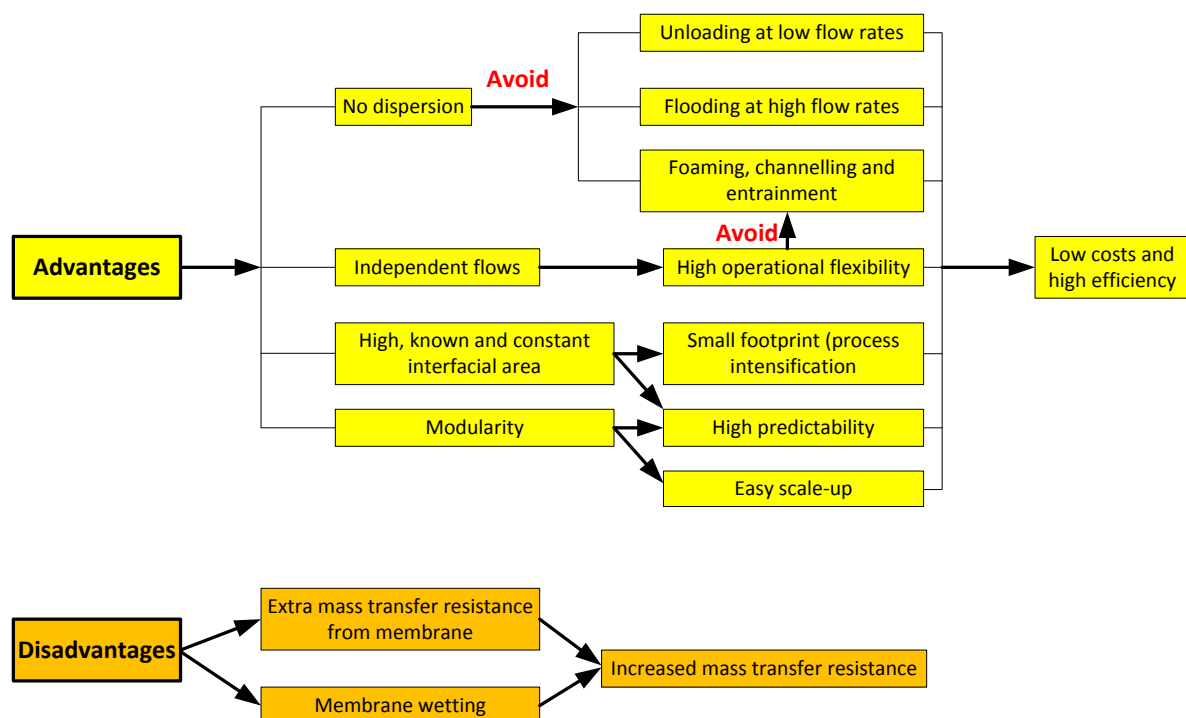


Figure 1.2 Summary of the advantages and disadvantages of the membrane contactors for ammonia based CO_2 absorption compared with conventional absorption columns (Zhao et al., 2016).

Specifically, HFMCs offer an indirect contact between gas and liquid, mitigating ammonia slip up to 2-fold if compared with conventional packed columns (McLeod et al., 2014) and present up to 30 times higher interfacial area, which leads to significant process intensification and

counterbalances the additional mass transfer resistance introduced by the membrane (Belaissaoui and Favre, 2018). However, the major issues encountered using membrane contactors for CCS were wetting (feed liquid passage through the membrane pores) and precipitation of ammonium bicarbonate (NH_4HCO_3) in the gas side, which increased mass transfer resistance and caused CO_2 flux instability (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018). McLeod et al., (2015) introduced a chemically reactive membrane crystallisation reactor (CR-MCr), proposing that controlled nucleation and growth of the CO_2 - NH_3 reaction product on the shell-side (liquid side) of the HFMC would offer the unique opportunity for water industries to remove nitrogen from NH_3 rich wastewater, upgrade biogas up to 98% pure methane and recover solid fertilizer by-product in a single process. Differently from physical membrane crystallisation, generally driven by a thermal gradient to initiate nucleation (Cheng et al, 2008), in their work McLeod et al., (2015) chemically induced shell-side nucleation of ammonium bicarbonate through counter diffusion of solute (carbon dioxide) from the gas phase to the crystallising fluid (aqueous ammonia), where the driving force was the enhancement in solubility provided by the reaction between $\text{CO}_2(\text{aq})$ and $\text{NH}_3(\text{aq})$ (Wang et al., 2011). Curiously, ammonia based CO_2 absorption studies undertaken within batch reactors, spray towers and packed columns observed ammonium bicarbonate precipitation at NH_3 concentration above $4 \text{ molNH}_3 \text{ L}^{-1}$, while liquid side precipitation of the ammonium salt occurred within the PTFE HFMC at $2 \text{ molNH}_3 \text{ L}^{-1}$, which suggests that the introduction of the membrane as a substrate facilitates an enhanced nucleation potential (Table 1.1).

Whilst evidencing a preference for shell-side over lumen-side (gas side) crystallisation, the mechanism to promote consistent and reproducible liquid side nucleation, growth and recovery of the CO_2 - NH_3 reaction product has not been yet described (McLeod et al., 2015). Additionally, several studies tried to recover a crystalline product such as NH_4HCO_3 or $(\text{NH}_4)_2\text{SO}_4$ from environmental solvents through reaction of ammonia and a counter oxyanion. Nevertheless, the concentration of the product was below its solubility limit, thus requiring a further step to proceed crystallisation, such as introduction of an antisolvent or a thermal gradient, which increases capital cost and process complexity (Ukwuani and Tao, 2016; He et al., 2017). Similarly, McLeod et al. (2014) achieved precipitation of a crystalline product through CO_2 absorption in NH_3 rich wastewater within a HFMC, followed by thermal treatment. Due to the high solubility of the ammonium bicarbonate (the preferred reaction product) and the presence of other cations, precipitation of sodium bicarbonate and calcium carbonate occurred, which can be ascribed to their thermodynamic preference for precipitation over NH_4HCO_3 . Even though not explicitly evidenced, Teichgraber and Stein (1994) proposed the adoption of thermal packed column stripping for environmental solutions treatment,

Table 1.1 Review of ammonia based CO₂ capture studies using various absorption technologies

Ref.	Operating conditions			Absorbent					Feed gas				Salt precipitation
	Technology type	Priming volume	Inner diameter	[NH ₃]	[NH ₃]	C* ^a	pH	T	[CO ₂]	T	Gas velocity	Liquid velocity	
				g L ⁻¹	mol L ⁻¹	mol L ⁻¹	-	°C	%	°C	m s ⁻¹	×10 ³ m s ⁻¹	
McLeod et al., 2015	PTFE HFMC ^c	2.5 ×10 ⁻³	1.5 ^b	34	2	2.4±0.2	>11	20	50	20	0.93	20	Liquid side
	PTFE HFMC ^c	2.5 ×10 ⁻³	1.5 ^b	51-85	3-5	2.4±0.2	>11	20	50	20	0.93	20	Gas side
Yeh et al., 2005	SBBR ^d	1.5	-	68-132	4-7.8	2.8±0.3	8.8-9.6	27	15	27	1.76	0	Observed
Yeh and Bai, 1999	SCBR ^e	0.2	60	68-306	4-18	2.8±0.3	>11	25	8-16	25	0.5-2.4	0	Observed
	SCBR ^e	0.2	60	252	14.8	1.9±0.1	>11	10	8-16	10	0.5-2.4	0	Observed
	SCBR ^e	0.2	60	252	14.8	3.8	>11	40	8-16	40	0.5-2.4	0	Observed
Quing et al., 2011	Spray column	3.9	100	77	4.5	2.4±0.2	>11	20	15	20	0.02	0.3	Observed
	Spray column	3.9	100	77	4.5	>5.3	>11	55	15	55	0.02	0.3	Not observed
	Spray column	3.9	100	20	1.2	2.4±0.2	>11	20	15	20	0.04	0.4	Not observed
	Spray column	3.9	100	150	8.8	2.4±0.2	>11	20	15	20	0.04	0.4	Observed
	Packed bed	3.9	100	77	4.5	2.4±0.2	>11	20	15	20	0.02	0.3	Observed
	Packed bed	3.9	100	77	4.5	>5.3	>11	55	15	55	0.02	0.3	Not observed
	Packed bed	3.9	100	20	1.2	2.4±0.2	>11	20	15	20	0.04	0.4	Not observed
	Packed bed	3.9	100	150	8.8	2.4±0.2	>11	20	15	20	0.04	0.4	Observed
Rotunno et al., 2017	Water scrubber	5 ×10 ³	800	0.01	0.0004	1.6±0.1	8	5	25-60	60	0.07	0.02-0.006	Not observed
	Water scrubber	5 ×10 ³	800	0.01	0.0004	2.8±0.3	8	25	25-60	60	0.07	0.02-0.006	Not observed

^a Ammonia concentration at supersaturation for given absorbent temperature (Perry and Green, 2007; Trypuc and Kielkowska, 1998; PubChem, 2004).^b Fibre inner diameter.^c Hollow fibre membrane contactor.^d Semi-batch bubble reactor with mixer.^e Semi-continuous bubble reactor.

where separation and concentration of the ammonia fraction could be achieved to deliver a final concentration of up to $130 \text{ gNH}_3^+ \cdot \text{N L}^{-1}$ ($\approx 9 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, ammonia solubility limit in water at 70°C , O'Neil et al., 2013), which is considerably higher than has been previously identified in the literature to date. We propose that with the use of this technology to pre-concentrate ammonia from return liquors, a reactive solution in similar concentration to those employed for CCS can be produced, which is sufficiently concentrated to enable direct crystallisation of the reaction product, CO_2 separation and product conversion in a single stage HFMC process. Since thermal separation favours the volatile fraction (ammonia, NH_3), we also suggest that pre-treatment of return liquor will limit ionic competition issues encountered by McLeod et al. (2014), thus facilitating in this case ammonium bicarbonate thermodynamic preference as reaction product formed with ammonia recovered from wastewater.

1.4 Aim and objectives

The aim of the thesis is to demonstrate that an integrated system comprised of thermal stripper and HFMC enables concentration of aqueous ammonia from wastewaters to facilitate simultaneous CO_2 absorption, ammoniacal nitrogen removal and production of ammonium bicarbonate as marketable product within a single and low-cost process. A pictorial representation of the thesis, including the integrated system proposed, is illustrated in Figure 1.3.

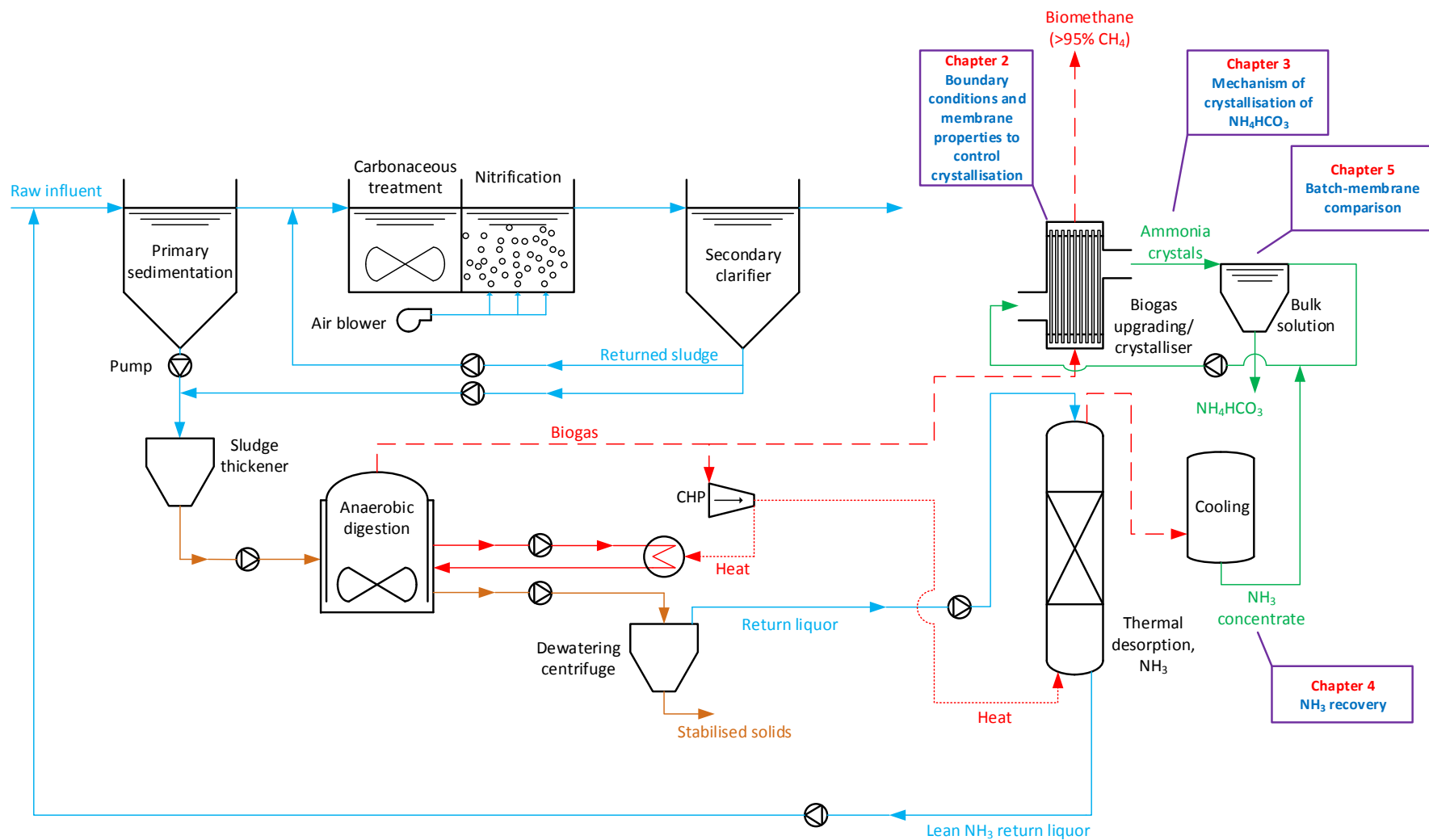


Figure 1.3 Pictorial representation of the thesis including a proposed approach for simultaneous biogas upgrading, NH₃ removal from return liquor and ammonium bicarbonate production.

To address this overall aim, the following objectives have been developed:

- (1) Determine the boundary conditions and membrane properties to avoid lumen-side (gas side) crystallisation and promote controlled nucleation and growth of the $\text{CO}_2\text{-NH}_3$ reaction product on the membrane-absorbent interface.
- (2) Explore the thermodynamic and kinetics of the gas-liquid-solid equilibria in the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system to establish the mechanism needed to induce consistent and reproducible shell-side (liquid side) nucleation and growth of ammonium bicarbonate within a CR-MCr.
- (3) Identify the boundary conditions to concentrate ammonia from concentrated wastewater, explore CO_2 absorption and crystallisation behaviour of the recovered ammonia solution compared with synthetic absorbent of equal reactivity, and prove NH_4HCO_3 formation, to evidence reduced cation competition in the solution recovered compared with raw return liquor.
- (4) Demonstrate, through comparison of membrane and batch crystallisation kinetics, that primary heterogeneous nucleation occurs at the membrane-solution interface in membrane crystallisation, reducing the Gibbs free energy barrier for nucleation, and is decoupled by secondary nucleation and growth, contrarily to batch operation, where primary and secondary homogeneous nucleation are followed by growth and agglomeration in the same system.

1.5 Thesis structure

The chapters of the thesis have been formatted as journal papers, which correspond to established research objectives, including four technical papers (Chapter 2, 3, 4 and 5) (Figure 1.4). Chapter 2, *“Identifying boundary conditions and membrane properties to promote crystallisation of ammonia- CO_2 reaction products in membrane contactors for biogas upgrading”*, investigates the operational conditions, such as gas-liquid temperature and absorbent in single pass or recycle mode to prevent wetting and lumen side crystallisation. Furthermore, it compares membranes of different pore sizes to facilitate sustained shell-side crystallisation of ammonium bicarbonate in CR-MCr. Chapter 3, *“Chemically reactive membrane crystallisation reactor for $\text{CO}_2\text{-NH}_3$ absorption and ammonium bicarbonate crystallisation: Kinetics of heterogeneous crystal growth”*, examines the chemistry of the solid-liquid equilibria in the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system and determines the kinetics of heterogeneous nucleation and crystal growth, which evidence the mechanism for chemically reactive membrane crystallisation. Chapter 4, *“ $\text{NH}_3(\text{aq})$ recovery from raw return liquor to induce in situ NH_4HCO_3 shell-side crystallisation and harvesting during CO_2 absorption within an hollow fibre membrane contactor”*, identifies and uses the boundary conditions required to concentrate ammonia from wastewater through thermal stripping, examines the absorption behaviour of

recovered ammonia compared with synthetic equivalent, evidences the formation of good quality NH_4HCO_3 and consequent reduction in cationic competition, due to pre-treatment. Chapter 5, “*Evidencing heterogeneous nucleation in membrane crystallisation through comparison with conventional batch crystallisation kinetics*”, demonstrates the introduction of the membrane to induce primary heterogeneous nucleation at the membrane-liquid interface, thus reducing the Gibbs free energy barrier for nucleation, disconnected by secondary nucleation and growth downstream, contrarily to batch crystallisation, where primary and secondary homogeneous nucleation, growth and agglomeration occur in the same domain. Chapters 6 and 7 include an overall discussion of the thesis, coupled with conclusions and proposed future work.

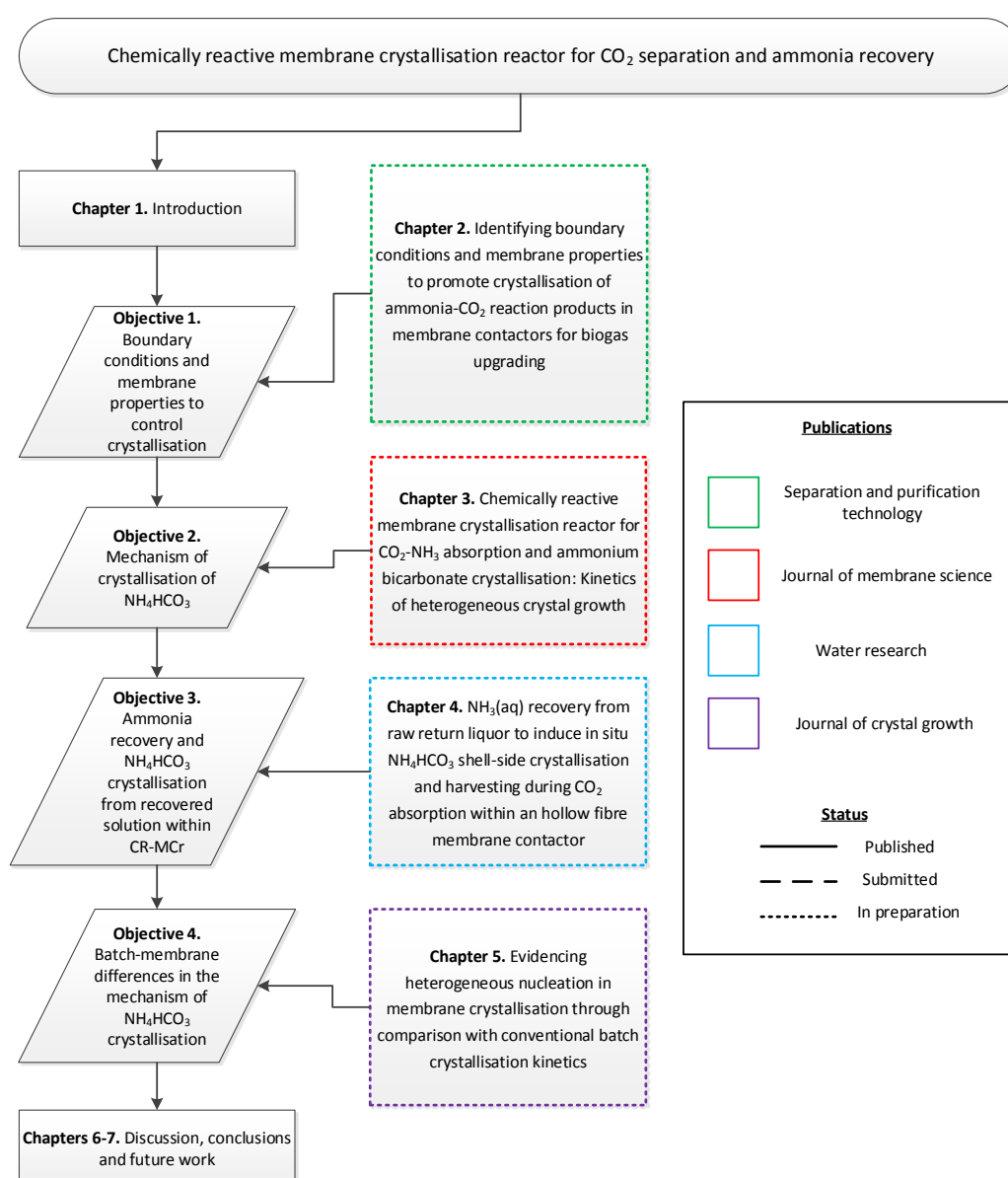


Figure 1.4 Thesis plan

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Chapter 2

Identifying boundary conditions and membrane properties to promote crystallisation of ammonia-CO₂ reaction products in membrane contactors for biogas upgrading

For submission to: Separation and Purification Technology

Identifying boundary conditions and membrane properties to promote crystallisation of ammonia-CO₂ reaction products in membrane contactors for biogas upgrading

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Abstract

A chemically reactive membrane crystallisation process for enhanced carbon dioxide (CO₂) absorption into aqueous ammonia (NH₃) has been upgraded to prevent process blockage and promote sustained heterogeneous nucleation, growth and harvesting of the reaction product ammonium bicarbonate at the membrane-solvent interface. Aqueous ammonia absorbents (0.6 - 3 M) were initially used in single pass for CO₂ absorption, where gas flow obstruction due to ammonium bicarbonate formation in the lumen of the hollow fibre was observed. The suggested mechanism for lumen-side crystallisation was ammonia slip into the gas phase, due to its high saturated vapour pressure, which can be suppressed in favour of preferential shell-side nucleation and growth by (1) reducing absorbent temperature; (2) recirculating the absorbent to shift ammonia-ammonium equilibrium toward non-volatile ammonium. In addition, selection of a membrane with a tight and regulated pore structure dissipates solvent ingress into the pore, facilitating consistent and reproducible shell-side crystallisation. This was evidenced using a 3 M NH₃ chilled absorbent in recirculation on the shell-side of a tight pore structure hollow fibre, where lumen-side crystallisation was avoided in favour of controlled heterogeneous crystallisation on the liquid side, followed by collection in the bulk solution. Importantly, this work demonstrates that chemically reactive membrane crystallisation reactors (CR-MCr) offer a unique opportunity for water industries for concurrent biogas upgrading, nitrogen removal from environmental solvents, and reaction product recovery as a further economic value within a single and low-cost stage.

Keywords: *biogas; aqueous ammonia; membrane crystallisation; ammonium bicarbonate; heterogeneous nucleation*

2.1 Introduction

Anaerobic digestion (AD) produces biogas comprising a 60:40 mixture of methane (CH₄) and carbon dioxide (CO₂). Through removal of CO₂ and other trace gases, biogas can be converted into biomethane, which can be introduced into the national grid or used as an alternative vehicle fuel (Persson et al., 2007). Significant investment in biogas upgrading infrastructure has been undertaken, which in Europe has been underpinned by governmental incentivisation policies such as the Renewable Heat Incentive and Renewable Transport Fuel Obligation in the UK (Read and Hofmann, 2011). Whilst upgrading technology was primarily based on physical absorption in the early installations (McLeod et al., 2014), there is now increased interest in chemical absorption systems, due to the process intensification provided.

The chemical reaction between ammonia and CO₂ has been successfully demonstrated to facilitate an absorption capacity for CO₂ three times higher than for conventional organic chemicals (Makhloufi et al., 2014), with the overall reaction provided by:

$$CO_2 + NH_3 + H_2O \leftrightarrow NH_4 HCO_3 \quad (1)$$

However, when applied to conventional packed column absorption technology, the high saturated vapour pressure of ammonia has been shown to introduce NH₃ slip into the gas phase, potentially demanding a further stage of gas phase treatment for clean-up (Shuangchen et al., 2013). Microporous hollow fibre membrane contactors (HFMC) can support the same overall chemical reaction, but the introduction of a hydrophobic membrane is used to initiate indirect contact between gas and liquid phases, with the CO₂ free to diffuse through the membrane pores (Heile et al., 2014). Whilst the membrane introduces an additional resistance to mass transfer, the higher specific surface area that can be achieved enables a process intensification of around 15 times (Belaissaoui and Favre, 2018). McLeod et al. (2014) identified around a two order of magnitude reduction in NH₃ slip using membrane contactors, which the authors proposed to be due to the development of laminar flow in the liquid phase which limited NH₃ transport to radial diffusion from the absorbent bulk to the boundary layer where chemical reaction proceeded. Latterly, simple recovery of an aqueous ammonia product from the gas-side of the membrane, has also been proposed to further limit slip (Villeneuve et al., 2018).

Early research of NH₃-CO₂ absorption in packed columns, focussed on forming ammonium bicarbonate (NH₄HCO₃) as the solid phase reaction product, to reduce the mass flow of stripper solution thereby reducing the heat requirement but also limiting NH₃ slip (Gazzani et al., 2014). However, problems in managing solid precipitate within the column was demonstrated to be difficult due to clogging (Sutter et al., 2015). Consequently, NH₃-CO₂ column studies typically seek to implement strategies to eliminate formation of a solid phase reaction product (Yu et al., 2012; Gazzani et al., 2014). In studies utilising hollow fibre membrane contactors to facilitate NH₃-CO₂ absorption, the formation of a problematic solid

phase reaction product has been observed to preferentially form in the gas-phase side of the membrane (typically the lumen-side), which blocked the lumen, subsequently limiting further gas-side flow (Table 2.1) (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018). To illustrate, Makhloufi et al. (2014) was unable to generate a stable CO_2 absorption flux due to lumen-side (gas side) NH_4HCO_3 precipitation, which has been similarly evidenced elsewhere (Cui and deMontigny, 2017).

Biogas upgrading facilities are ordinarily co-located with ammonia rich wastewater that have been demonstrated as a sustainable source for chemical reaction (McLeod et al., 2014; He et al., 2017). In addition to minimising chemical cost, stabilisation of a crystalline solid phase $\text{NH}_3\text{-CO}_2$ reaction product from this process, offers several advantages: (i) the need for absorbent regeneration is obviated, simplifying capital cost and unit operation; (ii) ammonia wastewater treatment is facilitated through CO_2 reaction rather than requiring conventional biological aeration, which will reduce energy demand; (iii) ammonium bicarbonate is formed as the final crystalline product, which possesses value as a commodity, as well as locking CO_2 into the solid phase, which introduces a local carbon benefit. McLeod et al. (2015) proposed that application of a hydrophobic microporous membrane could lower the activation energy sufficiently to induce heterogeneous nucleation and growth of the reaction product. It was proposed that the phase separation provided by the membrane, simplified the harvesting and recovery of the crystalline reaction product versus columns. Rather than membrane assisted crystallisation, which generally uses a thermal gradient to develop the concentration gradient needed to initiate nucleation (Cheng et al., 2008), the authors propose here a chemically reactive membrane crystallisation reactor (CR-MCr) in which counter diffusion of the ammonia and carbon dioxide introduces a concentration gradient at the three phase line, where gas-solid-liquid interaction at the pore mouth mediate induction and growth of crystalline NH_4HCO_3 (McLeod et al., 2015). The authors investigated both solution chemistry and ammonia concentration, which demonstrated a preference for shell-side (absorbent) crystallisation over lumen-side crystallisation, previously observed by other authors (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018). Although the explicit mechanism of crystal growth was not fully articulated, the authors suggested that control of solution surface tension and membrane pore size could enhance the sustained operation of CR-MCr.

Whilst the potential for preferential shell-side crystallisation has been demonstrated, the specific mechanism to consistently and reproducibly favour shell-side (liquid side) crystallisation over lumen-side crystallisation whilst facilitating $\text{NH}_3\text{-CO}_2$ reactions has not yet been described, and specifically in conjunction with the recovery of the final crystalline reaction product from the liquid phase. In this study, we therefore seek to identify the boundary conditions and membrane properties required for CR-MCr to facilitate CO_2 separation, reaction product formation and crystalline ammonium bicarbonate recovery in a single stage. Specific

Table 2.1. Review of ammonia based CO₂ capture studies using hollow fibre membrane contactors (HFMCs).

Ref.	Operating conditions				Absorbent				Feed gas				Salt precipitation
	Membrane / ID ^b	Pore size	Gas C.S.A. ^c	Liquid flow / Gas side	[NH ₃] ^d	C* ^a	pH	T ^e	[CO ₂]/ RH _{inlet}	T ^e	Gas velocity	Liquid velocity	
	mm	µm	×10 ⁶ m ²		mol L ⁻¹	mol L ⁻¹	-	°C	%	°C	m s ⁻¹	×10 ³ m s ⁻¹	
McLeod et al., 2015	PTFE/1.5	0.32	1.8	Recycle / lumen	2	2.4±0.2	>11	20	50/0	20	0.93	20	Liquid side
	PTFE/1.5	0.32	1.8	Recycle / lumen	3-5	2.4±0.2	>11	20	50/0	20	0.93	20	Gas side
Makhloufi et al., 2014	PP/0.3	0.2	0.07	S.P. ^f / lumen	0.6-1.8-2.9	2.4±0.2	>11	21	15/0	21	0.4-1.1	0.086-0.24	Gas side
Villeneuve et al., 2018	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	1.9±0.1	>11	10	15/100	10	2	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	1.9±0.1	>11	10	15/0	10	2	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	2.4±0.2	>11	21	15/100	21	2	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	2.4±0.2	>11	21	15/0	21	2	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	2.4±0.2	>11	21	15/0	21	1.3	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	2.4±0.2	>11	21	15/100	21	1.3	2	Gas side
	PP+PMP/0.2	-	0.03	S.P. ^f / lumen	2.9	3.8	>11	40	15/0	40	1.3	2	Not observed
Cui et al., 2017	PTFE/1.5	2.6	450	S.P. ^f / shell	1 to 3.7	2.4±0.2	>11	21	10-15-20/0	21	0.11	5-40	Gas side
This study	PP/1.2	0.36-0.2	1.1	Recycle / lumen	3	1.6±0.1	10	5	100/0	20	14.7	60	Liquid side
	PTFE/2.4	3.4-0.5	4.5	Recycle / lumen	3	1.6±0.1	10	5	100/0	20	3.7	60	Liquid side
	PTFE/2.4	3.4-0.5	4.5	S.P. ^f / lumen	2.3-3	2.4±0.2	>11	20	100/0	20	0.2	1.4	Gas side

^a Ammonia concentration at supersaturation for given absorbent temperature (Perry and Green, 2007; Trypuc and Kielkowska, 1998; PubChem, 2004).^b ID = Inner diameter^c C.S.A. = Cross sectional area^d [NH₃] = Ammonia concentration^e T = Temperature^f S.P. = Single pass

objectives are to: (i) determine the boundary conditions to prevent wetting and lumen side crystallisation; (ii) compare membranes of different pore sizes to promote sustained shell-side crystallisation; (iii) characterise shell-side nucleation and growth of the crystalline ammonium bicarbonate product within a chemically reactive membrane crystallisation reactor.

2.2 Materials and methods

2.2.1 Fabrication, equipment setup and operation

The micro-porous PTFE hollow fibre (Zeus Industrial Products, Letterkenny, Ireland) comprised pores with a nominal pore size of 0.5 μm . The maximum stretched pore length was also characterised (d_{max} , 3.4 μm) as the pores were oval rather than circular. The PP hollow fibre (Membrana GmbH, Wuppertal, Germany), comprised a nominal pore size of 0.2 μm (d_{max} , 0.36 μm) (Table 2.2).

Table 2.2. Dimensions and surface characteristics of the single membrane fibre

		PP	PTFE
Fibre characteristics			
Membrane material	-	Polypropylene (PP)	Polytetrafluoroethylene (PTFE)
Inner diameter	mm	1.2	2.4
Outer diameter	mm	1.8	2.8
Wall thickness	μm	300	200
Active length	mm	165	165
Surface area ^b	m^2	9.33×10^{-4}	1.44×10^{-3}
Porosity	%	72 ± 2^a	60 ± 10^a
$\Delta G_{\text{het}} / \Delta G_{\text{hom}}$	%	60	90
Minimum pore size, (d_{min})	μm	0.2 ^a	0.5 ^c
Maximum pore size, (d_{max})	μm	0.36 ^c	3.4 ^c
Geometrical factor, B	-	0.56	0.15
Contact angle, (θ)	$^\circ$	117 ^d	135 ^d
Breakthrough pressure, ($\Delta P_{\text{B.P.}}$)	bar	2.0	0.1
Lumen cross sectional area	m^2	1.13×10^{-6}	4.5×10^{-6}
Shell side characteristics			
Height	mm	5	5
Width	mm	12	12
Shell cross sectional area	m^2	6.0×10^{-5}	6.0×10^{-5}
Priming volume	ml	11.0	10.4
Operational characteristics			
Flow regime		Counter-current	Counter-current
Shell-side	M NH_3 (aq)	3	3 - 2.3 - 0.6
Lumen-side		99.8% CO_2	99.8% CO_2
Liquid temperature	$^\circ\text{C}$	5 ± 1	20 ± 1^e
Gas temperature	$^\circ\text{C}$	20 ± 1	20 ± 1
Liquid velocity	m s^{-1}	0.06	0.06 - 0.0014
Gas velocity	m s^{-1}	14.7	3.7 - 0.2
Gas humidity	%	38	47 - 100

^a Data provided by manufacturer.

^b Based on fibre outer diameter.

^c Data statistically determined using log-normal distribution

^d Bougie and Iliuta, (2013)

^e For comparison with PP and chilled absorbent in recycle, liquid recirculated on PTFE was at $5 \pm 1^\circ\text{C}$

$$\Delta P_{B.P.} = \frac{-4By_L \cos \theta}{d_{max}} \quad (2)$$

The diagram illustrates the experimental setup for CO₂ crystallization on a single carbon nanofiber. The system includes a CO₂ cylinder connected to a mass flow controller, which regulates the flow of ambient temperature gas into a single fiber. A temperature sensor and a humidity sensor are positioned to monitor the gas conditions. The gas flow is controlled by a mass flow controller and a bubble flow meter. The single fiber is connected to a peristaltic pump that circulates cold liquid (Cold liquid inlet) through it. The cold liquid is then collected in bulk (Crystals collected in bulk) and can be analyzed using a magnetic stirrer and a chiller. The system also features a cold liquid outlet and an ambient temperature gas outlet. A data acquisition module is connected to the sensors and the peristaltic pump, with data being recorded on a laptop computer. The setup is designed to study the crystallization of CO₂ on a single carbon nanofiber under controlled conditions.

Carbon dioxide (99.8%, BOC gases, Ipswich, UK) was introduced into the lumen of the hollow-fibre at a flow rate of 1000 ml min⁻¹ using a laminar mass flow controller (0.01-1 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK). Absorbent was pumped counter-current on the shell-side of the membrane at 200 ml min⁻¹ with a peristaltic pump (520Du, Watson-Marlow Ltd., Falmouth, UK). The absorbent temperature was fixed with a refrigerated bath and circulator (R1 series, Grant Instruments Ltd., Cambridge, UK). Thermocouples (K-type, Thermosense Ltd., Bucks, UK) were sited in the gas and liquid phase both upstream and downstream of the cell.

2.2.2 Chemical preparation, sampling and analysis

Absorbent ammonia concentration was fixed by addition of aqueous NH₃ concentrate (35% Fisher Chemicals, Loughborough, UK) to de-ionised water (15.0 MΩ cm⁻¹) (Table 2.2). The absorbent pH was fixed at pH 10 with addition of hydrochloric acid (HCl, 37%, Fisher Scientific, Loughborough, UK), which is typical of that employed in aqueous ammonia packed column processes (Yeh et al., 2005). Ammonia concentration was confirmed using ammonium cell test (VWR International Ltd., Poole, UK) coupled with spectrophotometric determination (Spectroquant Nova 60, Merck-Millipore, Darmstadt, Germany). Manual volumetric flow meters of 50 mL (Restek, Bellefonte, US) and 1000 mL volume (SKC, Blandford Forum, UK) were used to measure the gas flow rate and to calculate the carbon dioxide flux (J_{CO_2} , mol m⁻² s⁻¹):

$$J_{CO_2} = \frac{(Q_{G,in} - Q_{G,out}) \times 273.15 \times 1000}{22.4 \times A_m T_G} \quad (3)$$

where $Q_{G,in}$ and $Q_{G,out}$ are gas flow rate (m³ s⁻¹) before and after HFMC, A_m is the membrane surface area for absorption (m²) and T_G is the gas temperature (K) (Atchariyawut et al., 2007). The error for gas flow measurement was around 2% of the reported value.

Solution pH was monitored using a Jenway epoxy bodied pH electrode (bulb end type) connected to a pH meter (Jenway 4330, Cole-Parmer, Stone, UK). The solution UV absorbance was determined at 215 nm (Jenway 6715 UV/Vis. Spectrophotometer, Cole-Parmer, Stone, UK) which corresponds to the absorption of bicarbonate (Wilson et al., 2001). To characterise the development of the crystalline solids phase, experiments were terminated at different levels of supersaturation (C/C^*), which was defined as the ratio between the CO₂ absorbed into solution and the CO₂ required to form ammonium bicarbonate at the solubility limit. For each level of supersaturation, sacrificial experiments were undertaken in triplicate and the crystal size distribution (CSD) determined. The absorbent was initially filtered through a 0.45 µm Whatman filter and weighed (Camlab Ltd., Cambridge, UK). Crystals were then immersed in anhydrous alcohol to minimise agglomeration during counting (Veiga et al., 1999) and transferred to a microscope slide consisting of a 1 mm grid for counting under an optical microscope (Optech Microscope Services Ltd., Thame, UK), equipped with PL 5/0.12 lens and digital camera (Infinity 3, Lumenera, Ottawa, Canada). Images were analysed with an image processing software (Image Pro Plus, Media Cybernetics, Cambridge, UK) to determine crystal numbers and sizes. Each image analysed corresponded to around 50 crystals. For each sacrificial test, at least 600 crystals were classified to achieve sufficient accuracy for the CSD (Ji et al., 2010), which was determined assuming a log-normal distribution (Li et al., 2000).

2.2.3 Chemistry of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system

Throughout CO_2 absorption into aqueous ammonia solutions, the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system is thermodynamically controlled by the following equilibria (Millero and Roy, 1997; Sander, 2015):



In the liquid phase, Wang et al. (2011) explored the kinetics of the reactions of $\text{NH}_3(aq)$ with $\text{CO}_2(aq)$ and carbonate species, comprising the reversible reactions of ammonium carbamate/ carbamic acid formation. Interactions of $\text{CO}_2(aq)$ with water and hydroxide ions, carbonic species equilibria and ammonia ionisation proceed by:



The relative proportion of dissolved CO_2 available as carbonic acid (H_2CO_3) and the relative proportion of ammonia present in protonated form (NH_4^+) are dependent on both solution pH and temperature (Figure 2.2).

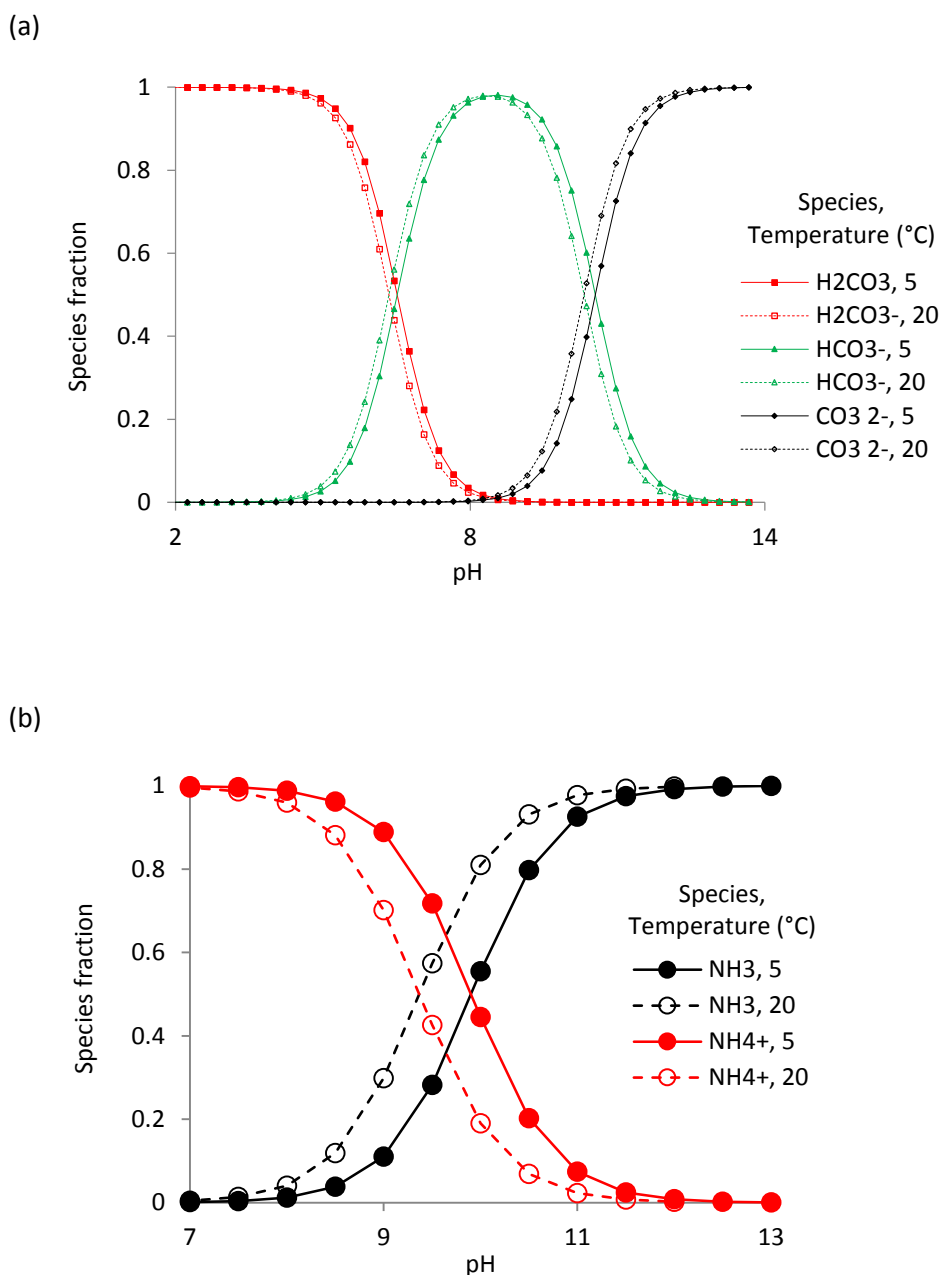


Figure 2.2. Distribution of carbonic acid, bicarbonate and carbonate (H_2CO_3 , HCO_3^- , CO_3^{2-}) (a) and of ammonium-ammonia (b) as functions of pH and absorbent temperature. Additional information available in appendix.

Whilst five solid reaction products may potentially form (Sutter et al., 2015), ammonium bicarbonate is thermodynamically favoured, due to the lower solubility of the salt (Mani et al., 2006), which exhibits some dependency upon temperature (Figure 2.3).

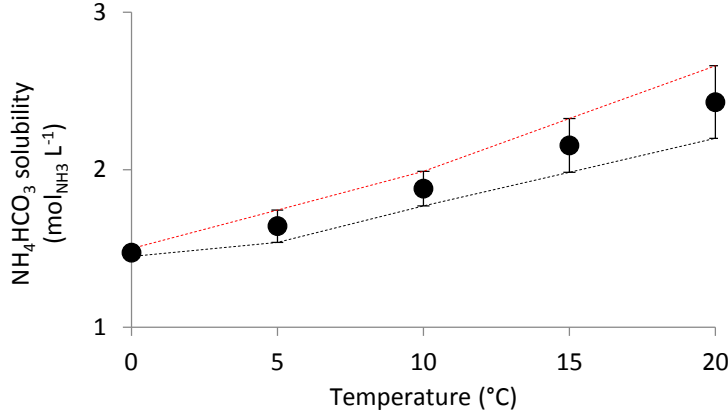


Figure 2.3. Ammonium bicarbonate (NH_4HCO_3) solubility line in water. Symbols correspond to the mean calculated between experimental data from PubChem, (2004) and Perry and Green, (2007).

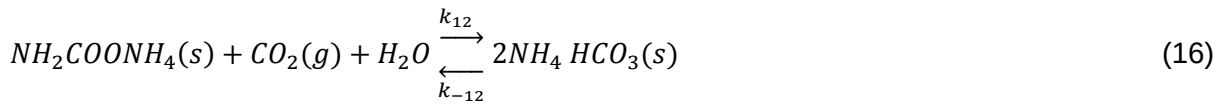
Ammonium bicarbonate is formed from the ionic bond between NH_4^+ and HCO_3^- (Niu et al., 2012):



The formation of carbamate and its protonation to the carbamic acid are described by:



In the gas phase, carbon dioxide and ammonia can produce ammonium carbamate ($\text{NH}_2\text{COONH}_4$). Through hydrolysis, $\text{NH}_2\text{COONH}_4$ successively converts into ammonium bicarbonate (NH_4HCO_3) (Li et al., 2003):



Nevertheless, due to the high solubility of ammonium carbamate in water (Mani et al., 2006), ammonium bicarbonate formation in the gas phase is more likely to proceed by (Li et al., 2003; Han et al., 2013):



An increase in aqueous ammonia concentration raises ammonia volatility, thus facilitating NH_3 slip in the gas phase and increasing the likelihood for gas side crystallisation of NH_4HCO_3 (Figure 2.4; Perman, 1903).

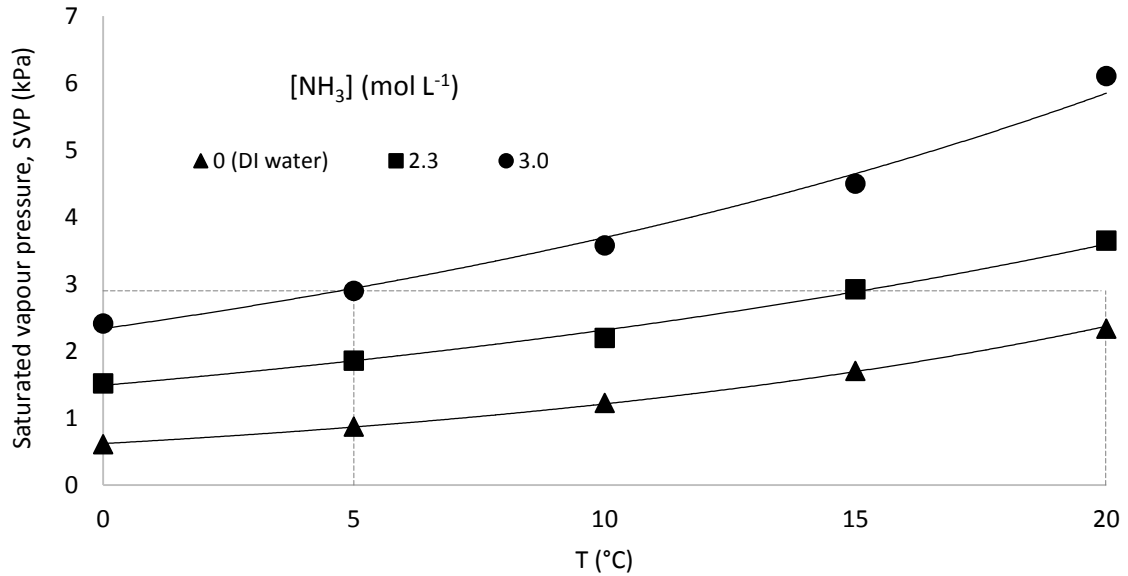


Figure 2.4. Saturated vapour pressure (SVP) of NH_3 over aqueous ammonia solution as a function of solution temperature. An increase in ammonia concentration or temperature induces a gain in SVP and consequently NH_3 slip through the pores, into the gas phase, rising the likelihood for lumen side crystallisation.

2.3 Results

2.3.1 Diagnosis of liquid absorbent operation to prevent lumen side crystallisation

The PTFE HFMC was initially tested in single pass operation with absorbent and gas temperatures at $20 \pm 1^\circ\text{C}$. Ammonia concentration was varied between 0.6 and 3 $\text{mol NH}_3 \text{ L}^{-1}$ whilst liquid and gas velocity (V_L and V_G) were fixed at 0.2 m s^{-1} and $1.4 \times 10^{-3} \text{ m s}^{-1}$, respectively (Figure 2.5).

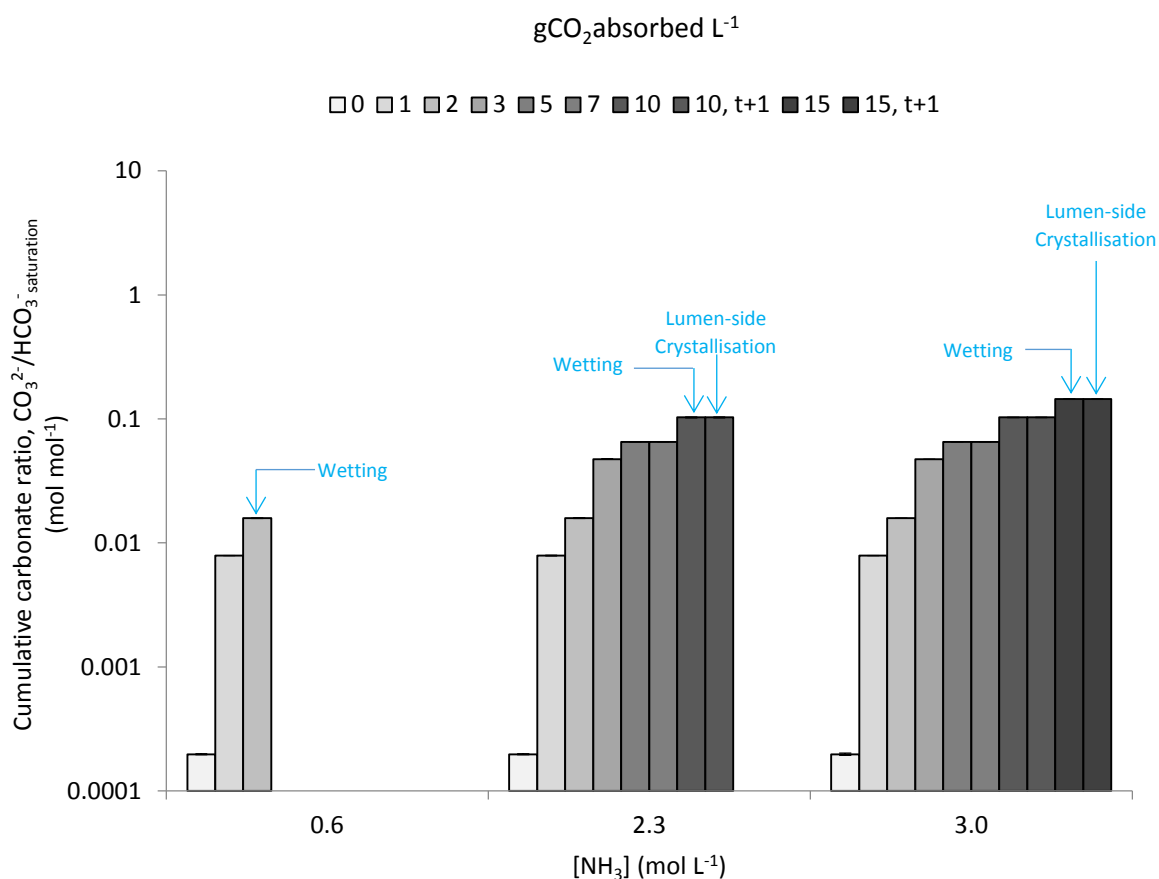


Figure 2.5. Impact of ammonia concentration on wetting and lumen side crystallisation (observed immediately after wetting, $t+1$) for PTFE membrane in single pass operation. Cumulative carbonate ratio calculated assuming CO_2 absorbed fully converted into CO_3^{2-} . Hydrodynamic conditions: G/L 11; V_G 0.2 m s⁻¹; V_L 1.4×10^{-3} m s⁻¹. Gas and absorbent at 20°C. Gas humidity: 100%. Error bars indicate standard deviation.

Lumen-side crystallisation was observed at the two highest ammonia concentrations examined (2.3 and 3 molNH₃ L⁻¹), which corresponded to 10 and 15 gCO₂absorbed L⁻¹. The EDX analysis of the crystals grown in the lumen using absorbent at 3 molNH₃ L⁻¹, comprised O, N and C in a ratio indicative of ammonium bicarbonate (Figure 2.6).

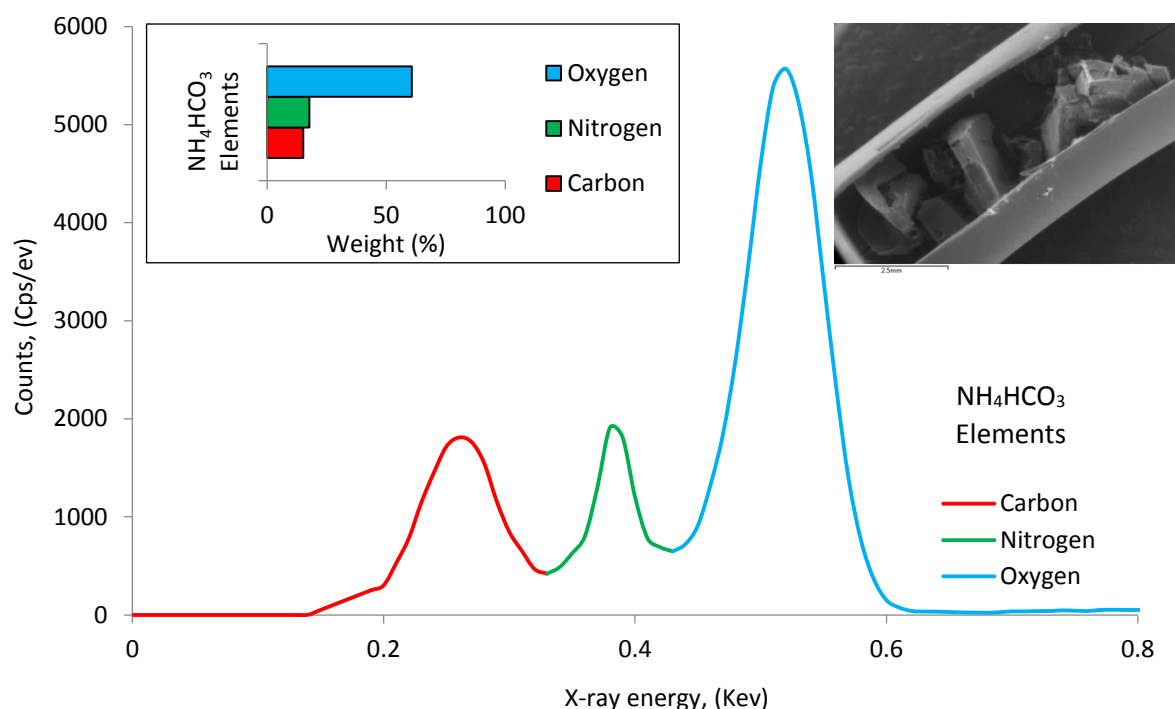


Figure 2.6. EDX analysis of NH_4HCO_3 crystals formed in the lumen of the PTFE hollow fibre membrane. In the right inset is shown the dissected section of the fibre subsequent to blockage, which occurred after 8 hours of operation, using absorbent at 3M NH_3 in single pass.

During tests under identical hydrodynamic conditions, ammonia concentrations and gas/liquid temperatures, but following absorbent recirculation (rather than single pass), lumen side crystallisation was not observed at 0.6 and $2.3 \text{ molNH}_3 \text{ L}^{-1}$ corresponding to 26 and 120 gCO_2 absorbed L^{-1} , respectively (where NH_4HCO_3 solubility is equivalent to 101 gCO_2 absorbed L^{-1} at 20°C and 1 atm), while it was detected when using absorbent at $3 \text{ molNH}_3 \text{ L}^{-1}$, below NH_4HCO_3 solubility limit (Figure 2.7).

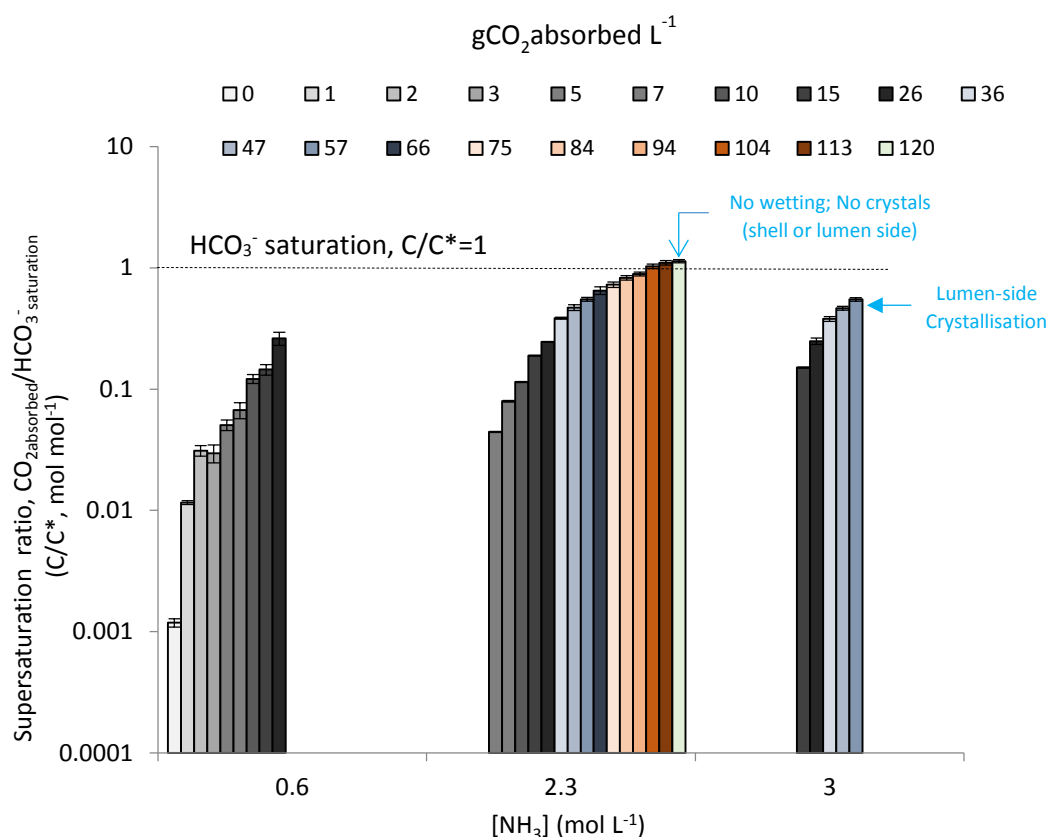


Figure 2.7. Influence of ammonia concentration on lumen side crystallisation observed with PTFE membrane following absorbent recirculation. Supersaturation ratio C/C^* calculated assuming CO₂ absorbed fully converted in HCO₃⁻. Hydrodynamic conditions: G/L 11; V_G 0.2 m s⁻¹; V_L 1.4 x 10⁻³ m s⁻¹. Gas and absorbent at 20°C. Gas humidity: 100%. Error bars indicate standard deviation.

Chilled absorbent recirculation at 5±1°C and 3 molNH₃ L⁻¹ within the same PTFE HFMC induced multiple advantages, including reduction of NH₄HCO₃ solubility to 75 gCO₂ absorbed L⁻¹, prevention of lumen-side crystallisation and promotion of shell-side crystallisation, which commenced at 104 gCO₂ absorbed L⁻¹ (Figure 2.8). Specifically, the ammonia saturated vapour pressure dropped from 6.11 to 2.9 kPa when refrigerating the aqueous ammonia solution at 3 molNH₃ L⁻¹ from 20 to 5°C, which significantly reduced ammonia slip in the gas phase (Figure 2.4). Nevertheless, at 113 gCO₂ absorbed L⁻¹, wetting occurred, facilitating CO₂ mass transfer (Figures 2.8 and 2.9).

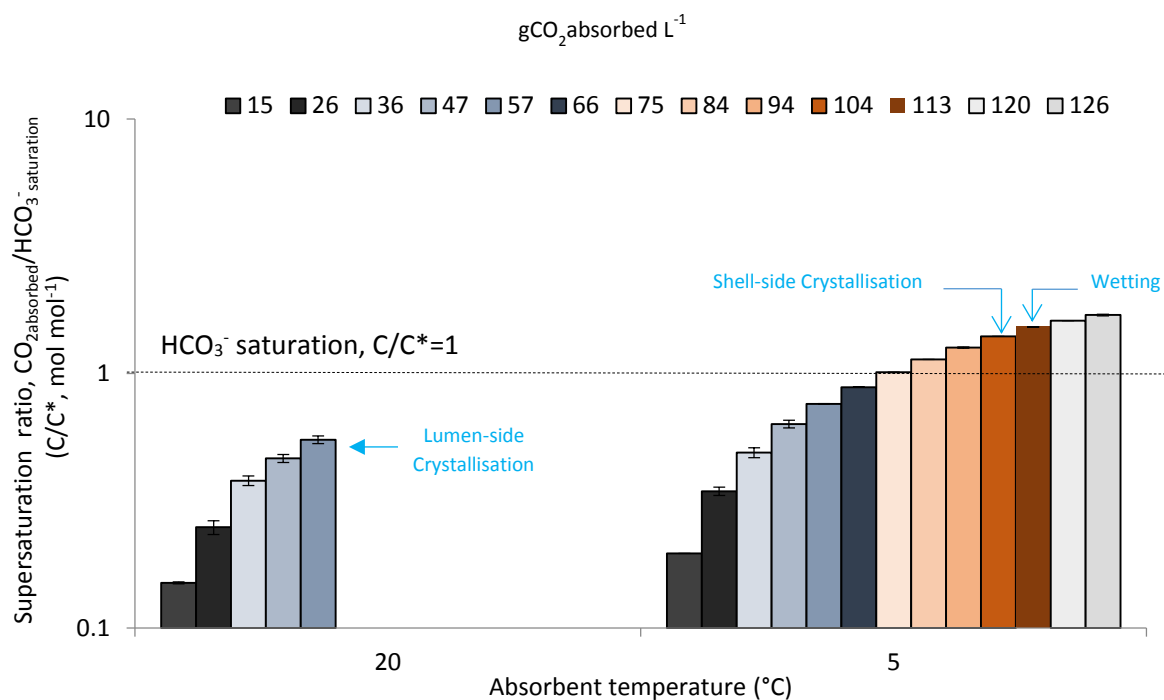


Figure 2.8. Effect of absorbent temperature ($3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, in recirculation) upon lumen side crystallisation observed with PTFE membrane. Supersaturation ratio C/C^* calculated assuming CO_2 absorbed fully converted in HCO_3^- . (Left) Gas and absorbent at 20°C . (Right) Gas temperature 20°C ; Liquid temperature 5°C . Error bars indicate standard deviation.

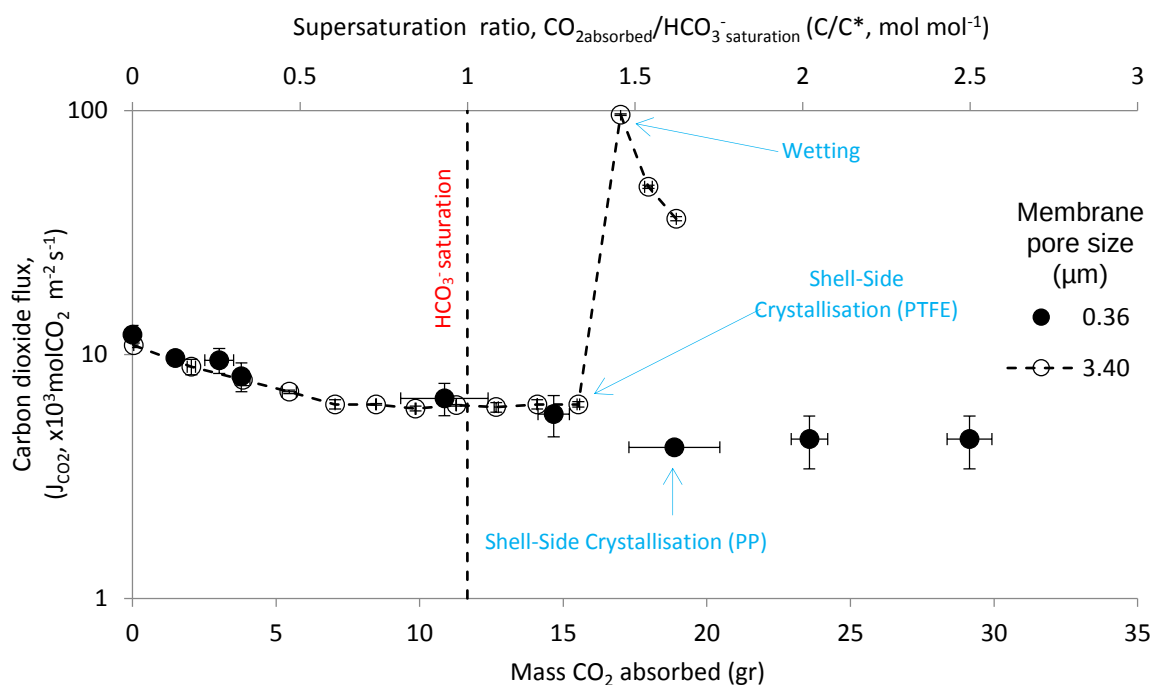


Figure 2.9. Impact of pore size reduction (from 3.4 μm in PTFE to 0.36 μm in PP membrane) on wetting prevention, following NH_3 absorbent recirculation at 3M. Hydrodynamic conditions: G/L 5; V_L 0.06 m s^{-1} ; V_G 14.7 m s^{-1} for PP and 3.7 m s^{-1} for PTFE. Shell-side crystallisation occurred for both the materials. Membrane wetting observed only with PTFE following shell-side crystallisation. Error bars indicate standard deviation.

2.3.2 Investigation of vapour-liquid-solid equilibria throughout CO₂ absorption within chilled aqueous ammonia in recirculation

Reduction of pH from 10 to 7.3 ($0 < C/C^* < 1.7$) was observed when recirculating chilled aqueous ammonia at 3 molNH₃ L⁻¹, corresponding to ammonia-ammonium transition up to 100% ionised ammonia (hence, 3 molNH₄⁺-N L⁻¹) (Figure 2.10).

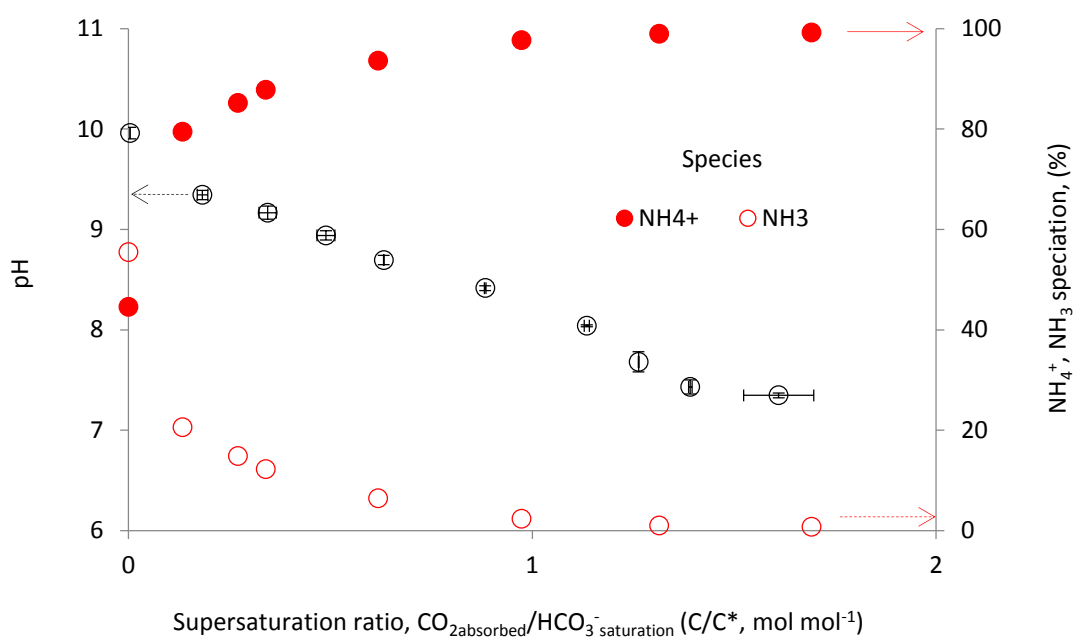


Figure 2.10. pH drop and ammonia-ammonium speciation as a function of supersaturation ratio for PTFE hollow fibre membrane following aqueous ammonia absorbent recirculation at concentration of 3M. Error bars indicate standard deviation.

In the same pH range, bicarbonate concentration initially raised up to 3 molHCO₃⁻ L⁻¹ at pH 8 (where HCO₃⁻ ≈ 100% within the carbonic acid speciation; Figure 2.2a), corresponding to a supersaturation ratio $C/C^*=1$ (HCO₃⁻ saturation), followed by a decline, where shell-side crystal nucleation and growth of ammonium bicarbonate occurred (Figure 2.11), coupled with 13% reduction of bicarbonate converted into carbonic acid (Figure 2.2a). In particular, in C/C^* range between 1 and 1.7, overall bicarbonate drop was approximately 85%, furtherly exacerbated in C/C^* range between 1.7 and 2.5, with an overall HCO₃⁻ decrement of 3-fold (Figure 2.11).

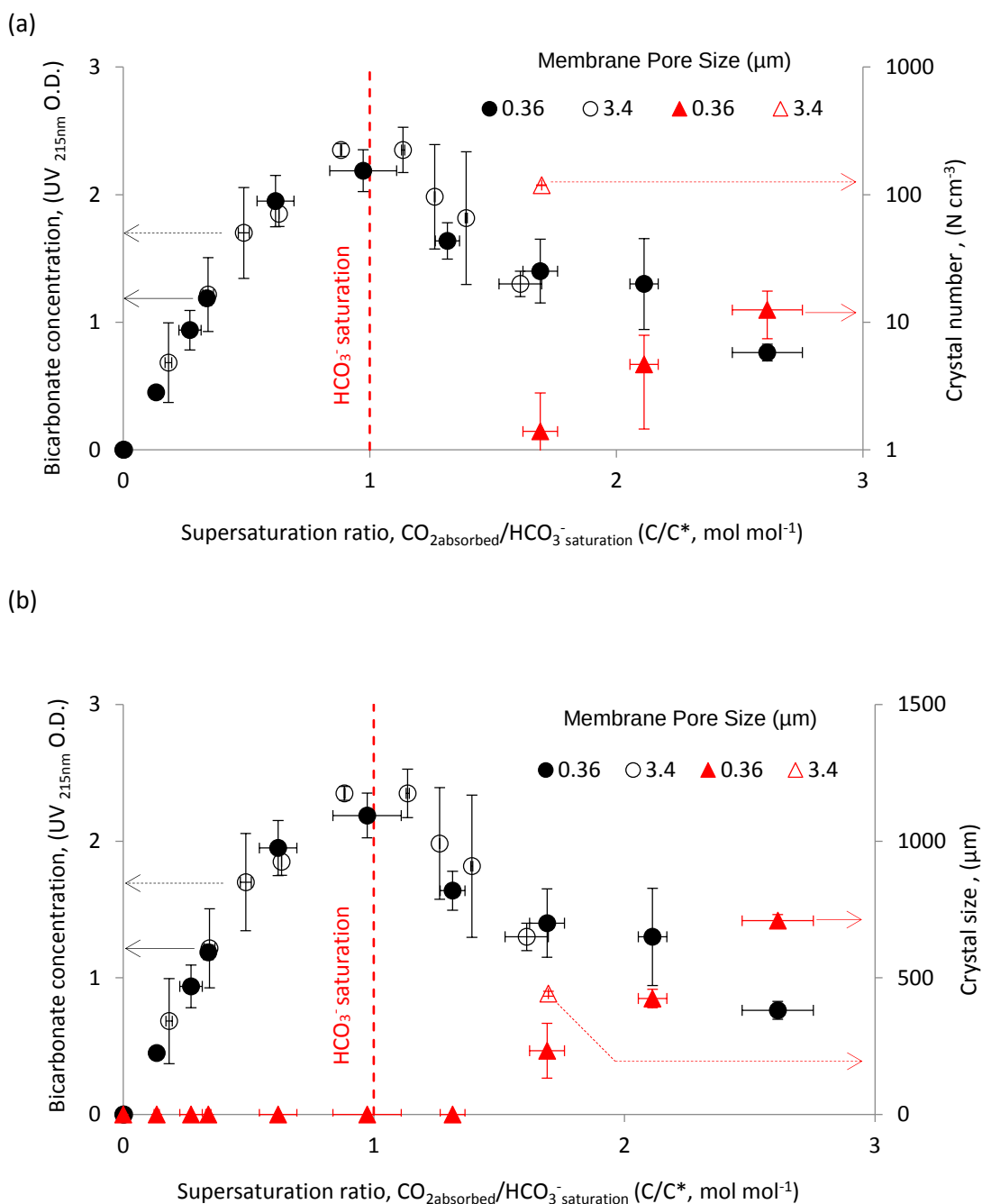


Figure 2.11. Impact of pore size on shell-side nucleation and growth of NH_4HCO_3 crystals expressed as crystal number (a) and crystal size (b) at ammonia concentration of 3M in recycle. Absorbent and gas temperature of 5 and 20 °C respectively. Bicarbonate peak indicates the induction time where CO_2 absorbed is equal to NH_4HCO_3 solubility ($\approx 1.5 \text{ mol NH}_3 \text{ L}^{-1}$ at 5°C and 1atm, assuming CO_2 absorbed fully converted in HCO_3^-) and nucleation initiates. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate for both PTFE and PP membranes (corresponding to pore size 3.4 and 0.36 μm respectively).

2.3.3 Influence of membrane properties to prevent wetting and promote shell-side nucleation and growth

Membrane pore size reduction from 3.4 to 0.36 μm , following recirculation of aqueous ammonia at 5°C ($G/L = 5$), enabled stable CO_2 flux and prevented wetting until complete

exhaustion of the absorbent ($C/C^* = 2.5$) (Figure 2.9), facilitating consistent and reproducible shell-side crystallisation (Figure 2.11). In particular, the decrement in pore size accomplished (from PTFE to PP), induced an increase in the geometrical factor B from 0.15 to 0.56, boosting the liquid breakthrough pressure by 20-fold (Table 2.2). Once exceeded bicarbonate saturation limit ($C/C^*=1$), heterogeneous nucleation and growth commenced on both the fibres ($\Delta G_{het}/\Delta G_{hom}$, ~90% for PTFE and ~60% for PP; Table 2.2) (Curcio et al., 2006), followed by collection in the bulk. When using the membrane with wide pore structure, wetting occurred subsequent to growth (Figure 2.9), resulting in crystal precipitation of 100 crystals cm^{-3} of 440 μm mean size at $C/C^*=1.7$, compared with only 1 crystal cm^{-3} of 230 μm mean size at the same supersaturation ratio within the tight pore structure (Figures 2.11 and 2.12b). In the latter case, in particular, ammonium bicarbonate crystal number increased from 1 crystal cm^{-3} at $C/C^*=1.7$ to 10 crystal cm^{-3} at $C/C^*=2.5$, while crystal size raised from 233 to 709 μm within the same C/C^* range. Analogously, a gain in mean crystal mass recovered was detected within the 0.36 μm pore size fibre from 12 mg at $C/C^*=1.7$ to 491 mg at $C/C^*=2.5$, whilst 815 mg have been recovered from the test with 3.4 μm pore size fibre at $C/C^*=1.7$ (Figure 2.12).

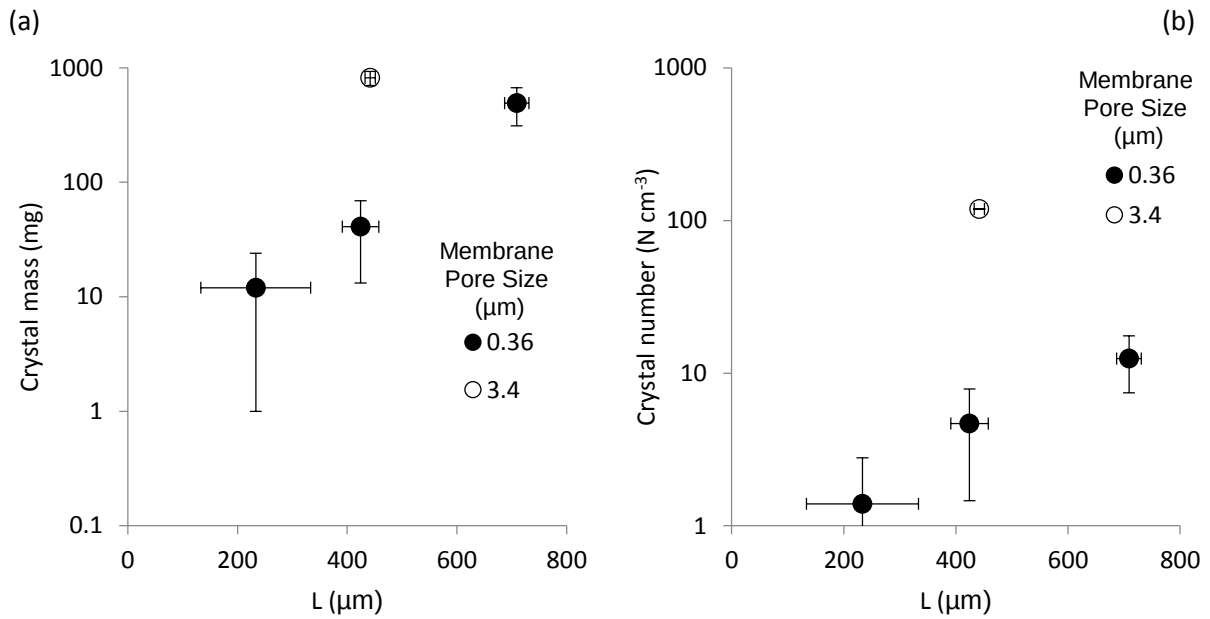


Figure 2.12. Experimental results of the crystal mass (a) and number (b) vs. mean size using PP and PTFE hollow fibre membranes, corresponding to pore size 3.4 and 0.36 μm respectively. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate for each membrane material.

2.4 Discussion

This study has demonstrated that by limiting the transport of free ammonia into the gas phase through suppressing ammonia vapour pressure using temperature, coupled with recirculation of the absorbent to shift the equilibrium toward the non-volatile ionised ammonium form,

consistent and reproducible induction and growth of ammonium bicarbonate crystals can be achieved on the shell-side of the membrane. When absorbent flow was operated in single pass, NH_4HCO_3 crystallisation was observed in the gas phase, on the lumen-side of the membrane (Figures 2.5 and 2.6), and corresponded to conditions in which the 2.3 M NH_3 absorbent solution was below the solubility limit ($C/C^*, 1$) required to facilitate crystallisation within the liquid phase. This is similar to earlier investigation in which CO_2 mass transfer was studied using single pass NH_3 absorbent flow (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018). A previous investigation has demonstrated crystalline ammonium bicarbonate can result from gas phase reaction via formation of ammonium carbamate ($\text{NH}_2\text{COONH}_4$) as an intermediate solid (Equations 15 and 16) (Li et al., 2003; Han et al., 2013). Consequently, gas-phase crystallisation could proceed through one of two mechanisms: direct reaction between CO_2 and slipped NH_3 in the gas phase; or wetting and breakthrough of solvent into the gas phase followed by CO_2 dissolution. At equivalent absorbent concentration and hydrodynamic conditions (where constant gas velocity maintains unvaried gas humidity; Table 2.2), lumen side crystallisation was prevented through recycling the absorbent, which suggests lumen side precipitation of NH_4HCO_3 to be independent from gas humidity (Figure 2.7). As CO_2 absorbs, it quickly reacts with free $\text{NH}_3(\text{aq})$ to form carbamic acid (NH_2COOH) (Equation 13; $k_9, 4.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$; Wang et al., 2011), which then transforms to carbamate liberating a hydrogen ion (Equation 14). The resultant reduction in pH shifts the ammonia-ammonium equilibrium toward the non-volatile ionised ammonium form (Capodaglio et al., 2015; Wang et al., 2011; Figure 2.2b). It is this conversion of NH_3 into its ionised form (Equation 11) which dissipates NH_3 slip, reducing the probability for ammonium bicarbonate formation in the gas phase.

Since $2.3 \text{ molNH}_3 \text{ L}^{-1}$ was not sufficient to induce crystallisation of the reaction product on the shell-side at ambient temperature ($20 \pm 1^\circ\text{C}$), an increase in aqueous ammonia to $3 \text{ molNH}_3 \text{ L}^{-1}$ was trialled which again promoted lumen side crystallisation (Figure 2.7). At $3 \text{ molNH}_3 \text{ L}^{-1}$, the saturated vapour pressure for ammonia is 65% higher than for $2.3 \text{ molNH}_3 \text{ L}^{-1}$ which increased the probability for transport to the gas phase (Figure 2.4) (Perman, 1903). This is supported by the observations of McLeod et al. (2015) in which lumen side (gas-phase) crystallisation occurred during absorbent recirculation at ambient temperature for 3 to 5 $\text{molNH}_3 \text{ L}^{-1}$ but not at 2 $\text{molNH}_3 \text{ L}^{-1}$ (Table 2.1). For the CR-MCr, the reduction in absorbent temperature affords two advantages: a reduction in NH_3 vapour pressure will limit the probability for gas-phase crystallisation; and at lower temperature NH_4HCO_3 becomes less soluble, which should advantage induction and crystal growth on the shell-side (absorbent side) of the membrane (Figure 2.3) (Perry and Green, 2007). This was demonstrated through recirculation of $3 \text{ molNH}_3 \text{ L}^{-1}$ absorbent at $5 \pm 1^\circ\text{C}$, where lumen-side crystallisation was prevented in favour of shell-side nucleation (Figure 2.8). The point of induction was observed

close to the solubility limit for CO₂ (C/C*), which was coincidental with around 100% of the nitrogen present as ammonium since solution pH had reduced to pH 8 (Figure 2.10; Millero and Roy, 1997; Capodaglio et al., 2015); at this point both ammonium and bicarbonate concentrations were twice the solubility limit (1.5mol L⁻¹), enabling shell side nucleation to occur on the PTFE fibre (PubChem, 2004).

Shortly after saturation was achieved for the PTFE membrane, shell-side crystal growth was determined. Polytetrafluoroethylene exhibits a contact angle of around 135° (Bougie and Iliuta, 2013) which is thought to promote heterogeneous nucleation at the membrane wall ($\Delta G_{het}/\Delta G_{hom}$, ~90%; Curcio et al., 2006):

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = 0.25(2 + \cos\theta)(1 - \cos\theta)^2 \left[1 - \varepsilon \frac{(1 + \cos\theta)^2}{(1 - \cos\theta)^2} \right]^3 \quad (16)$$

Once nucleation and growth was observed, a sudden peak in CO₂ flux occurred due to breakthrough of ammonia solution into the gas phase, in response to surface wetting subsequently enabling direct chemical reaction with CO₂ (Figure 2.9). Through microscopic surface characterisation, McLeod et al. (2015) were able to confirm nucleation to initiate at the edge of the pore, where the membrane (solid phase), liquid and gas phases intersect. It is proposed that the concentration gradient developed within the boundary layer coupled with the material promotion of heterogeneous nucleation, initiated substantive nucleation within the membrane pores. The extent of nucleation was confirmed in the bulk, where the crystal number was two orders of magnitude higher than for the polypropylene membrane at an equivalent supersaturation level (Figures 2.11 and 2.12). Crystallisation around the membrane pores modified the contact angle, reducing the breakthrough pressure which was already limited by the large pore size, subsequently inducing wetting and the transfer of solvent into the gas phase (Rangwala, 1996). Application of a smaller pore size membrane (polypropylene) in conjunction with chilled recirculating absorbent to limit slip, enabled consistent and reproducible crystallisation on the shell-side (liquid side) of the membrane (Figure 2.9). Specifically, the stretched pore length of the membrane reduced from 3.4 to 0.36 µm, which increased the breakthrough pressure by 20-fold. The lower crystal number and size observed for the polypropylene membrane can be ascribed to the smaller contact angle of the material (117°) which reduced the thermodynamic potential for induction (Di Profio et al., 2010; Bougie and Iliuta, 2013). Analogous to the trend identified for crystal growth with the 0.36 µm stretched pore size membrane, Di Profio et al. (2003) also recorded an increase in crystal number and crystal size over time when using a similar polypropylene membrane in osmotic crystallisation of organic macromolecules, and inferred the trend to be that of heterogeneous nucleation. Nitrogen mass balance demonstrated that 5 % of the nitrogen lost from the NH₃ absorption solvent was recovered within the crystallised product in the bulk solution, which

suggests negligible NH₃ slip to have occurred and insignificant crystalline surface deposition on the surface of the membrane.

2.5 Conclusions

Recirculation of a chilled absorbent within hollow fibre membrane contactors has been introduced to prevent lumen-side blockage and enable consistent and reproducible shell-side nucleation and growth of ammonium bicarbonate through chemical CO₂ absorption from the gas phase. This represents the first chemically reactive membrane crystallisation study to describe the specific mechanism for controlling preferential liquid side over gas side crystallisation, coupled with recovery of the NH₃-CO₂ reaction product from the liquid phase. Lumen-side crystallisation can be precluded and shell-side crystallisation facilitated by (1) suppressing ammonia volatility through absorbent refrigeration and (2) shifting ammonia-ammonium equilibrium toward the non-volatile NH₄⁺ through liquid recirculation. Additionally, selection of a membrane with tight and regulated pore structure quenches solvent ingress into the pores, thus promoting sustained crystallisation on the membrane-liquid interface. Preferential heterogeneous nucleation on the tight pore structure fibre, driven by a concentration gradient, demonstrated to favour nucleation over growth (Di Profio et al., 2003). Future biogas upgrading applications could envision the implementation of CR-MCr at WWTWs down-stream the anaerobic digestion, where heterogeneous nucleation and growth of ammonium bicarbonate is followed by collection in the bulk solution. Discharge of the CO₂ saturated solution (rich in ammonium bicarbonate) and subsequent introduction of fresh aqueous ammonia in the cycle, would then allow long term high CO₂ flux and concurrent crystals recovery (as fertilizer by-products), ammonia removal and biogas upgrading up to 98% pure CH₄ within a single and low-cost process (McLeod et al., 2014).

Acknowledgements

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

Appendix

Carbonic acid, bicarbonate and carbonate equilibria

The distributions of H₂CO₃, HCO₃⁻ and CO₃²⁻ as a function of pH (Figure 2.2a) have been determined through the following equations (Millero and Roy, 1997; Millero, 1995):

$$\frac{[H_2CO_3]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A1)$$

$$\frac{[HCO_3^-]}{C_T} = \frac{[H^+]K_{-5}}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A2)$$

$$\frac{[CO_3^{2-}]}{C_T} = \frac{K_{-4}K_{-5}}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A3)$$

Where $C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$, while K_{-4} and K_{-5} are the dissociation constants of bicarbonate and carbonic acid, given by (Equations 8 and 9; Millero and Roy, 1997):

$$K_{-4} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (A4)$$

$$K_{-5} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (A5)$$

The value of the dissociation constants is significantly dependent on temperature and salinity of water (Millero and Roy, 1997). Specifically, at temperature $T = 5^\circ\text{C}$ and salinity $S = 0\%$, $K_{-4} = 2.84 \times 10^{-11}$; $K_{-5} = 3.069 \times 10^{-7}$, whilst at temperature $T = 20^\circ\text{C}$ and salinity $S = 0\%$, $K_{-4} = 4.3 \times 10^{-11}$; $K_{-5} = 4.188 \times 10^{-7}$ (Millero, 1995).

Dissociation of ammonia and ammonium ion

The distributions of NH_3 and NH_4^+ as a function of pH have been evaluated as follows (Ukwuani and Tao, 2016):

$$\alpha_{NH_3} = 1/(1 + 10^{pK_a^S - pH}) \quad (A6)$$

$$\alpha_{NH_4^+} = 1 - \alpha_{NH_3} \quad (A7)$$

Where pK_a^S is given by (Bates and Pinching, 1949):

$$pK_a^S = -\log K_a^S = \frac{A}{T} + B \quad (A8)$$

Specifically, the values of the constants A and B are 2727.42 and 0.0973, respectively, while T is temperature in K (Bates and Pinching, 1949).

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Chapter 3

Chemically reactive membrane crystallisation reactor for CO₂–NH₃ absorption and ammonium bicarbonate crystallisation: Kinetics of heterogeneous crystal growth

For submission to: Journal of Membrane Science

Chemically reactive membrane crystallisation reactor for CO₂–NH₃ absorption and ammonium bicarbonate crystallisation: Kinetics of heterogeneous crystal growth

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Abstract

The feasibility of gas-liquid hollow fibre membrane contactors for the chemical absorption of carbon dioxide (CO₂) into ammonia (NH₃), coupled with the crystallisation of ammonium bicarbonate has been demonstrated. In this study, the mechanism of chemically facilitated heterogeneous membrane crystallisation is described, and the solution chemistry required to initiate nucleation elucidated. Induction time for nucleation was dependent on the rate of CO₂ absorption, as this governed solution bicarbonate concentration. However, for low NH₃ solution concentrations, a reduction in pH was observed with progressive CO₂ absorption which shifted equilibria toward ammonium and carbonic acid, inhibiting both absorption and nucleation. An excess of free NH₃ buffered pH suitably to balance equilibria to the onset of supersaturation, which ensured sufficient bicarbonate availability to initiate nucleation. Following nucleation, an increase in crystal population density and crystal size was observed at progressive levels of supersaturation which contradicts the trend ordinarily observed for homogeneous nucleation in classical crystallisation technology, and demonstrates the role of the membrane as a physical substrate for heterogeneous nucleation during chemically reactive crystallisation. Both nucleation rate and crystal growth rate increased with increasing levels of supersaturation. This can be ascribed to the relatively low chemical driving force imposed by the shift in equilibrium toward ammonium which suppressed solution reactivity, together with the role of the membrane in promoting counter-current diffusion of CO₂ and NH₃ into the concentration boundary layer developed at the membrane wall, which permitted replenishment of reactants at the site of nucleation, and is a unique facet specific to this method of membrane facilitated crystallisation. Free ammonia concentration was shown to govern nucleation rate where a limiting NH₃ concentration was identified above which crystallisation induced membrane scaling was observed. Provided the chemically reactive membrane crystallisation reactor was operated below this threshold, a consistent (size and number) and reproducible crystallised reaction product was collected downstream of the membrane, which evidenced that sustained membrane operation should be achievable with minimum reactive maintenance intervention.

Keywords: nucleation; solid phase; chemical absorption; precipitation; ammonia

3.1 Introduction

The use of packed columns for the absorption of carbon dioxide (CO₂) has received significant attention over the past decade, for their potential to facilitate carbon capture and storage (CCS) as well as enabling CO₂ separation from biogas for the production of biomethane; this latter application representing one of the fastest growing areas for gas-liquid separation technology (IEA, 2016). In both applications, chemically reactive solvents have been employed as a method of process intensification (Makhloufi et al., 2014; McLeod et al., 2015). Aqueous ammonia has been shown to achieve higher CO₂ loadings than sterically free primary alkanolamines such as monoethanolamine (Yeh and Bai, 1999). However, the absorption and reaction kinetics between CO₂ and aqueous ammonia are complex, and the resultant species formed in a CO₂-NH₃-H₂O system are poorly understood (Mani et al., 2006), despite the commercial significance of the overall reaction in the industrial production of crystalline ammonium bicarbonate (NH₄HCO₃), for the food, fertiliser, pharmaceutical and manufacturing sectors (Veiga et al., 1999 after Kirk-Othmer, 1982). Veiga et al. (1999) were amongst the first to report on a three phase (gas-liquid-solid) system for the controlled production of crystalline NH₄HCO₃ in which governance over crystal size and morphology was evaluated. The overall chemical reaction can be described as:



In packed column studies for NH₃-CO₂ absorption, the formation of an NH₄HCO₃ solid was also considered as this has the potential to improve CO₂ solvent capacity, thereby reducing the mass flow of stripper solution and lowering the specific energy demand for CCS (Gazzani et al., 2014). However, managing formation and recovery of the crystalline solid within packed columns was found to be difficult (Sutter et al., 2015), and demands explicit investigation of the underpinning science to define the kinetics of solids formation in CO₂-NH₃-H₂O systems for CO₂ absorption (Darde et al., 2010; Sutter and Mazzotti, 2017). Subsequent investigations of NH₃-CO₂ absorption for CCS have therefore sought to implement strategies that eliminate solid phase formation to obviate clogging of the packed media bed (Yu et al., 2012; Gazzani et al., 2014).

Several authors have now investigated microporous hollow-fibre membrane contactors (HFMC) for the absorption of CO₂ into ammonia (Cui and deMontigny, 2017; Villeneuve et al., 2018; McLeod et al., 2014). In membrane contactors, the hydrophobic membrane permits non-dispersive contact between the gas phase (CO₂) and NH₃ rich solvent, with the gas filled pores of the microporous membrane mediating CO₂ transport from gas to liquid phase. Whilst inclusion of the membrane increases the overall resistance to mass transfer, the increase in specific surface area afforded by membrane contactors, provides a process intensification of over an order of magnitude compared with packed columns (Zhao et al., 2016). McLeod et al. (2015) successfully evidenced that the nucleation and growth of crystalline ammonium

bicarbonate on the solvent-side (shell-side) of a microporous HFMC was feasible in a CO_2 - NH_3 - H_2O system. In this proposed application for biogas upgrading, the reaction enabled separation of ammonia from wastewater and the formation of a new by-product to provide new value for the water industry (McLeod et al., 2014). Unlike in packed columns, the driving force for crystallisation is facilitated by counter-current diffusion of CO_2 and NH_3 into a chemically reactive concentration boundary layer developing at the solvent-membrane interface. The authors proposed that the membrane behaved as a physical substrate to lower the free energy barrier sufficient to initiate nucleation at the entrance of the pores where gas, liquid and solid (the membrane) interact such that heterogeneous nucleation was initiated in a controlled pathway (McLeod et al., 2015; Di Profio et al., 2010; Curcio et al., 2006).

The improved governance over nucleation provided by the membrane, coupled with the advantage of partitioning of the crystalline NH_4HCO_3 into the liquid phase, rather than a two-phase fluid as with packed columns, presents a simpler and more controlled method for reaction product recovery. However, whilst the thermodynamic behaviour of the CO_2 - NH_3 - H_2O system has been generally described, neither the solution chemistry required to initiate heterogeneous nucleation, or the crystallisation kinetics of a chemically reactive membrane crystalliser have been determined, which help to identify suitable boundary conditions for exploitation in CO_2 separations, as well as to indicate downstream processing requirements for product recovery. Supersaturation is the driving force for both nucleation and growth and the rate at which an excess of solute is achieved, is dependent upon the flux (Di Profio et al., 2010). In this configuration, chemical reactivity will define flux, thus the free ammonia concentration will influence the kinetic trajectory of the final crystalline product. Whilst membrane assisted crystallisers have been developed using osmotic or vapour pressure gradient as the driving force, the only chemically reactive membrane crystallisation reactor reported to date used the membrane to facilitate mixing of two solutions (Kieffer et al., 2009). The proposed configuration therefore represents a new chemically reactive membrane crystallisation reactor (CR-MCr) configuration. In this study we aim to characterise the chemistry and crystallisation kinetics underpinning crystal nucleation and growth in a membrane contactor for CO_2 absorption using NH_3 , to enable consistent and reproducible recovery of the final crystalline solid reaction product. Specific objectives are to: (i) characterise the kinetics of crystal nucleation and growth in a chemically reactive membrane crystallisation reactor, driven by gas phase reaction; (ii) establish the significance of driving force on membrane crystallisation through variation in ammonia concentration; (iii) identify the chemistry demanded to initiate nucleation in CR-MCr for ammonia mediated CO_2 separation; and (iv) provide confirmation of the reaction product identity and populate a mass balance to validate the successful separation of the crystalline reaction product from the membrane.

3.2 Materials and methods

3.2.1 Fabrication, equipment setup and operation

The module comprised of a single 165mm long polypropylene (PP) micro-porous hollow-fibre membrane (Membrana GmbH, Wuppertal, Germany) with a nominal pore size of 0.2 μm and membrane area of $9.33 \times 10^{-4} \text{ m}^2$ (based on the outer diameter) (Table 3.1).

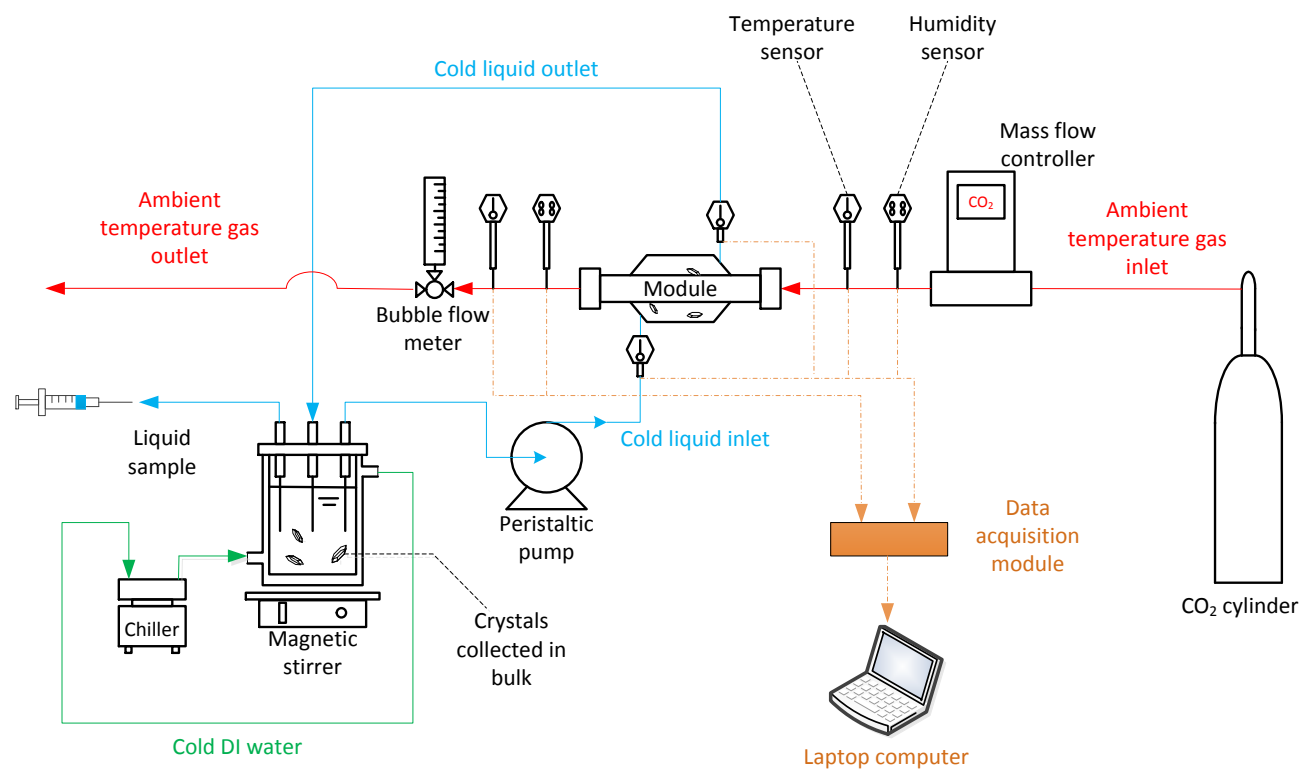
Table 3.1. Dimensions and characteristics of the hollow-fibre membrane

Fibre characteristics		
Membrane material	-	polypropylene
Inner diameter	mm	1.2
Outer diameter	mm	1.8
Wall thickness	μm	300
Active length	mm	165
Surface area ^b	m^2	9.33×10^{-4}
Nominal pore size ^a	μm	0.2
Lumen cross sectional area	m^2	1.13×10^{-6}
Shell side characteristics		
Height	mm	5
Width	mm	12
Shell cross sectional area	m^2	6.0×10^{-5}
Priming volume	ml	11.0
Operational characteristics		
Flow regime		Counter-current
Shell-side		1, 1.9, 3.3, 4.6 M NH_3 (aq)
Lumen-side		99.8% CO_2
Liquid temperature	$^{\circ}\text{C}$	5 - 7
Gas temperature	$^{\circ}\text{C}$	18 - 20
Liquid velocity	m s^{-1}	0.06
Gas velocity	m s^{-1}	14.7
Gas humidity	%	38

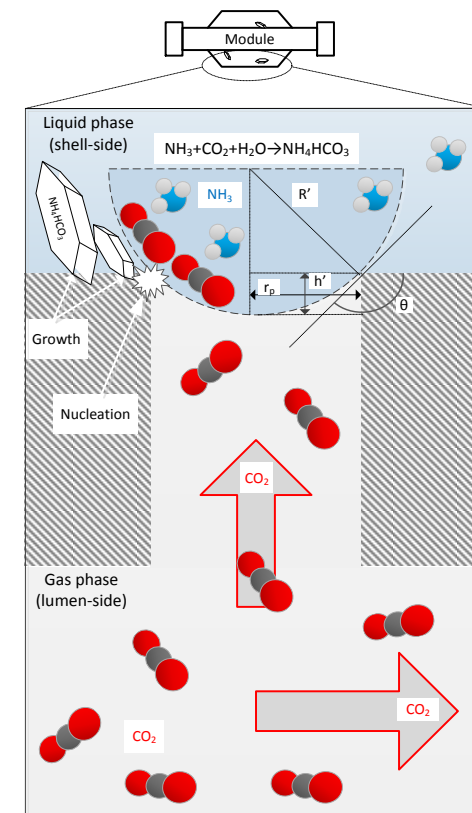
^a Data provided by manufacturer.

^b Based on fibre outer diameter.

The hollow-fibre membrane was potted in epoxy resin (Bostick Ltd., Stafford, UK) and sited within a 12mm diameter channel within the Perspex cell (Figure 3.1). To allow direct observation of shell-side crystallisation, a viewing window was engineered into a recess within the upper section of the cell (Autin et al., 2016). A Nikon SMZ-2T stereomicroscope with a 0.5x objective lens (Nikon UK Ltd., Surrey, UK) was fixed above the viewing window and images captured with a high-resolution camera (Leica EC3 Microsystems, Milton Keynes, UK). Membrane experiments were conducted sacrificially for each supersaturation level reached (C/C^*). The supersaturation level (C/C^*) is defined as the ratio between the CO_2 absorbed into solution and the CO_2 required to form ammonium bicarbonate at the solubility limit. Thus for each supersaturation level, a new single hollow-fibre was mounted into the Perspex cell. Sacrificial experiments were conducted in triplicate for each supersaturation level, and the mean and standard deviation reported.



(a)



(b)

Figure 3.1. (a) Experimental setup for the chemically reactive membrane crystallisation reactor; and (b) CO₂ absorbed within NH₃ rich solution induced supersaturation at the three phase line where gas, liquid and solid (membrane) intersect which initiates nucleation. Additionally, ammonia and water transport from liquid to gas phase could also occur.

Carbon dioxide (99.8%, BOC gases, Ipswich, UK) was introduced into the lumen of the hollow-fibre at a flow rate of 1000ml min⁻¹ using a laminar mass flow controller (0.01-1 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK). Absorbent was pumped counter-current on the shell-side of the membrane at 200ml min⁻¹ with a peristaltic pump (520Du, Watson-Marlow Ltd., Falmouth, UK). The absorbent temperature was fixed at 5°C with a refrigerated bath and circulator (R1 series, Grant Instruments Ltd., Cambridge, UK). Gas and liquid phase temperatures were measured across the membrane system (K-type thermocouples, Thermosense Ltd., Bucks, UK). Inlet temperatures for the gas and liquid phase were 20°C and 5°C respectively, with losses across the membrane noted to be around 0.4±0.2°C for both liquid and gas.

3.2.2 Chemical preparation, sampling and analysis

Absorbent ammonia concentrations ranging between 1 and 4.6 molNH₃ L⁻¹, were prepared through addition of aqueous NH₃ concentrate (35% Fisher Chemicals, Loughborough, UK) to de-ionised water (15.0 MΩ cm⁻¹). The absorbent pH was fixed at pH 10 with addition of hydrochloric acid (HCl, 37%, Fisher Scientific, Loughborough, UK) as this is typical of the pH employed in aqueous ammonia packed column processes (Yeh et al., 2005). Ammonia concentration was confirmed using an ammonium cell test which pre-acidifies the sample (VWR International Ltd., Poole, UK) before determination by spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darnstadt, Germany). A 1000 ml bubble flow meter (SKC, Blandford Forum, UK) was used to measure gas flow rate in order to calculate CO₂ flux (J_{CO2}, mol m⁻² s⁻¹):

$$J_{CO_2} = \frac{(Q_{G,in} - Q_{G,out}) \times 273.15 \times 1000}{22.4 \times A_m T_G} \quad (2)$$

where $Q_{G,in}$ and $Q_{G,out}$ are the inlet and outlet gas flow rates (m³ s⁻¹) respectively, A_m is the membrane surface area (m²) and T_G is the gas temperature (K) (Atcharyawut et al., 2007). The error for gas flow measurement was less than 2% of the reported value. Absorption solvent pH was monitored using a Jenway epoxy bodied pH electrode (Jenway 4330, Cole-Parmer, Stone, UK). The development of bicarbonate in solution was determined by UV absorbance at 215 nm (Jenway 6715, Cole-Parmer, Stone, UK) which corresponds to the absorption region for bicarbonate (Wilson et al., 2001). A crystal size distribution was developed for each sacrificial experiment which corresponded to a specific level of supersaturation (C/C*). Prior to counting, the absorbent was filtered through a 0.45 µm filter (Whatman, Camlab Ltd., Cambridge, UK) and then immersed in anhydrous alcohol to minimise agglomeration (Veiga et al., 1999). The crystals were transferred onto a microscope slide consisting of a 1 mm counting grid, and placed under an optical microscope (Optech Microscope Services Ltd., Thame, UK) equipped with PL 5/0.12 lens and digital camera

(Infinity 3, Lumenera, Ottawa, Canada). Images were analysed with image processing software (Image Pro Plus, Media Cybernetics, Cambridge, UK) to determine crystal number and size. Around 50 crystals were quantified with each image and a minimum of 600 crystals counted to develop one size distribution to minimise standard error (Ji et al., 2010). A Siemens D5005 X-ray diffractometer with Cu Ka1 radiation (Bruker UK Ltd., Coventry, UK) was used for crystal analysis, using a step size of 0.04° with diffraction patterns recorded in the 2θ range 15-40° (Meng et al., 2005).

3.2.3 Chemistry of the NH₃-CO₂-H₂O system

The absorption of carbon dioxide into aqueous ammonia solutions is thermodynamically controlled by the following equilibria (Millero and Roy, 1997; Sander, 2015):



Upon absorption of CO₂ into solution, the interactions between CO₂ and water can be described by:



The relative proportion of dissolved CO₂ available as carbonate (CO₃²⁻), bicarbonate (HCO₃⁻) or carbonic acid (H₂CO₃) is dependent upon solution pH, assuming a fixed liquid temperature of 5°C (Figure 3.2).

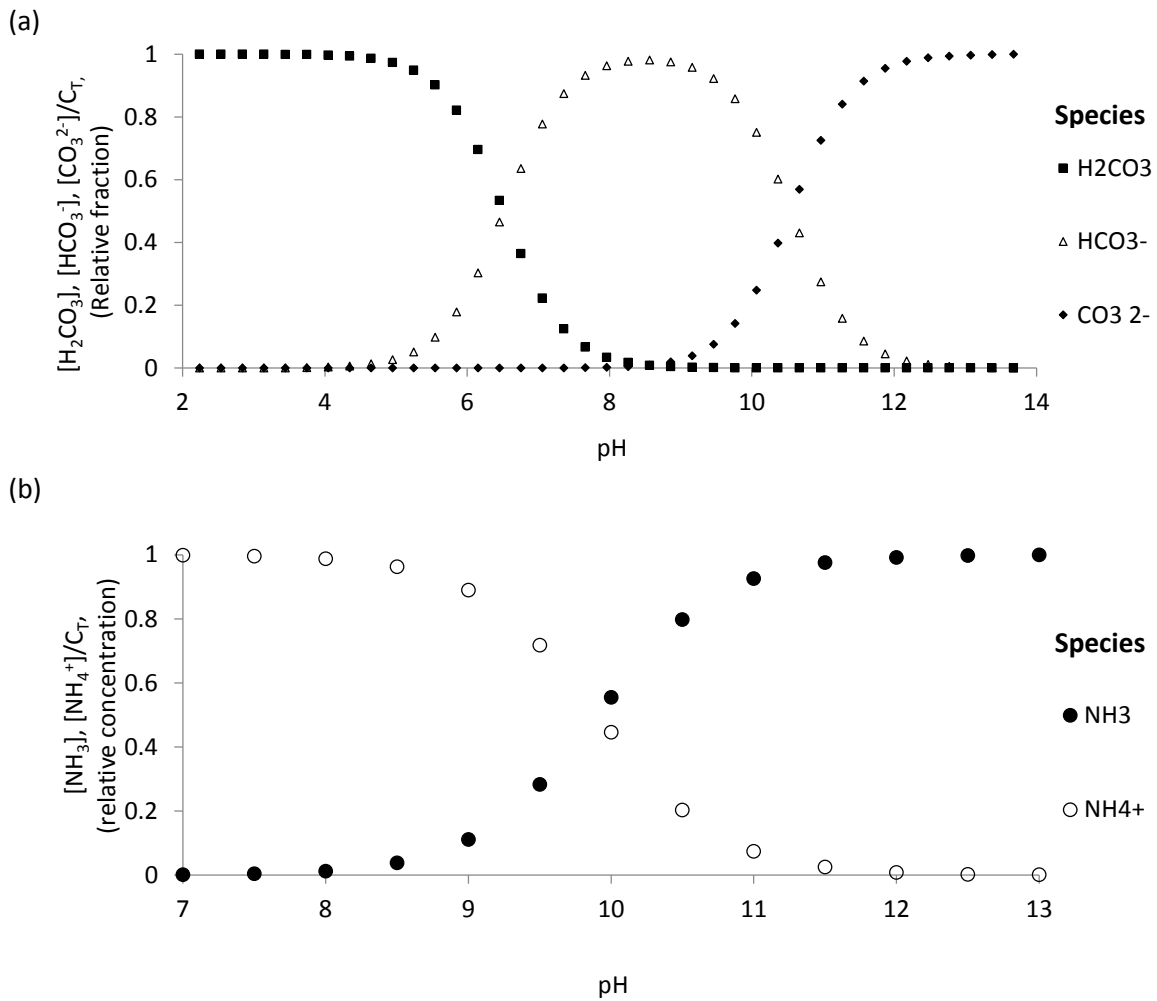


Figure 3.2. Dependency of: (a) carbonate equilibria; and (b) ammonium-ammonia equilibrium (b) on pH, for a fixed solution temperature of 5°C. Additional information available in appendix.

The equilibrium between unprotonated ammonia (NH_3) and protonated ammonium (NH_4^+) is similarly dependent on solution pH (Figure 3.2):



Wang et al., (2011) investigated NH_3 - CO_2 reaction kinetics in the liquid phase, comprising the reversible reactions of ammonium carbamate and carbamic acid formation:



Whilst five solid reaction products may form within the NH_3 - CO_2 - H_2O system (Sutter et al., 2015), ammonium bicarbonate is thermodynamically favoured, due to the lower solubility of the salt (Equation, 1; Mani et al., 2006).

3.2.4 Crystallisation kinetics

In a supersaturated solution, the nucleation rate (B) and crystal growth rate (G) can be determined by (Chen et al., 2014):

$$B = K_B G^b \quad (13)$$

$$G = K_G (c_{fm} - c^*)^g \quad (14)$$

where K_B ($\text{No m}^{-3-b} \text{s}^{-1+b}$) and K_G ($\text{kg}^{-g} \text{m}^{3g+1} \text{s}^{-1}$) are the rate constants for nucleation and growth respectively, while c_{fm} and c^* (kg m^{-3}) are the $\text{CO}_2(\text{aq})$ concentrations adjacent to the membrane surface and the equilibrium-saturated concentration at the membrane wall. Exponents g and b can be obtained from experimental data regression. Through determining the change in crystal number (ΔN) over a prescribed time period (Δt), the average nucleation rate becomes:

$$B(L, t) = \Delta N / \Delta t \quad (15)$$

Applying the experimentally derived values for B, into the logarithmic transformation of Equation 13, then permits determination of the kinetic nucleation constant K_B and exponent b from the intercept and slope respectively:

$$\log B = \log K_B + b \log G \quad (16)$$

Similarly, crystal growth rate can be defined as the change in size (m) over a prescribed time period (Δt), thus the average growth rate becomes:

$$G(L, t) = \Delta L / \Delta t \quad (17)$$

Following the determination of G from the linear slope (Söhnel et al., 1996), the crystal growth rate constant K_G and the exponent g can then be respectively derived from the intercept and slope of Equation 14, following logarithmic transformation:

$$\log G = \log K_G + g \log(c_{fm} - c^*) \quad (18)$$

3.3 Results

3.3.1 Impact of ammonia concentration on shell-side ammonium bicarbonate crystallisation

Carbon dioxide absorption was determined at four liquid phase ammonia concentrations ranging 1 to 4.6 molNH₃ L⁻¹ with the NH₃ solution in recirculation (Figure 3.3a). For each NH₃ concentration, CO₂ flux followed a similar two-stage profile, characterised by a rapid initial decline in CO₂ flux followed by a slow progressive decline in CO₂ flux. Whilst the initial CO₂ flux was lower for the 1M NH₃ solution, the flux profile was similar for NH₃ solutions ranging 1.9 to 4.6M. A spike in CO₂ flux was observed for the 4.6M NH₃ solution, corresponding to a supersaturation level of 1.2 (Figure 3.3b) and was coincident with the onset of substantive shell-side crystallisation which covered the membrane surface (Figure 3.4). Within the 3.3M NH₃ solution, shell-side crystallisation was observed at C/C^* 1.7, with no observable impact on CO₂ flux. Shell-side crystallisation did not occur in NH₃ solutions ranging 1-1.9M.

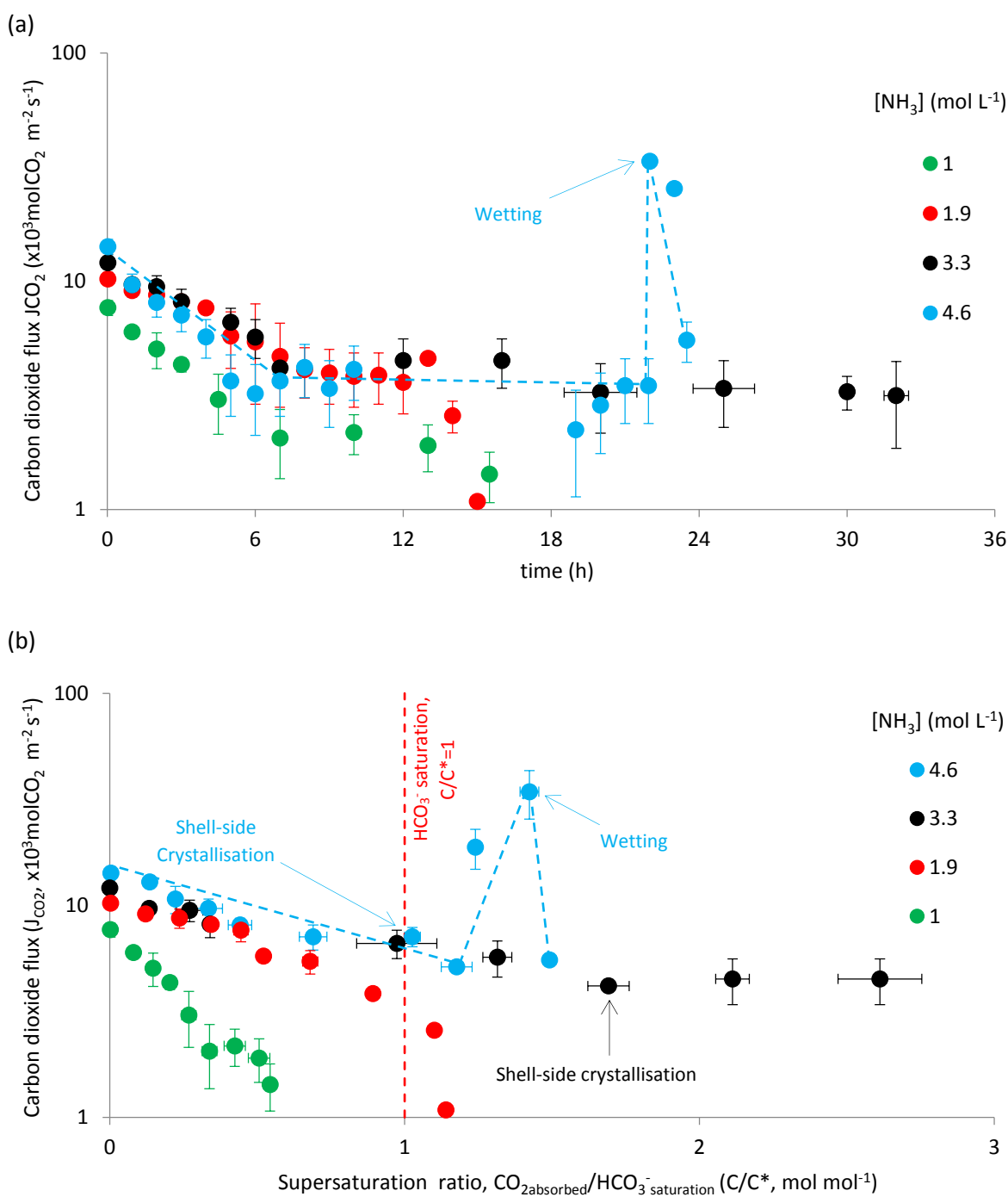


Figure 3.3. Carbon dioxide (CO_2) flux determined for the polypropylene membrane with four concentrations of NH_3 absorbent (1–4.6M NH_3) whilst operating absorbent in recirculation. Flux data plotted versus: (a) time; and (b) the supersaturation level (C/C^*), which assumes complete conversion of CO_2 to HCO_3^- . Error bars represent standard deviation of sacrificial experiments undertaken in triplicate at each supersaturation level. Conditions: G/L 5; V_G 14.7 m s^{-1} ; V_L 0.06 m s^{-1} .

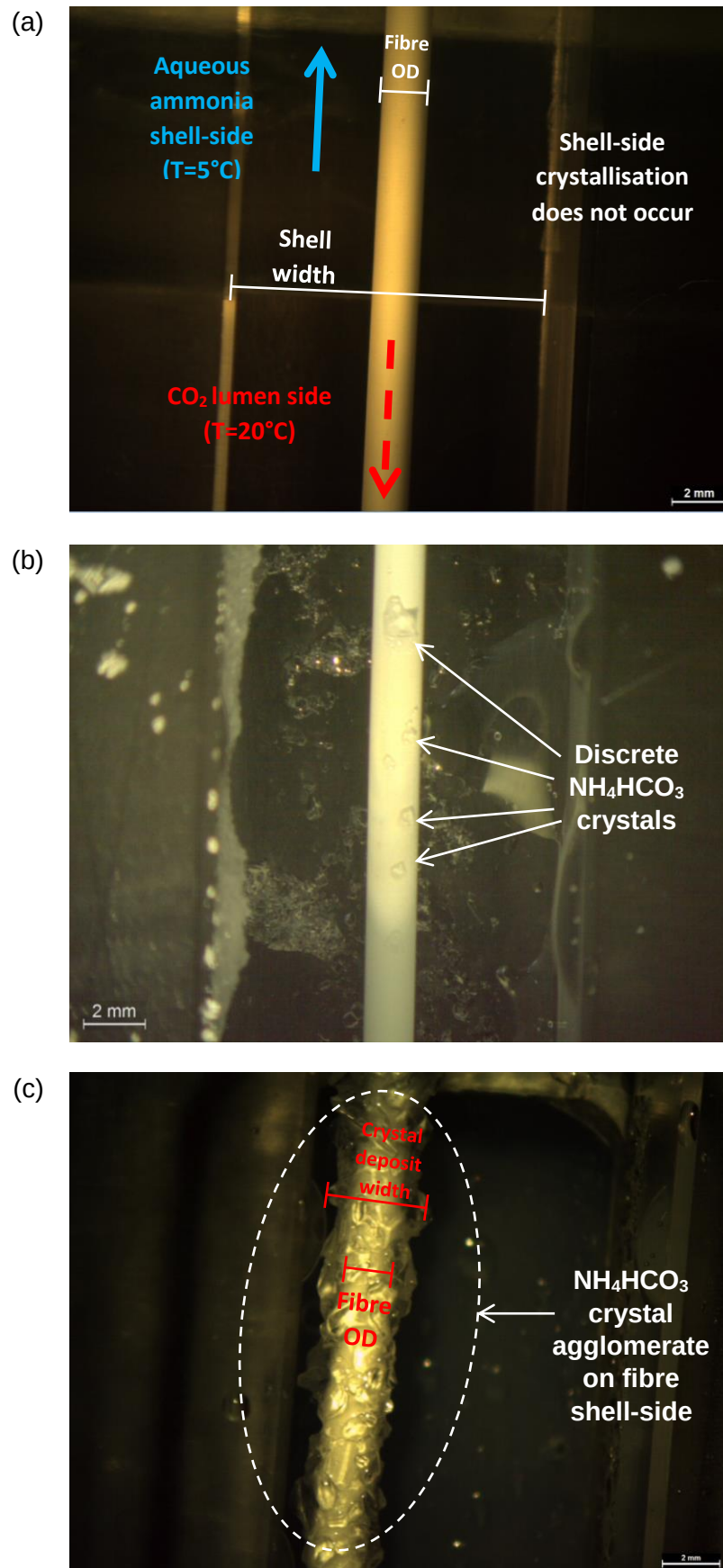
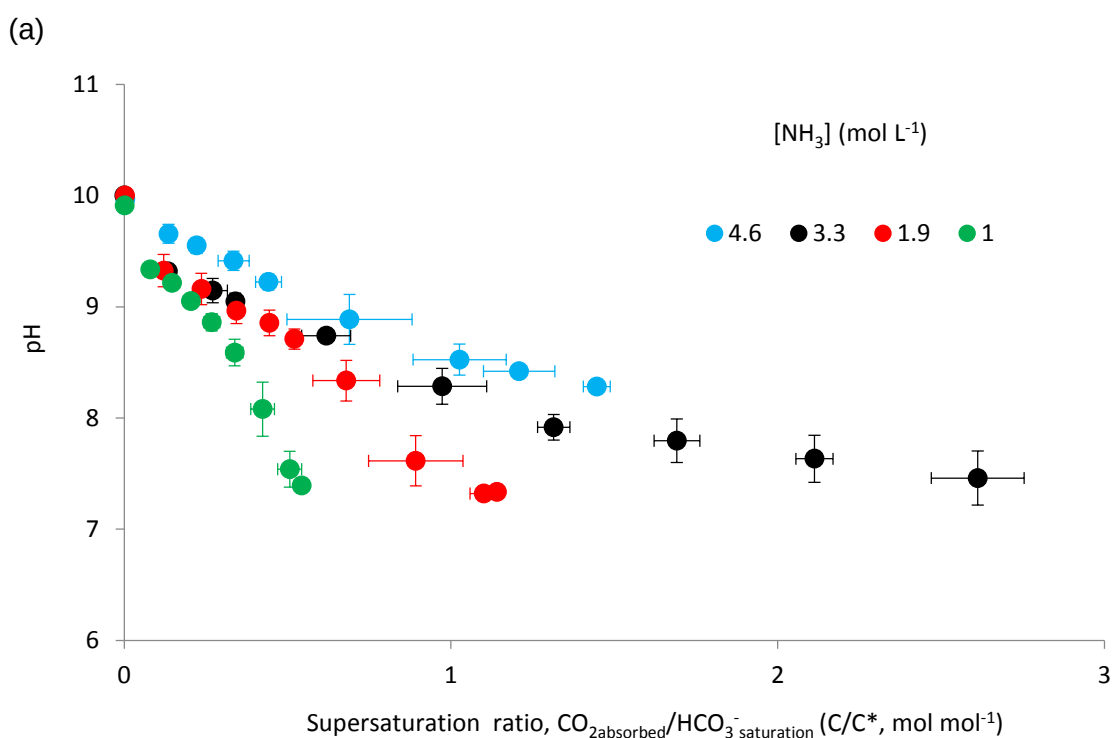


Figure 3.4. Direct observation of membrane surface crystallisation in real time once supersaturation (C/C^*) exceeded 1. Aqueous ammonia concentrations of: (a) 1.9M; (b) 3.3M; (c) 4.6M. Conditions: G/L 5; V_G 14.7 m s^{-1} ; V_L 0.06 m s^{-1} .

3.3.2 Chemistry governs induction of NH_4HCO_3 in $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ system

As CO_2 absorption progressed, the solution pH declined (Figure 3.5a). The reduction in pH was more evident for the lower ammonia concentrations (1 and 1.9M) despite the absorption of an equivalent amount of CO_2 . To illustrate, a minimum pH value of 7.4 was reached at C/C^* 0.55 with 1M NH_3 absorbent, whilst that pH was reached at C/C^* 2.6 for the 4.6M NH_3 solution. However, normalisation of the cumulative CO_2 absorption data to the initial free ammonia concentration of solution (CO_2 solution loading, mol mol^{-1}) evidenced that the reduction in pH exhibits an analogous trend independent of initial NH_3 solution concentration (Figure 3.5b). Shell-side crystallisation occurred at CO_2 loadings of 0.77 and 0.44 for 3.3 and 4.6 $\text{mol NH}_3 \text{ L}^{-1}$ respectively.



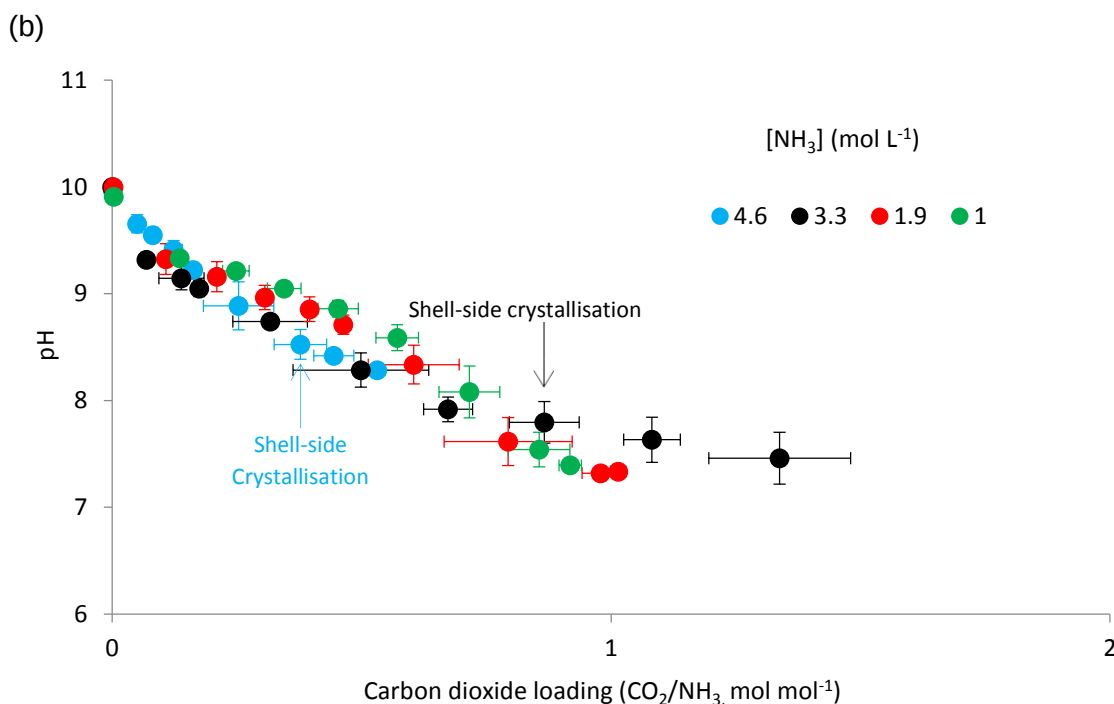


Figure 3.5. Reduction in pH observed following progressive CO₂ absorption, analysed by: (a) supersaturation level; and (b) carbon dioxide loading normalised for initial ammonia concentration. Error bars indicate standard deviation from sacrificial experiments undertaken in triplicate at each supersaturation level.

The arising pH data was developed to estimate ammonia and bicarbonate equilibria during CO₂ absorption (Figure 3.6). The ammonia-ammonium equilibrium had shifted primarily toward NH₄⁺ for each absorbent at supersaturation (C/C^* , 1), independent of initial NH₃ concentration (Figure 3.6). During the initial CO₂ absorption phase, the carbonate equilibrium shifts toward bicarbonate, due to the decrease in solution pH. However, as solution pH continued to decline with further CO₂ absorption, the water-CO₂ equilibrium shifts away from bicarbonate toward carbonic acid. For the lower NH₃ solution concentrations, this results in a peak in HCO₃⁻ concentration in advance of supersaturation (C/C^* , 1). This was corroborated by UV_{215nm} in which the bicarbonate concentration was noted to peak for both the 1 and 1.9M NH₃ solutions prior to supersaturation, and was evidently a contribution of the initial ammonia concentration (Figure 3.6b, c). The UV_{215nm} absorbance provided a surrogate for HCO₃⁻ concentration and demonstrated the 4.6M NH₃ solution to comprise the highest concentration at the point of supersaturation.

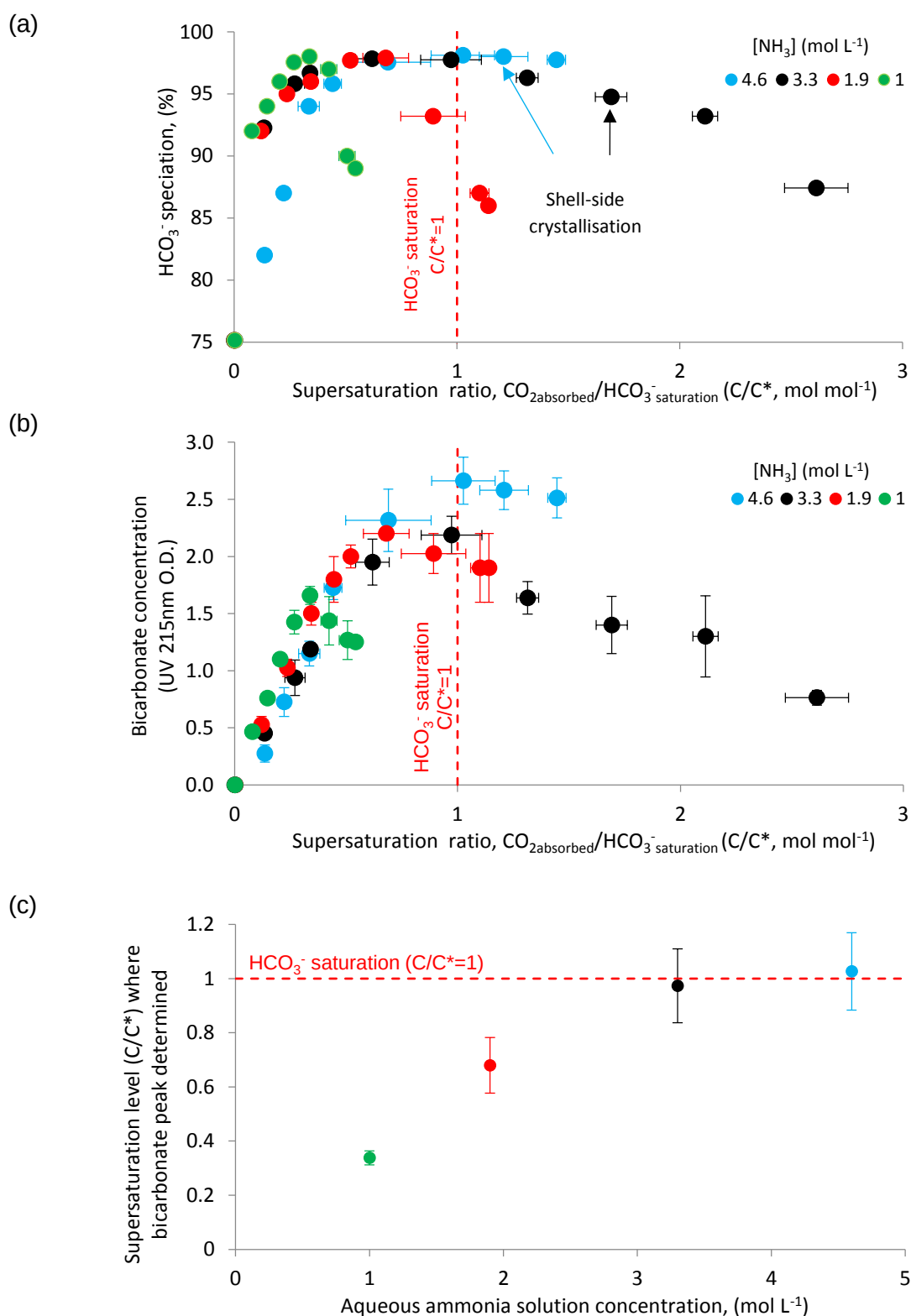
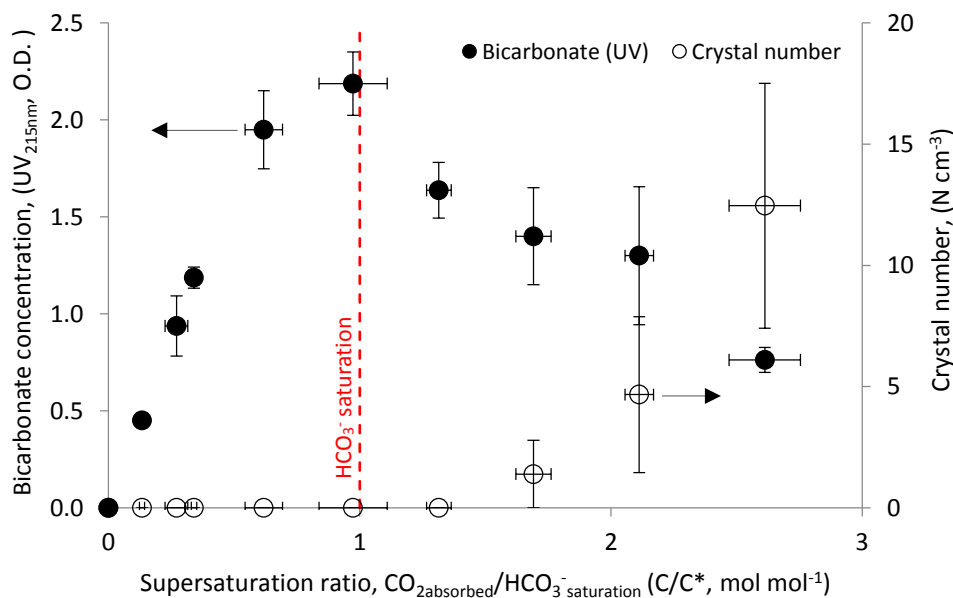


Figure 3.6. Ongoing CO₂ absorption lowers pH which shifts carbonate equilibria generating a dynamic bicarbonate concentration: (a) bicarbonate speciation determined from literature equilibria data; (b) bicarbonate concentration determined at UV215nm, which confirms shift in HCO₃⁻ speciation and indicates relative concentration; and (c) the supersaturation level at which the peak in bicarbonate concentration is achieved. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate for each ammonia concentration.

3.3.3 Kinetics of nucleation and growth for chemically assisted membrane crystallisation

For the 3.3M NH_3 solution, an increase in crystal number and crystal size was observed with an increase in supersaturation level and was coincident with a decrease in $\text{UV}_{215\text{nm}}$ (Figure 3.7).

(a)



(b)

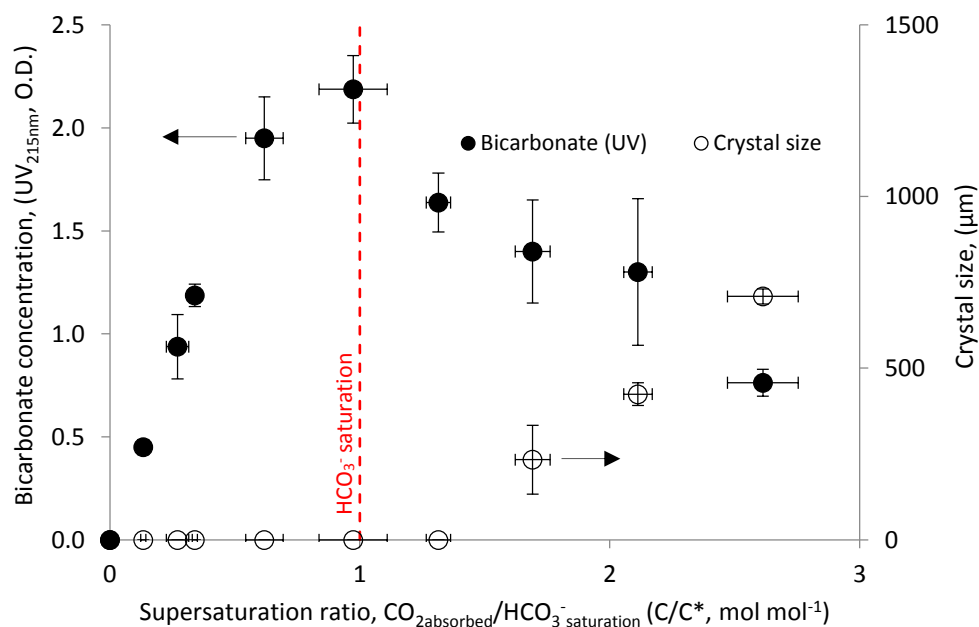


Figure 3.7. Transition in (a) crystal number; and (b) crystal size, determined at progressive levels of supersaturation (saturation demands conversion of 1.5M CO_2 into HCO_3^-) for an NH_3 concentration of 3.3M. Bicarbonate concentration shown for reference as this is important for induction. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate for each ammonia concentration

The average crystal growth rate (G) was determined at each supersaturation level, which enabled derivation of the crystal growth rate constant K_G $1.7 \times 10^{-14} \text{ Kg}^{-g} \text{ m}^{3g+1} \text{ s}^{-1}$ and exponent g , 2.64 (Figure 3.8). The nucleation rate (B) was also determined at each supersaturation level, to provide the nucleation rate constant K_B $1.9 \times 10^5 \text{ No m}^{-3-b} \text{ s}^{-1+b}$ and exponent b 0.38.

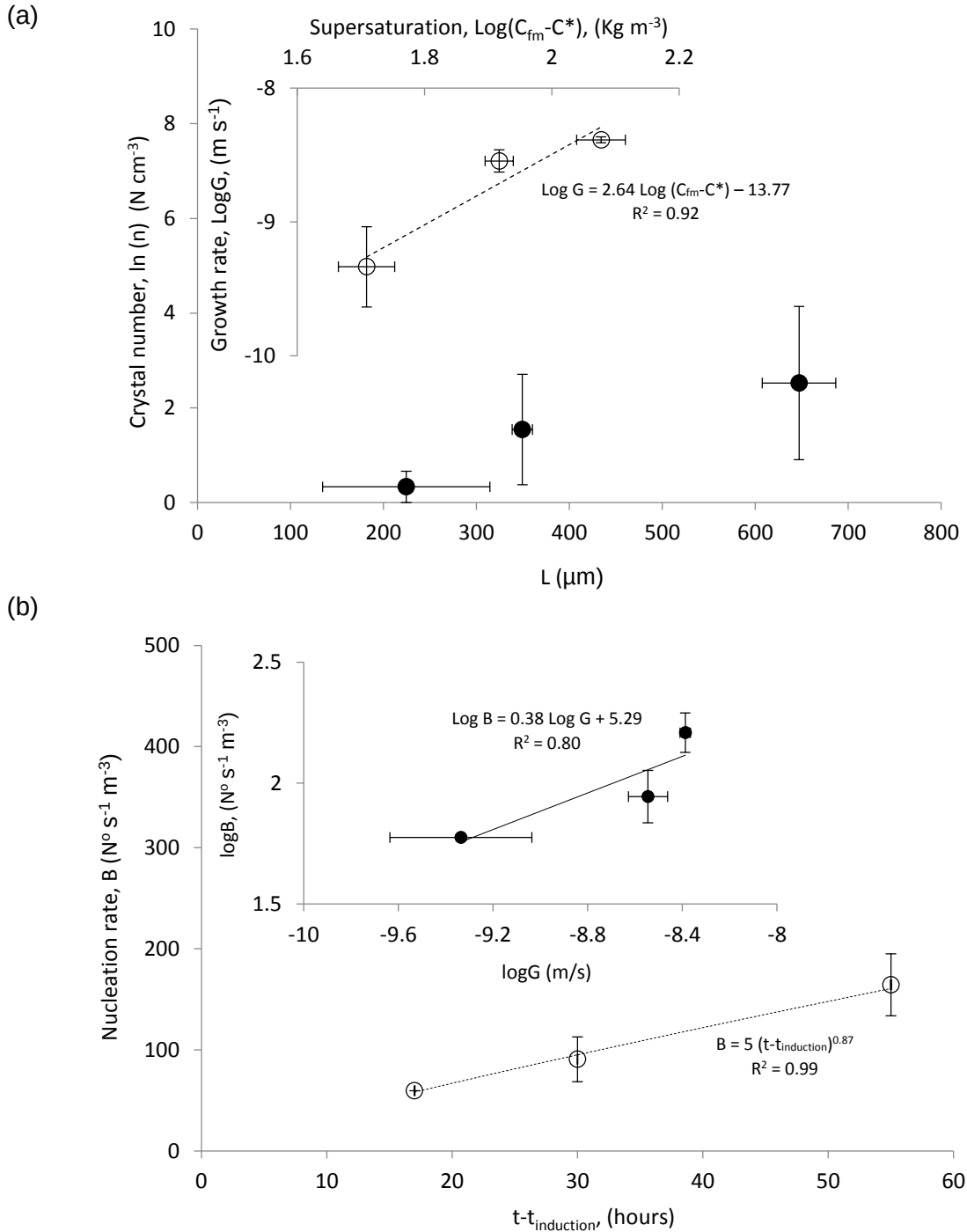


Figure 3.8. (a) Crystal population density versus crystal size observed at progressively increasing levels of supersaturation, and inset the determination of crystal growth rate from this data; (b) nucleation rate determined from the onset of induction and inset, the relationship between nucleation rate and growth rate is evaluated.

Nitrogen mass balance indicated that >99% of the nitrogen reduction in the absorbent was contained within the recovered crystalline product. X-ray diffraction was used to compare pure ammonium bicarbonate to crystals produced following CO₂ absorption into 3.3M NH₃ solution, which evidenced crystals obtained through the CR-MCr to be ammonium bicarbonate (Figure 3.9).

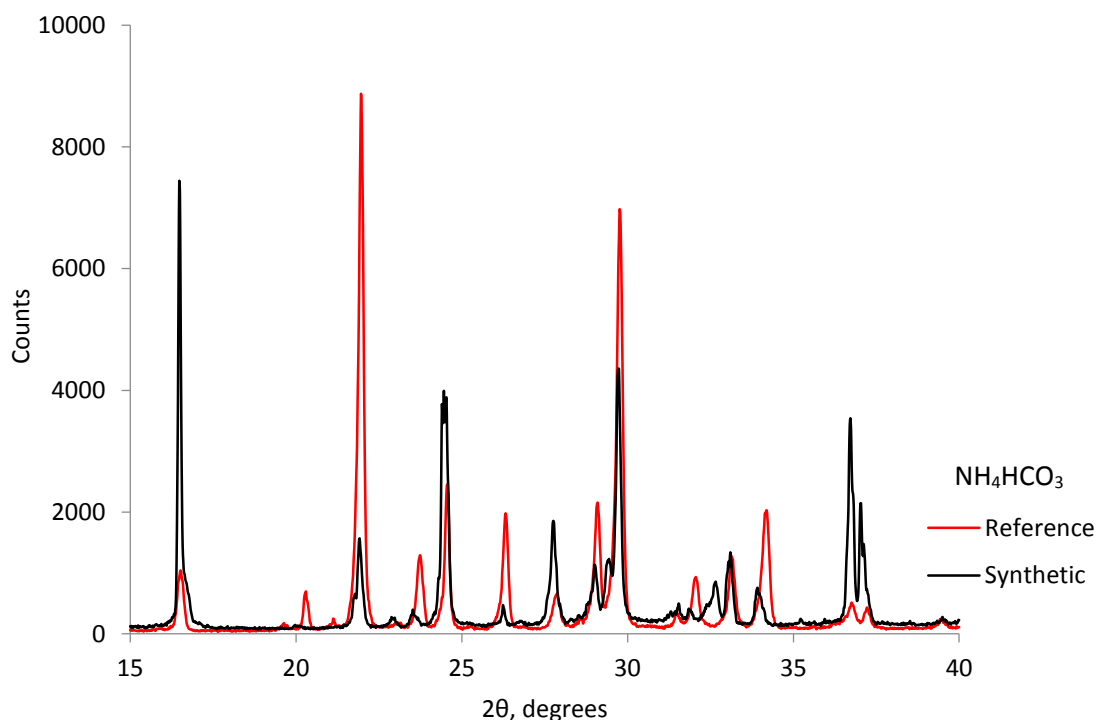


Figure 3.9. X-Ray Diffraction (XRD) analysis for comparison of pure ammonium bicarbonate (Reference) with the ammonium bicarbonate produced from chemically reactive membrane crystallisation (Synthetic) using 3.3M NH₃ solution.

3.4 Discussion

In this study, the underpinning chemistry required to simultaneously absorb CO₂ and initiate nucleation of crystalline ammonium bicarbonate in a hollow-fibre membrane contactor has been ascertained, and the kinetics of heterogeneous nucleation and crystal growth determined, which evidence the mechanism for chemically reactive membrane crystallisation. Both crystal population density and crystal size increased with increasing levels of supersaturation (Figure 3.8). This is in contrast to Veiga et al. (1999) who crystallised ammonium bicarbonate in batch and observed a decline in crystal population density with particle size which is characteristic of conventional crystalliser configurations where homogeneous primary and secondary nucleation is favoured (Mydlarz and Briedis, 1993; Curcio et al., 2001). The increase in population density observed in the present study (Figure 3.8), in parallel with crystal growth, is indicative of sustained primary heterogeneous nucleation, promoted by the membrane substrate through a reduction in the free energy

barrier. Di Profio et al. (2003) also identified an increase in population density following supersaturation when operating membrane crystallisation for lysozyme recovery through an osmotic gradient. However, as their process was operated in batch, nucleation rate declined due to solute consumption at increasing levels of supersaturation for all but the lowest driving force. Whilst nucleation rates cannot be directly compared due to geometric differences amongst other considerations, the nucleation rate constant in this study was $1.9 \times 10^5 \text{ No m}^{-3} \cdot \text{s}^{-1+b}$ which is thirteen orders of magnitude below that reported by Curcio et al. (2001) for a conventional crystalliser (Figure 3.8). It is therefore asserted that the increasing nucleation rate and growth rate observed at increasing levels of supersaturation is due to: (i) the low driving force of the chemical reaction, which limited consumption of NH_3 in the initial phase of crystallisation; and (ii) the counter-current diffusion of CO_2 and NH_3 into the concentration boundary layer, which provided consistent replenishment of reactant to the site of preferential nucleation. This latter contribution is a unique facet of this chemically reactive membrane crystallisation reactor configuration. For the 4.6M NH_3 solution, encrustation (or scaling) of the fibre occurred too quickly for the nucleation rate to be determined (Figure 3.4). Chen et al. (2014) asserted that crystallisation induced scaling arose from Ostwald ripening in which an agglomeration of fine particles occurred immediately after nuclei breeding, followed by the supported growth of coarser crystals through supply of small crystal particles that become more stable on the membrane surface. As the CO_2 flux profiles for both 3.3 and 4.6 M NH_3 solutions (Figure 3.3) were similar, it is the free ammonia concentration and not CO_2 transport which determines the nucleation rate. It is suggested for this study, that the higher NH_3 concentration increased nucleation rate which induced an analogous effect to Ostwald ripening. The resultant effect was a change in surface contact angle which subsequently induced wetting and a breakthrough of solution NH_3 into the gas phase which temporarily increased flux (Figure 3.3; Franken et al., 1987). In contrast, whilst several discrete crystals were observed to have formed on the membrane fibre at 3.3M (Figure 3.4b), most crystals were collected downstream of the membrane, which was confirmed by nitrogen mass balance. When coupled with the consistent flux profiles sustained over the duration of experiments, this would suggest that provided nucleation rate can be specific below a critical threshold, sustained membrane operation should be achievable with minimum reactive maintenance intervention.

The highest CO_2 flux recorded was similar to that of McLeod et al. (2015) who used a wider pore size PTFE membrane for CO_2 - NH_3 absorption. For initial NH_3 concentrations equal to or above 1.9M, CO_2 flux was apparently independent of NH_3 concentration (Figure 3.3) which implies the liquid phase imparted negligible resistance to mass transfer, as is commonly reported for chemical absorption where the reactant is in excess (Esquiroz-Molina et al., 2013). However, a two-stage decline in CO_2 flux was observed following progressive CO_2

absorption. In the initial phase of CO₂ absorption, carbamic acid forms alongside ammonium carbonate (Mani et al., 2006; Ahn et al., 2011; Wang et al., 2011). The carbamic acid deprotonated to form carbamate (Equation 12), whilst a fraction of the CO₂ reacted with hydroxide to form bicarbonate (HCO₃⁻), the cumulative effect being a reduction in solution pH (Figure 3.5a) (Wang et al., 2011). The lower pH shifted the equilibrium toward NH₄⁺ (Figure 3.2) which is favourable for crystallisation (Equation 1) but reduced the rate of reaction with CO₂. The onset of the second slower phase of CO₂ flux decline occurred at a pH of between 8.2 and 8.5 for each NH₃ concentration studied (Figure 3.5b) which corresponded to a shift in equilibrium from NH₃ to NH₄⁺ prior to supersaturation. It is this reduction in reactivity which constrained nucleation rate. The rate of pH decline was dependent upon CO₂ loading (CO₂/NH₃, Figure 3.5b) where a relative excess of CO₂ drives a faster decline in pH as was observed in this study with a lower NH₃ absorbent concentration (Figure 3.5a). The 4.6M NH₃ solution therefore sustained a higher pH at supersaturation which subsequently favoured HCO₃⁻ formation at induction (Figure 3.6b). We suggest that it is the increased availability of HCO₃⁻ provided by the buffering capacity of the 4.6M NH₃ solution which increased nucleation rate and induced surface scaling.

The thermodynamics of the crystalline reaction product were evaluated by Jänecke (1929) who identified that the intermediate solid products, ammonium carbonate monohydrate ([NH₄]₂CO₃H₂O), sesquicarbonate ([NH₄]₂CO₃ 2NH₄HCO₃) and ammonium carbamate (NH₂COONH₄) could form before the final reaction product (ammonium bicarbonate) dependent upon solution temperature and CO₂ loading (the molar ratio of CO₂/NH₃). The authors identified that at an absorbent temperature of 5°C, a CO₂/NH₃ loading exceeding 0.53 was required to induce crystallisation of ammonium bicarbonate (27% NH₃; Jänecke, 1929). In this study, this CO₂ loading was exceeded at each ammonia concentration (Figure 3.5b), however, crystallisation did not occur for NH₃ concentrations below 3.3M. For 1M absorbent, the solid phase transition is thermodynamically limited since the free ammonia concentration is below the solubility limit for NH₄HCO₃ of 1.5 M (5°C, Perry and Green, 2007). At 1.9M, NH₃ is not thermodynamically limiting. Instead the solid phase transition is kinetically limited by the pH transient which forces the equilibrium toward carbonic acid (H₂CO₃, Figure 3.3) such that upon reaching supersaturation (C/C* ~1), there is an insufficiency of bicarbonate to initiate heterogeneous nucleation (Figure 3.6). For NH₃ concentrations of 3.3 and 4.6M, the excess NH₃ reduced the CO₂/NH₃ ratio (Wang et al., 2011) and sustained pH through to supersaturation such that sufficient HCO₃⁻ was available to induce crystal growth at CO₂ loadings of 0.77 and 0.44 respectively. Confirmation of crystalline ammonium bicarbonate was provided by XRD analysis. The governance of this kinetic trajectory is in contrast to the thermodynamic description of NH₃-CO₂-H₂O crystallisation where NH₃ concentrations up to 27% wt. have been studied (Jänecke, 1929; Darde et al., 2010). In such cases, the NH₃

concentration is sufficient to sustain pH, and favour the crystallisation of the more soluble intermediate solid products of ammonium carbonate (320 g l^{-1}) and ammonium carbamate (790 g l^{-1}). Mani et al. (2006) identified a similar NH_3 concentration (2.5M) as the best compromise between CO_2 loading and ammonia slip for packed columns. As demonstrated in this study, a similar ammonia concentration of 3.3M permits maximum attainable flux to be achieved which will limit membrane area, whilst assuring continuity in the crystallisation of the ammonium bicarbonate product of reaction.

3.5 Conclusions

In this study, the kinetics and solution chemistry underpinning the chemically reactive membrane crystallisation reactor for gas-liquid absorption of CO_2 into ammonia has been described and the method to recover crystalline ammonium bicarbonate as the reaction product has been demonstrated:

- The two-stage decline in CO_2 flux caused by the reduction in solution pH and the subsequent shift in ammonia-ammonium and carbamate-carbonate-bicarbonate equilibrium demonstrated that a minimum free ammonia concentration is demanded to sustain pH to ensure there is sufficient bicarbonate in the reaction zone at supersaturation to facilitate heterogeneous nucleation.
- Free ammonia concentration greater than 1.9M did not improve CO_2 flux, which is similar to observations in CO_2 - NH_3 packed column investigation. Selection of the upper threshold for ammonia should therefore be based on limiting nucleation rate to avoid crystallisation induced scaling of the membrane.
- Increase in crystal population density and crystal size is indicative of the membrane acting as a physical substrate for heterogeneous nucleation during chemically reactive crystallisation.
- Both nucleation rate and crystal growth rate increased with progressing levels of supersaturation, which can be ascribed to the relatively low chemical reactivity and the unique counter diffusion mechanism fostered by this type of membrane crystallisation technology which provides continued reactant replenishment within the boundary layer where heterogeneous nucleation is promoted by the membrane through reduction in the free energy barrier.
- Provided an appropriate nucleation rate was specified, only limited crystals were observed to form at the membrane and were instead collected downstream of the membrane. Use of sacrificial experiments (i.e. replicates) at each level of supersaturation helped to evidence that consistent and reproducible crystallisation is achievable in this chemically reactive system, indicating limited maintenance intervention should be required.

Integration of the system for simultaneous crystallisation and gas treatment will require progress toward continuous crystallisation through metastable control, or the implementation of multi-stage gas treatment, where the latter option is most likely to achieve the higher crystal product yield.

Acknowledgements

The authors would like to thank our industrial sponsors: Anglian Water, Northumbrian Water and Severn Trent Water for their financial and technical support. We are further grateful for financial support from the Engineering and Physical Sciences Research Council (EPSRC) received through the STREAM Industrial Doctorate Centre and for a Cranfield School of Water, Energy and Environment PhD bursary.

Appendix

Carbonic acid, bicarbonate and carbonate equilibria

The distributions of carbonic acid, bicarbonate and carbonate vs. pH (Figure 3.2a) have been evaluated through the following equations (Millero and Roy, 1997; Millero, 1995):

$$\frac{[H_2CO_3]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A1)$$

$$\frac{[HCO_3^-]}{C_T} = \frac{[H^+]K_{-5}}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A2)$$

$$\frac{[CO_3^{2-}]}{C_T} = \frac{K_{-4}K_{-5}}{[H^+]^2 + K_{-5}[H^+] + K_{-4}K_{-5}} \quad (A3)$$

Where C_T is the sum of the carbonic species fractions in solution ($C_T = 1$), while K_{-4} and K_{-5} are the dissociation constants of bicarbonate and carbonic acid, given by (Equations 7 and 8; Millero and Roy, 1997):

$$K_{-4} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (A4)$$

$$K_{-5} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (A5)$$

In particular, at temperature $T = 5^\circ\text{C}$ and salinity $S = 0 \%$, $K_{-4} = 2.84 \times 10^{-11}$; $K_{-5} = 3.069 \times 10^{-7}$, (Millero, 1995).

Dissociation of ammonia and ammonium ion

The equilibrium between unprotonated ammonia and protonated ammonium as a function of pH has been evaluated as follows (Ukwuani and Tao, 2016):

$$\alpha_{NH_3} = 1/(1 + 10^{pK_a^S - pH}) \quad (A6)$$

$$\alpha_{NH_4^+} = 1 - \alpha_{NH_3} \quad (A7)$$

Where pK_a^S is given by (Bates and Pinching, 1949):

$$pK_a^S = -\log K_a^S = \frac{A}{T} + B \quad (\text{A8})$$

Specifically, A = 2727.42 and B = 0.0973, respectively, while T is temperature in K (Bates and Pinching, 1949).

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Chapter 4

NH₃(aq) recovery from raw return liquor to induce in situ NH₄HCO₃ shell-side crystallisation and harvesting during CO₂ absorption within an hollow fibre membrane contactor

For submission to: Water Research

NH₃(aq) recovery from raw return liquor to induce in situ NH₄HCO₃ shell-side crystallisation and harvesting during CO₂ absorption within an hollow fibre membrane contactor

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Abstract

An integrated system comprised of in-series thermal stripping and hollow fibre membrane contactor (HFMC) has been introduced to concentrate ammonia from return liquors and employ the condensate as an absorbent for simultaneous CO₂ absorption enhancement, ammonia removal, and controlled crystallisation and harvesting of ammonium bicarbonate within a single process. Synthetic solutions (0.5 - 2.7 mol_{NH₃} L⁻¹) were initially used to investigate the boundary conditions required to concentrate ammonia. In-series thermal stripping of the synthetic return liquor at high temperatures (~80°C) demonstrated to (1) shift the NH₃-NH₄⁺ equilibrium toward 100% free ammonia and raise the NH₃ saturated vapour pressure, thus increasing the overall liquid phase mass transfer coefficient; (2) produce a concentrated absorbent at significantly higher concentration than that required to initiate crystallisation; (3) offer the opportunity for water utilities to minimise the chemical demand for recovering NH₃, compared with low temperatures. Aqueous ammonia recovered from real return liquor showed sensibly lower surface tension compared with the synthetic solution of equivalent reactivity, which resulted in an enhanced nucleation potential on the membrane-liquid interface. Additionally, X-ray diffraction analysis of the crystals produced from real absorbent, indicated the reaction products to be reasonably pure ammonium bicarbonate, demonstrating that pre-treatment of the return liquor avoids ionic competition problems.

Keywords: *membrane; biogas; aqueous ammonia; return liquor; thermal stripping; crystallisation; ammonium bicarbonate*

4.1 Introduction

Biogas produced through anaerobic digestion is a mixture of methane (CH₄, ~60%) and carbon dioxide (CO₂, ~40%). Through facilitating CO₂ removal, biogas can be upgraded into biomethane for injection into the national grid (Persson et al., 2007). Following introduction of incentivisation for biomethane, there are now a large number of biogas upgrading plants operating across Europe. Most large scale facilities advocate absorption technology, using either water or chemical solvents as the scrubbing solution. Chemical solvents provide a higher absorption capacity and increased rate of mass transfer, which introduces considerable process intensification. Whilst a relatively new technology for water utilities, chemical absorption is a mature technology in other sectors and has been extensively investigated for carbon capture and storage (CCS). In CCS, ammonia (NH₃) has been identified as an alternative solvent to organic amines since it exhibits greater absorption capacity, lower energy requirement for regeneration and is favourable from a cost perspective. However, due to the low molecular weight of ammonia, the saturation vapour pressure is high in comparison to alkanolamines, which introduces NH₃ slip into the gas phase (Kozak et al., 2009). McLeod et al. (2014) evidenced that NH₃ slip could be limited by using a membrane contactor rather than a packed column. Hollow fibre membrane contactors (HFMC) employ a hydrophobic microporous membrane to facilitate non-dispersive contact between gas and liquid phases, permitting only gases to diffuse through the pores. The minimisation of slip in HFMC was proposed to be due to the promotion of laminar flow in the liquid phase which promoted radial diffusion of NH₃ from the absorbent bulk to the reactive boundary layer, facilitating overall stabilisation through the overall reaction (Budzianowski, 2011a):



Whilst the membrane introduces an additional resistance to mass transfer, the increased specific surface area in the HFMC provides substantive process intensification when compared to packed columns (Belaissaoui and Favre, 2018).

In biogas facilities operated by water utilities, there are ammonia rich wastewaters which have the potential to act as a sustainable source of absorption solvent for biogas upgrading. McLeod et al. (2014) illustrated an enhancement in CO₂ separation of up to 15 times versus water when employing NH₃ rich sludge liquor returns (around 2000 mgNH₄⁺-N L⁻¹, 0.11mol L⁻¹). He et al. (2017) introduced vacuum membrane distillation (VMD) to recover NH₃ from return liquors prior to their introduction into a packed column for biogas upgrading. Pre-concentration using VMD achieved a recovered ammonia concentration of 18,300 mgN L⁻¹ (1.3 mol L⁻¹), markedly enhancing CO₂ separation during biogas upgrading versus the untreated liquor. Whilst this remains below the ammonia concentration generally considered viable for CCS (4 to 6 mol L⁻¹) (Shuangchen et al., 2013; Budzianowski, 2011b), the authors

proposed discharge of the used absorbent for fertigation (Bonet-Ruiz et al., 2015), which would obviate the need for thermal regeneration, simplifying process design and energy requirements.

The cost of ammonia removal from wastewater has been valued between £ 1.7 and £ 73.1 per kgNH₄⁺ removed, dependent upon process scale (Oxera, 2006). Consequently, separation of the NH₃-CO₂ reaction product from solution presents several advantages:

- (i) avoiding the cost of wastewater treatment for ammonia;
- (ii) recovery of ammonium in a crystalline solid ammonium bicarbonate (NH₄HCO₃) product, which affords a potential resale value of up to € 0.11 kg⁻¹ due to its value as an industrial feedstock (e.g. fertiliser) (Budzianowski, 2011b);
- (iii) no thermal requirement for solvent regeneration;
- (iv) minimisation of disposal volume, which will reduce transport costs;
- (v) locking CO₂ into a solid phase which can improve sustainability credentials.

Crystallisation of the ammonium bicarbonate reaction product was first considered in the chilled ammonia process for CCS as a method to decrease NH₃ slip in the absorber (Darde et al., 2009). However, the homogeneous nucleation and growth of crystals within the mixed phase of a packed column introduced clogging of equipment, making implementation difficult (Sutter et al., 2015). McLeod et al. (2015) successfully demonstrated the feasibility to control the initiation of ammonium bicarbonate crystallisation in HFMC using a synthetic 2M ammonia solution. The high contact angle exhibited by the hydrophobic PTFE membrane employed, promoted heterogeneous nucleation at the micropores where gas, liquid and membrane interacted to induce surface growth of the reaction product. This enhanced nucleation potential offered by the HFMC versus packed columns (Budzianowski et al., 2011), coupled with the phase separation fostered by the membrane, enabled recovery of the reaction product in the liquid phase (McLeod et al., 2015). Therefore, HFMC technology offers the unique opportunity to simultaneously accomplish enhanced CO₂ separation, NH₃ removal from wastewater and fertiliser production within a single stage process.

Previous studies that have sought to produce a solid crystalline product following reaction of ammonia with a counter oxyanion in real solutions, have shown that the concentration of the reaction product is generally below the solubility limit, such that further processing is demanded before crystallisation can proceed. To illustrate, Ukwuani and Tao, (2016) coupled vacuum thermal stripping with acid absorption to recover ammonium sulphate ((NH₄)₂SO₄) as the crystalline product. However, due to the high solubility limit of ammonium sulphate (706 g(NH₄)₂SO₄ L⁻¹), the introduction of an antisolvent or thermal gradient was needed to initiate the phase change to a crystalline product (Ukwuani and Tao, 2016), introducing a third processing stage, which increases capital cost and process complexity. Similarly, following facilitation of an NH₃-CO₂ reaction in real wastewater using a HFMC,

McLeod et al. (2014) identified that to achieve the phase change into a crystalline product, thermal treatment was required. However, due to the high solubility of ammonium bicarbonate ($182 \text{ gNH}_4\text{HCO}_3 \text{ L}^{-1}$, $42 \text{ gNH}_4^+ \text{ L}^{-1}$ or 2.3M at 20°C) and the presence of other cations, more thermodynamically favourable products such as calcium carbonate and sodium bicarbonate were also formed, which limited ammonia transformation into the preferred solid reaction product. Whilst not explicitly demonstrated, Teichgraber and Stein (1994) proposed that using thermal packed column stripping for direct return liquor treatment, separation and concentration of the ammonia fraction could be achieved to deliver a final concentration of up to $130 \text{ gNH}_3^+\text{-N L}^{-1}$ ($\approx 9 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$), which is considerably higher than has been previously identified in the literature to date. We propose that utilisation of such technology to pre-concentrate ammonia from return liquors will provide a reactive solution in similar concentration to those employed for CCS that is sufficiently concentrated to enable direct crystallisation of the reaction product enabling CO_2 separation and product conversion in a single stage HFMC process. Since thermal separation favours the volatile fraction (ammonia, NH_3), we also suggest that pre-treatment will limit ionic competition, such that ammonium bicarbonate will become the thermodynamically favourable crystalline reaction product formed with ammonia recovered from wastewater. Consequently, in this study, we seek to demonstrate an integrated system comprised of thermal stripper and HFMC to promote chemically enhanced CO_2 separation with concentrated ammonia recovered from real wastewater, to deliver consistent and reproducible nucleation, growth and recovery of the crystalline NH_4HCO_3 reaction product, within a single stage HFMC (Figure 2.1). The following objectives have been identified: (i) determine the boundary conditions needed to concentrate ammonia from concentrated wastewater; (ii) use identified boundary conditions to demonstrate ammonia separation and recovery from real wastewater using thermal stripping; (iii) compare CO_2 absorption and crystallisation behaviour using synthetic and recovered ammonia solutions of equal reactivity; and (iv) confirm the crystalline reaction product derived from real wastewater to be NH_4HCO_3 to evidence the reduction in cationic competition through application of pre-treatment.

4.2 Materials and methods

4.2.1 Experimental set-up for thermal stripping of ammonia

Vacuum thermal stripping experiments were conducted using a rotary evaporator (Rotavapor R-100, Buchi Ltd, Oldham, UK) comprising vertical condenser, heating bath with a digital display and 1L evaporating flask for feed solution, 1L receiving flask for condensate (recovered), vacuum pump, and vacuum controller. Stripping experiments were initially conducted using synthetic wastewater to characterize the boundary conditions that maximize NH_3 recovery (Zeng et al., 2006). For all the experiments, the liquid feed was approximately

1L, pre-heated in the water bath and when its temperature approached the desired operating temperature (either $19 \pm 1^\circ\text{C}$ or $80 \pm 1^\circ\text{C}$), the vacuum pump was turned on to keep feed boiling. At the end of each sacrificial test conducted in triplicate, the volumes, pH, temperatures and NH_3 concentrations of residual feed and condensate recovered were determined through graduated cylinders (10ml to 2L, Fisher Scientific Ltd, Loughborough, UK), pH and conductivity meter (Jenway 4330, Cole-Parmer, Stone, UK), Digi-sense long-stem digital pocket thermometer (-50 to 150°C , Cole Parmer, St. Neots, UK), and ammonium cell test (4-80 mg L^{-1} , VWR International Ltd., Poole, UK) followed by determination with spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darnstadt, Germany) to enable ammonia mass balance among feed, recovered, residual and loss, and calculation of ammonia and water mass transfer kinetics (Ukwuani and Tao, 2016).

4.2.2 Membrane contactor experimental set-up

A Perspex cell, comprised of a 12mm diameter channel (Figure 2.1) was fed with a single micro-porous PP hollow fibre obtained from Membrana GmbH (Wuppertal, Germany), comprised of $0.2\mu\text{m}$ nominal pore size and active fibre length of 165mm (Table 4.1).

Table 4.1. Dimensions and surface characteristics of the single membrane fibre

Fibre characteristics		
Membrane material	-	polypropylene
Inner diameter	mm	1.2
Outer diameter	mm	1.8
Wall thickness	μm	300
Active length	mm	165
Surface area ^b	m^2	9.33×10^{-4}
Nominal pore size ^a	μm	0.2
Lumen cross sectional area	m^2	1.13×10^{-6}
Shell side characteristics		
Height	mm	5
Width	mm	12
Shell cross sectional area	m^2	6.0×10^{-5}
Priming volume	ml	11.0
Operational characteristics		
Flow regime		Counter-current
Shell-side		3.3 M NH_3 (aq)
Lumen-side		99.8% CO_2
Liquid temperature	$^\circ\text{C}$	6 ± 1
Gas temperature	$^\circ\text{C}$	19 ± 1
Humidity (Inlet)	%	2 ± 1
Humidity (Outlet)	%	38 ± 0.4
Dew Point	$^\circ\text{C}$	3.5 ± 0.5

^a Data provided by manufacturer.

^b Based on fibre outer diameter.

The upper section of the cell included a viewing window (Autin et al., 2016) to allow direct observation of shell-side crystallisation in real time. A Nikon SMZ-2T stereomicroscope with a 0.5x objective lens (Nikon UK Ltd., Surrey, UK) was fixed above the viewing window, and

images captured with a high-resolution camera (Leica EC3 Microsystems, Milton Keynes, UK). Epoxy resin (Bostick Ltd., Stafford, UK) and liquid PTFE (Flomasta, Screwfix, Yeovil, UK) were applied on hollow-fibre extremities to seal it into the crossflow cell.

Carbon dioxide (99.8%, BOC gases, Ipswich, UK) was fed into the lumen of the hollow-fibre at 1000 ml min^{-1} and $19\pm 1^\circ\text{C}$ using a laminar mass flow controller ($0.01\text{--}1\text{ L min}^{-1}$, Roxspur Measurement and Control Ltd., Sheffield, UK), while the absorbent was recirculated in counter-current on the shell-side of the membrane at 200 ml min^{-1} with a peristaltic pump (Watson-Marlow 520Du, Watson-Marlow Ltd., Falmouth, UK). The absorbent temperature was maintained refrigerated at $6\pm 1^\circ\text{C}$, through an R1 Series refrigerated bath and circulator (Grant Instruments Ltd., Cambridge, UK). Thermocouples (K-type, Thermosense Ltd., Bucks, UK) were positioned upstream and downstream of the cell in both the gas and liquid to record their temperatures on a PicoLog data acquisition module (Pico Technology, St. Neots, UK) each 10 minutes. The PicoLog was connected to a laptop computer to monitor the data in real time (Figure 2.1).

4.2.3 Reagents and analytical methods

Synthetic wastewater at $1.8\text{ g N-NH}_4^+ \text{ L}^{-1}$ ($\sim 0.1\text{ mol L}^{-1}$) and concentrated aqueous ammonia absorbents ranging between 7 and $38\text{ g N-NH}_4^+ \text{ L}^{-1}$ (~ 0.5 and 2.7 mol L^{-1}) were prepared for vacuum thermal stripping by dissolving NH_3 (35%, 2.5 L, Fisher Chemicals) into de-ionised water. Ammonia concentration in the feed was confirmed through ammonium cell test and spectrophotometry, following the same procedure adopted for feed residual and condensate recovered previously described. For experiments evaluating pH effect, the feed solutions were pre-adjusted to different pH values between 8.2 and 11.2 by addition of hydrochloric acid (HCl, 37%, Fisher Scientific, Loughborough, UK). Once determined the boundary conditions to concentrate ammonia, return liquor (real wastewater) was then collected from a digestate dewatering centrifuge at a local WWTW, stored at 4°C and sampled for analysis prior to use for dual stage vacuum thermal stripping (Table 4.2).

Table 4.2. Operational characteristics of the double stage ammonia recovery from raw return liquor

	Stage		
	First	Second	
Feed temperature		80	$^\circ\text{C}$
Vacuum pressure	420	470	mbar
Desorption time	60	45	min
Volume initial feed		1000	mL
pH initial feed	11*	11.5	(-)
$[\text{NH}_3]_{\text{initial feed}}$	0.14	2.8	$\text{mol}_{\text{NH}_3} \text{ L}^{-1}$
	2.0	39.2	$\text{gN-NH}_3 \text{ L}^{-1}$
$[\text{NH}_3]_{\text{condensate}}$	2.8	6.4	$\text{mol}_{\text{NH}_3} \text{ L}^{-1}$
	39.2	89.6	$\text{gN-NH}_3 \text{ L}^{-1}$

*Addition of NaOH (1%)

Synthetic and real concentrated absorbents for membrane crystallisation were prepared in the first place by addition of NH_3 into de-ionised water and in the other instance through opportune mixture of first ($2.8 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$) and second ($6.4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$) stage condensate. Both the crystallising fluids at a concentration of $4 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, were finally buffered with HCl concentrate to fix pH at 10, as typical value in commercial aqueous ammonia packed column processes (Yeh et al., 2005) and ammonia concentration at $3.3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$. Major chemical and physical properties of raw sewage, condensate, crystallising fluid and synthetic fluid (analysed for comparison) are given in Table 4.3.

Table 4.3. Characterisation of raw return liquor and condensate from first and second stage of $\text{NH}_3(\text{aq})$ recovery process

		Raw Sewage	Condensate		Crystallising fluid ^a	Synthetic fluid
			First Stage	Second Stage		
pH	(-)	8.4	11.5	11.5	11.3	12.6
COD	mg L^{-1}	6100	486	1767	913	<25
SCOD	mg L^{-1}	4500	427	1678	844	<25
TSS	mg L^{-1}	6600	12 ± 7	3 ± 3	3 ± 3	3 ± 3
Conductivity	mS cm^{-1}	2.05	1.59	0.87	1.35	0.19
$[\text{NH}_3]_{\text{initial feed}}$	$\text{mol}_{\text{NH}_3} \text{ L}^{-1}$	0.14	2.8	6.4	4 ^b	4 ^b
	$\text{gN-NH}_3 \text{ L}^{-1}$	2.0	39.2	89.6	56	56

^a Mixture between first and second stage condensates to fix $[\text{NH}_3] = 4\text{M}$.

^b Eventually lowered at 3.3M with addition of HCl 37% (w/w) to fix pH = 10.

A manual volumetric flow meter (Bubble flow meter, 1000 mL, SKC, Blandford Forum, UK) was used to measure gas flow rate and to calculate carbon dioxide flux (J_{CO_2} , $\text{mol m}^{-2} \text{ s}^{-1}$) during membrane crystallisation tests:

$$J_{\text{CO}_2} = \frac{(Q_{G,\text{in}} - Q_{G,\text{out}}) \times 273.15 \times 1000}{22.4 \times A_m T_G} \quad (2)$$

where $Q_{G,\text{in}}$ and $Q_{G,\text{out}}$ are gas flow rate ($\text{m}^3 \text{ s}^{-1}$) before and after HFMC, A_m is the membrane surface area for absorption (m^2) and T_G is the gas temperature (K) (Atchariyawut et al., 2007). The solution pH and UV absorbance trend (Jenway 6715 UV/Vis. Spectrophotometer, Cole-Parmer, Stone, UK) were obtained through regular liquid sampling of 3% of the whole bulk solution during absorption experiment (Figure 2.1). UV reading was fixed at 215 nm, which is the wavelength for absorption of bicarbonate (Wilson et al., 2001). Each experimental trial with synthetic absorbent was terminated at a different level of supersaturation (C/C^*), defined as the ratio between the CO_2 absorbed into solution and the CO_2 required to form ammonium bicarbonate at the solubility limit. For each sacrificial test, the absorbent was filtered through a $0.45 \mu\text{m}$ Whatman filter (Camlab Ltd., Cambridge, UK) and weighed. Crystals were immersed in anhydrous alcohol to minimise agglomeration during counting (Veiga et al., 1999) and deposited onto a microscope slide consisting of a 1 mm grid. The slide was placed under an optical microscope (Optech Microscope Services Ltd., Thame, UK), equipped with PL 5/0.12 lens and digital camera (Infinity 3, Lumenera, Ottawa, Canada). Images were analysed

with image processing software (Image Pro Plus, Media Cybernetics, Cambridge, UK) to determine crystal number and size. Each image analysed corresponded to around 50 crystals. For each sacrificial test, at least 600 crystals were classified to develop a robust crystal size distribution (CSD) which was constructed using a log-normal distribution (Li et al., 2000; Ji et al., 2010). Each sacrificial experiment was carried out in triplicate. The mean crystal size values obtained from CSDs at each supersaturation ratio (C/C^*) were then used to characterize ammonium bicarbonate crystal growth (Chen et al., 2014). Analogously, real absorbent was recirculated until its complete exhaustion under identical conditions and procedures to the synthetic solution. The experiment was carried out in triplicate. However, due to its limited availability, sacrificial tests at different supersaturation levels to characterize shell-side nucleation and growth were not conducted. Solvent surface tension was determined using a Du Noüy ring tensiometer (Kruss K6, Bristol, UK). A Siemens D5005 X-ray diffractometer with Cu Ka1 radiation (Bruker UK Ltd., Coventry, UK) was used for the XRD analysis of crystals collected from the bulk solutions (synthetic and real) and pure ammonium bicarbonate (>99%, Fisher Scientific, Loughborough, UK). The step size was 0.04° and diffraction patterns were recorded in the 2θ range $15-40^\circ$ (Meng et al., 2005).

4.2.4 Chemical equilibria

Ammonium ion (NH_4^+) and free ammonia (NH_3) are in equilibrium within the aqueous ammonia absorbents, which is strongly dependent on pH and temperature as shown in Figure 4.1, as a result of the following equations (Bates and Pinching, 1949; Perry and Green, 2007):

$$\alpha_{\text{NH}_3} = 1/(1 + 10^{pK_a^S - \text{pH}}) \quad (3)$$

$$pK_{a,T}^S = pK_{a,298}^S + 0.0324(298 - T) \quad (4)$$

$$pK_{a,P}^S = pK_{a,1}^S + 0.0415P/T \quad (5)$$

Where α_{NH_3} is the relative fraction of free ammonia in total ammonia; pK_a^S is the negative logarithm of stoichiometric acid dissociation constant of ammonium ion; $pK_{a,T}^S$ and $pK_{a,P}^S$ are the pK_a^S values at temperature T (K) and pressure P (atm), respectively ($pK_{a,298}^S = 9.25$; $pK_{a,1}^S = 9.9$). In particular, during stripping, ammonia volatilisation is driven by the difference between free ammonia saturation concentration and its actual concentration, which follows Fick's first law of diffusion, expressed by Lewis-Whitman model (Equation 6) (Tao and Ukwuani, 2015):

$$J_{\text{NH}_3 \text{ stripped}} = -K_L \frac{A}{V} (C - C_s) \quad (6)$$

Where $J_{\text{NH}_3 \text{ stripped}}$ = rate of ammonia mass transfer ($\text{mg L}^{-1} \text{ h}^{-1}$), K_L = overall liquid-phase mass transfer coefficient (m h^{-1}), C_s = saturation concentration of NH_3 in liquid (mg L^{-1}), C = free ammonia concentration in liquid at time t (mg L^{-1}), A/V = area-volume ratio of the liquid ($\text{m}^2 \text{ m}^{-3}$). Ammonia saturation concentration decreases with temperature as shown in Figure 4.2 (O'Neil, 2013), facilitating ammonia stripping, while its variation with vacuum in the absolute

pressure range of 10-101.3 kPa is negligible (Whitfield, 1974; Salavera et al., 2005). Integration of Equation 6 from ammonia concentration C_0 at time $t = 0$ to C at time t , provides the following analytical solution:

$$\ln\left(\frac{C-C_s}{C_0-C_s}\right) = -K_L \frac{A}{V} t \quad (7)$$

Where t = time into a stripping experiment (h); C_0 = initial free ammonia concentration in the feed (mg L^{-1}); C_s , K_L , A/V are the same as in Equation 6. The stripping experiments had an A/V ratio of $36.2 \text{ m}^2 \text{ m}^{-3}$, which closely approximates to the value obtained by (Tao and Ukwuani, 2015). Additionally, the water flux recovered $J_{\text{H}_2\text{O}}$ (g h^{-1}) in vacuum thermal stripping can be expressed as (He et al., 2018):

$$J_{\text{H}_2\text{O recovered}} = \frac{\Delta m_{\text{H}_2\text{O}}}{\Delta t} \quad (8)$$

Where $\Delta m_{\text{H}_2\text{O}}$ (g) is the mass of water transferred from the feed to the condensate during the time period Δt (h). The rates of ammonia loss $J_{\text{NH}_3 \text{ loss}}$ ($\text{mg L}^{-1} \text{ h}^{-1}$) and ammonia recovered $J_{\text{NH}_3 \text{ recovered}}$ ($\text{mg L}^{-1} \text{ h}^{-1}$), can be back-calculated as:

$$J_{\text{NH}_3 \text{ loss}} = \frac{C_0 V_0 - C_t V_t - C_{\text{rec},t} V_{\text{rec},t}}{\Delta t} \quad (9)$$

$$J_{\text{NH}_3 \text{ recovered}} = J_{\text{NH}_3 \text{ stripped}} - J_{\text{NH}_3 \text{ loss}} \quad (10)$$

where V_0 , V_t , C_0 and C_t are the feed volumes (L) and feed ammonia concentrations (mg L^{-1}) at time $t = 0$ and time t , while $V_{\text{rec},t}$ and $C_{\text{rec},t}$ are volume (L) and ammonia concentration (mg L^{-1}) in the condensate recovered (mg L^{-1}) at time t .

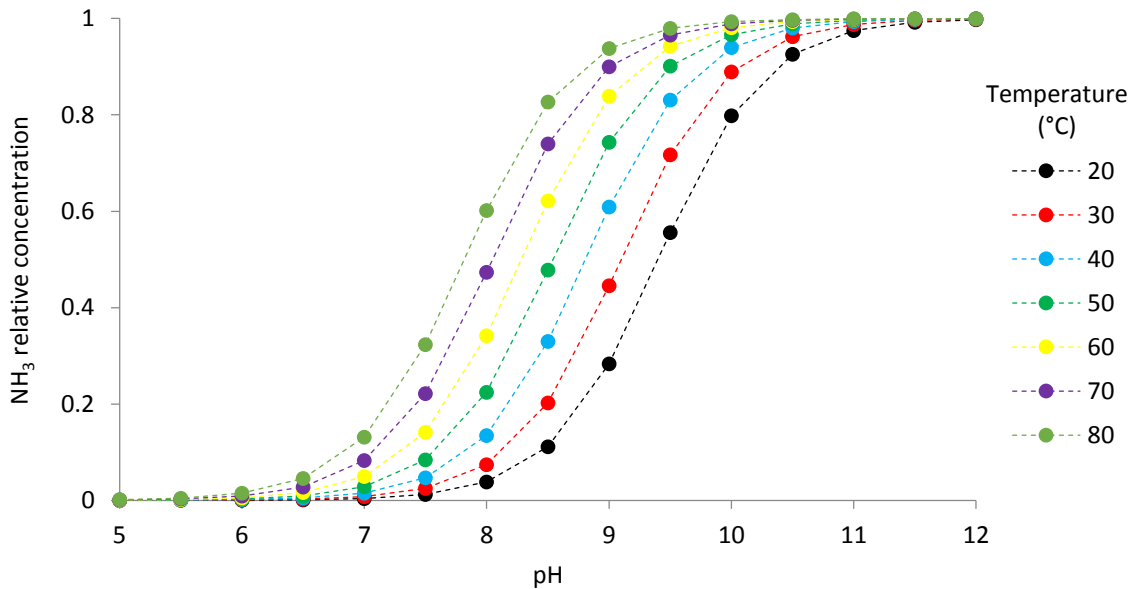


Figure 4.1. Influence of liquid temperature and pH on ammonia-ammonium speciation (Equations 3-5; Bates and Pinching, 1949).

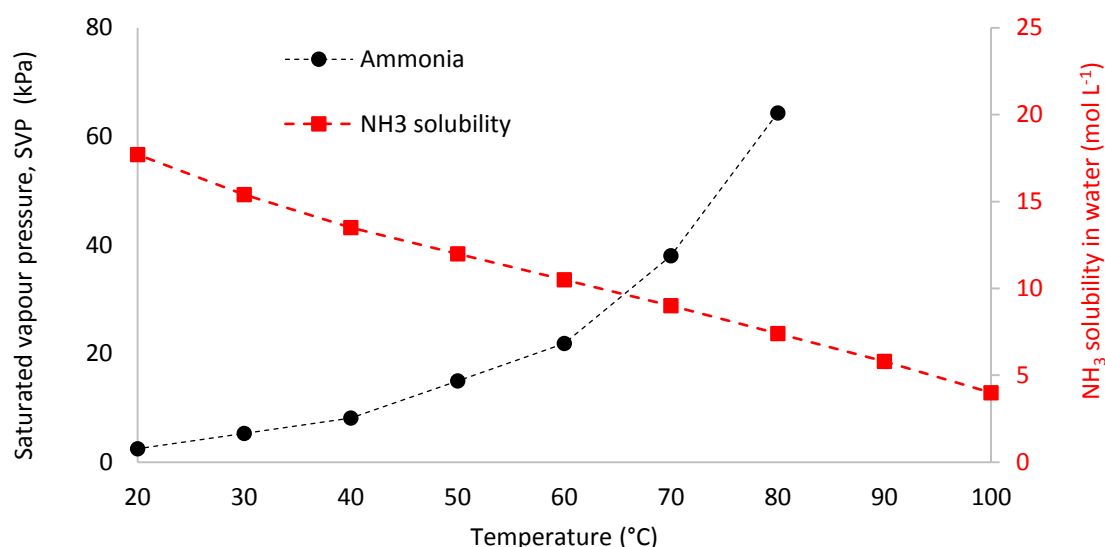


Figure 4.2. Impact of absorbent temperature on saturated vapour pressure of $\text{NH}_3(\text{aq})$ at $1.8\text{gNH}_3\text{-N L}^{-1}$ (black line; Wilson, 1925), and ammonia solubility in water (red line; O’Neil, 2013).

4.3 Results

4.3.1 Diagnosis of the boundary conditions needed to concentrate ammonia from wastewater for membrane crystallisation

An increase in solvent pH under fixed operational conditions induced a sharp gain in aqueous ammonia concentration recovered within the condensate (Figure 4.5). In particular, $\text{NH}_3(\text{aq})$ concentration boosted from $0.2 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ at pH 8.2 (80 °C) to $2.1 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ at pH 11.2 (80 °C). An increase in pH drives the ammoniacal nitrogen equilibrium toward free ammonia with approximately 60%, 90% and 99% present as free ammonia at pH 8, 9 and 11 respectively at 80 °C (Figure 4.1). Throughout single-stage stripping, lower temperatures achieved higher NH_3 condensate concentration, being equal the volume recovered (Figure 4.4). For example, at a fixed $V_{\text{recovered}}/V_{\text{initial feed}}$ ratio of 2.3%, $1.3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ was obtained at 50 °C, which reduced to $0.2 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ when stripping at 80 °C. Nevertheless, a significant gain in the overall liquid phase mass transfer coefficient (K_L) has been detected when increasing the temperature from 50 °C to 80 °C (Figure 4.3).

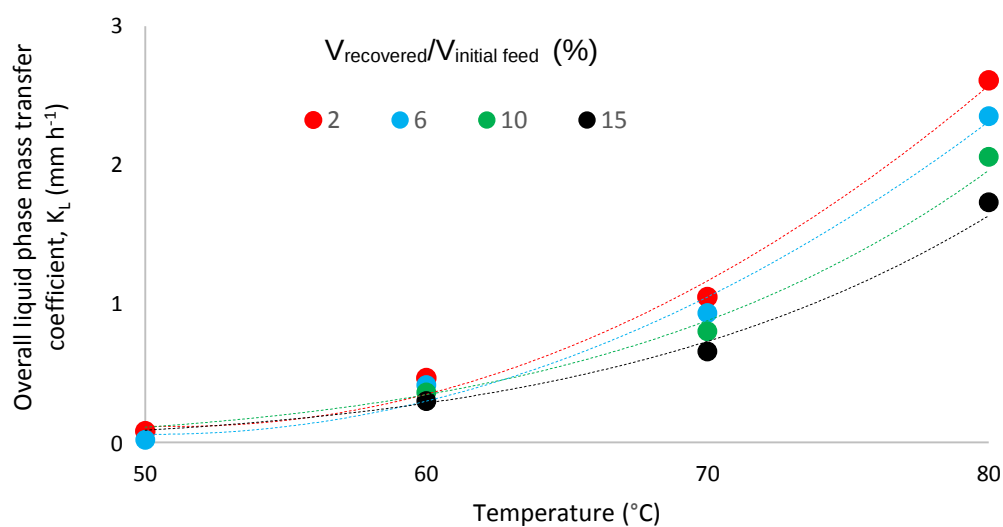


Figure 4.3. Effect of feed temperature and volume recovered on the overall liquid-phase mass transfer coefficient. Operational conditions: $[\text{NH}_3]_{\text{initial feed}} = 1.8 \text{ g L}^{-1}$; Initial feed temperature = 20°C ; Vacuum pressure = 100mbar; Volume initial feed = 1000 mL; pH initial feed = 11.

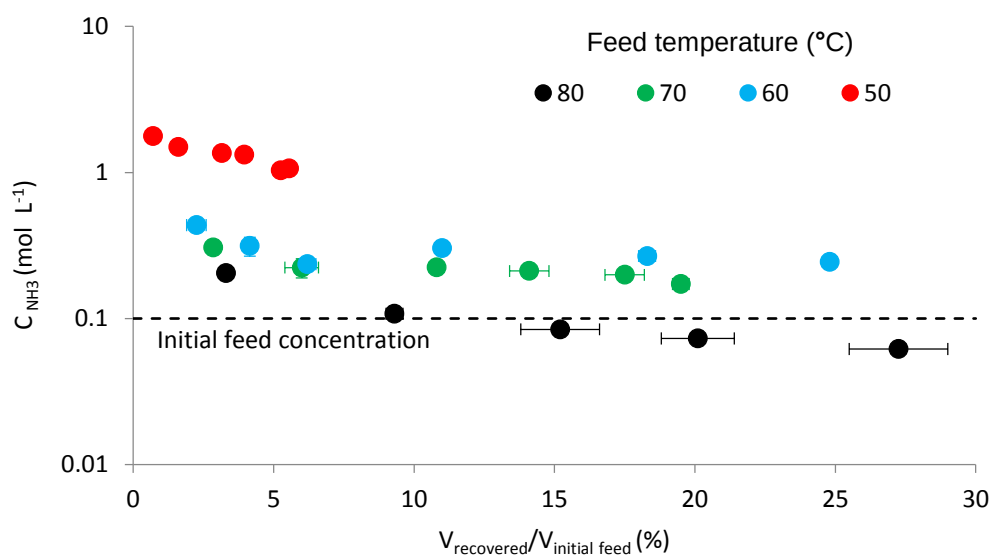


Figure 4.4. Effect of condensate volume harvested and heating temperature on single stage ammonia recovery. Operational conditions: $[\text{NH}_3]_{\text{initial feed}} = 1.8 \text{ g L}^{-1}$; Initial feed temperature = 20°C ; Vacuum pressure = 100mbar; Volume initial feed = 1000 mL; pH initial feed = 11. Error bars indicate standard deviation from sacrificial experiments undertaken in triplicate.

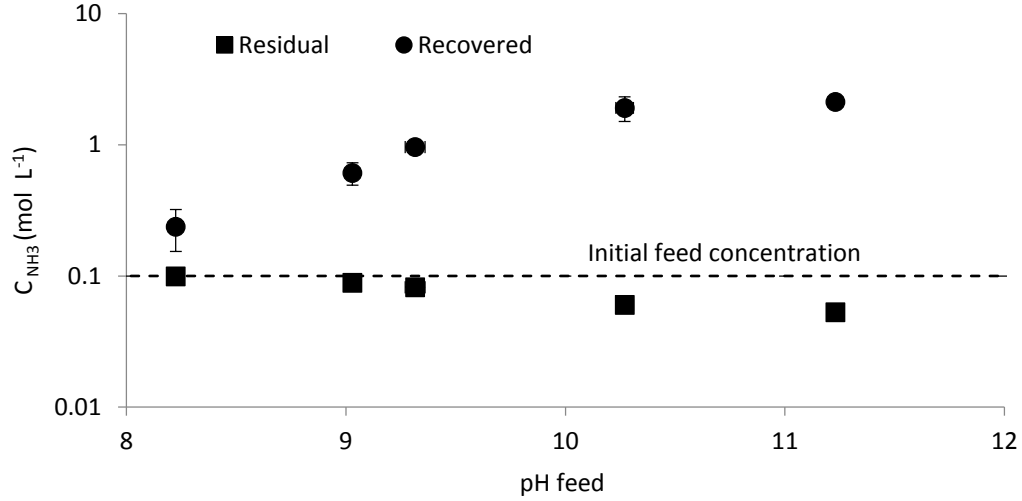


Figure 4.5. Impact of pH in the feeding solution on single stage ammonia recovery. Operational conditions: $[NH_3]_{\text{initial feed}} = 1.8 \text{ g L}^{-1}$; Desorption time = 45minutes; Temperature = 80 °C; Vacuum pressure = 420mbar. Error bars indicate standard deviation from sacrificial experiments conducted in triplicate.

Specifically, a temperature increase from 50 °C to 80 °C, raised K_L from 0.09 mm h⁻¹ to 2.6 mm h⁻¹ at fixed $V_{\text{recovered}}/V_{\text{initial feed}}$ ratio of 2%, and from ~0 mm h⁻¹ (below detection limit) to 1.7 mm h⁻¹ at $V_{\text{recovered}}/V_{\text{initial feed}}$ ratio of 15%. In the second stage of in-series thermal stripping, K_L showed a strong dependency with aqueous ammonia concentration in the feeding solution (Figure 4.6a). To illustrate, at feed temperature of 80 °C, a sharp increase in K_L was recorded from 1 mm h⁻¹ to 14 mm h⁻¹ corresponding to feed concentration between 0.5 mol_{NH₃} L⁻¹ and 2.7 mol_{NH₃} L⁻¹. This induced an increase in $V_{\text{recovered}}/V_{\text{initial feed}}$ ratio from 0.5% to 7%, whilst maintaining the concentration recovered at around 6 mol_{NH₃} L⁻¹, which is close to the NH₃ solubility limit in water at 80°C (~7.4 mol_{NH₃} L⁻¹, Figure 4.2). Furthermore, nitrogen mass balance showed that feed concentration increase caused a rise in NH₃ loss from 43% at 0.5 mol_{NH₃} L⁻¹ to 67% at 2.7 mol_{NH₃} L⁻¹, while ammonia residual (in the feed solution after stripping) dropped from 50% to 19% within the same feed concentration range (Figure 4.6b).

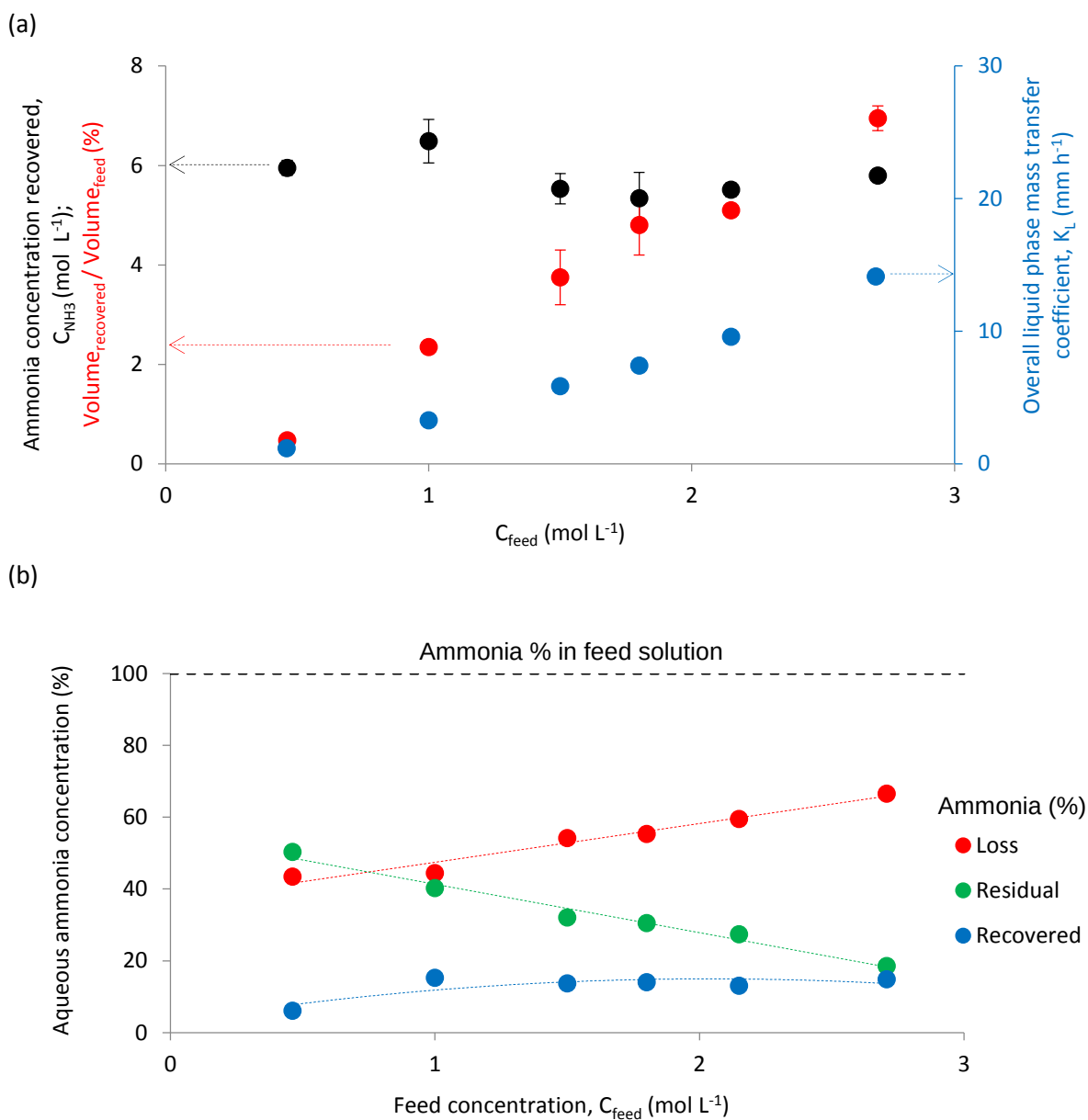


Figure 4.6. (a) Influence of $\text{NH}_3(\text{aq})$ concentration in the feeding solution on dual stage ammonia concentration recovered (black points) and volume recovered (red points), and on dual stage overall liquid phase mass transfer (blue points). (b) Effect of ammonia concentration in the feed on ammonia loss, residual and recovered (%). Operational conditions: desorption time = 45 minutes; temperature = 80°C ; vacuum pressure = 470mbar; volume initial feed = 1000mL; pH initial feed = 12 – 12.5. Error bars indicate standard deviation.

4.3.2 Surface tension characterization of real absorbents

The condensate derived from concentration of return liquor appeared significantly less turbid than raw feed, but slightly more than ultra-pure water, which suggests that during vacuum thermal stripping modest carry over of the feed into the condensate still occurred (Figure 4.7). A gain in ammonia concentration within the real absorbent resulted in a drop in surface tension significantly deeper than that recorded within the homologous synthetic in the same NH_3 range

(Figure 4.8). In particular, at $0.5 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, the change in surface tension relative to deionised water ($\Delta\sigma$) was about -1 mN m^{-1} for the synthetic absorbent compared with -7 mN m^{-1} for the real solution, while at fixed concentration of $3.3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, the discrepancy intensified to -5 mN m^{-1} for the synthetic up to -40 mN m^{-1} for the real liquid.

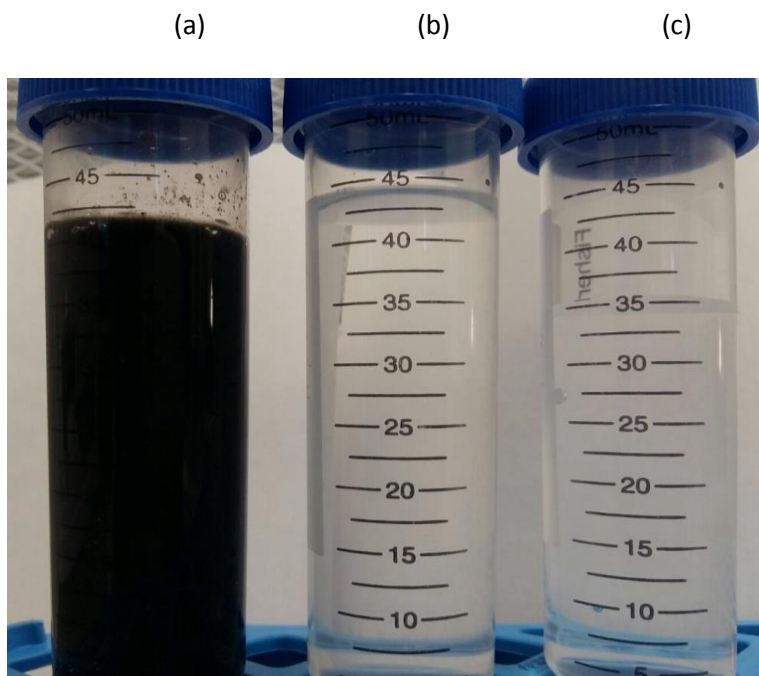


Figure 4.7. Image of raw return liquor used in this study (a), condensate produced for membrane chemically assisted crystallisation (b) and ultra-pure water (c).

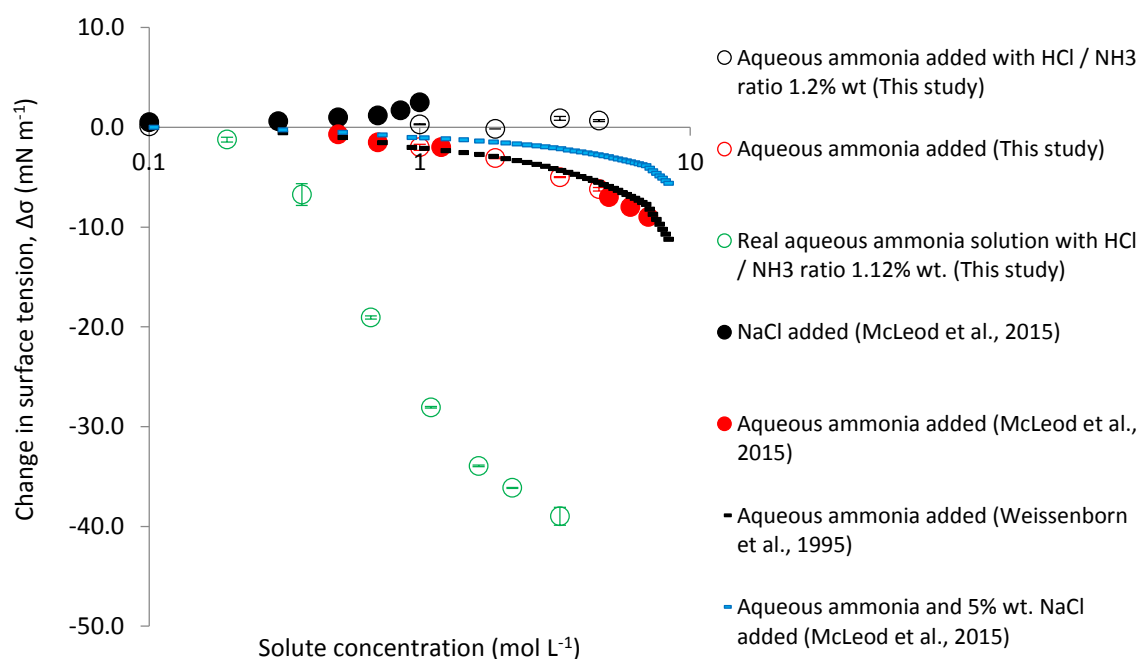


Figure 4.8. Changes in surface tension relative to deionised water driven by aqueous ammonia solute concentration in real (condensate produced from raw return liquor) and synthetic solutions.

4.3.3 Investigation of CO₂ absorption and crystallisation behaviour using synthetic and recovered ammonia solutions of equal reactivity

Carbon dioxide flux for both synthetic and real solutions was similar in the supersaturation range C/C^* between 0 mol mol⁻¹ and 0.4 mol mol⁻¹ with a J_{CO_2} decline from 13×10^{-3} molCO₂ m⁻² s⁻¹ to 5×10^{-3} molCO₂ m⁻² s⁻¹, followed by a sharper J_{CO_2} drop observed with the real solution, which achieved a plateau of approximately 2×10^{-3} molCO₂ m⁻² s⁻¹ compared with 4×10^{-3} molCO₂ m⁻² s⁻¹ detected with the synthetic counterpart in the same C/C^* range (Figure 4.9).

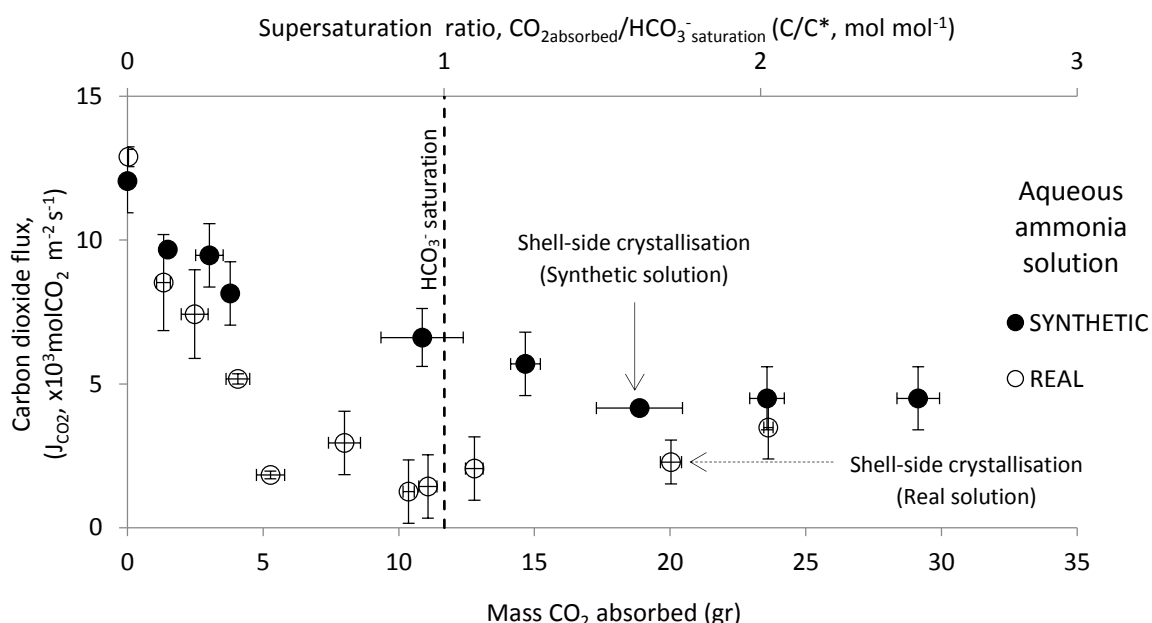


Figure 4.9. Carbon dioxide flux reduction following recirculation of synthetic and real aqueous ammonia solutions at 3.3M and 5°C on the shell-side of the PP HFMC. Supersaturation ratio calculated assuming CO₂ absorbed fully converted into HCO₃⁻. Hydrodynamic conditions: G/L 5; V_L 0.06 m s⁻¹; V_G 14.7 m s⁻¹. Shell-side crystallisation occurred at $C/C^* \approx 1.7$ for both solutions. Error bars indicate standard deviation from sacrificial experiments undertaken in triplicate.

Analogous pH decrement was observed with the 2 solutions from 10 to about 8, corresponding to complete exhaustion of the absorbents (Figure 4.10). Bicarbonate concentration achieved a peak at supersaturation ratio of 1 for both the solvents, following a decrease, which resulted in higher mass, number and mean size of ammonium bicarbonate crystals formed for the real solution (being equal C/C^*) (Figure 4.11). For example, at C/C^* of 2.1 ammonium bicarbonate mass recovered, number and mean size were 1800 mg, 75 crystal cm⁻³ and 600 μm respectively for the real solution, compared with 41 mg, 5 crystals cm⁻³ and 400 μm for the synthetic fluid.

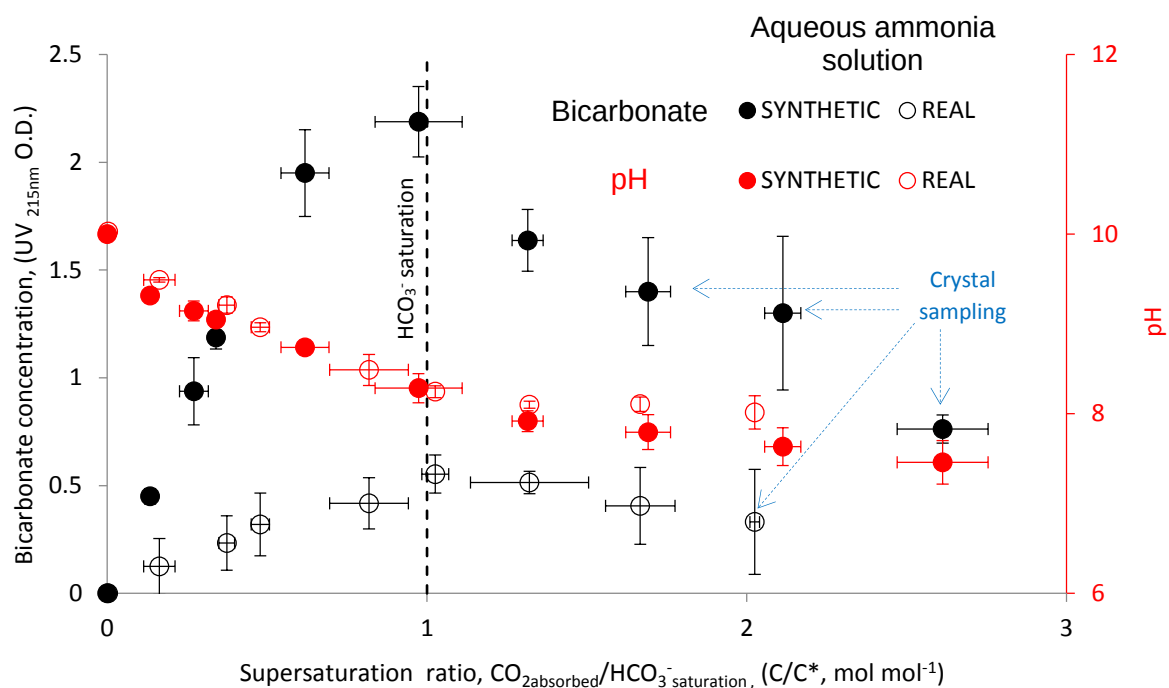


Figure 4.10. Impact of CO_2 absorbed on pH reduction, bicarbonate variation and liquid side crystallisation for synthetic and real solutions in recirculation at 3.3M and 5°C through the shell-side of the fibre. Error bars indicate standard deviation from sacrificial experiments undertaken in triplicate.

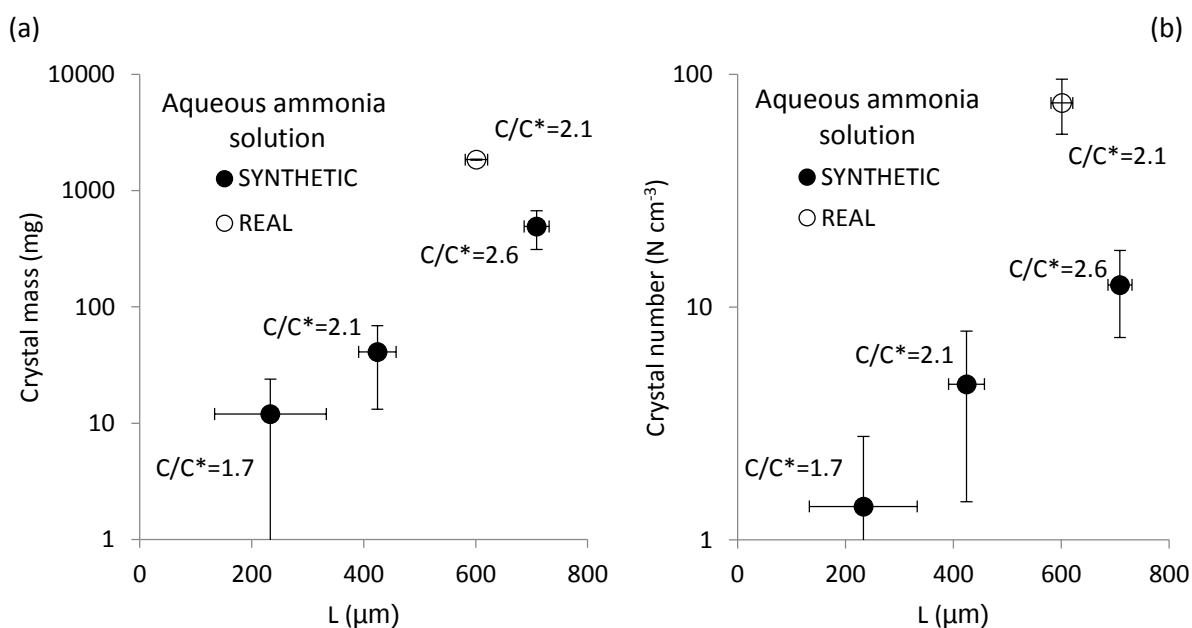


Figure 4.11. Impact of aqueous ammonia solution on crystal mass (a) and number (b). Aqueous ammonia solutions used in recirculation on the shell-side of a PP membrane were at 3.3 mol L^{-1} ($\approx 46.2 \text{ gN-NH}_3 \text{ L}^{-1}$) in both cases. Hydrodynamic conditions: G/L 5; V_L 0.06 m s^{-1} ; V_G 14.7 m s^{-1} . Absorbents and gas temperatures of 6 ± 1 and 19 ± 1 respectively. Error bars indicate standard deviation from sacrificial experiments undertaken in triplicate.

4.3.4 Identifying the reaction product derived from real wastewater

X-ray diffraction analysis undertaken on 3 different samples: pure ammonium bicarbonate crystals (>99%), crystals recovered from the synthetic solution, and crystals collected from real solution, suggested the crystals sampled from the 2 solutions to be reasonably pure ammonium bicarbonate (Figure 4.12; Meng et al., 2005), thus obviating cationic competition that prevented ammonium bicarbonate formation from wastewater in other studies (McLeod et al., 2014).

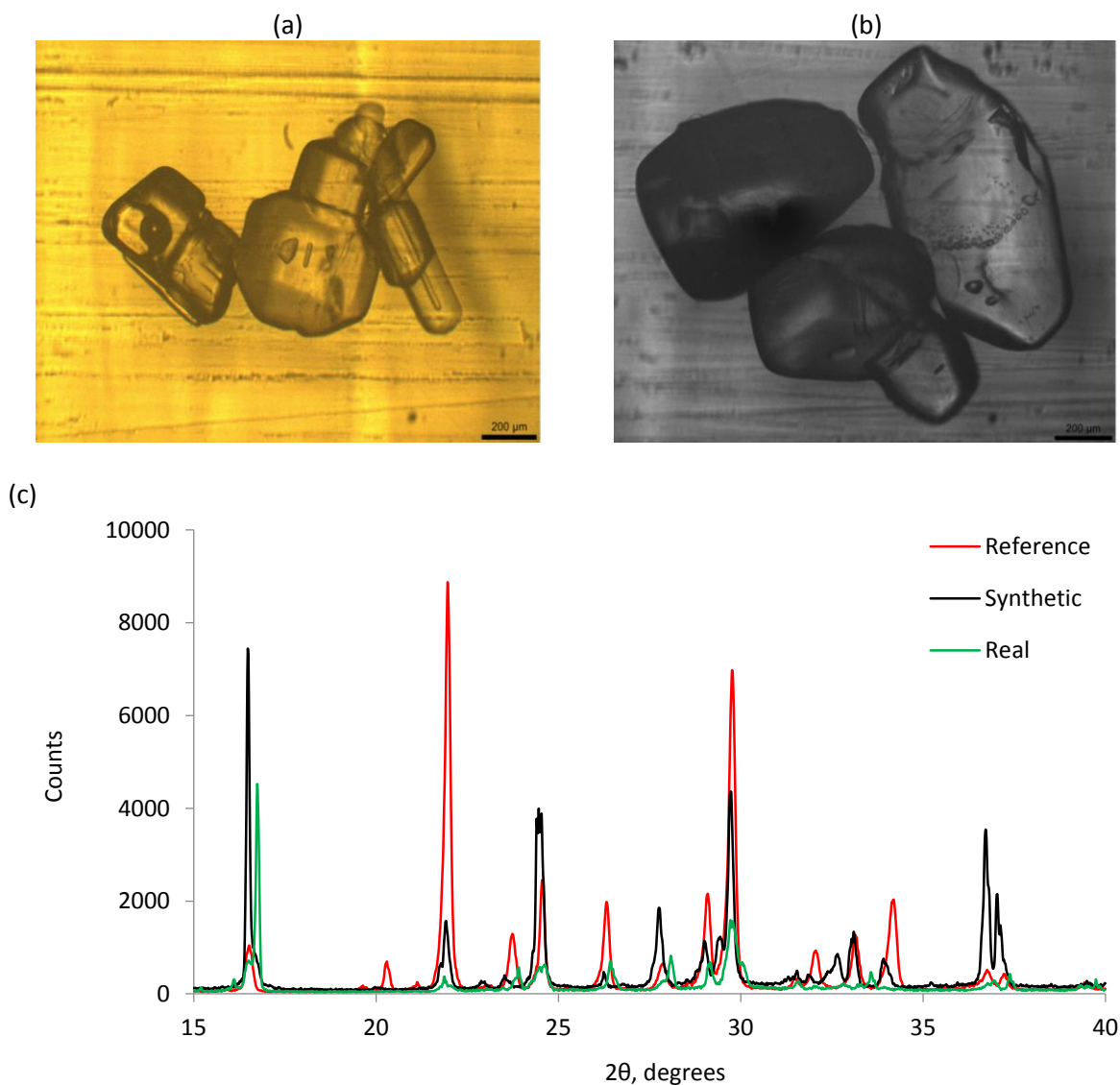


Figure 4.12. Optical microscope images of NH_4HCO_3 crystals collected from the synthetic (a) and real (b) bulk solutions. (c) XRD analysis of pure NH_4HCO_3 (Reference), ammonium bicarbonate produced from condensate recovered from raw return liquor (Real) and ammonium bicarbonate obtained from synthetic solution (Synthetic).

4.4 Discussion

In this study, the use of a concentrated $\text{NH}_3(\text{aq})$ condensate produced from thermal stripping of return liquor, as an absorbent for CO_2 separation in a chemically reactive membrane crystallisation reactor, was demonstrated to simultaneously enhance CO_2 flux, remove $\text{NH}_3(\text{aq})$ and control ammonium bicarbonate nucleation, growth and harvesting within a single stage process. For thermal stripping, the increase in ammonia recovery attributed to an increase in pH, can be accounted for by the transition beyond the acid-dissociation constant, in which the gaseous NH_3 form became the dominant fraction of the $\text{NH}_3/\text{NH}_4^+(\text{aq})$ equilibrium (Figures 4.1 and 4.5). At low temperature (50°C), a higher NH_3 condensate concentration was achievable in single-stage stripping due to the lower vapour pressure for water in the feed and higher NH_3 solubility in H_2O , which favoured both selective transport of NH_3 and larger dissolution of the volatile compound within the condensate (Figures 4.2 and 4.4) (O'Neil, 2013; Thurston et al., 1979). However, higher temperatures shifted the equilibrium further toward 100% NH_3 (Figure 4.1) and raised saturated vapour pressure of NH_3 (Wilson, 1925), which increased the overall mass transfer coefficient (Figure 4.3) and is comparable to observations by Tao and Ukwuani (2015). Using in-series stripping, mass transfer in the second stage was dependent upon the initial NH_3 concentration (Figure 4.6) and as a consequence, was considerably higher than recorded in the primary separation. At industrial scale, rectification has been proposed for this application, which can be thought of as multiple distillation columns in series (Teichgraber and Stein, 1994). Thus in practice, the overall rate of mass transfer within the rectifier will be an average of the two stages. Packed column technology has already been employed for ammonia separation from complex wastewater at commercial scale (Zeng et al., 2006; Heile et al., 2017), however, the recovery and concentration of ammonia has not been well described. The NH_3 concentration in the recovered concentrate was consistently around $6 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, which can be ascribed to the solution reaching the solubility limit for NH_3 , thus exacerbating NH_3 losses when increasing aqueous ammonia concentration in the feed (Figures 4.2 and 4.6; O'Neil, 2013). Importantly, the concentration recovered is significantly greater than the 1.5 M required to initiate crystallisation and is within the concentration range nominally proposed in CCS, indicating strong potential for CO_2 separation (Shuangchen et al., 2013; Budzianowski, 2011b). Approximately 40% of the energy produced from biogas is dissipated as waste heat from thermal hydrolysis coolers (in the case of advanced AD) and un-utilised waste heat from CHP, which represent an economically valuable source for thermal stripping (Auty and Moore, 2003). At 80°C , the pK_a for ammonia reduced such that at the natural pH of the return liquor studied (pH 8.4, Table 4.3), around 85% of the nitrogen is available as NH_3 , compared to only 10% of the nitrogen fraction at 20°C . Therefore whilst mass transfer may be partially limited at lower pH (Figure 4.1), the chemical demand for

recovering NH_3 can be minimised through application of waste heat making the overall process economically attractive and operationally simpler.

Whilst CO_2 flux for both synthetic and real solutions was initially similar, the decline in CO_2 flux observed as ammonia was progressively consumed, was more prominent for the real solution (Figure 4.9). The considerable reduction in surface tension of the real solution (Figure 4.8) could have reduced the breakthrough pressure, which introduced wetting of the micropores (Franken et al., 1987; Wang et al., 2005). However the comparable CO_2 flux data at the initial stage of separation coupled with the absence of gas-phase crystallisation, which is known to occur following solvent breakthrough, was not evident (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018). Instead we propose that the higher conductivity of the real condensate, reduced the solubility potential of the solvent following transition from chemical to physically mediated absorption (Table 4.3; Al-Anezi et al., 2008). Once dissolved, CO_2 quickly reacts with free ammonia $\text{NH}_3(\text{aq})$ to produce carbamic acid (NH_2COOH), subsequently releasing hydrogen ions (H^+) which lowers pH (Wang et al., 2011). The analogous trend in solvent pH with an increase in CO_2 saturation evidences that the reactivity of both solutions were therefore similar (Figure 4.10). The carbamate formed (NH_2COO^-) then decomposes into HCO_3^- and NH_3 which subsequently converts into the ionised form (NH_4^+) due to the reduced pH (Kim et al., 2008; Capodaglio et al., 2015; Wang et al., 2011). Crystallisation of NH_4HCO_3 can then proceed once sufficient concentration of the reactant is present. This was confirmed by growth of the crystalline solid which was first observed at a supersaturation ratio (C/C^*) of around 1.7 (Figures 4.10 and 4.11).

The delayed onset of crystallisation can be explained by the partial conversion of HCO_3^- into H_2CO_3 , which requires further dissolution of CO_2 to achieve sufficient supersaturation for induction (the initiation of nucleation) (Millero and Roy, 1997). The hydrophobicity exhibited by the membrane in this study (polypropylene, θ 117°) is proposed to promote heterogeneous nucleation on the membrane surface, which can be described by (Lucassen-Reynders, 1963; Curcio et al., 2006; Bougie and Iliuta, 2013):

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (11)$$

where θ is the contact angle of liquid on the membrane, while γ_L , γ_S and γ_{SL} are the surface tensions representing liquid-vapour, solid-vapour and solid-liquid interfaces, respectively. Since the membrane is hydrophobic, $\cos \theta$ is negative, thus a reduction of liquid surface tension will decrease γ_{SL} , implying the early onset of nucleation. In this study, we suggest that the higher crystal growth and crystal number observed in the real solution at an equivalent supersaturation ratio is therefore attributable to the reduction in surface tension observed. Specifically, the change in Gibbs free energy (ΔG) during critical nucleus formation is:

$$\Delta G^* \propto \gamma_{SL}^3 \quad (12)$$

in which a small decrease in γ_L (and consequently γ_{SL}), will increase both nucleation and growth rate (Wu and Nancollas, 1999). Characterisation of the solid product confirmed the crystal to be NH_4HCO_3 (Figure 4.12). McLeod et al. (2014) used thermal processing to crystallise NH_4HCO_3 in return liquors and ion-exchange regenerant following their use in biogas upgrading, which instead preferentially formed sodium bicarbonate and calcium carbonate respectively. Whilst some salts were transferred in this study due to carryover (an artefact of the experimental design), the comparatively small concentration of the salts relative to the concentrated ammonia were insufficient to inhibit preferential NH_4HCO_3 , which indicates thermal pre-concentration of ammonia as a viable solution to enable biogas upgrading, including crystallisation within a single stage process. Furthermore, ammoniacal nitrogen mass balance showed that about 99% of N lost was locked in the crystalline product recovered from the bulk solution, which demonstrated both ammonia lost and NH_4HCO_3 deposition on the hydrophobic surface of the membrane to be negligible.

4.5 Conclusions

A concentrated aqueous ammonia absorbent produced from in-series thermal stripping of return liquor has been employed for simultaneous CO_2 absorption enhancement, ammonia removal, and ammonium bicarbonate shell-side crystallisation and harvesting within a CR-MCr. This represents the first integrated system where a reactive solution in similar concentration to those adopted in CCS has been produced through thermal stripping of wastewaters and subsequently used for CO_2 separation and nutrient recovery within a single process. In-series thermal stripping of the return liquor at high temperatures ($\sim 80^\circ\text{C}$) (1) facilitates the overall liquid phase mass transfer; (2) produces a concentrated absorbent at $6 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, significantly greater than the $1.5 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ required to initiate crystallisation (PubChem, 2004; Perry and Green, 2007); (3) offers the opportunity for water utilities to minimise the chemical demand for recovering NH_3 through application of waste heat, due to the high availability of free ammonia at both 80°C and natural pH of return liquor (Thurston et al., 1979). Additionally, XRD analysis of the crystals produced from real absorbent, suggested the product to be good quality ammonium bicarbonate, demonstrating that pre-treatment of the return liquor overcomes ionic competition problems, which prevented the formation of the preferred reaction product (ammonium bicarbonate) in previous studies (McLeod et al., 2014). Further refinement is required to maximize the yield of ammonium bicarbonate recovered from the CR-MCr process. Future biogas applications can employ the CR-MCr, at commercial scale, down-stream the anaerobic digester, where the crystals grown on the hydrophobic surface of the membrane and detached by the shear stresses of the axial liquid flow, can be collected in the bulk solution. The bleeding of the bulk solution saturated with CO_2 and rich of settled crystals, would then enable simultaneous harvesting of ammonium salts (as

marketable products) and introduction of fresh $\text{NH}_3(\text{aq})$ into the recirculated solvent, which still guarantees high CO_2 removal and methane purity at the outlet of the HFMC up to 98% (McLeod et al., 2014).

Acknowledgements

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

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Chapter 5

Evidencing heterogeneous nucleation in membrane crystallisation through comparison with conventional batch crystallisation kinetics

For submission to: Journal of Crystal Growth

Evidencing heterogeneous nucleation in membrane crystallisation through comparison with conventional batch crystallisation kinetics

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Abstract

In this study, the crystallisation kinetics in membrane and batch operations have been compared to demonstrate that the membrane underpins primary heterogeneous nucleation at the membrane-liquid interface in an unseeded supersaturated solution characterised by laminar regime. On the contrary, in batch operation, characterised by direct enhanced mixing, primary and secondary homogeneous nucleation are followed by growth and agglomeration within the same system. This has confirmed the population density increase at progressing levels of supersaturation in membrane crystallisation, in contrast to batch crystallisation, where population density declined. Specifically, the primary nuclei formed in membrane crystallisation are then transported in the vessel downstream, through the axial liquid flow, where secondary nucleation and growth arise, whilst the newly free nucleation sites on the membrane surface enable the birth of additional nuclei. The interfacial energies (σ) calculation, resulted in $6.6 \times 10^{-3} \text{ J m}^{-2}$ with Ji (et al.)'s method for membrane crystallisation, and $7.7 \times 10^{-3} \text{ J m}^{-2}$ with Nakai's method for batch crystallisation, both in good agreement with the values of σ reported within the literature for several inorganic salts (Ji et al., 2010; Nakai, 1969). Furthermore, the σ calculation for batch crystallisation with Ji (et al.)'s method, resulted in $\sigma < 0$, contrarily to the positive values of σ for numerous crystals in the literature (Ji et al., 2010; Nakai, 1969). These results confirmed the hypothesis of primary heterogeneous nucleation, decoupled from secondary nucleation in membrane operation (Ji et al., 2010), against batch operation, where primary and secondary homogeneous nucleation occur within the same domain (Nakai, 1969). In batch crystallisation, earlier onset of ammonium bicarbonate precipitation, faster pH transient and higher yield of crystals recovered have been observed, due to higher probability of collision between solute and solvent, as compared with membrane operation. The yield of nitrogen precipitated in batch was indeed higher than in membrane at a maximum of 30%, which however can be enhanced up to 99% by increasing the pH, which would eliminate bicarbonate (solute) transition into carbonic acid. Importantly, an increase of the membrane interfacial surface area, would raise the nucleation rate and close the gap to control crystallisation in membrane operation. Nitrogen mass balance showed a complete conversion of ammonia from liquid to solid crystalline phase, contrarily to the batch crystallisation test, where only 60% of ammoniacal nitrogen was recovered, due to direct

gas/liquid contact which exacerbated ammonia slip in the gas phase, thus demonstrating the potential of membrane crystallisation for inclusion of ammonium bicarbonate crystallisation in CO₂ absorption applications.

Keywords: nucleation; crystal growth; chemical absorption; precipitation; ammonia

5.1 Introduction

In the last decade, packed columns have represented the most common technology for carbon dioxide (CO₂) separation, in both biogas upgrading and carbon capture and storage (CCS) applications, due to their simplicity and high efficiency (Sahota et al., 2018; Augelletti et al., 2017). Whilst monoethanolamine (MEA) was initially used as absorbent solution, aqueous ammonia (NH₃) has been subsequently identified as an excellent substitute (Bandyopadhyay, 2011), since it is not corrosive and does not degrade (McLeod et al., 2014). Furthermore, NH₃ is 6 times cheaper than MEA on a mass basis, it can lower energy demand up to 75% and offers 3 times higher absorption capacity (Makhloufi et al., 2014). In the first stage of CO₂ absorption into aqueous ammonia, CO₂ and NH₃ react to form carbamic acid (NH₂COOH), which releases the hydrogen ion (H⁺) and lowers the solution pH, thus shifting carbonate-bicarbonate (CO₃²⁻ - HCO₃⁻) equilibrium towards bicarbonate and ammonia-ammonium (NH₃ - NH₄⁺) equilibrium towards the non-volatile, ionised ammonium form, while a fraction of CO₂ reacts with hydroxide ion (OH⁻) to form HCO₃⁻ (Figure A5.1, Wang et al., 2011). The ionic bond between NH₄⁺ and HCO₃⁻ eventually leads to formation of ammonium bicarbonate (NH₄HCO₃) (Niu et al., 2012):



In the last 5 years, ammonium bicarbonate precipitation has been investigated in CCS studies using packed columns to lower the absorbent mass flow required for CO₂ stripping and therefore the heat for solvent regeneration (Gazzani et al., 2014). However, the solid product formed was difficult to manage due to packing material clogging (Sutter et al., 2015).

McLeod et al. (2015) introduced a chemically reactive membrane crystallisation reactor (CR-MCr) through which they successfully demonstrated the feasibility of nucleation and growth of the CO₂-NH₃ reaction product at the membrane-liquid interface (shell-side), therefore preventing process blockage. In this configuration, supersaturation is achieved by counter diffusion of solutes at the membrane-solution interface, also known as three phase line, where liquid (aqueous ammonia), gas (CO₂) and solid (membrane) interact, and solutes transport is driven by the enhancement in solubility provided by the reaction between NH₃ and CO₂ (Curcio et al., 2006; McLeod et al., 2015). Furthermore, the authors suggested that the microporous hydrophobic membrane is a substrate which can reduce the energy barrier to

activate heterogeneous nucleation and growth of the crystalline product, contrarily to applications where direct gas/liquid contact facilitates homogeneous nucleation (such as batch or packed columns) (McLeod et al., 2015; Di Profio et al., 2010). Whilst this mechanism has proposed, to our knowledge, a comparison between batch and membrane crystallisation kinetics of the same compound is not available in the literature to provide confirmatory evidence that the introduction of a hydrophobic membrane underpins heterogeneous nucleation. Therefore, the purpose of this study is to demonstrate that, in an unseeded supersaturated solution and laminar regime, the polymeric fibre is a substrate which induces primary heterogeneous nucleation and reduces the Gibbs free energy barrier, followed by secondary nucleation and growth downstream, as compared with mixing in batch operation, which facilitates primary and secondary homogeneous nucleation, growth and agglomeration in the same system. To address the overall aim, the following objectives have been developed: (i) characterise the divergences in the kinetics of crystal nucleation and growth between batch and membrane chemically assisted crystallisation; (ii) identify the impact of ammonia concentration on the driving force for solutes transport in batch operation; (iii) investigate the CO₂-NH₃-H₂O system underpinning batch crystallisation; (iv) determine, in both the applications, product yield and nitrogen transition from the liquid phase (absorbent) to the solid phase (crystal) recovered to evidence the diversity in the thermodynamic limit for nucleation and growth, and to demonstrate that non-dispersive gas/liquid contact reduces ammonia losses.

5.2 Materials and methods

5.2.1 Fabrication, equipment setup and operation for batch crystallisation

Carbon dioxide (99.8%, BOC gases, Ipswich, UK) was introduced into a jacketed Duran bottle (500 mL, Soham Scientific, Fordham, UK) through a head with filter disc (sparger of porosity 1, Hamilton Glass Products Ltd.) at 200ml min⁻¹ and bubbled within a 200 mL aqueous ammonia absorbent held in the same vessel. The solution was gently stirred through a Fisherbrand Microstirrer (Fisher Scientific, Loughborough, UK) and maintained refrigerated at 5±1°C through water recirculation from the jacket to a refrigerated bath and circulator (R1 Series, Grant Instruments Ltd., Cambridge, UK). The bottle head was equipped with temperature sensors (K-type, Thermosense Ltd., Bucks, UK) both upstream and downstream, connected to a data acquisition module (PicoLog, Pico Technology, St. Neots, UK) and a laptop computer, for gas and liquid temperature monitoring in real time (Figure 5.1).

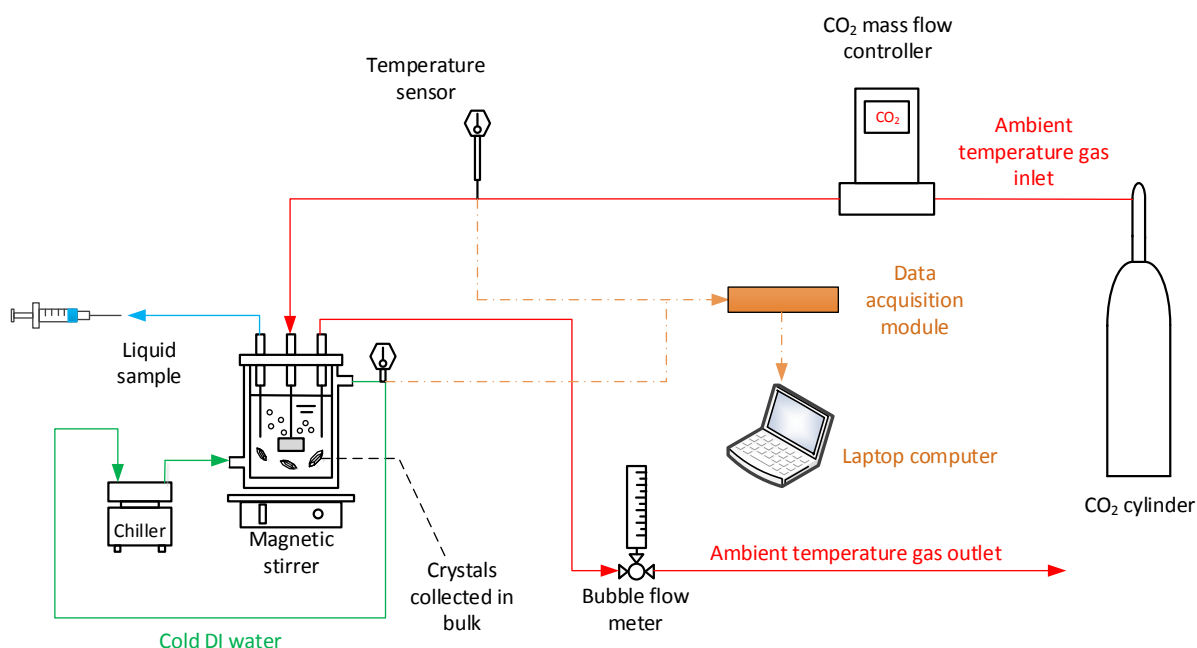


Figure 5.1. Setup diagram of the batch chemically assisted crystallisation process. Membrane operation setup has been reported in appendix.

5.2.2 Fabrication, equipment setup and operation for membrane crystallisation

The crossflow cell was constructed of Perspex, including a flow channel with a width of 12 mm and height 5 mm. A polypropylene (PP) hollow fibre membrane (Membrana GmbH, Wuppertal, Germany) with a nominal pore size of 0.2 μm , fractional porosity (ϵ) 72% and contact angle between liquid and membrane (θ) 117° was used in this study (Table 5.1). A laminar mass flow controller (0.01-1 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK) was adopted to flow pure carbon dioxide (99.8%, BOC gases, Ipswich, UK) into the lumen of the hollow-fibre at a flow rate of 1000ml min⁻¹, corresponding to a gas velocity (V_G) 14.7 m s⁻¹, while aqueous ammonia absorbent was pumped counter-current on the shell-side of the membrane at 200ml min⁻¹ (resulting in a liquid velocity, V_L 0.06 m s⁻¹) with a peristaltic pump (520Du, Watson-Marlow Ltd., Falmouth, UK). Absorbent temperature was maintained at 5±1°C by using a refrigerated bath and circulator (R1 series, Grant Instruments Ltd., Cambridge, UK). A data acquisition module (PicoLog, Pico Technology, St. Neots, UK) equipped with thermocouples (K-type, Thermosense Ltd., Bucks, UK) sited upstream and downstream of the cell recorded both gas and liquid temperatures each 10 minutes, and was connected to a laptop computer in order to monitor the data in real time (Figure A5.2).

Table 5.1. Dimensions and surface characteristics of the single hollow fibre membrane contactor (HFMC)

PP		
Fibre characteristics		
Membrane material	-	Polypropylene (PP)
Inner diameter	mm	1.2
Outer diameter	mm	1.8
Wall thickness	µm	300
Active length	mm	165
Surface area ^b	m ²	9.33 x 10 ⁻⁴
Porosity	%	72±2 ^a
ΔG _{het} / ΔG _{hom}	%	60
Minimum pore size, (d _{min})	µm	0.2 ^a
Maximum pore size, (d _{max})	µm	0.36 ^c
Contact angle, (θ)	°	117 ^d
Lumen cross sectional area	m ²	1.13 x 10 ⁻⁶
Shell side characteristics		
Height	mm	5
Width	mm	12
Shell cross sectional area	m ²	6.0 x 10 ⁻⁵
Priming volume	ml	11.0
Operational characteristics		
Flow regime		Counter-current
Shell-side	M NH ₃ (aq)	3.3
Lumen-side		99.8% CO ₂
Liquid temperature	°C	5±1
Gas temperature	°C	20±1
Liquid velocity	m s ⁻¹	0.06
Gas velocity	m s ⁻¹	14.7
Liquid volume in loop	ml	150
Liquid velocity	m s ⁻¹	0.06
Gas velocity	m s ⁻¹	14.7
Gas humidity	%	38

^a Data provided by manufacturer.^b Based on fibre outer diameter.^c Data statistically determined using log-normal distribution^d Bougie and Iliuta, (2013)

5.2.3 Chemical preparation, sampling and analysis

Ammonia concentrate (35% Fisher Chemicals, Loughborough, UK) was added to de-ionised water (15.0 MΩ cm⁻¹) to prepare aqueous ammonia solutions at fixed concentrations (ranging between 2.6 and 6.3 molNH₃ L⁻¹), while absorbent pH was fixed at pH 10 through addition of hydrochloric acid (HCl, 37%, Fisher Scientific, Loughborough, UK) as typically employed in aqueous ammonia packed column processes (Yeh et al., 2005). Ammonia concentration was confirmed using an ammonium cell test which pre-acidifies the sample (VWR International Ltd., Poole, UK) before determination by spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darnstadt, Germany). Gas flow rate was measured, in membrane and batch operations, through bubble flow meters of 1000 ml and 50 ml volume respectively (SKC, Blandford Forum, UK; Restek, Bellefonte, US) and the CO₂ flux (J_{CO₂}, mol m⁻² s⁻¹) was expressed as:

$$J_{CO_2} = \frac{(Q_{G,in} - Q_{G,out}) \times 273.15 \times 1000}{22.4 \times A_m T_G} \quad (2)$$

where $Q_{G,in}$ and $Q_{G,out}$ are the inlet and outlet gas flow rates ($\text{m}^3 \text{s}^{-1}$) respectively, A_m is the membrane or diffuser surface area (m^2) and T_G is the gas temperature (K) (Atchariyawut et al., 2007).

A pH meter (Jenway 4330, Cole-Parmer, Stone, UK) equipped with Jenway epoxy bodied pH electrode (bulb end type) was used to periodically monitor absorbent pH, while UV absorbance of the solvent was determined at 215 nm on a UV/Vis. Spectrophotometer (Jenway 6715, Cole-Parmer, Stone, UK), corresponding to the absorption region for bicarbonate (Wilson et al., 2001). Crystal size distribution (CSD) of the crystal product recovered from the bulk solution was determined through a sacrificial experiment for each level of supersaturation (C/C^*). Sacrificial experiments at a fixed supersaturation level were undertaken in triplicate. Prior to counting, the absorbent was filtered through a $0.45 \mu\text{m}$ filter and weighed (Whatman, Camlab Ltd., Cambridge, UK). The crystals were then immersed in anhydrous alcohol to minimise agglomeration (Veiga et al., 1999) and transferred onto a microscope slide consisting of a 1 mm grid for counting under an optical microscope (Optech Microscope Services Ltd., Thame, UK) equipped digital camera (Infinity 3, Lumenera, Ottawa, Canada). Images were analysed with image processing software (Image Pro Plus, Media Cybernetics, Cambridge, UK) to determine crystal number and size. Each image analysed corresponded to around 50 crystals. The crystal size distribution was determined assuming a log-normal distribution (Li et al., 2000) and for each sacrificial experiment at least 600 crystals were classified to minimise standard error of the CSD (Ji et al., 2010).

5.2.4 Crystallisation kinetics

Chen et al. (2014) proposed the following equations to determine the kinetics of nucleation and crystal growth in a supersaturated solution:

$$G = K_G (c_{fm} - c^*)^g \quad (3)$$

$$B = K_B G^b \quad (4)$$

The kinetic rate constant for crystal growth K_G ($\text{kg}^{-g} \text{m}^{3g+1} \text{s}^{-1}$), nucleation rate constant K_B ($\text{No m}^{-3-b} \text{s}^{-1+b}$), and exponents g and b can be experimentally determined through linear regressions. The parameters c_{fm} and c^* (kg m^{-3}) represent the $\text{CO}_2(\text{aq})$ concentrations adjacent to the membrane surface and the equilibrium-saturated concentration at the membrane wall temperature T_{fm} . If the crystal growth rate is defined as the size variation from $L(\text{m})$ at time t to $L+\Delta L$ at $t+\Delta t$, then the average crystal growth rate G , over the time interval Δt (s), can be calculated through the linear equation (Söhnel et al., 1996):

$$G(L, t) = \Delta L / \Delta t \quad (5)$$

where G can be experimentally determined at different time intervals and Equation 3 converted into its logarithmic form:

$$\log G = \log K_G + g \log(c_{fm} - c^*) \quad (6)$$

The crystal growth rate constant K_G and the exponent g can then be respectively derived from the intercept and slope of the linear regression.

Analogously, the nucleation rate can be defined as:

$$B(L, t) = \Delta N / \Delta t \quad (7)$$

Where ΔN is the crystal number variation over the same time interval Δt . The logarithmic form of Equation 4 is:

$$\log B = \log K_B + b \log G \quad (8)$$

The kinetic nucleation constant K_B and exponent b , can be derived through data regression of Equation 8, being the nucleation rates B at each sampling time experimentally determined.

The likelihood of preferential heterogeneous nucleation of a crystal on the membrane surface was expressed as (Curcio et al., 2006):

$$\frac{\Delta G_{het}}{\Delta G_{hom}} = 0.25(2 + \cos\theta)(1 - \cos\theta)^2 \left[1 - \varepsilon \frac{(1 + \cos\theta)^2}{(1 - \cos\theta)^2} \right]^3 \quad (9)$$

where ΔG_{het} and ΔG_{hom} are the Gibbs free energies of heterogeneous and homogeneous nucleation, θ is the contact angle between membrane and liquid surface and ε is the fractional porosity of the membrane. Specifically, $\Delta G_{het} / \Delta G_{hom}$ ratio was 60%, thus indicating heterogeneous nucleation to prevail over homogeneous nucleation at the membrane-solution interface.

5.2.5 Interfacial energies determination

In membrane crystallisation undertaken in this work, hydro-dynamically characterised by recirculation of absorbent solution in a laminar regime ($Re \sim 350$) and where unseeded crystallisation occurred at the membrane-liquid interface, primary heterogeneous nucleation of ammonium bicarbonate was assumed to initiate the crystallisation process at the three phase line, followed by secondary nucleation and growth in the vessel downstream (Ji et al., 2010). According to the classical nucleation theory (CNT), the primary nucleation rate B is related to supersaturation S ($= c_{fm}/c^*$) by the expression:

$$B = a \exp\left(\frac{-b}{\ln S^2}\right) \quad (10)$$

With a kinetic parameter and b the thermodynamic parameter for nucleation (Mersmann et al., 1992). The exponential part represents a free energy barrier for the formation of the nucleus while the pre-exponential part contains information on the kinetics of the barrier crossing. In conformity with Equation 10, $\ln B$ should be a linear function of $\ln^2 S$. The thermodynamic

parameter b can be estimated from the slope of the best fit straight line, while the kinetic parameter a can be derived from the intercept of that line, giving the value $\ln a$.

The coefficient b for heterogeneous nucleation can be expressed as in Gomez-Morales et al. (1996):

$$b = \frac{\phi 16\pi\sigma^3\vartheta^2}{3(k_B T)^3} \quad (11)$$

Where ϑ is the NH_4HCO_3 molecular volume ($8.26 \times 10^{-29} \text{ m}^3$), k_B the Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T the absolute temperature (278.15 K) and $\phi = \Delta G_{\text{het}}/\Delta G_{\text{hom}}$ (~ 0.6) the factor which accounts for the reduction of the Gibbs free energy of the system due to the heterogeneous nucleation on porous membranes (Equation 9). Based on the slope of the experimental data regression $\ln B$ vs. $\ln^2 S$, the value of σ (interfacial energy, J m^{-2}) can be derived using Equation 11.

Secondary nucleation could not be decoupled from primary nucleation within batch crystallisation undertaken in this study, due to combined action of direct mixing and CO_2 bubbling into the crystallising solution within the same environment, which increased chemical energy and frequency of collisions, and consequently raised the likelihood for generation of secondary nuclei in the same domain where primary nucleation initiated (Curcio et al., 2001; Agrawal and Paterson, 2015; Lewis et al., 2015). Interfacial energy for batch crystallisation in this work has been then evaluated through Nakai's method, which takes into account both primary and secondary nucleation (Nakai, 1969; Toyokura, 1995).

$$\frac{\beta\sigma}{K_B T} = K \quad (12)$$

Where K is a dimensionless parameter dependent on solute (CO_2) concentration and β (m^2) is the geometric factor of ammonium bicarbonate crystal assumed to be a cube (Nakai, 1969):

$$\beta_{\text{cube}} = \frac{\phi_{\text{cube}}}{\phi_{\text{sphere}}} \beta_{\text{sphere}} \quad (13)$$

Specifically, $\phi_{\text{cube}} / \phi_{\text{sphere}}$ is the ratio between the shape factors of cube and sphere, respectively and β_{sphere} can be expressed as a function of NH_4HCO_3 molecular volume as follows:

$$\beta_{\text{sphere}} = (4\pi)^{1/3} (3\vartheta)^{2/3} \quad (14)$$

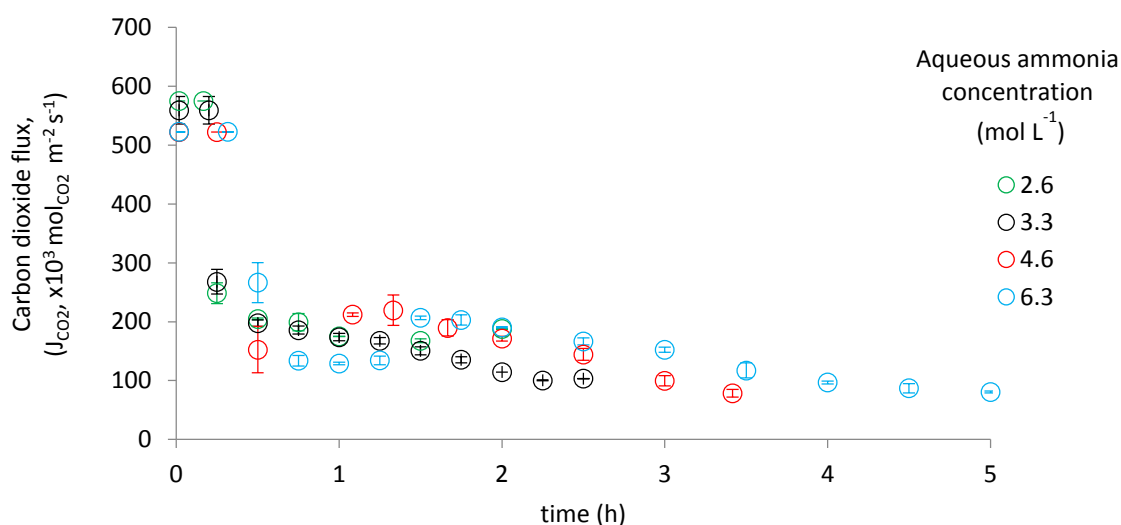
5.3 Results

5.3.1 Carbon dioxide absorption chemistry in batch operation

Maximum CO_2 flux, approximately constant at $550 \times 10^{-3} \text{ molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ was observed between 0.2 and 0.3 hours (or C/C^* between 0.2 and 0.5) for the whole range of $\text{NH}_3(\text{aq})$ concentrations, followed by a rapid CO_2 absorption decline, which was sustained between 2 and 5 hours, corresponding to absorbent concentrations between 2.6 and $6.3 \text{ molNH}_3 \text{ L}^{-1}$ (Figure 5.2). At an equivalent supersaturation level, expressed as CO_2 absorbed / HCO_3^-

saturation, lower ammonia concentration elicited steeper pH drop (Figure 5.3a). To illustrate, a minimum pH value of 7.1 was observed with 2.6 molNH₃ L⁻¹ absorbent at C/C* of 1.6, whilst the same minimum pH value of 7.1 was observed for the 6.3 molNH₃ L⁻¹ solution at C/C* of 3.2. Specifically, whilst the initial flux recorded was identical at 2.6 and 6.3 molNH₃ L⁻¹, the J_{CO₂} profile was sustained for a longer period of time at the higher concentration. A decrease of pH vs CO₂ loading, expressed as CO₂ absorbed / NH₃ molar ratio, resulted to be identical for all the ammonia concentrations adopted (Figure 5.3b).

(a)



(b)

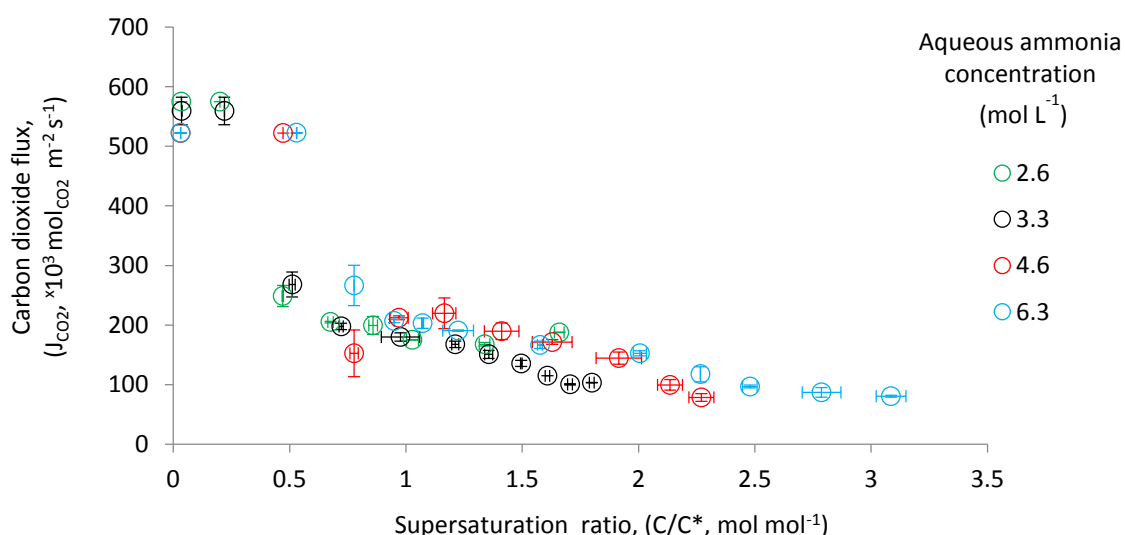


Figure 5.2. Influence of aqueous ammonia concentration on CO₂ flux decline in batch mode operation. (a) Carbon dioxide flux vs. time; (b) Carbon dioxide flux vs. supersaturation ratio (C/C^* , expressed as CO₂ absorbed / HCO₃⁻ saturation). Error bars indicate standard deviation from sacrificial tests conducted in triplicate.

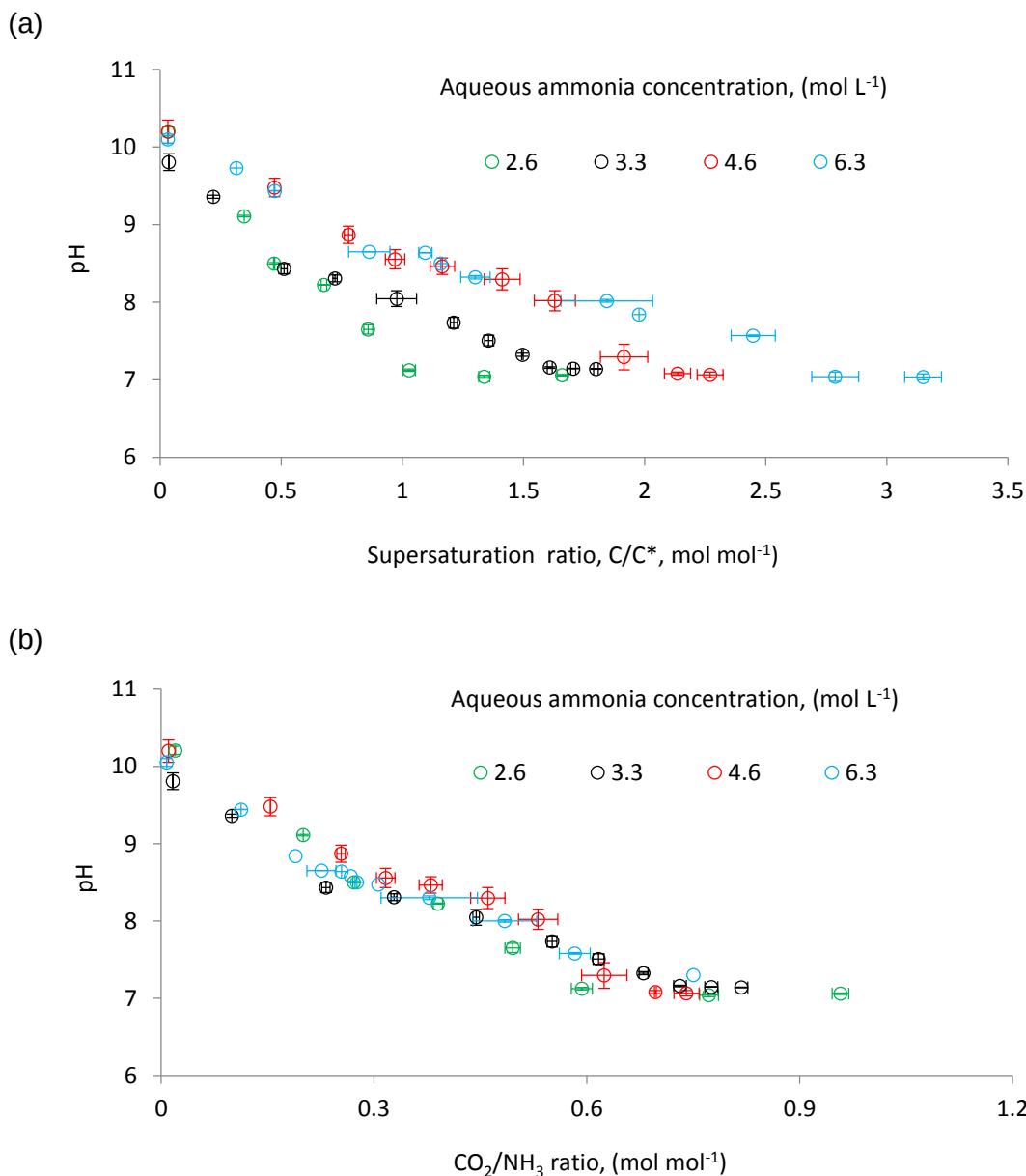


Figure 5.3. Impact of aqueous ammonia concentration on pH decline as function of supersaturation ratio ($C/C^* = \text{CO}_2 \text{ absorbed} / \text{HCO}_3^- \text{ saturation}$) (a) and CO_2/NH_3 ratio (b) through batch chemically assisted crystallisation. Error bars represent standard deviation of sacrificial experiments undertaken in triplicate.

Ammonium bicarbonate precipitation was observed in all the absorbent concentrations above 3 molNH₃ L⁻¹. In particular, bicarbonate peak was achieved before HCO₃⁻ saturation with the 2.6 molNH₃ L⁻¹ solution. On the contrary, the adoption of absorbents above 3 molNH₃ L⁻¹ showed HCO₃⁻ peak at $C/C^* = 1$ prior drop, following nucleation and growth of NH₄HCO₃ (Figure 5.4).

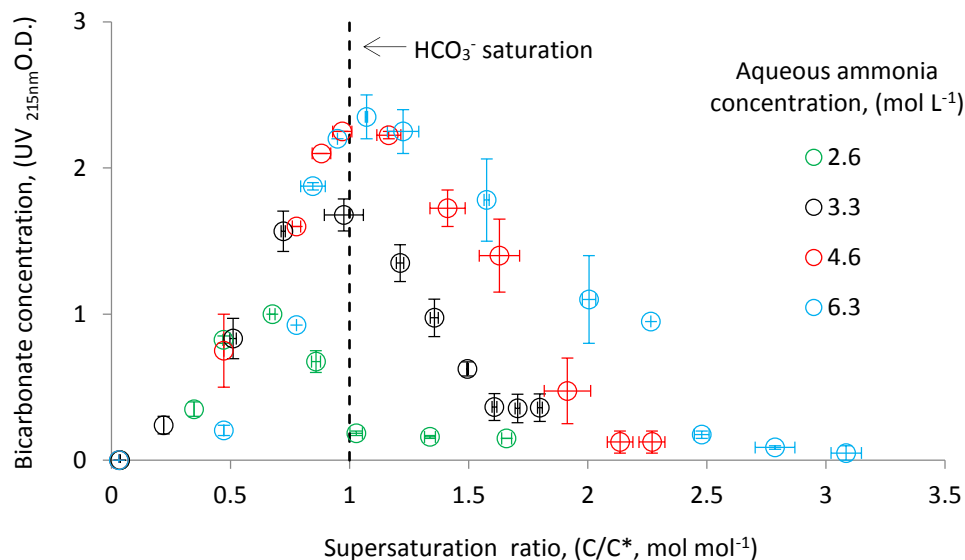


Figure 5.4. Effect of aqueous ammonia concentration on bicarbonate variation and NH_4HCO_3 crystallisation in batch chemically assisted crystallisation. Carbon dioxide absorbed in solution assumed fully converted into bicarbonate. Error bars indicate standard deviation of sacrificial experiments undertaken in triplicate.

5.3.2 Comparison of batch and membrane applications at fixed aqueous ammonia absorbent concentration

Maximum CO_2 fluxes were observed at the beginning of the test, which corresponded to $559 \times 10^{-3} \text{ molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ (CO_2 flow rate, 200 ml min^{-1}) and $12 \times 10^{-3} \text{ molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ (CO_2 flow rate, 1000 ml min^{-1}) respectively for both batch and membrane operations (Figure 5.5), prior to a decline, which achieved a minimum in 2.5 hours ($C/C^* = 1.8$) for batch operation and 68 hours ($C/C^* = 2.6$) for membrane operation (Figure 5.5). A pH decline as function of C/C^* resulted to be more accentuated in batch crystallisation (where direct mixing occurred) at $C/C^* > 1$, as compared with membrane operation (Figure 5.6).

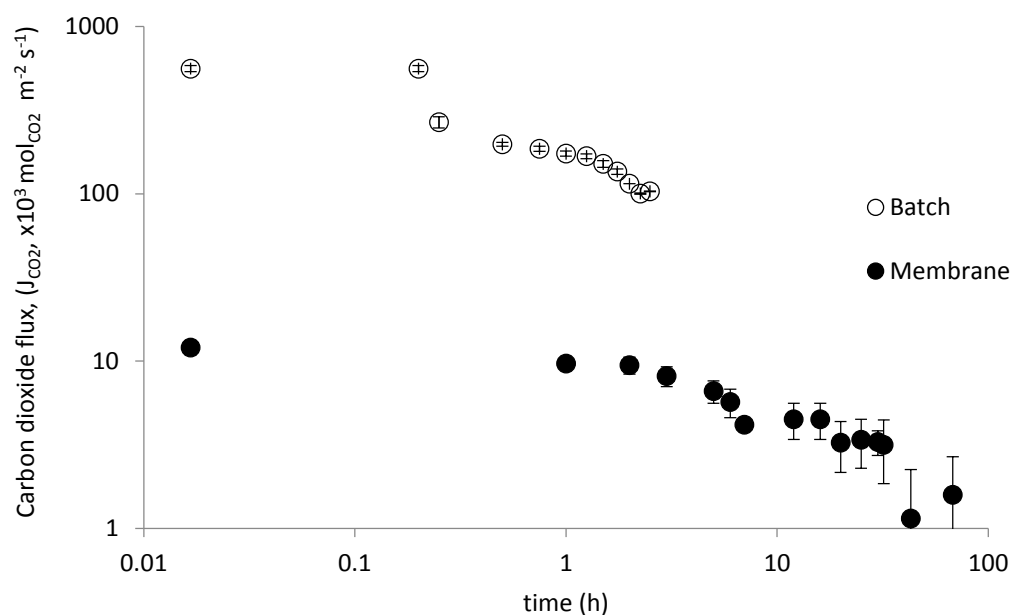


Figure 5.5. Influence of membrane and batch absorption operations on CO₂ flux decline vs. time. Aqueous ammonia absorbent temperature and concentration of 5°C and 3.3molNH₃ L⁻¹ respectively. Error bars indicate standard deviation from sacrificial tests conducted in triplicate.

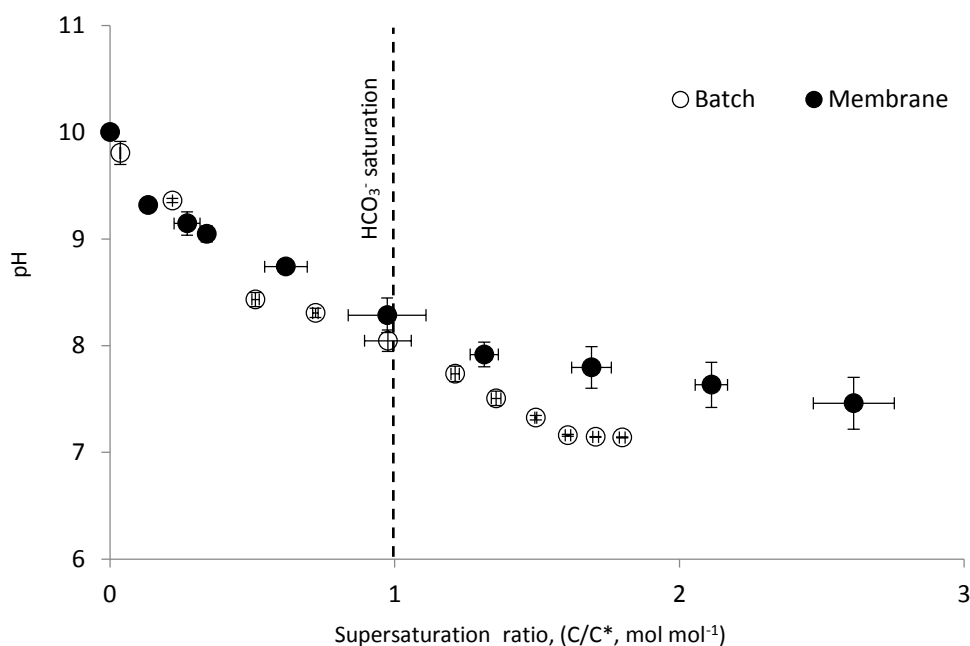


Figure 5.6. Impact of batch and membrane operation on pH decline as function of supersaturation ratio. Aqueous ammonia absorbent temperature and concentration of 5°C and 3.3molNH₃ L⁻¹ respectively. Hydrodynamic conditions: G/L 5, V_L 0.06 m s⁻¹ and V_G 14.7 m s⁻¹ for membrane crystallisation, while V_L 0.0 m s⁻¹ and V_G 0.01 m s⁻¹ for batch test (sparger surface area 3x10⁻⁴ m²). Error bars represent standard deviation of sacrificial experiments undertaken in triplicate.

Furthermore, an increase in bicarbonate concentration from $C/C^* = 0$ to $C/C^* = 1$ (bicarbonate saturation) was observed in both operations, followed by an exacerbated decline in batch operation. To elucidate, being equal the supersaturation level $C/C^*=1.8$, UV_{215nm} was 0.36 O.D. in batch and 1.4 O.D. in membrane (Figure 5.7).

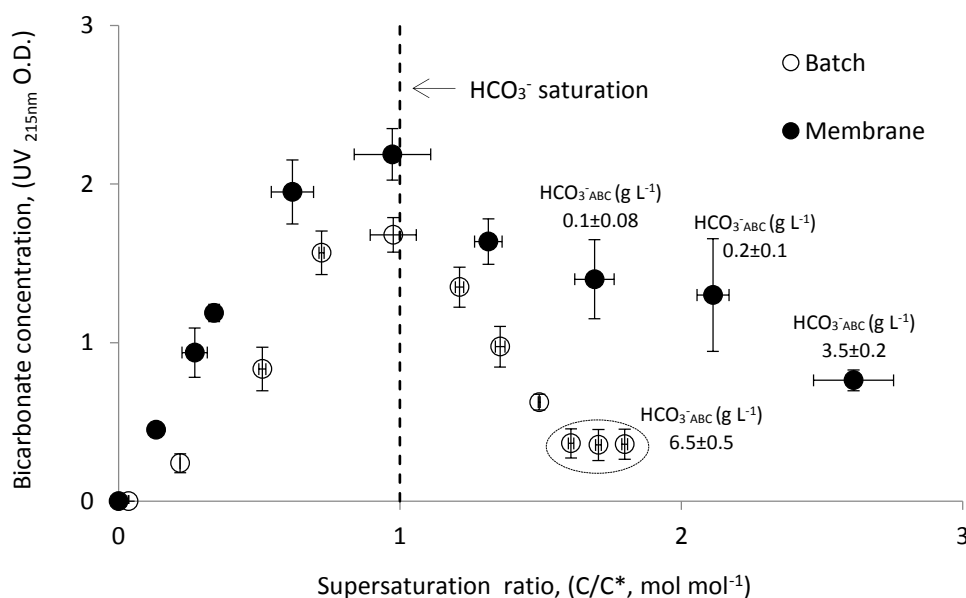


Figure 5.7. Effect of membrane and batch operation on bicarbonate consumption, where $HCO_3^-_{ABC}$ (g L⁻¹) indicates bicarbonate converted into crystal. Liquid volumes are 0.2L and 0.15L for batch and membrane test, respectively. Error bars indicate standard deviation of sacrificial experiments undertaken in triplicate.

5.3.3 Ammonium bicarbonate crystallisation in batch and membrane operations

A linear regression of the experimental mean crystal growth rate G , obtained from Equations 5 and 6 at time interval $t-t_{induction}$ from 17 to 55 hours for membrane test and from 0.75 to 1.5 hours for batch test (where $t_{induction}$ is the absorption time at $C/C^* = 1$; $t_{induction} = 13$ hours and 1 hour for membrane and batch tests, respectively), enabled to derive the crystal growth rate constant K_G and exponent g , as $1.7 \times 10^{-14} \text{ Kg}^{-g} \text{ m}^{3g+1} \text{ s}^{-1}$ and 2.64, for membrane crystallisation, and as $9.5 \times 10^{-8} \text{ Kg}^{-g} \text{ m}^{3g+1} \text{ s}^{-1}$ and -0.32, for batch operation, respectively (Figure 5.10). Similarly, from the experimental data of the crystal number (Figure 5.8), at the same time interval considered for crystal growth, nucleation rate has been determined (Equation 7; Figure 5.9), which led to the nucleation rate constant K_B and exponent b , as $1.9 \times 10^5 \text{ No m}^{-3-b} \text{ s}^{-1+b}$ and 0.38 for membrane test, and as $9.5 \times 10^{43} \text{ No m}^{-3-b} \text{ s}^{-1+b}$ and 5.06 for batch test, through linear regression of $\text{Log}B$ vs $\text{Log}G$ (Equation 8).

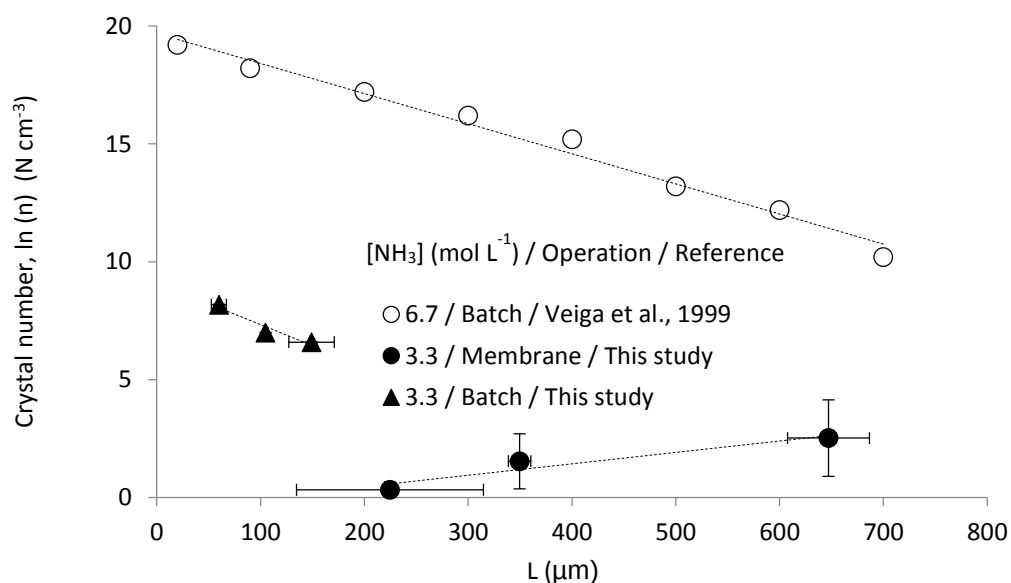


Figure 5.8. Crystal population density as a function of crystal size undertaken in this study through batch and membrane crystallisation with absorbent concentration of $3.3 \text{ mol NH}_3 \text{ L}^{-1}$ and temperature of 5°C (black data points), and in Veiga et al. (1999) through batch operation, using aqueous ammonia concentration of $6.7 \text{ mol NH}_3 \text{ L}^{-1}$ and temperature of 25°C (white data points). Batch crystallisation operations presented similar population density slopes.

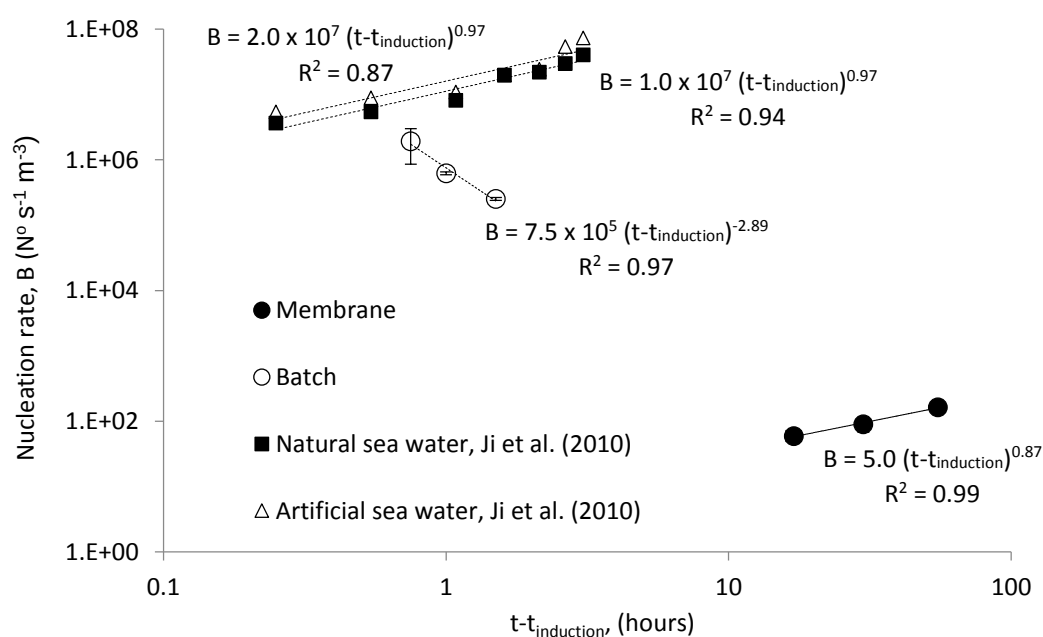


Figure 5.9. Nucleation rate vs. time (once supersaturation was achieved at induction time) for crystals precipitated in batch and membrane operations. In this study, batch and membrane chemically assisted crystallisation was carried out using aqueous ammonia absorbent temperature and concentration at 5°C and $3.3 \text{ mol NH}_3 \text{ L}^{-1}$, respectively. In Ji et al. (2010), membrane distillation crystallisation of natural and artificial sea water was undertaken through evaporation-migration-condensation mechanism.

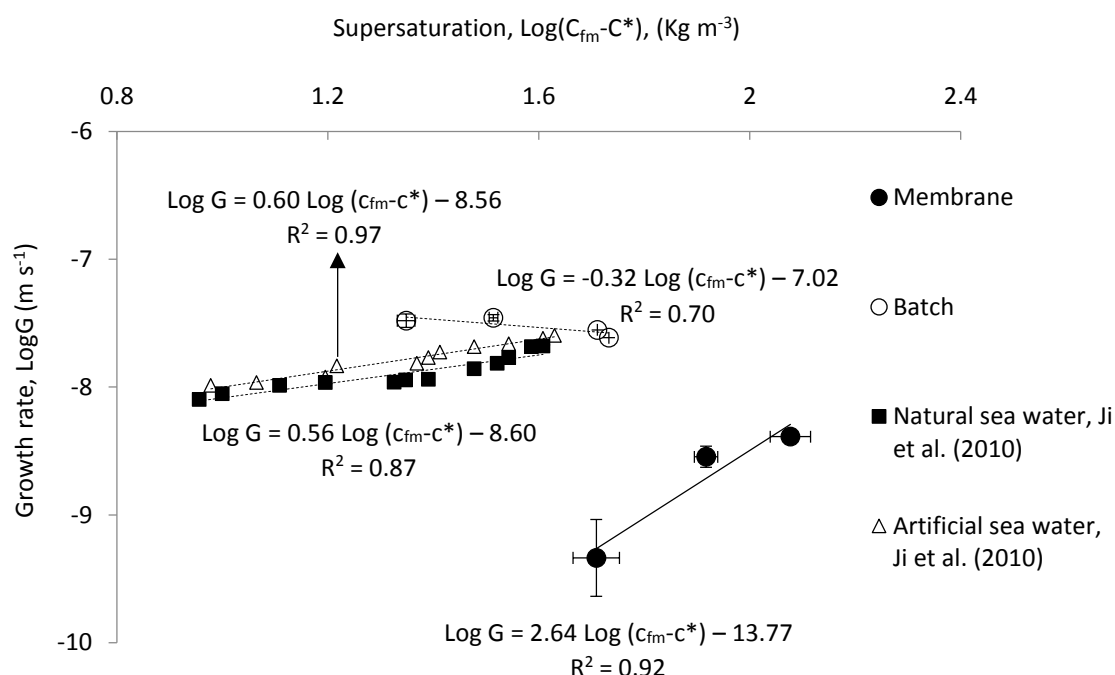


Figure 5.10. Crystal growth rate vs. supersaturation, where the crystal growth rate constant K_G and exponent for crystal growth g are derived from intercept and slope of experimental data regression. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate in this study.

A summary of the kinetic expressions for nucleation and growth is illustrated in Table 5.2. Nitrogen mass balance revealed that nitrogen conversion from the liquid phase to solid NH_4HCO_3 achieved a maximum value above 90% for membrane crystallisation and of approximately 60% in batch crystallisation, while nitrogen removal recorded a maximum of about 30% in batch test and 5% in membrane test (Figure 5.11).

Table 5.2. Kinetic expressions for nucleation and growth

Reference	Crystallisation technology	$G = K_G(C_{fm} - C^*)^g$	$B = K_B G^b$
Ji et al., 2010	MDC ^a	$G = 2.8 \times 10^{-9} (C_{fm} - C^*)^{0.60 \text{ b}}$	$B = 3.7 \times 10^{49} G^{5.52 \text{ b}}$
	MDC ^a	$G = 2.5 \times 10^{-9} (C_{fm} - C^*)^{0.56 \text{ c}}$	$B = 8.5 \times 10^{37} G^{3.96 \text{ c}}$
This study	Batch	$G = 9.5 \times 10^{-8} (C_{fm} - C^*)^{-0.32}$	$B = 9.5 \times 10^{43} G^{5.06}$
	CR-MCr	$G = 1.7 \times 10^{-14} (C_{fm} - C^*)^{2.64}$	$B = 1.9 \times 10^5 G^{0.38}$

^a Membrane distillation-crystallization.

^b Crystals nucleated from artificial brines.

^c Crystals nucleated from natural brines.

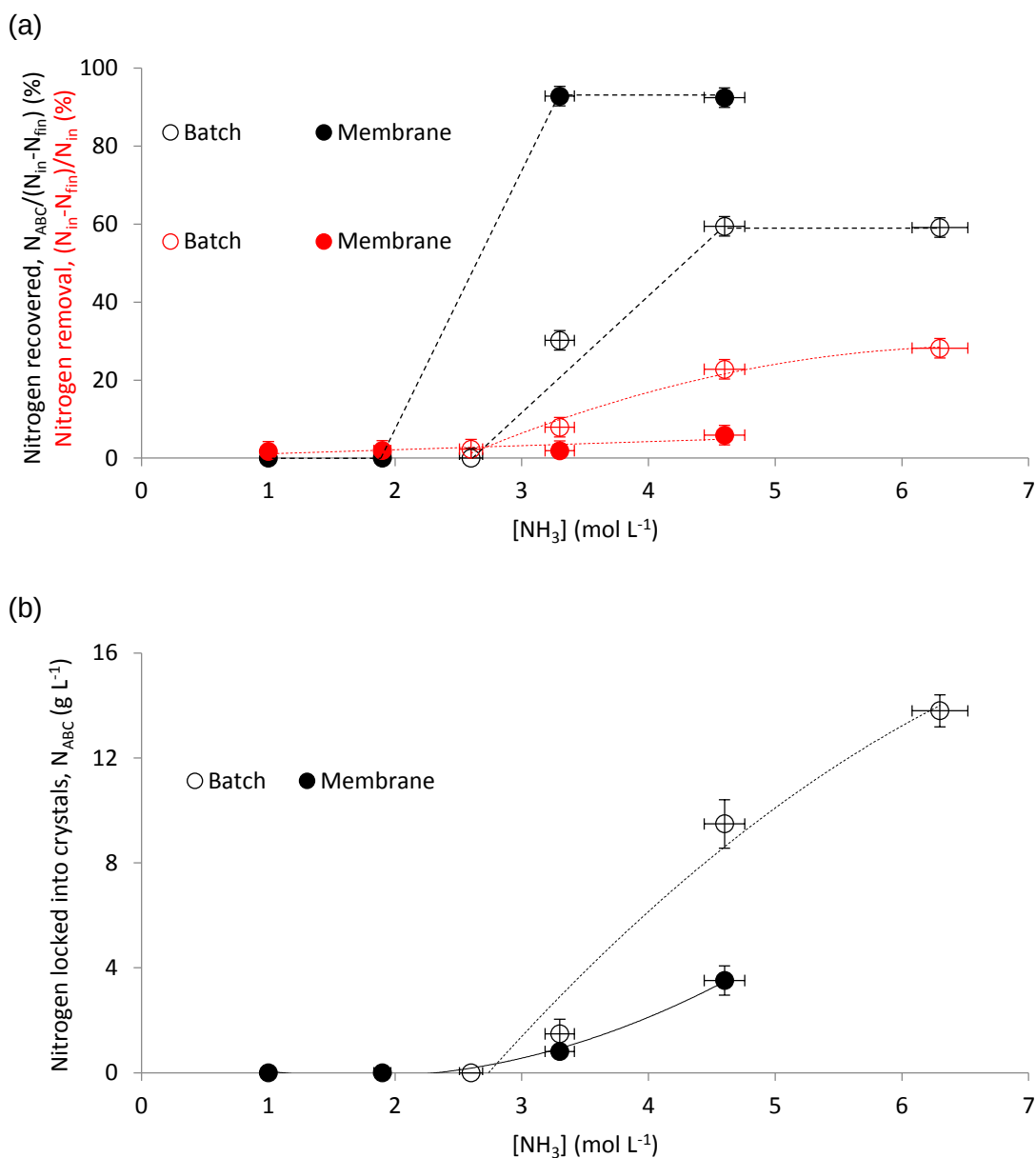


Figure 5.11. (a) Impact of aqueous ammonia concentration on ammoniacal nitrogen removal, calculated as $(N_{in}-N_{fin})/N_{in}$ (%), where N_{in} and N_{fin} are initial and final ammoniacal nitrogen concentrations (g L⁻¹) (red data points), and recovered, calculated as $N_{ABC}/(N_{in}-N_{fin})$ (%) (black data points), where N_{ABC} is nitrogen concentration locked into the crystals (g L⁻¹, figure b). Liquid volumes: 0.2L and 0.15L for batch and membrane operation, respectively. Error bars indicate standard deviation obtained from sacrificial experiments carried out in triplicate.

5.4 Discussion

In this study, the kinetics of nucleation and growth of ammonium bicarbonate product during CO₂ absorption in membrane and batch operations have been determined. Specifically, throughout CO₂ absorption in aqueous ammonia within the CR-MCr, when supersaturation has been achieved in the unseeded solution, primary heterogeneous nucleation initiates at the three phase line (Curcio et al., 2006; Ji et al., 2010). This phenomenon is followed by particle harvesting, facilitated by the shear stress of the liquid flow, which elicits nuclei

transport from the hydrophobic surface to the vessel downstream (Appendix; McLeod et al., 2015; Di Profio et al., 2010). Whilst the newly free nucleation sites on the fibre-liquid interface enable the birth of additional primary nuclei, therefore increasing nuclei number at raising levels of supersaturation, crystal growth downstream also takes place, facilitated by surface integration of secondary nuclei (mainly produced through attrition breeding) and primary nuclei, transported downstream by the liquid flow, leading to an increase in population density vs. crystal size (Figure 5.8; Lewis et al., 2015; Ji et al., 2010). On the other hand, during CO₂ absorption into aqueous ammonia in unseeded batch operation, once supersaturation is achieved, primary homogeneous nucleation occurs within the CO₂-NH₃-H₂O system, followed by secondary nucleation in the same environment (Agrawal and Paterson, 2015). When the supersaturation level further increases, combined surface integration and volume diffusion controlled growth take place, coupled with particle agglomeration, which is facilitated by high frequency of particle collisions (mainly orthokinetic and inertial collisions for particle mean length $L > 10 \mu\text{m}$ as in this work), promoted by the shear generated from CO₂ bubbling into the crystallising fluid (Appendix; Lewis et al., 2015; Elimelech et al., 1995). Thus, the initiation of primary nucleation in batch crystallisation, followed by secondary nucleation, growth and agglomeration within the same domain caused a reduction in population density (contrarily to membrane operation) as mean crystal size increased (Veiga et al., 1999; Mydlarz and Briedis, 1993). Di Profio et al. (2003) also detected a gain in population density when operating membrane crystallisation of lysozyme driven by an osmotic gradient. Nevertheless, since their crystallisation process was in batch, nucleation and growth rate declined, due to consumption of reagents with increasing levels of supersaturation (similarly to batch operation in this work, Figures 5.9 and 5.10). Contrarily, the increasing nucleation rate vs. supersaturation observed in the CR-MCr (Figure 5.9) can be ascribed to the low driving force of the chemical reaction, which limited the consumption of NH₃ whilst simultaneously developing the concentration gradient at the membrane-liquid interface, due to continuous replenishment of NH₃(aq) and CO₂ at the three phase line (Curcio et al., 2006). Furthermore, the raising nucleation rate in the present membrane study increased the nuclei integration per unit of time on the crystal surface (which enables growth in a supersaturated solution at an energy level below activation energy), therefore leading to a gain in crystal growth rate vs. C/C^* (Figure 5.10; Lewis et al., 2015). Analogously to the trends observed in membrane crystallisation, Ji et al. (2010) also reported a rise in nucleation rate vs. time and growth rate vs. C/C^* (Figures 5.9 and 5.10), due to continuous recirculation of feed into the lumen-side and distillate on the shell-side of the membrane module to induce membrane distillation crystallisation of sodium chloride from natural and artificial sea water. The interfacial energy σ calculated for membrane crystallisation in this work through Ji (et al.)'s method was $6.6 \times 10^{-3} \text{ J m}^{-2}$ (Equations 10 and 11; Ji et al., 2010), whilst for batch crystallisation σ calculated with Nakai's method (Equations

12 to 14; Nakai, 1969), was $7.7 \times 10^{-3} \text{ J m}^{-2}$. These σ values obtained, nicely compare with the experimental values of interfacial energy for NaCl crystals in Ji et al. (2010) and other inorganic salts reported in Toyokura, 1995, ranging between $7.3 \times 10^{-3} \text{ J m}^{-2}$ for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $10.5 \times 10^{-3} \text{ J m}^{-2}$ for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Table 5.3).

Table 5.3. Calculated values of interfacial energies σ

Reference	Crystallisation technology	Interfacial energy, σ (J m^{-2})	Crystal formed
Toyokura, 1995	Fluidized seed bed	10.5×10^{-3}	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
	Fluidized seed bed	8.9×10^{-3}	K-Alum
	Fluidized seed bed	7.3×10^{-3}	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Ji et al., 2010	MDC ^a	9.6×10^{-3} ^b ; 10.2×10^{-3} ^c	NaCl
This study	CR-MCr	$(6.6 \pm 0.2) \times 10^{-3}$	NH_4HCO_3
	Batch	$(7.7 \pm 0.2) \times 10^{-3}$	NH_4HCO_3

^a Membrane distillation-crystallization.

^b Crystals nucleated from artificial brines.

^c Crystals nucleated from natural brines.

Furthermore, the interfacial energy calculation with Ji (et al.)'s method for batch crystallisation, led to $\sigma < 0$, in contrast to the positive values of interfacial energies reported in the literature for several types of crystals, thus confirming that Ji (et al.)'s method cannot be used for batch operation, since in this case primary and secondary nucleation cannot be decoupled (Figure A5.3; Ji et al., 2010; Nakai, 1969). Therefore, the values σ obtained corroborates the hypothesis made of primary heterogeneous nucleation at the membrane-liquid interface decoupled by secondary nucleation and growth, which mainly occur downstream, in membrane operation, in contrast to primary homogeneous nucleation followed by secondary homogeneous nucleation and growth, within the same environment, in batch crystallisation. Even though membrane and batch chemically assisted crystallisation, and membrane distillation crystallisation are governed by distinct mechanisms of crystallisation, the growth rate G (m s^{-1}) among them still ranged in the order of $10^{-9} - 10^{-7} \text{ m s}^{-1}$, as exhibited by most inorganic salts (Figure 5.10; Garside and Shah, 1980). Furthermore, nucleation rates B ($\text{N}^0 \text{ s}^{-1} \text{ m}^{-3}$) reported for batch crystallisation in this study and membrane distillation in Ji et al. (2010) ranged between 10^5 and $10^8 \text{ N}^0 \text{ s}^{-1} \text{ m}^{-3}$, analogously to the values measured by Garside and Shah, (1980) for several inorganic salts in MSMPR crystallisers (Figure 5.9). On the other hand, nucleation rate B for membrane chemically assisted crystallisation was 3 orders of magnitude below the conventional range reported in the literature (Figure 5.9), due to its low counter-diffusional driving force, which approximately provides between 20 to 50 times lower solute flux, if compared with the turbulent system in batch operation (Figure 5.5). Further evidence on the distinct crystallisation mechanism within the applications investigated is provided by a comparison among nucleation rate constants K_B and exponents b for batch and

membrane chemically assisted crystallisation in this work, and membrane distillation crystallisation studies in Ji et al. (2010) (Table 5.2). Membrane distillation crystallisation values of K_B (8.5×10^{37} and 3.7×10^{49} $\text{No m}^{-3-b} \text{s}^{-1+b}$) and b (3.96 and 5.52) in Ji et al. (2010), for natural and artificial sea water respectively, were analogous to those in batch operation calculated in this study ($K_B = 9.5 \times 10^{43}$ $\text{No m}^{-3-b} \text{s}^{-1+b}$ and $b = 5.06$), which were in turn about 38 orders of magnitude higher than CR-MCr nucleation rate constant K_B and 13 times higher than CR-MCr nucleation rate exponent b , respectively. Nevertheless, wide ranges of nucleation rate constant K_B and exponent b have been reported in the literature for inorganic salts (Timm and Cooper, 1971; Murray and Larson, 1965; Song and Douglas, 1975). To illustrate, within MSMPR crystallisers, if considering only tests with exponent of magma density $j=0$ in order to have the same units reported in this study for K_B and b , then the values of K_B would range between the order of 10^{-10} and 10^{78} $\text{No m}^{-3-b} \text{s}^{-1+b}$, and b between -2.48 and 9 (reported for barium soap and sodium chloride, respectively; Garside and Shah, 1980; Timm and Larson, 1968), where the sensible discordance on the values of K_B and b , can be strongly influenced by the different hydraulic and geometric characteristics of the crystallisation systems (Curcio et al., 2001). The delayed onset of crystallisation in both batch and membrane operations in this study, compared with membrane distillation crystallisation tests in Ji et al. (2010) (Figure 5.10), can be explained by the partial conversion of HCO_3^- into carbonic acid (H_2CO_3) (Figure A5.1, a), caused by solution pH drop, which occurs throughout CO_2 absorption (Figure 5.6; Wang et al., 2011). Thus, further dissolution of CO_2 is required to achieve sufficient supersaturation for induction (the initiation of nucleation) (Millero and Roy, 1997). Additionally, a delayed onset of crystallisation in the CR-MCr has been detected compared with batch crystallisation in this study (Figure 5.10), which can be ascribed to the direct mixing operated in batch crystallisation, that lowers the metastable zone width (MSZW) and elicits earlier crystallisation (O'Grady et al., 2007). To elucidate, the probability of collision between CO_2 and NH_3 is $P(\text{CO}_2\text{-NH}_3) = 1$ in the whole liquid volume within the batch reactor, facilitated by direct enhanced mixing and shear produced by CO_2 bubbling in aqueous ammonia, which significantly raise the rate of molecules collision, but do not affect the activation energy for nucleation, defined as the minimum amount of kinetic energy for an effective collision to occur (O'Grady et al., 2007; Appendix). On the other hand, in membrane operation $P(\text{CO}_2\text{-NH}_3) = 1$ at the thin membrane-liquid interface, where $V_{\text{boundary layer}} / V_{\text{solution}}$ fraction (Litre / Litre) < 0.01 if considering $V_{\text{solution}} = 0.15$ L and assuming boundary layer thickness $L_{\text{B.L.}} < 0.01$ dm:

$$V_{\text{boundary layer}}(\text{Litre}) = V_{\text{boundary layer+membrane}}(\text{Litre}) - V_{\text{membrane}}(\text{Litre}) \quad (15)$$

$$V_{\text{membrane}} = \frac{\pi D^2}{4} \times L \quad (16)$$

Where D and L are outer diameter and active length of the fibre, respectively (dm), while:

$$V_{\text{boundary layer+membrane}} = \frac{\pi(D+2L_{\text{B.L.}})^2}{4} \times L \quad (17)$$

While $P(\text{CO}_2\text{-NH}_3)$ is significantly lower in the remaining solution volume ($\approx 99.9\%$ of the total solution volume, V_{solution}), which induces a lag time on pH transient associated with poor mixing between CO_2 and NH_3 , if compared with batch crystallisation (Figure 5.6). As a result, the single fibre adopted in membrane crystallisation in this work, thermodynamically limited the precipitation of NH_4HCO_3 crystals, due to a restricted boundary layer volume, if compared with batch operation, where the entire liquid volume contributes to nucleation and growth, inducing N removal (%) in batch higher than in membrane (Figure 5.11). Specifically, the maximum yield of $\text{NH}_3\text{-N}$ precipitated was about 30% (in batch; Figure 5.11), which however can be enhanced up to 99% through simplification of the chemistry (no acid addition in the crystallising fluid), since the $\text{CO}_2\text{-NH}_3$ reaction would initiate at higher pH, therefore eliminating HCO_3^- to H_2CO_3 transition observed in both membrane and batch operation in this study (Figures 5.6 and A5.1). As a consequence of faster pH transition, which converts part of HCO_3^- into H_2CO_3 , and higher NH_4HCO_3 yield, once supersaturation was achieved, a steeper decline of HCO_3^- vs. C/C^* was observed in batch operation as compared with membrane crystallisation (Figure 5.7). Nevertheless, nitrogen mass balance in both membrane and batch chemically assisted crystallisation showed in the first case that about 95% of N lost was locked in the crystalline product recovered from the bulk solution, which demonstrated both ammonia lost and NH_4HCO_3 deposition on the hydrophobic surface of the membrane to be negligible, whilst in the second case only about 60% of N lost was converted into solid (Figure 5.11). This can be explained by the fact that, differently from the direct gas-liquid contact in batch operation, the hydrophobic membrane facilitates non-dispersive contact between the chemical absorbent and gas phase, providing a reduction in NH_3 slip up to two orders of magnitude (McLeod et al., 2014). Importantly, an increase of the membrane-solution interfacial surface area, at constant CO_2 flux, would expand the boundary layer volume and raise the probability of collision between solute and solvent, thus leading to higher nucleation rate and closing the gap to control nucleation in membrane operation (Curcio et al., 2006). The peak CO_2 flux recorded in batch crystallisation was initially similar for the NH_3 concentrations ranging between 2.6 and 6.3M due to excess of $\text{NH}_3(\text{aq})$ in the $\text{CO}_2\text{-NH}_3$ reaction (Wang et al., 2011). Analogously to the CO_2 fluxes observed in membrane crystallisation in this study, a two-stage decline was also observed in batch (Figure 5.2a and b). Specifically, in the first stage, where CO_2 and NH_3 react to form carbamic acid, the pH decline is governed by CO_2/NH_3 ratio (Figure 5.3b), where a relative excess of CO_2 enables a quicker pH drop as observed with a lower ammonia concentration in Figure 5.3a. As a consequence of NH_3 consumption, the CO_2 flux reduces, leading to the second stage reaction, where the higher is the aqueous ammonia concentration, the longer the CO_2 flux is sustained, due to the formation of carbamate with excess of free NH_3 (Figure 5.2a and b; Ahn et al., 2011). Even though all the aqueous ammonia concentrations used were above the ammonium bicarbonate solubility limit of

approximately 1.5 M (119 g l⁻¹, 5°C; PubChem, 2004; Perry and Green, 2007), the solid phase conversion was not observed for NH₃ at 2.6M (Figure 5.11), since it was kinetically limited by the pH transient, which forced HCO₃⁻ to a maximum before saturation and then converted part of the bicarbonate into carbonic acid, such that once supersaturation was achieved ($C/C^* = 1$), there was not enough bicarbonate available for NH₄HCO₃ nucleation (Figures 5.4). For ammonia concentrations above 3M, the pH was sustained above 8 at $C/C^* = 1$, therefore leading to dissolved CO₂ mainly available as HCO₃⁻ and enabling nucleation and growth of ammonium bicarbonate (Figures 5.3 and 5.11). This demonstrates that similarly to CR-MCr, batch crystallisation is also governed by allowing sufficient free NH₃ to sustain the pH (and thus HCO₃⁻) at bicarbonate supersaturation limit ($C/C^* = 1$).

5.5 Conclusions

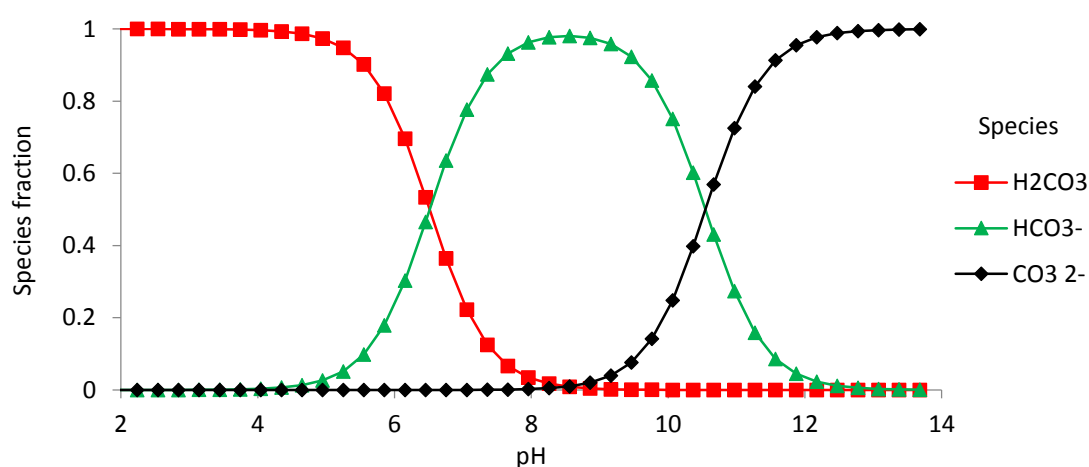
A comparison between batch and membrane crystallisation kinetics in this study, evidenced that in the CO₂-NH₃-H₂O system, the hydrophobic membrane is a substrate which induces heterogeneous nucleation of ammonium bicarbonate at the three phase line and reduces the Gibbs free energy for nucleation. Specifically, whilst in membrane crystallisation, for an unseeded supersaturated solution, characterised by laminar regime, primary heterogeneous nucleation occurs at the membrane-liquid interface, decoupled by secondary nucleation and growth which mainly arise in the vessel downstream, in batch operation, homogeneous primary and secondary nucleation are followed by growth and agglomeration within the same system. As a result, an increasing trend in population density vs. crystal size was recorded with the CR-MCr, in contrast with the decline observed in batch crystallisation. The hypothesis of primary heterogeneous nucleation disconnected by secondary nucleation in membrane test against primary and secondary homogeneous nucleation within the same domain in batch were furtherly confirmed through interfacial energies values obtained, in good agreement with those reported in the literature for some inorganic salts (Toyokura, 1995; Ji et al., 2010). Additionally, in batch crystallisation, direct mixing induced an earlier onset of precipitation, as compared with membrane operation, whilst faster pH transient and higher yield of NH₄HCO₃ formed in batch, were promoted by higher probability of collision between CO₂ and NH₃. This, however, can be compensated by increasing the membrane-solution interfacial area, which would lead to higher nucleation rate and close the gap to control crystallisation in membrane operation. Nitrogen mass balance showed complete conversion of ammoniacal nitrogen from liquid to solid phase (NH₄HCO₃), whilst only about 60% was recovered in batch operation. This can be ascribed to the fact that the introduction of the membrane offers non-dispersive gas/liquid contact, facilitating ammonia slip reduction up to two orders of magnitude, if compared with direct gas/liquid contact applications (McLeod et al., 2014).

Acknowledgements

The authors would like to thank our industrial sponsors: Anglian Water, Northumbrian Water and Severn Trent Water for their financial and technical support. We are further grateful for financial support from the Engineering and Physical Sciences Research Council (EPSRC) received through the STREAM Industrial Doctorate Centre and for a Cranfield School of Water, Energy and Environment PhD bursary.

Appendix

(a)



(b)

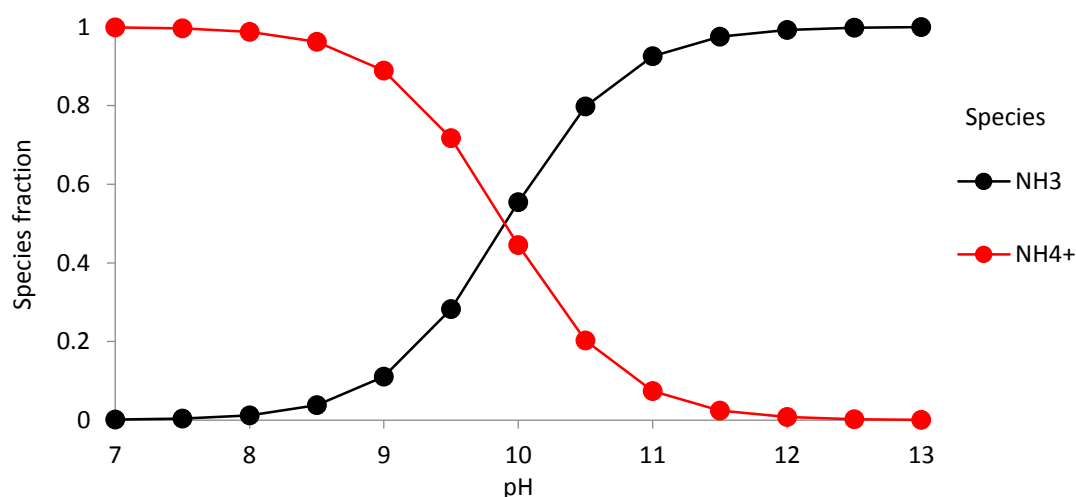


Figure A5.1. Distribution of carbonic acid, bicarbonate and carbonate (H_2CO_3 , HCO_3^- , CO_3^{2-}) (a) and of ammonium-ammonia (b) as functions of pH at absorbent temperature of 5°C (Millero, 1995; Bates and Pinching, 1949).

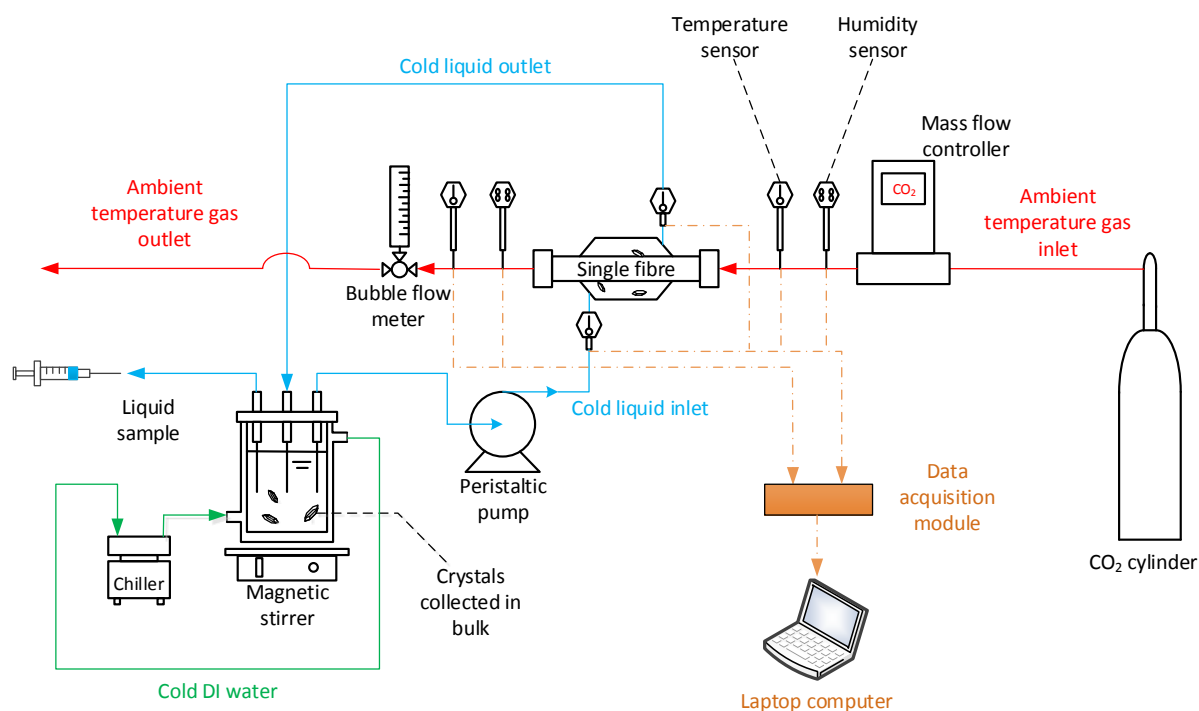


Figure A5.2. Setup diagram of the membrane chemically assisted crystallisation process.

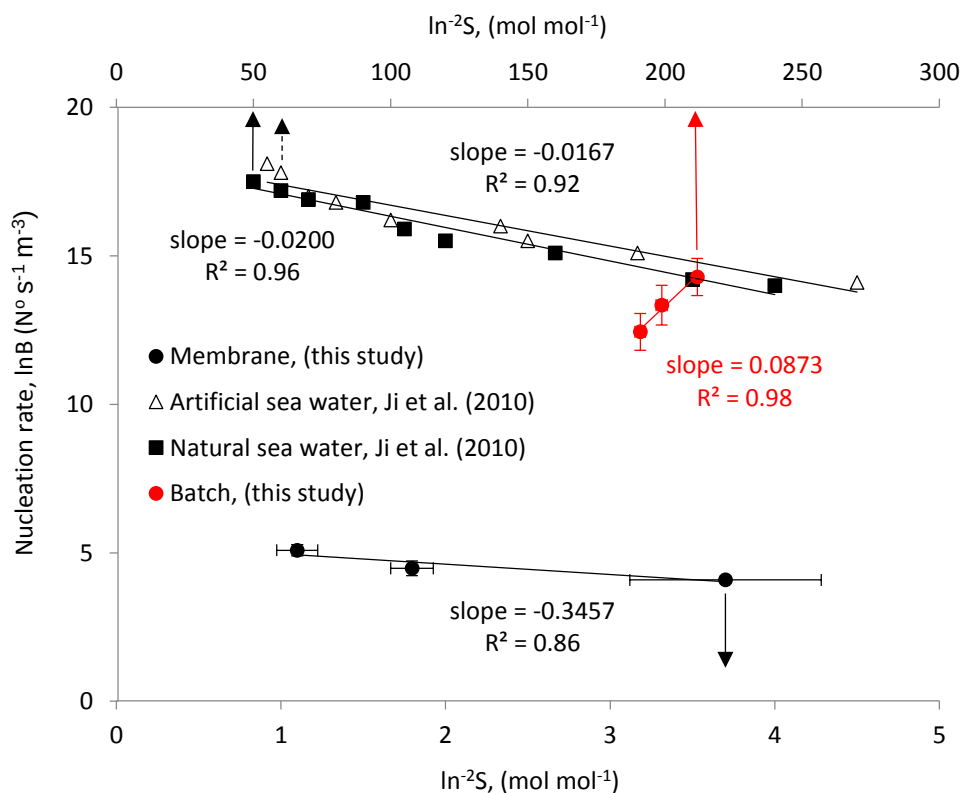


Figure A5.3. Experimental nucleation rate of NH_4HCO_3 crystals (this study) and $NaCl$ crystals (Ji et al., 2010) vs. supersaturation. Error bars represent standard deviation of sacrificial experiments carried out in triplicate.

Shear rate in a bubble reactor

The mean shear rate in the reactor G_b (s^{-1}) produced by bubbles assumed small (diameter ≈ 0.01 cm) and with low rise velocity ($Re \ll 1$) can be determined by (Logan, 2012):

$$G_b = \left(\frac{Q_{CO_2} h g}{V_T \vartheta_w} \right)^{1/2} \quad (A4)$$

Where Q_{CO_2} ($L s^{-1}$) is the gas flow rate, h (cm) is the height of aqueous ammonia, g ($cm s^{-2}$) is the acceleration due to gravity, V_T (L) is the volume of aqueous ammonia in the reactor and ϑ_w ($cm^2 s^{-1}$) is the kinematic viscosity of the liquid at $5^\circ C$. As a result, the shear rate in the bubble reactor used in this study was about $66 s^{-1}$ which is in good agreement with the typical values reported in the literature for bubble reactors without baffles, ranging between $70 s^{-1}$ and $50 s^{-1}$ (Camp, 1968; Lai et al., 1975).

Wall shear rate in CR-MCr

The mean shear rate in the CR-MCr G_L (s^{-1}) produced by the liquid flow on the shell side of the microporous membrane can be determined by (Jaffrin, 2008):

$$G_L = 0.23 \frac{v_w^{3/2}}{L} L^{5/4} e^{-1/4} \vartheta_w^{-1/2} \quad (A5)$$

Where v_w ($m s^{-1}$) is the liquid velocity, L (m) is the active length of the fibre, e (m) is the gap between the membrane and shell, ϑ_w ($m^2 s^{-1}$) is the kinematic viscosity of the liquid at $5^\circ C$. As a result, the shear rate in the CR-MCr used in this study was about $22 s^{-1}$ which is sensibly lower than that the values reported in the literature ($> 1000 s^{-1}$, Zsirai et al., 2016). Furthermore, the Taylor number in the membrane reactor was calculated as follows (Taylor, 1936):

$$Ta = \frac{\left(\frac{v_w}{L} \right) (L^{1/2}) (e^{3/2})}{\vartheta_w} \quad (A6)$$

This parameter indicates that instabilities, also called Taylor vortices, appear when $Ta > 42$. Specifically, in this work $Ta \approx 6$, thus confirming that the liquid on the membrane-solution interface was in laminar regime, which promoted primary heterogeneous nucleation at the three phase line, followed by secondary nucleation and growth in the bulk downstream (Ji et al., 2010).

Nucleation probability

When supersaturation level $C/C^* > 1$, the solution $pH \approx 8$ for both batch and membrane operations (Figure 5.6), corresponding to CO_2 fully converted into HCO_3^- and $NH_3-NH_4^+$ equilibrium shifted towards about 100% NH_4^+ (Figure A5.1). Consequently, the probability of effective collisions between CO_2 and NH_3 , $P(CO_2-NH_3)$, becomes equivalent to the probability of effective collisions between HCO_3^- and NH_4^+ , $P(HCO_3-NH_4^+)$, also known as nucleation probability (Equation 1), which can be expressed as follows (Lewis et al., 2015):

$$P(t) = 1 - e^{-BV(t-t_0)} \quad (A7)$$

Where t is reaction time (s), t_0 induction time (3600 s in batch, 46800 s in CR-MCr), V is the active liquid volume (m^3), corresponding to the whole liquid volume in batch (0.2 L), and the membrane-solution interface in CR-MCr (about 1% of 0.15 L), and B is the nucleation rate at time t ($N^0 s^{-1} m^{-3}$). As a result, $P(t)=1$ in both batch (within the whole liquid volume) and membrane (at the thin boundary layer) from the onset of crystallisation until the end of the test (corresponding to 1.75 hour $< t < 2.5$ hours in batch and 30 hours $< t < 65$ hours in CR-MCr).

Activation energy and frequency factor in batch and membrane crystallisation

The critical Gibbs free energy (ΔG^* , J molecule $^{-1}$) and activation energy (E_a , J mol $^{-1}$) for homogeneous and heterogeneous nucleation can be determined as (Lewis et al., 2015):

$$\Delta G_{homo}^* = \frac{16\pi\sigma^3\vartheta^2}{3(k_B T)^2(\ln S)^2} \quad (A8)$$

$$\Delta G_{hetero}^* = \phi \times \Delta G_{homo}^* \quad (A9)$$

$$E_{a,homo} = \Delta G_{homo}^* N_A \quad (A10)$$

$$E_{a,hetero} = \Delta G_{hetero}^* N_A \quad (A11)$$

Where N_A = Avogadro's number (6.02×10^{23} molecules mol $^{-1}$), S = supersaturation ratio (C/C^*), ϑ is the NH_4HCO_3 molecular volume ($8.26 \times 10^{-29} m^3$), k_B the Boltzmann's constant ($1.38 \times 10^{-23} J K^{-1}$), T the absolute temperature (278.15 K) and $\phi = \Delta G_{het}/\Delta G_{hom}$ (~ 0.6) the factor which accounts for the reduction of the Gibbs free energy of the system due to the heterogeneous nucleation on porous membranes (Equation 9). At an equivalent supersaturation level, $S = 1.7$, the critical Gibbs free energy in batch was $\Delta G_{homo}^* = 1.2 \times 10^{-20} J molecule^{-1}$, whilst in membrane, $\Delta G_{hetero}^* = 4.7 \times 10^{-21} J molecule^{-1}$, corresponding to $E_{a,homo} = 7.5 \times 10^3 J mol^{-1}$, $E_{a,hetero} = 2.8 \times 10^3 J mol^{-1}$, respectively. These values enable, through Arrhenius equation, to calculate the frequency factor A ($No m^{-3-b} s^{-1+b}$), a parameter which indicates the rate of molecules collision and the fraction of collisions with the proper orientation for the reaction to occur (Chemistry LibreTexts, 2016):

$$K_{B,batch} = A_{homo} e^{\frac{-E_{a,homo}}{RT}} \quad (A12)$$

$$K_{B,membrane} = A_{hetero} e^{\frac{-E_{a,hetero}}{RT}} \quad (A13)$$

Where K_B ($No m^{-3-b} s^{-1+b}$) is the nucleation rate constant at $S = 1.7$, R is the gas constant ($8.314 J mol^{-1} K^{-1}$) and T the temperature (K). As a result, $A_{homo} = 2.6 \times 10^{45} No m^{-3-b} s^{-1+b}$ in batch and $A_{hetero} = 6.5 \times 10^5 No m^{-3-b} s^{-1+b}$ in membrane operation. To summarise, whilst E_a order of magnitude was the same in membrane and batch crystallisation ($10^3 J mol^{-1}$), the frequency factor A in batch was 40 orders of magnitude higher than in membrane (10^{45} vs. $10^5 No m^{-3-b} s^{-1+b}$), confirming that mixing rate, CO_2 bubbling and the fact that the probability of collisions between solute and solvent is 1 in the whole liquid volume in batch, if compared with the only

boundary layer in CR-MCr, simultaneously contribute to increase the rate of molecules collisions and the fraction of effective collisions for nucleation to occur, but do not affect the activation energy for nucleation (O'Grady et al., 2007; Logan, 2012; Chemistry LibreTexts, 2016).

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Chapter 6

Discussion

6.1 Discussion

The chapters comprised within this thesis have collectively tested the initial hypothesis, ‘*can the synergy between a thermal stripper to concentrate ammonia from wastewater and a HFMC designed to deliver chemically enhanced CO₂ separation, also enable recovery of the CO₂-NH₃ reaction product (ammonium bicarbonate) through consistent and reproducible crystal nucleation and growth?*’ Activated sludge systems designed for wastewater treatment post primary clarification generally consume 50 to 80% of the whole plant’s power supply, corresponding to a range between 15 and 20 kWh PE⁻¹ (population equivalent) (Figure 1.1). Around 35% of the energy demanded is used for ammonia removal (McAdam et al., 2011), translating into a cost ranging between £1.7 and 73.1 per KgNH₄⁺ removed, dependent upon process scale (Oxera, 2006). As a consequence, separation of the CO₂-NH₃ reaction product from wastewater presents multiple advantages, including:

- (i) avoiding the cost of wastewater treatment for ammonia;
- (ii) recovery of ammonium in a crystalline solid ammonium bicarbonate (NH₄HCO₃) product, which affords a potential resale value of up to €0.11 kg⁻¹ due to its value as an industrial feedstock (e.g. fertiliser) (Budzianowski, 2011b);
- (iii) minimisation of disposal volume, which will reduce transport costs; and
- (iv) locking CO₂ into a solid phase which can improve sustainability credentials.

In comparison to the existing infrastructure available for biogas upgrading, which ordinarily consists of a pressurised water scrubber, several advantages of the investigated scheme are also proposed (Figure 1.3):

- (v) no solvent regeneration is required, reducing one stripper column which can be repurposed for the thermal recovery of ammonia;
- (vi) the chemical reaction minimises methane slip and precludes the need for a flash tank;
- (vii) inclusion of a chemical reaction enhances mass transfer, reducing process scale;
- (viii) the high packing fraction of the membrane furtherly promotes process intensification compared with conventional packed columns;
- (ix) the membrane reduces the pressure drop for pumping and inclusion of the chemical reaction lessens the liquid flow rate, both of which limit the specific energy requirement.

To contextualise the impact of the research toward an implementable solution, the contribution to knowledge is explored around a set of operational questions.

1. How can product recovery and product yield be delivered at scale?

Previous studies of CO₂-NH₃ absorption for carbon capture and storage in packed columns and in HFMC evidenced gas phase precipitation leading to clogging and eventual process failure (Makhloufi et al., 2014; Cui and deMontigny, 2017; Villeneuve et al., 2018; Sutter et al., 2015). As a result, most research now focuses on identifying strategies to avoid crystallisation

(Villeneuve et al., 2018; Sutter et al., 2015), which precludes taking advantage of the benefits that solid-phase recovery presents for both applications. However, some progress toward solid phase recovery has recently been made. Sutter et al. (2017) recently introduced a separate crystalliser into the recycle line of a packed column to enable controlled crystallisation. In this thesis, inclusion of the membrane improves process intensification and simultaneously behaves as a physical structure to promote heterogeneous nucleation, enabling controlled crystallisation within a single stage process (Chapter 5). The research builds upon the technical feasibility demonstrated by McLeod et al. (2015), to provide the kinetic trajectory of crystallisation and the explanation of the underpinning chemistry that elicits the driving force for supersaturation, whilst also evidencing the technical pathway for the recovery and concentration of ammonia from wastewater. Whilst only applied as a single hollow fibre, the polypropylene membrane material identified that limited wetting and promoted liquid-side crystallisation (Chapter 2) is a commercially available product which suggests economies of scale are already achievable. Furthermore, to control cost, the same company (and a number of competitors) have modularised the technology into modules comprised of up to 330m² of membrane area with a specific surface area of almost 10000 m² m⁻³. This implies that process intensification can be achieved with commercially available technology. The packing fraction is considerably higher than employed in this research (85 m² m⁻³), which could be thought to influence product recovery. However, it is demonstrated that crystallisation takes place in a two-stage process: the membrane promoting heterogeneous nucleation, followed by crystal growth downstream (Chapter 5). Whilst further analysis is required, this should limit intra-fibre clogging and is coincident with observation made of membrane assisted crystallisation previously (Di Profio et al., 2010).

The nitrogen mass balance evidenced that nitrogen lost from the aqueous ammonia absorbent was predominantly recovered within the crystallised product recovered in the bulk solution (~99%, Chapter 2), which indicates two aspects: (i) insignificant crystalline surface deposition occurred on the membrane fibre surface; and (ii) negligible ammonia slip occurred. This is similar to the observations of Mani et al. (2006), who identified less than 1.3% NH₃ slip following partial reaction for a 2.5M solution. However, the crystalline yield of around 5% of the total ammonia load in solution was less than projected (Chapter 2). This was due to the low bicarbonate concentration which limited the reaction and was induced by the pH reduction from the formation of carbamic acid which facilitated a conversion of HCO₃⁻ into H₂CO₃ (Figure 2.2a). In this thesis solution pH was fixed to 10, typical for commercial aqueous ammonia packed column, through addition of acid in the absorbent (Yeh et al., 2005). However, future work could forecast avoidance of acid addition in the solution, inducing multiple advantages, which include: capital cost reduction, process simplification, and up to 100% of theoretical yield of ammonium bicarbonate produced, eliciting NH₄⁺-N reduction from initial NH₃(aq)

concentration (either 3 or 6 mol_{NH₃} L⁻¹) to ammonium bicarbonate solubility (1.5 mol_{NH₃} L⁻¹), through complete NH₄⁺-N transition from liquid to crystalline phase. In particular, adopting the natural pH of the ammonia concentrate (>11), the pH profile throughout CO₂ absorption will terminate at a higher pH value, leading to more HCO₃⁻ and closer proximity to 100% of theoretical yield. To illustrate, a 3 mol_{NH₃} L⁻¹ aqueous absorbent in recycle at 5°C, would lead to NH₃ removal of 50%, but it could increase up to 75% if adopting 6 mol_{NH₃} L⁻¹ (maximum concentration recovered from return liquor in this study), since NH₄HCO₃ solubility at 5°C is constant at 1.5 mol_{NH₃} L⁻¹ (PubChem, 2004; Perry and Green, 2007). Nevertheless, a gain in ammonia concentration above 3 mol_{NH₃} L⁻¹ evidenced a raise of the specific nucleation rate (N° m⁻² s⁻¹) on the membrane-liquid interface, which sufficiently reduced the contact angle to induce wetting (Figure 3.5; Rangwala, 1996). Chapter 3 showed that by controlling aqueous ammonia concentration, heterogeneous nucleation of ammonium bicarbonate on the membrane surface can be regulated, thus avoiding wetting and facilitating consistent and reproducible shell-side crystallisation and harvesting. An opportune design of a HFMC, where the membrane area is based on controlling the same specific nucleation rate per unit area as that achieved at 3 mol_{NH₃} L⁻¹, can enable an equivalent productivity through the adoption of a 6 mol_{NH₃} L⁻¹ absorbent, but with a higher yield, correspondent to around 75% ammonia removal from solution (Curcio et al., 2006). Furthermore, a comparison between membrane and batch crystallisation in Chapter 5, showed a slower pH transient in the first case, due to the probability of collisions between solute and solvent P(CO₂-NH₃)=1 in the whole liquid volume in batch, whilst P(CO₂-NH₃)=1 at the thin membrane-liquid interface, but sensibly lower in the bulk in membrane crystallisation (Figure 5.6). Therefore, the combined increase of membrane interfacial area and absorbent concentration proposed would maintain constant the specific nucleation rate per unit area of membrane (N° m⁻² s⁻¹), whilst raising the overall nucleation rate per unit volume of liquid (N° m⁻³ s⁻¹), which would simultaneously enable to control shell-side nucleation, growth and harvesting within the CR-MCr and to close the kinetic gap between membrane crystallisation and conventional batch operation.

2. *How do we engineer a membrane crystallisation process for simultaneous biogas upgrading and controlled NH₄HCO₃ precipitation and harvesting?*

Up to date, ammonium bicarbonate crystallisation is undertaken through batch operation, where the precipitated solid is used as fertilizer or as a chemical fermentation agent in the bakery products (Veiga et al., 1999). However, membrane crystallisation, a hybrid separation-crystallisation process that supports heterogeneous rather than homogeneous nucleation, enables the production of crystals with a narrower CSD and improved quality (Curcio et al., 2001). In particular, CR-MCr technology offers the opportunity for water utilities to simultaneously precipitate and harvest NH₄HCO₃, remove ammonia from wastewater and

upgrade biogas. In this work, the mechanism to control chemically assisted membrane crystallisation of NH_4HCO_3 has been demonstrated, using pure CO_2 as inlet gas, fed into the lumen of the fibre at around 15 m s^{-1} . If using an inlet gas mixture such as biogas (60:40 $\text{CH}_4\text{:CO}_2$), this velocity would be too high to guarantee methane purity above 90% (McLeod et al., 2015). The employment of membrane contactors in series is a practical solution to accommodate loss of biogas upgrading performance, since an increase in membrane length is known to facilitate CO_2 extraction from biogas (Reed et al., 1995). Specifically, a design for biogas upgrading comprised of two in series absorption modules has been demonstrated to improve CO_2/CH_4 separation performance, as compared with the parallel connection (Kim et al., 2016). Additionally, the modularity of HFMCs favours an easy-scale up, thus enabling an appropriate design, where the first stage induces crystallisation, while the second step further promotes CO_2 removal from biogas (Zhao et al., 2016). Furthermore, in this project has been identified how the crystallisation process is governed by pH and bicarbonate, where the latter in particular can be measured by UV spectrophotometry. Both UV and pH are common on-line measurements used by the water industry, therefore allowing easy adoption.

3. How significant is the energy demand for the thermal pre-concentration of ammonia?

A conventional flow diagram of a WWTW is illustrated in Figure 1.1, against a proposed approach shown in Figure 1.3. The transition between the two schemes would avoid the use of the desorption column for CO_2 rich water regeneration and convert the water scrubber column uptake into thermal stripping of ammonia from return liquor, leading to equivalence of the process complexity. Biogas produced from AD contains approximately 6 kWh m^{-3} of heat energy (Aqper, 2018). When directed towards CHP, it produces about $1.5 - 2 \text{ kWh m}^{-3}$ of electricity and 3 kWh m^{-3} of heat, depending on CHP conversion efficiency (EPA, 2018). Water utilities that have introduced upgrading, often exploit around 75% of biogas for CHP and 25% for upgrading into biomethane (McLeod et al., 2014). If considering a WWTW that treats $500,000 \text{ m}^3 \text{ d}^{-1}$ influent ($50 \text{ NH}_4^+\text{-N m}^{-3}$) and produces $3400 \text{ m}^3 \text{ h}^{-1}$ raw biogas (60:40 / $\text{CH}_4\text{:CO}_2$), then $2,550 \text{ m}^3 \text{ h}^{-1}$ will be used for electricity and heat production and $850 \text{ m}^3 \text{ h}^{-1}$ for biogas refinement. The energy required to heat the return liquor exiting the dewatering centrifuge from 25°C to 80°C in order to produce a concentrated absorbent up to $6 \text{ molNH}_3 \text{ L}^{-1}$ (Table 4.2) can be calculated from the following equation:

$$\text{Energy required} \left(\frac{\text{kWh}}{\text{d}} \right) = c_{\text{water}} \left(\frac{\text{kWh}}{\text{L}^\circ\text{C}} \right) \times \Delta T \left(^\circ\text{C} \right) \times Q_{\text{Return liquor}} \left(\frac{\text{L}}{\text{d}} \right) \quad (1)$$

Where c_{water} is the specific heat capacity of water ($\sim 4.2 \text{ kJ L}^{-1} \text{ }^\circ\text{C}^{-1}$), $\Delta T = 55^\circ\text{C}$, and return liquor flow rate, $Q_{\text{return liquor}}$ around $2100 \text{ m}^3 \text{ d}^{-1}$ (Water Environment Federation, 1987), thus resulting in about $135,000 \text{ kWh d}^{-1}$ of energy required. Generally, 60% of the biogas energy

used for CHP is dissipated as waste heat from TH coolers and un-utilised heat (Auty and Moore, 2003), and can be calculated as:

$$\text{Waste heat energy} \left(\frac{\text{kWh}}{\text{d}} \right) = 0.6 \times \text{biogas specific energy} \left(\frac{\text{kWh}}{\text{m}^3} \right) \times Q_{\text{Biogas CHP}} \left(\frac{\text{m}^3}{\text{d}} \right) \quad (2)$$

Where biogas specific energy is 6 kWh m⁻³, biogas flow rate used for CHP, $Q_{\text{biogas CHP}}$ is 2,550 m³ h⁻¹, resulting in waste heat energy of around 220,000 kWh d⁻¹, which can be used as a free source of heat, with an excess of about 65%, to heat up the return liquor and improve the overall energy efficiency of the WWTW. This can be considered a conservative estimate of available heat as it neglects heat recovery from the exit of the stripper, using shell and tube heat exchangers, which are now common place technology unit operations for large scale AD installations in the sludge line.

4. What is the financial benefit to incorporating NH₄HCO₃ crystalline product recovery?

A summary of the financial gains expected over a baseline case scenario comprised of 75% CHP and 25% biogas upgrading with water scrubber, is shown in Table 6.1. Specifically, partial upgrading and recovery of NH₄HCO₃ with HFMC, would increase the total income by 0.8 M£ y⁻¹ in the new case scenario, if using 3 molNH₃ L⁻¹ absorbent, which raises up to 1.1 M£ y⁻¹ with adoption of 6 molNH₃ L⁻¹, due to its higher NH₄⁺-N removal capacity (up to 75% circa, against 50% at 3 molNH₃ L⁻¹ and 0% with secondary effluent, since the solubility limit of the product is constant at 1.5 molNH₃ L⁻¹) (PubChem, 2004; Perry and Green, 2007), which also reduces aeration costs for nitrification through ammonium transition into solid product. Aqueous ammonia absorbents at 3 molNH₃ L⁻¹ and 6 molNH₃ L⁻¹ are typical concentrations used in CCS (Shuangchen et al., 2013; Budzianowski, 2011b). Interestingly, the revenue estimated for full upgrading, in comparison with the baseline, would raise by 6.8 M£ y⁻¹ with utilisation of a highly reactive absorbent at 3 molNH₃ L⁻¹, and further up to 8.8 M£ y⁻¹ with the adoption of 6 molNH₃ L⁻¹ solution. On the other hand, assuming replacement of the water scrubber with PP HFMCs (3M Capillary Membrane MF-PP Series, Type 300/1200) at a typical cost for purchase and installation of 40 £ m² membrane area and a conservative 3 years lifetime (Prasad and Sirkar, 1989; McLeod et al., 2014), full upgrading for a 95% CH₄ biomethane output would lead to an expenditure of around 18,900 £ y⁻¹ with adoption of a 3 molNH₃ L⁻¹ solution, which would lower to 13,300 £ y⁻¹ with employment of a 6 molNH₃ L⁻¹ absorbent (due to process intensification), and further down to either 4,700 or 3,300 £ y⁻¹ if operating a partial upgrading through absorbents at 3 or 6 molNH₃ L⁻¹, respectively. All these costs are around three orders of magnitude lower than the correspondent financial gains esteemed over the baseline, thus offering a payback time lower than 3 days for all the possible scenarios. Furthermore, pre-treatment of return liquor to produce concentrated aqueous ammonia, demonstrated to preclude cationic competition, enabling the formation of high purity

solid fertilizer. According to market regulations, NH_4HCO_3 should contain about 17% of N and hygroscopic water less than 5% to become a sellable commodity (Li and Chen, 1980). Nevertheless, this compound is generally formed as very hygroscopic powder, which is apt to cake. Its poor physical properties can be overcome by pressing it into pills, through a small double-roll machine, which are stable during storage and resistant to crushing (Institute of Soil Science, 1974). Additionally, NH_4HCO_3 pills coating with Ca-Mg-phosphate from powder rock phosphate fused with dolomitic limestone, would make the product a slow-release fertilizer, enabling the plants to uptake most of the N and limiting wastes after application in the soil (Li, 1976). In particular, ammonium bicarbonate wholesale offers an additional revenue over the baseline ranging between 0.5 and 3.7 M€ y^{-1} depending on absorbent concentration and percentage of biogas upgrading (Budzianowski, 2011b; Table 6.1).

Table 6.1 Operational costs, capital costs and net benefits of several scenarios against baseline case (75% CHP, 25% upgrading with water scrubber). For all the scenarios, the WWTW treats 500,000 m³ d⁻¹ influent (50 NH₄⁺-N m⁻³) and produces 3400 m³ h⁻¹ raw biogas (60:40 / CH₄:CO₂).

Scenario / Upgrading technology	Biogas utilisation	[NH ₃] molNH ₃ L ⁻¹	CHP ^c M£ y ⁻¹	Upgrade ^c M£ y ⁻¹	NH ₄ HCO ₃ ^d M£ y ⁻¹	Aeration ^a M£ y ⁻¹	Membrane ⁱ M£ y ⁻¹	Total M£ y ⁻¹	Net gain ^e M£ y ⁻¹
Baseline: partial upgrading / Water scrubber ^h	75% CHP 25% upgrade ^b	0.0004	4.2	2.4	0	-2.9	0	3.7	0
Partial upgrading and recovering NH ₄ HCO ₃ / HFMC ^g	75% CHP 25% upgrade ^b	3	4.2	2.4	0.5	-2.6	-0.005	4.5	0.8
Partial upgrading and recovering NH ₄ HCO ₃ / HFMC ^g	75% CHP 25% upgrade ^b	6	4.2	2.4	0.7	-2.5	-0.003	4.8	1.1
Full upgrading / Water scrubber ^h	0% CHP 100% upgrade	0.0004	0	9.5	0	-2.9	0	6.6	2.9
Full upgrading and recovering NH ₄ HCO ₃ / HFMC	0% CHP 100% upgrade	3	0	9.5	2.5 ^f	-1.5 ^f	-0.019	10.5	6.8
Full upgrading and recovering NH ₄ HCO ₃ / HFMC	0% CHP 100% upgrade	6	0	9.5	3.7 ^f	-0.7 ^f	-0.013	12.5	8.8

[NH₃] – Aqueous ammonia concentration, CHP – Combined heat and power.

^a Aeration cost based on nitrification demand using 4.34 KgO₂ KgN⁻¹, oxygen transfer efficiency 15%, water depth 5 m (McLeod et al., 2014).

^b Biogas split based on ammonia availability in return liquor using concentration and flow from Water Environment Federation, (1987) and McLeod et al., (2014).

^c Biogas revenues based on Read and Hofmann, (2011).

^d Ammonium bicarbonate value based on Budzianowski, (2011b).

^e Net gain over baseline scenario (75% CHP, 25% upgrading with water scrubber).

^f Assumes 100% NH₄ use (concentrated at 3 or 6 molNH₃ L⁻¹) for biogas upgrading, where 1.5molNH₃ L⁻¹ saturated absorbent (CO₂ rich) leaves the upgrading system and is redirected towards aeration due to NH₄HCO₃ solubility limit (PubChem, 2004; Perry and Green, 2007). Mass balance demonstrates a mole ratio of 0.9:1 CO₂:NH₄⁺-N which is sufficient for NH₄HCO₃ precipitation and biogas upgrading into biomethane (PubChem, 2004; Perry and Green, 2007; McLeod et al., 2015).

^g Using return liquors concentrated up to 3 or 6 molNH₃ L⁻¹. Mass balance demonstrates a mole ratio of 1:1 CO₂:NH₄⁺-N.

^h Using secondary effluent.

ⁱ Assumes HFMCs cost at 40£ m⁻² and a conservative 3y membrane life time (Prasad and Sirkar, 1989). Membrane surface area required has been calculated considering maximum CO₂ flux achieved in this work when adopting absorbent at 3 and 6 molNH₃ L⁻¹ respectively.

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Chapter 7

Conclusions and further work

7.1 Conclusions

The present thesis has introduced an integrated system to concentrate aqueous ammonia from wastewater and adopt the condensate recovered to consistently and reproducibly crystallise and harvest ammonium bicarbonate within a CR-MCr. The following conclusions can be drawn from this work:

1. Recirculation of chilled aqueous ammonia absorbent on the shell-side of a HFMC reduces free ammonia introduction into the gas phase and shifts $\text{NH}_3\text{-NH}_4^+$ equilibrium toward non-volatile NH_4^+ , which avoids gas side crystallisation and promotes liquid side crystallisation of the $\text{CO}_2\text{-NH}_3$ reaction product (**Objective 1**).
2. The employment of a tight pore size membrane coupled with chilled absorbent recirculation, prevents wetting (induced by shell-side crystallisation), facilitating consistent and reproducible shell-side (liquid side) crystallisation and harvesting of NH_4HCO_3 (**Objective 1**).
3. Nitrogen mass balance showed complete conversion of $\text{NH}_3\text{-N}$ lost from the absorbent to the crystals recovered, indicating negligible ammonia slip in the gas phase and insignificant crystalline surface deposition on the fibre (**Objective 1**).
4. The use of aqueous ammonia absorbents ranging between 1 and $4.6 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, maintained in recycle at 5°C within a CR-MCr, demonstrated that concentrations below $3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ (twice ammonium bicarbonate solubility at 5°C) were either thermodynamically or reaction limited. Absorbents with concentrations above $3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ showed to successfully enable crystallisation. Nevertheless, following shell-side crystallisation, wetting occurred at $4.6 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$, while at $3.3 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ consistent and reproducible shell-side crystallisation was observed, due to the reduced mass and number of crystals formed, which lowered the likelihood for wetting (**Objective 2**).
5. A rise of aqueous ammonia concentration increases the yield for ammonium bicarbonate crystallisation, which is reaction limited by HCO_3^- concentration due to dynamic reaction zone. Simplification of the chemistry would terminate CO_2 absorption at a higher pH value, favouring an elevated bicarbonate concentration and closer proximity to 100% of theoretical yield (**Objective 2**).
6. In-series thermal stripping of return liquor at high temperatures ($\sim 80^\circ\text{C}$) evidenced to (1) increase the overall liquid phase mass transfer coefficient; (2) produce a concentrated absorbent at concentration about 4 times higher than that required to

initiate crystallisation; (3) offer the opportunity for water utilities to minimise the chemical demand for recovering NH_3 , compared with low temperatures. Waste heat at WWTWs can be utilised to strip ammonia at 80°C from return liquors, facilitating economical production of a crystallising fluid from wastewater (**Objective 3**)

7. Pre-treatment of return liquor demonstrated to reduce ionic competition, allowing the precipitation of reasonably pure ammonium bicarbonate as a marketable product (**Objective 3**).
8. The hydrophobic membrane underpins primary heterogeneous crystallisation at the membrane-liquid interface in membrane crystallisation (thus reducing the Gibbs free energy barrier for nucleation) disconnected by secondary nucleation and growth downstream, contrarily to batch crystallisation, where primary and secondary homogeneous nucleation are followed by growth and agglomeration (promoted by enhanced mixing and CO_2 bubbling) within the same domain. As a result, an increase of population density vs. supersaturation occurs in membrane crystallisation, against a population density decline in conventional batch operation (**Objective 4**).
9. Raising the membrane interfacial surface area and ammonia absorbent concentration would enable to control shell-side crystallisation, to increase ammonia removal, and to close the kinetic gap between membrane and batch crystallisation (**Objective 4**).

7.2 Further work

Areas where further research would be beneficial have been identified during this work and summarised as follows:

1. In this work, absorbent pH was fixed at 10 through addition of acid. Adopting the natural pH of aqueous ammonia (>11 , obviating acid addition in the solution), would lead to a higher pH value at the end of the absorption process, a raised bicarbonate concentration and therefore higher yield that could be evaluated at different $\text{NH}_3(\text{aq})$ concentration adopted. Simplification of the chemistry might also improve technological acceptance with water utilities.
2. Further investigation on the scale up of the technology would be essential to ensure that a commercial module comprised of numerous fibres will be able to deliver equivalent results to those achieved with a single HFMC adopted in this project.

3. Investigation of other membrane matrices with reduced pore size to maximize ammoniacal nitrogen removal and ammonium bicarbonate yield.
4. A maximum concentration of $6 \text{ mol}_{\text{NH}_3} \text{ L}^{-1}$ was recovered from real wastewater in this study, where both desorption temperature and vacuum pressure affected the solubility of ammonia in water. A deeper investigation of these two parameters would be beneficial to further optimise ammonia recovery from wastewater.
5. This research identified the boundary conditions to produce a concentrated absorbent with a rotary-evaporator. The adoption of a different absorption technology, such as a packed column, could increase the liquid mass transfer, due to higher interfacial area. It may be pertinent to assess the impact of this technology on ammonia stripping, to identify new boundary conditions that can maximize ammonia concentration recovered and minimise ammonia slip in the gas phase.
6. Chemically assisted membrane crystallisation of ammonium bicarbonate has been undertaken with pure carbon dioxide as inlet gas. The adoption of a binary gas (60:40 $\text{CH}_4:\text{CO}_2$) would be necessary to assess CO_2 absorption and NH_4HCO_3 crystallisation performance with a more complex feed, similar to real biogas.
7. Once determined the optimum conditions for biogas upgrading and ammonium bicarbonate crystallisation (with the adoption of a synthetic biogas), larger scale on-site testing of an integrated thermal stripper coupled with CR-MCr, would be beneficial to provide more detail on the optimization of the process.