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**Recovery of volatile fatty acids (VFA) from
complex waste effluents using membranes**

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Introduction

- Low Carbon Research Institute (LCRI)

Project “Cymru H2 Wales”

- Swansea University Group is involved in Liquid/Solid Separations from Complex Effluent Sources

Development of a number of process to recover useable materials in solid or liquid form and chemical intermediates from waste sources.

Swansea University Group

Swansea University
Prifysgol Abertawe

The Centre for
Complex Fluids Processing

CWATER

Volatile Fatty Acids (VFA)

- VFA are fatty acids with a carbon chain of six or fewer carbons, straight chain and branched.
- Also known as carboxylic acids due to the carboxylic group they have
- Also named low molecular weight (LMW) organic acids due to their small molar mass
- They are of great industrial importance applied in the field of food and beverages and in the pharmaceutical and chemical fabrication field.
- They play a central role in the metabolism of carbon in the environment especially in acidogenic fermentations

Commercial applications of VFA

Fig.1. Commercial Applications of VFA

VFA market size and methods of production

Volatile Fatty Acids	Market size (tonnes/ year)	Price per tonne (USD, \$)	Chemical Synthesis Methods	Bioprocess Methods
Formic HCOOH	30.000	800-1200	Oxidation of Alkanes Hydrogenation of Carbon dioxide Methanol carbonylation	Oxidative Fermentation Anaerobic Fermentation
Acetic CH₃COOH	3.500.000	400-800	Methanol Carbonylation Acetaldehyde Oxidation Ethylene Oxidation	Oxidative Fermentation Anaerobic Fermentation
Propionic CH₃CH₂COOH	180.000	1500-1650	Hydrocarboxylation of Ethylene Aerobic oxidation of Propionaldehyde	Anaerobic Fermentation
Butyric CH₃ (CH₂)₂COOH	30.000	2000-2500	Chemical Oxidation of Butyraldehyde	Fungal Fermentation of Glucose
Caproic CH₃ (CH₂)₄COOH	25.000	2250-2500	Ethylene Oxidation	Anaerobic Fermentation
Lactic CH₃CHOHCOOH	120.000	1000-1800	Chemical Synthesis Fermentation	Anaerobic Fermentation

Table 1. Commercial Applications of VFA

Anaerobic digestion, a source of VFA?

- Anaerobic digestion (AD), or acidogenic fermentation,
 - Traditional treatment, it can be performed on various solid or liquid substrates, such as silage or manure leading to the production of biogas, methane CO₂ used in energy generation.
 - Acidogenesis represents one of the stages towards methanogenesis. VFA are the main soluble compounds generated
 - VFA could represent a source of valuable carbon materials for chemicals products provided they can be recovered economically.

Fig.2. Schematic diagram of AD process

Advantages and commercial benefits of VFA recovery

- The reduced demand on waste treatment plants as reduced carbon is extracted so reducing costs and energy requirements of oxidation and the release of CO₂
- The extraction of reduced carbon (as VFA) for reuse and substitution of acetate and other VFA's derived from petrochemicals so reducing reliance on fossil carbon for chemicals of favourable nutrients
- Chemical based industry becomes uncoupled of fossil carbon and its increasing cost
- Valorisation of waste carbon
- Fixation of carbon as chemicals rather than their release as CO₂ Reduces economical and environmental impact of waste treatment.

Project overview

Recovery strategy

Membrane Filtration was the chosen recovery methodology

Suitable technology for pre-treatment and separation

Technology quite well developed but not widely industrially applied for waste processing

Benefits of membrane filtration include:

- Physical separation (water does not change phase)
- No additives (chemicals and/or other materials) are added other than when membranes are manufactured
- There is a wide range of membrane processes based on the membrane pore size

Fig.4. Processing and recovery scheme for VFA and nutrients

Lovitt & Zacharof, Proceedings 4th International Symposium on Energy from Biomass and Waste, IWWG publications, 2012

Microfiltration process

Fig.5. PID of the MF membrane filtration. The physical dimensions are annotated together with standards symbols for the various components (vessel, valves, heat exchanger, membrane module) in the system. P1 and P2 – pressure gauges; A and B – Centrifugal pumps

Effect of treatment scheme on sludge composition

Parameters	Agricultural Sludge							
	Untreated Sludge		Treated Sludge		Microfiltered (0.2µm) Sludge Retentate		Microfiltered (0.2µm) Sludge Permeate	
Total Solids (TS, g/L)	15.13		11.99	↓ 21%	10.40		5.15	↓ 50.5%
Total Suspended Solids (TSS, mg/L)	612.50		252.60	↓ 59%	258.00		190.00	↓ 26.35%
Conductivity (mS/cm)	9.37		9.11		9.01		8.3	
Zeta Potential (mV)	-33.25		-30.06		-29.60		-24.2	
Sizing (µm)	27.17		13.97	↓ 48.6%	13.49		4.93	↓ 63.5%
Optical Density (580nm ¹)	0.86		0.34		0.27		0.10	
Concentration	mg/L	mmols/L	mg/L	mmols/L	mg/L	mmols/L	mg/L	mmols/L
Acetic Acid	1650.17	27.48	1464.02	24.38	1083.30	18.04	1265.85	21.08
Butyric Acid	1781.58	19.22	1666.16	18.91	1163.93	13.21	1393.02	15.81

Table 2 The effect of pretreatment and microfiltration on the physical characteristics and chemical composition of the anaerobically digested agricultural sludge. The collected samples were diluted 100 times with deionised water and measured in a 1 cm light path¹

Selection of nanofiltration membranes

Fig.6. Factors affecting the separation efficiency of nanofiltration/reverse osmosis

Fig.7. Mechanisms governing the separation of nanofiltration/reverse osmosis

Characteristics of selected nanofiltration membranes

Characteristics	Membranes					
	General Electric -Osmonics USA			Dow FilmTech USA		Nitto Denko Japan
Manufacturer						
Model	HL	DL	DK	NF 270	LF10	
Distributors	Sterlitech Corporation http://www.sterlitech.com			Desal Supplies http://www.desal.co.uk		SOMICON AG WKL http://www.somicon.com
Material	Thin film composite piperazine –based polyamide microporous polysulfone			Thin film composite- Aromatic polyamide		Thin film composite Polyvinyl alcohol-aromatic cross linked polyamides
Applications	Water Softening, Acid Purification, Detergent removal, Heavy metal removal					
Geometry	Flat Sheet			Flat Sheet		Flat Sheet
Effective Membrane area (cm²)	14.60			14.60		14.60
Flux rate (L/m²h) @689 kPa	66.3	52.7	37.4	122.0		11.9
Charge (at neutral pH)				Negative		
pH	2-10		2-11	3-10		2-10
Ion rejection (%)	98	96	98	97		99.5
MWCO	150-300			150-200		<150
Maximum Operating Temperature (°C)	50			45		40

Table 3 Membranes characteristics provided by the manufacturers

Nanofiltration process

Fig.8. Schematic representation of the high pressure stirred cell unit [1] nitrogen cylinder, [2] pressure regulator valve, [3] pressure indicator, [4] waterbath with coils, [5] stirred cell unit equipped with membrane disc, [6] stirrer, [7] stirring plate, [8] permeate collection vessel, [9] electronic scale, [10] personal computer.

Permeate flux of characterising solutions

Permeate Flux (L/m ² h)				
Solutions		Deionised Water	Dihydrogen Orthophosphate Solution (10mM)	Microfiltered (0.2µm) Sludge Permeate
pH		7.2	6.5	8.25
Membranes	DK	69.61	27.54	16.49
	DL	84.04	34.43	14.91
	HL	121.43	82.97	14.37
	NF270	61.66	20.21	15.40
	LF10	15.95	06.78	06.00

Table 4 The influence of membrane type on permeate flux of deionised water, phosphate buffer solution and standardised anaerobically digested fluid using a variety of nanofiltration membranes at 1500 kPa operating pressure.

The effect of membrane type on acetate and butyrate retention of the waste effluent

Membranes	Acids					
	Acetic Acid			Butyric Acid		
	Permeate Concentration (mM)	Retentate Concentration (mM)	Retention* (%)	Permeate Concentration (mM)	Retentate Concentration (mM)	Retention* (%)
DK	17.27	40.38	57.23	10.86	19.81	45.18
DL	14.25	26.49	46.22	13.61	20.76	34.44
HL	20.09	26.57	24.40	8.58	14.28	39.92
NF270	14.00	29.56	52.64	8.03	26.54	69.74
LF10	14.98	53.94	72.23	10.74	28.38	62.16

Table 5 The effect of membrane type on acetate and butyrate from standardised permeate derived from microfiltered digested agricultural sludge (see Table 2) at 1500 kPa. Initial concentration in the feed (pH 8.25) is 21.10 mM and 15.81 mM of acetic and butyric acid respectively.

$$*R_{(\%) } = \left[1 - \left(\frac{C_{p,i}}{C_{r,i}} \right) \right] * 100$$

The effect of pH on permeate flux of the waste effluent

		Permeate Flux (L/m ² h)				
		Microfiltered (0.2µm) Sludge Permeate				
pH		4.0	5.5	7.0	8.5	9.0
Membranes	DK	21.48	21.42	17.64	16.49	02.09
	DL	18.33	17.92	16.78	14.91	05.06
	HL	25.48	22.55	20.04	14.37	11.42
	NF270	21.70	20.75	19.05	15.40	03.04
	LF10	12.09	13.35	05.44	06.00	04.14

Table 6 The effect of pH on permeate flux of standardised anaerobically digested fluids using a variety of nanofiltration membranes. The filtration fluids were derived from microfiltered sludge (see Table 2)

The effect of pH on VFA retention

Fig.8. [a, b]: The effect of pH on VFA retention **(a) acetic acid (b) butyric acid** of a variety of NF membranes using standardised anaerobically digested fluids. The filtered fluids are permeates derived from microfiltration of agricultural sludge (see Table 2)

Concluding remarks

- This study investigates spent digester fluids and developing a recovery strategy solely devoted on the recovery of VFA from anaerobic digestates, might not be as easy as from an acidogenic digester where the VFA concentration will be substantially higher, up to 100 mM.
- It has been pointed out that farming waste effluents do represent an environmental hazard as well as a good source virtually in abundance of useful nutrients and metals. Developing a complete recovery strategy for these substances, with a waste treatment system placed *in situ* could be of great benefit for the industry.
- NF can be used as a method of isolation and recovery of VFA from complex effluent streams, provided a pretreatment scheme that will remove coarse particles, so the effluents can be easily filtered.
- Alkali conditions enhance the, isolation and retention of VFA, with DK and NF270 representing the best option among the five membranes tested.
- These findings show potential and could be applied to the biotechnological production of VFA and their recovery.

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Questions

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