

**NOVEL MEMBRANE-BASED PROCESSES
FOR NUTRIENTS, ENERGY AND WATER
RECOVERY FROM SOURCE SEPARATED
HUMAN URINE**

by Federico Volpin

Thesis submitted in fulfilment of the requirements for
the degree of

Doctor of Philosophy

under the supervision of Prof. Ho Kyong Shon and Dr.
Sherub Phuntsho

University of Technology Sydney
Faculty of Engineering and Information Technology

June 2020

STATEMENT OF ORIGINAL AUTHORSHIP

I, **Federico Volpin**, declare that this thesis, is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy in the School of Civil and Environmental Engineering/Faculty of Engineering and IT** at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

Signature: Production Note:
 Signature removed prior to publication.

Federico Volpin

Date: **30/06/2020**

I dedicate this Thesis to my parents

Emanuela Lollo and Stefano Volpin

And my sister

Margherita Volpin

ACKNOWLEDGEMENTS

I owe many people my gratitude for the creation of this PhD Thesis. This work would not have been possible without the support and guidance of who supported me along the way. First, I would like to thank Prof. Ho Kyong Shon for providing me with all the resources, knowledge, and technical support to prove myself as a researcher. His advice, passion for research and never-ending strive for excellence allowed me to achieve the best possible outcome in my work. I would also like to express my gratitude Dr Sherub Phuntsho for always being supportive and caring.

I am also grateful to Prof. Hokyong Shon for providing me with a scholarship throughout my whole candidature tenure, and for supporting two fantastic overseas research experience in South Korea. In South Korea, I had the honour and pleasure to be hosted by two excellent researchers, Prof. Jaeweon Cho (UNIST) and Dr Yunchul Woo (KICT). I sincerely acknowledge Dr MD Johir and Dr Nirenkumar Pathak for their help in the laboratory and the administrative support from Maya, Trish and Van. I would also like to thank all my good friends and colleagues at UTS. All of you have always made me feel at home. I also want to send a special thanks to Seong Chul, Cristo and Ralph for the fantastic time spent together.

Last but not least, I would like to thank my family for their support throughout the whole duration of my PhD degree. They have always shown me just love and affection, in a truly selfless way. Finally, a special thanks to my girlfriend. Your joyful nature and company have been greatly valued, especially during these recent stressful and challenging times.

FEDERICO VOLPIN

Journal Articles Published or Submitted (*)

Part of the work performed during the PhD project resulted in peer-reviewed publications and presentations, which are listed hereafter in the order of acceptance and by category. They are directly or indirectly related to the main topics of this Thesis, and all of them have been accepted and published by the end of that project.

1. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, N. Ghaffour, J.S. Vrouwenvelder, H. K. Shon, Simultaneous phosphorous and nitrogen recovery from source-separated urine: A novel application for fertiliser drawn forward osmosis, *Chemosphere*, 203 (2018) 482-489.
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5. **F. Volpin**, S. Phuntsho, N. Ghaffour, J.S. Vrouwenvelder, H. K. Shon, Optimisation of a forward osmosis and membrane distillation hybrid system for the treatment of source-separated urine, *Separation and Purification Technology*, 212 (2019), 368-375.

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Conference Papers and Presentations

1. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, H. K. Shon, "Simultaneous Nutrients Recovery and Osmotic Concentration of Source-Separated Urine via Fertilizer drawn Forward Osmosis", **Oral Presentation at the 10th International Desalination Workshop (IDW 2017)**, 22-25 November 2017, Busan, Republic of Korea.
2. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, N. Ghaffour, J. S. Vrouwenvelde, H. K. Shon, "Simultaneous Phosphorous and Nitrogen Recovery from Source-Separated Urine: A novel application for Fertiliser Drawn Forward Osmosis", **Oral Presentation at the 4th IWA Specialised International Conference - Ecotechnologies for Wastewater Treatment (ecoSTP 2018)**, 25-28 June 2018, London, Canada.
3. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, H. K. Shon, "Simultaneous Nutrients Recovery and Osmotic Concentration of Source-Separated Urine via Fertilizer drawn Forward Osmosis", **Oral Presentation at the 2018 School Research Showcase**, 27 April 2018, Sydney, Australia.
4. **F. Volpin**, H. Yu, J. Cho, C. Lee, S. Phuntsho, N. Ghaffour, J. S. Vrouwenvelder, H. K. Shon, "Human urine as a novel draw solution for forward osmosis processes and its application to dewater microalgae solution.", **Oral Presentation at The 11th Conference of the Aseanian Membrane Society (AMS 11)**, 3-6 July 2018, Brisbane, Australia.
5. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, H. K. Shon, "Simultaneous Nutrients Recovery and Osmotic Concentration of Source-Separated Urine via Fertilizer drawn Forward Osmosis", **Oral Presentation at the Membrane Society of Australasia (MSA) Early Career Symposium (ECR)**, 30th of January to 2nd of February 2019, Melbourne, Australia.

6. **F. Volpin**, L. Chekli, S. Phuntsho, J. Cho, H. K. Shon, "Techno-economic feasibility of recovering phosphorous, nitrogen from urine via forward osmosis.", **at the Oral Presentation 9th International Water Association (IWA) Membrane Technology Conference and Exhibition for Water and Wastewater treatment and reuse**, 23-27 June 2019, Toulouse, France.

Presentations made during the PhD candidature including proceedings, oral and poster presentations.

LIST OF ABBREVIATIONS

AL-DS	Active Layer facing Draw Solution
AL-FS	Active Layer facing Feed Solution
AEMs	Anion Exchange Membranes
CAPEX	Capital Costs
COD	Chemical Oxygen Demand
CEMs	Cation Exchange Membranes
DCMD	Direct Contact Membrane Distillation
DI	Deionised water
DOC	Dissolved Organic Carbon
DS	Draw Solution
ED	Electrodialysis
EDX	Energy Dispersive X-ray spectroscopy
EPS	Extracellular Polymeric Substances
ES	Electrolyte Solution
FO	Forward Osmosis
FDFO	Fertilizer Driven Forward Osmosis
FS	Feed Solution
FU	Fresh Urine (Nitrogen as urea)
HC	High Concentration
HU	Hydrolysed Urine (Nitrogen as ammonia)
HRT	Hydraulic Retention Time
IEMs	Ion Exchange Membranes
ISS	International Space Station
LC	Low Concentration
LC-OCD	Liquid Chromatography-Organic Carbon Detection
LMW	Low Molecular Weight
MBR	Membrane Bioreactor
MD	Membrane Distillation
MLSS	Mixed Liquor Suspended Solids
NOB	Nitrite Oxidizing Bacteria
NF	NanoFiltration
OCV	Open Circuit Voltage
OPEX	Operational Costs
PD	Power Density
RED	Reverse Electrodialysis
RSF	Reverse Salt Flux
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SRSF	Specific Reverse Salt Flux
TAN	Total Ammoniacal Nitrogen

TDS

TFC

UF

UPA

WWTP

Total Dissolved Solids

Thin-Film Composite

Ultrafiltration

Urine Processor Assembly

Wastewater Treatment Plant

ABSTRACT

Worldwide, the combined effect of urban intensification and ageing infrastructure is seriously challenging all utility providers. Wastewater treatment infrastructures are no different. The integration of novel decentralised solutions with the current centralised status quo is becoming an essential measure across the whole utility board, from energy production and storage to potable water harvesting, treatment, and supply and even to waste treatment. Decentralising the treatment of our wastes is especially of interest as it has the potential of transforming the water sector into a net producer of energy, water, and raw materials.

Urine source-separation is especially attractive due to urine low volume, high nitrogen (N) and phosphorus (P) concentrations (80% of N and 50% of P inputs into sewers), and the relative ease of collection and storage. As such, it has the potential of being a suitable raw material from the production of fertiliser, energy, and water.

While conventional technologies often struggle in dealing with urine alkalinity, high total ammoniacal nitrogen (TAN) and dissolved organic carbon (DOC) concentration (i.e. 3 to 5 g.L⁻¹) and high salinity (i.e. 1 to 4%), the strong chemical resistance, small footprint, tuneable selectivity and versatility in the operation of membrane processes makes them suitable for extracting value from human urine. As such, this Thesis looked at novel stand-alone and membrane-based hybrid processes for the extraction of nutrients, energy, and clean water from source-separated human urine.

The Thesis begins by studying the use of moderate flux-opposing hydraulic pressure in forward osmosis (FO) and optimal membrane morphology in membrane distillation (MD), to minimise the leakage of nitrogen to the distilled water produced by the hybrid FO-MD process. Experimental results with both fresh and hydrolysed urine found that this novel approach can

decurtate the nitrogen flux in FO by up to 33%. Combining flux-opposing hydraulic pressure with optimum urine pH and draw solution (DS) salt concentration achieved FO water fluxes as high as $28 \text{ L.m}^{-2}.\text{h}^{-1}$ while bringing the nitrogen leakage to a minimum of 1.4 g.L^{-1} (Starting from an initial nitrogen concentration of 6.4 g/L).

While extracting water from urine is paramount on the International Space Station (ISS), producing sustainable and low-energy fertilisers from urine would help to alleviate the impacts of climate change by creating a more resilient food production network. This was addressed through the use of fertiliser driven-FO (which uses a concentrated fertiliser solution as DS) and a combination of membrane bioreactor (MBR) with MD. Each process was designed to cope with a specific “type” of urine: fresh or hydrolysed.

Firstly, it was shown that the combination of MBR and MD can produce an odourless concentrated liquid fertiliser with a concentration of nutrients similar to the commercial liquid products. The results showed that MBR was able to acidify the urine, removing $> 95\%$ of its DOC and oxidising 50% of its ammonia to NO_3^- . By converting the volatile NH_3 into ionic $\text{NH}_4^+(\text{l})$ and $\text{NO}_3^-(\text{l})$, the MBR process enabled the MD dewatering step to achieve 95% water recovery without nitrogen losses. When tested for the growth of lettuce and Pak Choi, this fertiliser solution achieved plant biomass comparable to those from commercial fertilisers.

Alternatively, when treating diluted fresh urine, the Fertiliser Driven Forward Osmosis process (FDFO) proved to be an economical alternative to recover urine nutrients. In FDFO, a fertiliser DS is used to draw water from a less concentrated solution (in this case urine). One of the drawbacks of the FO process is the high reverse salt flux (RSF) or reverse diffusion of draw solutes but this was advantageously exploited to promote N and P recovery as liquid fertiliser and struvite, respectively. Using real urine as FS and a commercial fertiliser as DS, it was demonstrated that 50% urine concentration could be achieved, with 93% P recovery as struvite

and 50% N recovery as liquid urea. Operational and capital costs analysis showed that the benefit from the savings to the downstream wastewater treatment plant costs are of better value than any return from the sale of produced fertiliser.

Finally, the last two technical chapters of this Thesis looked at a novel use of FO and reverse electrodialysis (RED) processes to convert the urine salinity into osmotic driving force and electric energy, respectively. Where RED is a process that allows to convert an ionic flux into an electron flux thanks to the use of a stack of cation and anion exchange membranes.

For the first time, the use of a compact reverse electrodialysis (RED) system to convert the chemical potential energy of urine dilution into electric energy was explored. The results showed that 1 m³ of real hydrolysed urine could produce 0.05 - 0.04 kWh of electrical energy. Also, when using urine as an electrolyte solution, it was demonstrated that the net chemical reactions occurring at the electrode compartments lead to TOC, TAN and urea removal of up to 13%, 6% and 4.4%. Overall, this process has the potential of providing off-grid urine treatment or energy production at a household or building level.

To conclude, in the last technical chapter it was proven that urine can be used as DS to dewater a microalgae solution. The combination of urine osmotic pressure (i.e. > 2000 kPa) and the high concentration of species with high self-diffusivity resulted in water flux as high as 16.7 ± 1.1 L.m⁻².h⁻¹ (with DI water was used as feed solution). Additionally, when dewatering a 0.2 g.L⁻¹ *Chlorella vulgaris* culture, urine DS achieved a fourfold increase in algal concentration with an average flux of 14.1 L.m⁻².h⁻¹ and no support layer membrane fouling. The advantages of this process are that, once diluted during, urine could itself be used as growing media for microalgae cultivation.

Overall, this Thesis investigated the proof-of-concept of utilising multiple emerging technologies for the treatment of human urine. It was identified that, while processes like FO and RED so far seems to have a limited effectiveness in treating human urine, the combination of MBR with MD has showed to be a promising candidate in producing a fertiliser that is suitable for use in hydroponic cultivation.

Keywords: Human urine, urine treatment, membrane technology, membrane bioreactor, forward osmosis, membrane distillation, reverse electrodialysis, microalgae, International Space Station.

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