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

by **Federico Volpin**

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Doctor of Philosophy

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

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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.

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Federico Volpin

Date: **30/06/2020**

I dedicate this Thesis to my parents

Emanuela Lollo and Stefano Volpin

And my sister

Margherita Volpin

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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.
2. **F. Volpin**, E. Fons, L. Chekli, K. Jung Eun, J. Am, H. K. Shon, Hybrid forward osmosis-reverse osmosis for wastewater reuse and seawater desalination: Understanding the optimal feed solution to minimise fouling, ***Process Safety & Environmental Protection: Transactions of the Institution of Chemical Engineers Part B***, 117 (2018) 523-532.
3. **F. Volpin**, L. Chekli, S. Lim, N. Pathak, S. Phuntsho, H. K. Shon, GreenPRO: A novel fertilizer driven osmotic power generation process for fertigation, ***Desalination***, 447 (2018) 158-166.
4. **F. Volpin**, H. Heo, M. A. H. Johir, J. Cho, S. Phuntsho, H. K. Shon, Techno-economic feasibility of recovering phosphorus, nitrogen and water from dilute human urine via forward osmosis, ***Water Research***, 150 (2019), 47-55.
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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8. (*) **F. Volpin**, Y. Woo, H. Kim, S. Freguia, N. Jeong, J. S. Choi, J. Cho, S. Phuntsho and H. K. Shon, Energy recovery through reverse electrodialysis: Harnessing the salinity gradient from the flushing of human urine, *Submitted for publication on* ***Water Research***.
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10. M. M. Damtie, **F. Volpin,** M. Yao, L. D. Tijing, R. H. Hailemariam, T. Bao, K. Park, H. K. Shon, J. S. Choi, Ammonia recovery from human urine as liquid fertilizers in hollow fiber membrane contactor: Effects of permeate chemistry, ***Environmental Engineering Research***, vol. 26, no. 1, pp. 190523-0.

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	**A**ctive **L**ayer facing **D**raw **S**olution
AL-FS	**A**ctive **L**ayer facing **F**eed **S**olution
AEMs	**A**nion **E**xchange **M**embranes
CAPEX	**C**apital **C**osts
COD	**C**hemical **O**xygen **D**emand
CEMs	**C**ation **E**xchange **M**embranes
DCMD	**D**irect **C**ontact **M**embrane **D**istillation
DI	**D**eionised water
DOC	**D**issolved **O**rganic **C**arbon
DS	**D**raw **S**olution
ED	**E**lectrodialysis
EDX	**E**nergy **D**ispersive **X**-ray spectroscopy
EPS	**E**xtracellular **P**olymeric **S**ubstances
ES	**E**lectrolyte **S**olution
FO	**F**orward **O**smosis
FDFO	**F**ertilizer **D**riven **F**orward **O**smosis
FS	**F**eed **S**olution
FU	**F**resh **U**rine (Nitrogen as urea)
HC	**H**igh **C**oncentration
HU	**H**ydrolysed **U**rine (Nitrogen as ammonia
HRT	**H**ydraulic **R**etention **T**ime
IEMs	**I**on **E**xchange **M**embranes
ISS	**I**nternational **S**pace **S**tation
LC	**L**ow **C**oncentration
LC-OCD	**L**iquid **C**hromatography-**O**rganic **C**arbon **D**etection
LMW	**L**ow **M**olecular **W**eight
MBR	**M**embrane **B**ioreactor
MD	**M**embrane **D**istillation
MLSS	**M**ixed **L**iquor **S**uspended **S**olids
NOB	**N**itrite **O**xidizing **B**acteria
NF	**N**ano**F**iltration
OCV	**O**pen **C**ircuit **V**oltage
OPEX	**O**perational **C**osts
PD	**P**ower **D**ensity
RED	**R**everse **E**lectrodialysis
RSF	**R**everse **S**alt **F**lux
RO	**R**everse **O**smosis
SEM	**S**canning **E**lectron **M**icroscopy
SRSF	**S**pecific **R**everse **S**alt **F**lux
TAN	**T**otal **A**mmoniacal Nitrogen

TDS	**T**otal **D**issolved **S**olids
TFC	**T**hin-**F**ilm **C**omposite
UF	**U**ltrafiltration
UPA	**U**rine **P**rocessor **A**ssembly
WWTP	**W**astewater **T**reatment **P**lant

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 $L.m^{-2}.h^{-1}$ 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 NH_4^+(l) and NO_3^-(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 m^3 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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