Simultaneous Phosphorous and Nitrogen Recovery from Source-Separated Urine: A novel application for Fertiliser Drawn Forward Osmosis

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Abstract

The transition of thinking wastes as resources is likely to become one of the major challenges of this century. Because of its exceptionally high nitrogen (N) and phosphorous (P) concentration, human urine is particularly suitable to be processed for fertiliser production. In the present study, forward osmosis (FO) was employed to mine the P and N from human urine. Two Mg^{2+}-fertilisers, i.e. $MgSO_4$ and $Mg(NO_3)_2$ were selected as draw solution (DS) to dewater synthetic non-hydrolysed urine. In this process, the Mg^{2+} reverse salt flux (RSF) were used to recover P as struvite. Simultaneously, the urea was recovered in the DS as it is poorly rejected by the FO membrane. The results showed that, after 60% urine concentration, about 40% of the P and 50% of the N were recovered. XRD and SEM – EDX analysis confirmed that P was precipitated as mineral struvite. If successfully tested on real urine, this process could be applied to treat the urine collected in urban areas e.g., high-rise building. After the filtration, the solid struvite could be sold for inland applications whereas the diluted fertiliser used for direct fertigation of green walls, parks or for urban farming. Finally, reduction in the load of N, P to the downstream wastewater treatment plant would also ensure a more sustainable urban water cycle.

2

1. Introduction

Sustainability in wastewater treatment is one of the significant issues of this century (Xie et al. 2016). In particular, rethinking wastewater as a valuable resource is crucial in meeting adequate sanitation, water and fertilier demand to feed a growing population (Elser and Bennett 2011, Xie et al. 2016). For these reasons, the efficient separation, treatment and reuse of human urine have gained increasing attention due to its inherent value potential (Maurer et al. 2006, Udert and Wächter 2012, Zhang et al. 2014). In fact, despite the low volumetric load of urine (i.e., less than 1% of the overall wastewater volume), it accounts for approximately 80% of the nitrogen (N), 50% of the phosphorus (P) and 55% of the potassium (K) load in most of the wastewater treatment plants (Liu et al. 2016, Maurer et al. 2006, Udert and Wächter 2012, Zhang et al. 2014). In particular, the amount of P contained in the urine is the single most significant source from urban areas (Zhang et al. 2014). Given the forecasted depletion of minable phosphorous rocks, reusing the P from waste streams could significantly enhance the sustainability of the urban water cycle (Xie et al. 2014, Xie et al. 2016). Additionally, with the increase in the size and densities of modern cities high-rise buildings are already becoming necessary. In these, urine separation and gravity-driven collection might become a feasible choice. After treatment, the recovered nutrients could be reused in several urban applications such as green walls, parks or urban farming. Simultaneously, the load of N, P to the downstream wastewater treatment plants would be reduced, possibly making their operation less energy demanding (Ishii and Boyer 2015, Kavvada et al. 2017).

Despite the applicability of raw human urine for direct fertigation, its nutrients imbalance (i.e., mainly N), and low nutrients concentration (i.e., N: 0.9%, P: 0.06%, K: 0.3%) as well as possible contamination of unwanted xenobiotic (e.g. hormones and pharmaceuticals), makes

62   its large-scale application challenging. Besides, if transportation were required, then the costs

63   of those above only, would offset the market value of urine as fertiliser (Maurer et al. 2006,

64   Udert and Wächter 2012). Therefore, up-concentration of urine and/or selective nutrients

65   recovery has recently attracted increased attention from the scientific community. Several

66   technologies are currently studied to achieve these goals. Among them, nutrients precipitation

67   as mineral fertiliser, or concentration as liquid fertiliser, have shown to be the most mature.

68   While recovering P, K as solid fertiliser is generally performed via struvite or K-struvite

69   precipitation (Etter et al. 2011, Wilsenach et al. 2007), recovering N, P, K as liquid fertiliser

70   has shown to be more challenging. Among the technologies investigated, nitrification-

71   distillation (Udert and Wächter 2012), nanofiltration (NF) (Pronk et al. 2006), reverse osmosis

72   (RO) (Maurer et al. 2006), adsorption (Tarpeh et al. 2017) and stripping (Tarpeh et al. 2018,

73   Xu et al. 2017) were the most promising ones.

74   However, despite the high potential of the nitrification-distillation process, at present, its costly

75   operation makes its applicability limited (Fumasoli et al. 2016). Pressure-driven NF/RO are not

76   often employed due to their unsatisfactory rejection of urea and ammonia (the most

77   predominant compounds in human urine) as well as high capital and operational costs (Maurer

78   et al. 2006, Zhang et al. 2014). While conventional ammonia stripping is high energy and

79   chemical intensive, electrochemical stripping in combination with electrodialysis and

80   membrane stripping might be a more feasible approach (Tarpeh et al. 2018). However, the

81   production of chlorination by-products (e.g., ClO_3^-, ClO_4^-) would still be a significant drawback

82   of mediated electro-oxidation of urine (Zöllig et al. 2015). Finally, adsorption using ion

83   exchange resins could be a useful technology to recover the N in the urine once the engineering

84   questions about post-treatment of the eluent or eluate for pharmaceutical removal are

85   addressed.

86 On the other hand, the process of P-recovery via struvite precipitation has been adequately

87 addressed and understood, showing its cost-effectiveness, simple operation and safety in the

88 final product (de Boer et al. 2018, Etter et al. 2011, Wilsenach et al. 2007, Xu et al. 2017). The

89 downside of this process is that it does not alleviate the issue related to the large volume of

90 human urine, and the recovery of both N and K is not addressed. Finally, this process also

91 requires the addition of extra magnesium source to recover >90% of phosphorous, which comes

92 at an additional cost (Maurer et al. 2006).

93 With these premises, to achieve the ambitious goal of combining urine volume reduction with

94 nutrients recovery, while maintaining low operational costs, the feasibility of using osmotically

95 driven forward osmosis (FO) process was recently investigated (Zhang et al. 2014). The

96 principle of FO relies on the natural water transport across a semi-permeable membrane from

97 a low concentration solution (feed) to a higher one (draw) until the thermodynamic equilibrium

98 is reached (Phuntsho et al. 2012). The advantages of FO consist of lower fouling propensity as

99 well as possible lower energy demand, especially when there is no need for draw solution

100 regeneration or further feed brine management (Van Der Bruggen and Luis 2015). In particular,

101 the concept of fertiliser driven forward osmosis (FDFO) has shown to be a viable FO

102 application to reclaim and reuse wastewater and impaired waters for agriculture application

103 (Chekli et al. 2017, Valladares Linares et al. 2016, Van Der Bruggen and Luis 2015). However,

104 the primary inherent drawback of this process was identified as the reverse draw solute

105 diffusion (RSF). In fact, the RSF of the fertiliser draw solution to the feed can compromise the

106 final quality of the brine (i.e., by exceeding the nutrients concentration standards for direct

107 brine discharge) but also can cause an economic loss of valuable fertiliser. Moreover, in the

108 context of urine dewatering via FO, if RO brine is selected as DS, the loss in rejection of small

109 and uncharged compound (e.g. urea) can contaminate the diluted DS thereby jeopardising the
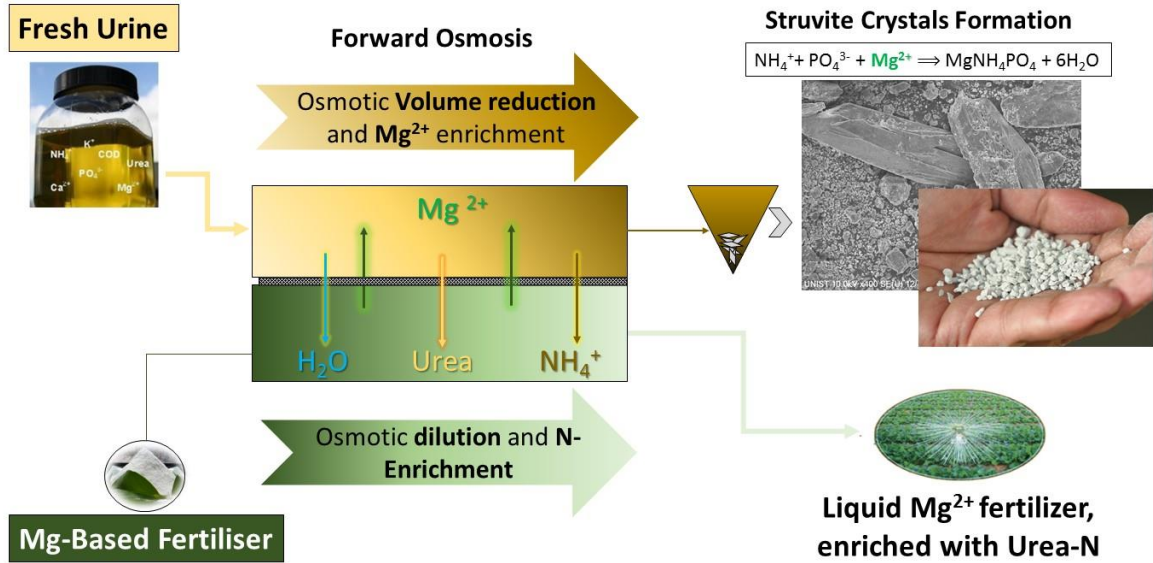
110   process (Liu et al. 2016, Zhang et al. 2014). Zhang et al. (Zhang et al. 2014) have already tried

111   to apply FO to concentrate human urine, using RO brine as DS. Their study showed that urea

112   is practically not rejected by the FO membrane, therefore, impeding a safe discharge of the

113   diluted RO brine in the environment.

114   We herewith present a novel FDFO concept for concentrating human urine, where both

115   limitations of FO (i.e., RSF of the draw solutes and urea/NH_3 rejection loss), are beneficial to

116   recover both nitrogen and phosphorous from urine. In fact, in this study, the feasibility of using

117   a Mg^{2+}-based fertiliser draw solution to dewater fresh (i.e. non-hydrolysed) human urine is

118   investigated. In this concept, the reverse solute diffusion will trigger P-recovery via struvite

119   precipitation, while the rejection loss of urea/NH_3 will enrich the Mg-fertiliser with valuable

120   nutrients. At the same time, the final volume of urine will be reduced thereby improving the

121   efficiency in downstream processes for N-recovery (e.g. ammonia stripping). This initial study

122   will address the following: (1) Screening of suitable Mg^{2+}-fertiliser draw solutions based on

123   FO performance, (2) Comparison between experimental results and model-based predictions

124   and, finally, (3) Critical analysis of the process efficiency and feasibility regarding

125   nutrients/water recovery and waste volume reduction.

126

127 **2. Materials and Methods**

128 **2.1 Feed and draw solution**

Fresh Urine

Forward Osmosis

Osmotic **Volume reduction** and **Mg²⁺** enrichment

Mg²⁺

H_2O Urea NH_4^+

Osmotic **dilution** and **N-Enrichment**

Mg-Based Fertiliser

Struvite Crystals Formation

$NH_4^+ + PO_4^{3-} + Mg^{2+} \Longrightarrow MgNH_4PO_4 + 6H_2O$

Liquid Mg²⁺ fertilizer, enriched with Urea-N

129

130 **Figure 1 Schematic diagram of the process.**

131 In Figure 1 the schematic representation of the system is displayed for a better understanding

132 of the process. The synthetic fresh urine feed solution (FS) was prepared according to the recipe

133 of Udert et al. (Udert et al. 2006), and its composition is displayed in

134   Table 1. Fresh urine was selected over stored urine because of several reason. Firstly, fresh

135   urine has a about half the osmotic pressure compared to hydrolysed urine. This means that,

136   theoretically, higher J_w and concentration can be achieved when fresh urine is chosen. Secondly

137   the acidic pH of fresh urine (i.e. 5.5 - 6.5), caused by the presence of uric and oxalic acids,

138   would likely reduce membrane scaling during the operation. Nevertheless, real urine is a very

139   dynamic solution in which urea, if stored in non-sterile conditions, is hydrolysed to NH_3/NH_4^+

140   and carbonate. The urea hydrolisation process causes a rise in the pH to around 9 triggering the

141   precipitation of Mg^{2+} and Ca^{2+} in the form of carbonates and phosphates (Maurer et al. 2006,

142   Randall et al. 2016). Therefore, the experiments conducted in this study aim at validating the

143   initial hypothesis but further investigations using real urine should be performed. $MgSO_4$ and

144    $Mg(NO_3)_2$ were finally selected as suitable Mg-fertiliser DS for this application. In fact, to our

145   knowledge, the only other soluble Mg-fertilisers are $MgCl_2$ and $Mg(H_2PO_4)_2$. However, the

146   high Cl_2 concentration of the first makes it applicability as fertiliser limited and, for the second,

147   the P-recovery as from the urine would likely be jeopardised by the PO_4 RSF of $Mg(H_2PO_4)_2$.

148   Similarly, one intrinsic limitation of using $Mg(NO_3)_2$ is the RSF of NO_3^- that could offset the

149   urea/NH_4^+-N gained from the feed rejection loss. Additionally, the high osmotic pressure of

150    $Mg(NO_3)_2$ (i.e. 84 bars at 1 M) would ensure high water flux and urine up-concentration. Non

151   Mg^{2+}-based fertilisers could also be used if the ultimate target is urine concentration and N-

152   recovery. However, that is outside the scope of the present work. All chemicals used in this

153   study were reagent grade and purchased from Sigma-Aldrich Australia. Draw and feed

154   solutions were prepared by dissolving the salts in deionised (DI) water.

155

Table 1 Composition and characteristics of the synthetic (non-hydrolysed) urine feed solution(Udert et al.

157 **2006). *Calculated with OLI System Analyser. ** Based on Udert et al. (Udert et al. 2006).**

Composition	Concentration [g/L]	Characteristics		
Urea	16.2	pH*	4.51	[-]
NH$_4$Cl	1.80	Osmotic Pressure*	13.4	[bar]
Na$_2$SO$_4$ (anhydrous)	2.30	Alkalinity**	0.02	[M]
NaH$_2$PO$_4$ (anhydrous)	2.90	Ionic Strength**	0.18	[M]
KCl	4.20	TDS*	9.1	[g/L]
NaCl	0.18			

158 **2.2 Forward osmosis experimental set-up**

159 An FO set-up, similar to the one used in our previous study (Phuntsho et al. 2012), was

160 employed in the present research. In particular, for the bench-scale experiments, commercially

161 available thin-film composite (TFC) polyamide (PA) membranes (Toray Chemical Korea Inc.,

162 South Korea) were tested. Transport and structural parameters of the FO membranes (A, B and

163 S values) were determined using both traditional pressure driven method (at 8 bars pressure)

164 and the FO method proposed by Tiraferri et al. (Tiraferri et al. 2013). The results are displayed

165 in

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9

167   **Table 2**. The crossflow membrane unit consisted of an FO cell with channels dimension of 2.6

168   cm width x 7.7 cm length x 0.3 cm depth, with an active membrane area of 20.02 cm^2. The DS

169   tank was placed on a digital scale connected to a computer to record the transported volume. A

170   conductivity and pH meter (Hach, Germany) were connected to the feed tank to record the pH

171   and conductivity of FS. Triplicates of each experiment were conducted.

172

173   **Table 2 Key proprieties of the FO membranes and draw solutions used for this study.**

	Unit	TFC
Active layer	[-]	Polyamide
Manufacturer	[-]	Toray Industry Inc.
A	[L.m^{-2}.h^{-1}.bar^{-1}]	6.64
B$_{NaCl}$	[L.m^{-2}.h^{-1}]	1.17
B$_{MgSO4}$	[L.m^{-2}.h^{-1}]	0.91
B$_{Mg(NO3)2}$	[L.m^{-2}.h^{-1}]	3.58
S	[μm]	409
D$_{MgSO4}$	[m^2.h^{-1}]	1.70×10^{-6}
D$_{Mg(NO3)2}$	[m^2.h^{-1}]	3.31×10^{-6}

174   **2.3 Modelling of water flux, reverse salt flux and achievable P-recovery**

175   To better understand and comment the experimental results, the water flux (J_w), specific

176   reverse salt flux (SRSF) have been modelled via the classical solution-diffusion model coupled

177   with the diffusion-convection transport in the membrane support layer (Tang et al. 2010).

178   Membrane pure water permeability (A) and the MgSO$_4$ and Mg(NO$_3$)$_2$ salt permeability

179   coefficients (i.e., B$_{MgSO4}$, B$_{Mg(NO3)2}$) were determined via equation 1 based on the

180   corresponding water flux and RO rejection data (at 8 bar pressure) (Zhang et al. 2014). The

181   diffusivity coefficients of MgSO$_4$ (i.e., D$_{MgSO4}$) and Mg(NO$_3$)$_2$ (i.e., D$_{Mg(NO3)2}$) have then been

182   calculated using OLI Stream Analyzer software. The results are displayed in

183

184   **Table 2**.

185    $$B = \frac{J_w(1-R)}{R} \qquad (1)$$

186   The impact of the internal concentration polarisation (ICP), on the porous support layer of the

187   FO membrane, needs to be considered to obtain a more realistic theoretical J_w and J_s values.

188   Since all the experiments have been carried out in FO mode (i.e., active layer (AL) facing the

189   feed solution (FS)), equation two was used to predict the water flux (Tang et al. 2010, Zhang

190   et al. 2014).

191    $$J_w = \sigma K_m \ln\left(\frac{A\pi_D + B_s}{A\pi_F + J_w + B_s}\right) \quad \text{(AL-facing FS)} \qquad (2)$$

192   Where σ is the reflection coefficient, assumed as unity (complete rejection of the solute), K_m

193   is the mass transfer coefficient, of the selected DS, given by the ratio between the diffusivity

194   of the salt and the structural parameter (S) of the membrane (i.e. $K_m = D/S$). The transport

195   coefficients for water and solutes are expressed as A and B_s. Finally, π_D and π_F are the DS and

196   FS bulk osmotic pressure, respectively. Assuming that the osmotic pressure of the DS follows

197   the van't Hoff equation, the reverse salt flux (J_S) can be calculated using equation 3. Where β

198   is the van't Hoff coefficient (i.e., 2 for $MgSO_4$ and 3 for $Mg(NO_3)_2$), R_g is the universal gas

199   constant, and T is the absolute temperature (Tang et al. 2010).

200    $$J_S = \frac{B_s}{A \cdot \beta R_g T} J_w \qquad (3)$$

201   The specific reverse salt flux (SRSF) can then be calculated as SRSF = J_s/J_w.

202   The theoretical minimum Mg^{2+} dose to precipitate 99%, 90% or 80% of PO_4^{3-} as struvite

203   (ammonium magnesium phosphate hexahydrate = $NH_4MgPO_4.6\ H_2O$ was calculated assuming

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204   Mg^{2+}/PO_4^{3-} the molar ratio of 1.1 ± 0.1 mol (Etter et al. 2011). In fact, the theoretical molar

205   Mg^{2+}/PO_4^{3-} the ratio of 1 mol often not enough to achieve a good P-recovery. Given the initial

206   PO_4^{3-} concentration in the synthetic urine the minimum required Mg^{2+} - SRSF was calculated

207   via equation 4. The variable in this equation is the feed up-concentration factor. The FS

208   concentration factor defines the transported water volume, which determines the amount of

209   Mg^{2+} supplied to the urine during the FO operation.

210
$$Minimum\ required\ Mg^{2+} - SRSF \left[\frac{g_{Mg^{2+}}}{L}\right] = \frac{(Mg^{2+}_{Required} - Mg^{2+}_{In\ urine})}{\left[1 - \left(\frac{V_{Feed}}{Feed_{Up-concentration}}\right)\right]} \qquad (4)$$

211   By substituting the required stoichiometric Mg^{2+} on equation 4 ($Mg_{Required}$) with the amount

212   of magnesium already present in the urine ($Mg_{In\ urine}$), and considering 1L of urine, the

213   minimum Mg^{2+}-SRSF required to achieve PO_4^{3-} recovery of 99%, 90% and 80% was

214   calculated. In Figure S2 the minimum Mg^{2+} - SRSF is plotted as a function of the feed up-

215   concentration. From this figure, it can be seen that above 50% FS up-concentration, there is

216   little variation in the required SRSF. That is because after 2 times FS up-concentration already

217   50% of the volume is moved from the FS to the DS.

218   **2.4 Experimental protocol and performance evaluation**

219   Given this required Mg^{2+}-SRSF, short-term experiments, with 1 M $MgSO_4$ and 1 M $Mg(NO_3)_2$

220   as DS and DI water as FS were performed. Water flux and Mg^{2+} - SRSF were measured in each

221   experiment.

222   For the experiments with synthetic urine as FS, the concentration of $MgSO_4$ was increased to

223   2 M to be able to reach at least 50% FS concentration (Figure S1). Also, both FS and DS were

224   acidified to a pH of 4, with a 4 M HCl solution, to avoid precipitation of Mg^{2+} salts on the

225   surface of the membrane. This acidification step, however, might not be necessary using real

226   fresh urine due to the presence of organic acids (mostly uric acid). Yet, this has to be further

227   investigated. Water flux, urine volume reduction were then recorded by weight measurements.

228   Feed and draw samples were collected over time to measure urea and NH$_3$ rejection as well as

229   the magnesium RSF. After the FO filtration, the pH of the concentrated FS was increased to

230   9.5, to trigger the mineral precipitation, by slowly adding 4 M NaOH solution. This step is not

231   necessary when real urine is used since the remaining urea in the feed would spontaneously

232   hydrolyse causing pH to rise to 9.5. Afterwards, the FS was then stirred for 2 hours and later

233   filtered using a 0.45 µm pore-size filter (Merck, Millipore).

234   Additionally, PO$_4$$^{3-}$ was measured in the feed (1) at the beginning of the experiment (2) after

235   the FO concentration and (3) after mineral precipitation and filtration to calculate the P-

236   recovery.

237   **2.5 Analytical methods**

238   The reverse flux of magnesium was measured using microwave plasma atomic emission

239   spectrometry (MP-AES) (Agilent Technologies, Australia), while sulphate (SO_4^{2-}), nitrate

240   (NO_3^-) and orthophosphate (PO_4^{3-}) anions were measured via ionic chromatography (IC

241   Thermo Fisher Scientific, Australia). The forward flux of ammonium (NH_4^+) and urea was

242   measured via spectrophotometer, at 340 nm wavelength, using urea/ammonium Megazime kit.

243   The crystals produced after the FO process were analysed by X-Ray diffraction (XRD)

244   (Siemens D5000), over a Bragg angles ranging from 6° to 60° (Cu Kα, λ=1.54059 Å), and

245   energy-dispersive X-ray spectroscopy (EDX) (Zeiss Supra 55VP, Carl Zeiss AG, Germany).

246   The surface of the scaled membrane was analysed by scanning electron microscopy (SEM,

247   Zeiss Supra 55VP, Carl Zeiss AG, Germany). Samples were firstly dried under air purging and

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248   then lightly coated with Au/Pd. The SEM imaging was performed at an accelerating voltage of

249   10 kV at different magnifications and at various points.

3. Results and Discussion

3.1   Magnesium fertilisers screening and performance prediction

As previously discussed, the initial criteria for the selection of suitable DS where that the chosen fertilisers should contain Mg^{2+} in their chemical formula while being fully water-soluble and lacking a phosphate group. Only two fertilisers were selected as DS for this application, i.e., $MgSO_4$ and $Mg(NO_3)_2$. Firstly, the osmotic pressure of the two DS was investigated. Between the two, $Mg(NO_3)_2$ generates by far the highest osmotic pressure at the same concentration (Figure S1) while having a higher diffusivity coefficient (

258   Table 1) (i.e., inducing less dilutive ICP). This means that a concentrated $Mg(NO_3)_2$ DS, could

259   potentially achieve greater urine volume reduction with higher water flux compared to $MgSO_4$.

260   The higher water flux was confirmed experimentally (Figure 2). On the other hand, it has to be

261   verified that the RSF of NO_3-N from $Mg(NO_3)_2$ does not offset the nitrogen recovered from the

262   rejection loss of urea-N/NH_3-N. Overall, $Mg(NO_3)_2$ showed almost three times the water flux

263   of $MgSO_4$ at same concentrations. Higher SRSF were also measured with $Mg(NO_3)_2$, probably

264   due to its higher diffusivity.

265   After testing the DS with DI water as FS, the experimental results were then used to validate

266   the model described in the previous section. Having a precise model, able to predict the

267   performance of the selected DS, is important when it comes to developing an economic analysis

268   of the FDFO under different operating conditions. By looking at Figure 2, it can be seen that

269   the model shows good agreement with the J_w and SRSF measured during the bench-scale study.

270   Given this good agreement, the developed model was then applied to predict the water flux of

271   long-term tests using fresh urine as FS.

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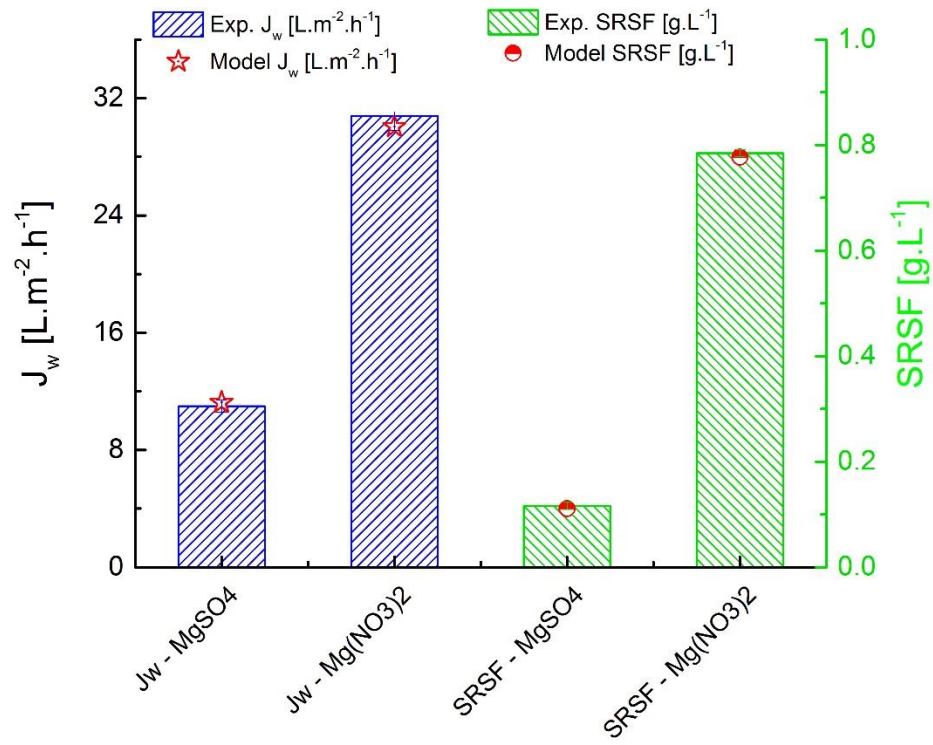
Figure 2. Experimental J_w and SRSF, with 1 M MgSO₄ or Mg(NO₃)₂ as DS and DI-water as FS (columns) are plotted against the J_w and SRSF predicted using equations 2 and 3 (symbols). The input data for the modelling are displayed in

276

Table 2. FO operational conditions: Commercial TFC PA membrane, DS concentration 1 M, DS and FS

**volume 1 L, cross-flow velocity 8.5 cm/s; temperature 25 ± 1 °C; membrane orientation: AL - FS.**

279 **3.2 Experiments with fresh urine as feed solution**

280 Once the model was validated with DI water as FS, long-term tests with fresh synthetic urine

281 were conducted to measure J_w, FS up-concentration, Mg^{2+} - SRSF, P and N recovery data. The

282 DS concentration used for these tests were: 2 M $MgSO_4$ and 1 M $Mg(NO_3)_2$. Feed up-

283 concentration of 60% was targeted for both fertilisers.

284 Starting with the effectiveness of the model when urine is used as FS, Figure 3 shows that the

285 model generally well predicted the J_w, especially when $Mg(NO_3)_2$ is used. However, for

286 $MgSO_4$, after approximately 40% feed up-concentration the measured flux is higher than the

287 modelled one. A possible explanation is the loss in osmotic pressure of the FS due to the urea

288 movement to the DS, thereby increasing the osmotic pressure difference ($\Delta\pi$) between FS and

289 DS. The loss in osmotic pressure due to urea transport might be particularly evident for $MgSO_4$

290 due to its longer experimental time (due to the average lower water flux). Previous findings by

291 Zhang et al. (Zhang et al. 2014) have already noticed this difference between experimental and

292 modelled water flux during concentration of fresh synthetic urine with NaCl as DS. Another

293 explanation could be due to the stripping of NH_3 during the experiment, due to the relatively

294 fast feed recirculation rate (i.e. 300 mL/min). However, ammonia volatilisation should not

295 significantly affect the system since at pH ≤ 5, the equilibrium $NH_3 \xrightleftharpoons[]{pK_a=9.25} NH_4^+$ should be

296 heavily shifted on NH_4^+ which is non-volatile. Besides, the NH_3/NH_4^+ concentration is

297 relatively low comapred to urea. Finally, 60% FS volume reduction was achieved without any

298 sign of membrane damage. In fact, decrease a in the water flux was mainly due to the increase

299 in the osmotic pressure of urine (from about 11-13 bar to around 30 bar) and the decrease in

300   the osmotic pressure of the DS (due to dilution). Flushing the membrane with DI-water was

301   generally enough to clean the membrane surface and restore the initial performances (Figure

302   S3). Nonetheless, experiments having real urine as FS are necessary to better assess membrane

303   fouling in this process.

304   Overall, the model showed an acceptable agreement with the measured data and the

305   experimental tests confirmed that at least 60% FS concentration was achievable without any

306   sign of scaling on the membrane.
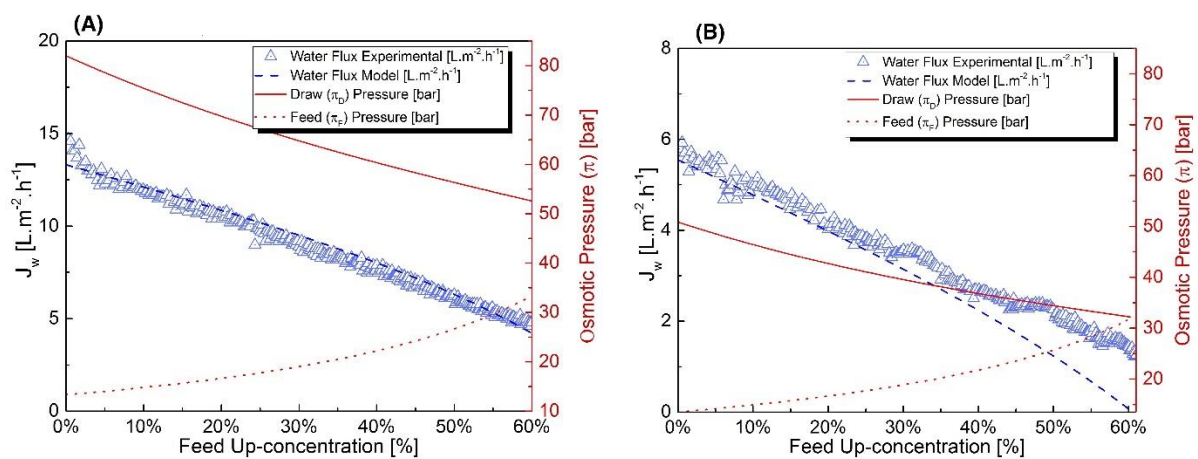
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308 **Figure 3: J_w and FS up-concentration factor for the long-term FO experiment using 1 L of synthetic FU as**

309 **feed and 1 L of 2 M MgSO$_4$ (B) and 1 L of 1 M Mg(NO$_3$)$_2$ (A) as DS.**

310 **3.3 Mineral phosphorous recovery**

311   Once the targeted FS concentration was reached, the pH of the feed was increased to 9.5 via

312   the addition of a 4 M NaOH solution that resulted in a sudden mineral formation (Xie et al.

313   2014). The FS was then left to stir at 500 rpm for 2 hours to allow full nucleation and crystals

314   growth. This alkalinisation step expected to be unnecessary when real urine is used. In fact, the

315   enzymatic hydrolysis of urea, which has spontaneously happens in real urine, would itself

316   increase the pH up to 8.5 - 9.5 (Mehta et al. 2015, Randall et al. 2016, Udert et al. 2003). In

317　this process, the urea concentration after the FDFO process is about the same as in the diluted

318　urine (i.e. 50% urea removal was achieved but also 60% volume reduction). Therefore, it is

319　expected that, after the urea hydrolysation process, the concentrated urine would yield a similar

320　final pH. Phosphorous and magnesium concentrations were measured before and after the

321　alkalinisation of the feed, and the insoluble minerals produced were analysed via XRD and

322　SEM - EDX. Figure 4 shows the amount of Mg^{2+} and PO_4^{3-} before and after the mineral

323　precipitation. Both draw solutions achieved around 40% PO_4^{3-} removal despite the different

324　DS molar concentrations and water fluxes. All the magnesium that diffused through the

325　membrane during the process was removed after precipitation.

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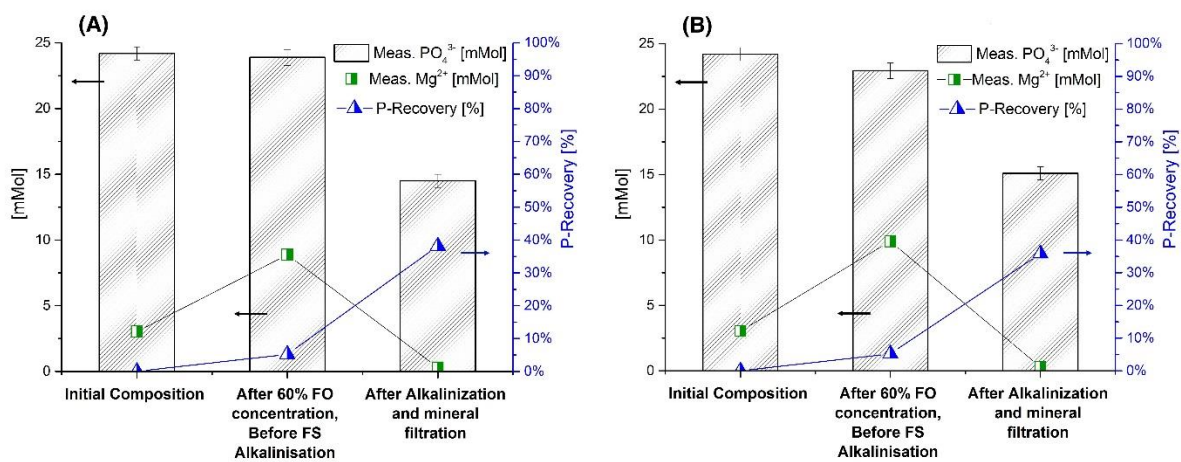
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329　**Figure 4 Magnesium and phosphorous in the urine before the FO, after the FO and after the NaOH addition**

330　**in the concentrated urine. Figure 4 (A) refers to the tests with 1 M Mg(NO₃)₂ and Figure 4 (B) to the ones**

331　**with 2 M MgSO₄.**

332　After desiccating at room temperature, the solids obtained from the alkalinised FS, SEM - EDX

333　and XRD were used to identify the elemental composition and structure of the crystals. Figure

334　5 shows the XRD spectrum of the precipitates while Figure 6 the SEM - EDX. In the XRD, the

335 peaks of the sample match quite well with the standard peaks of struvite, according to the

336 literature, while the EDX shows that the molar ratio of Mg and P is almost 1:1 (Xie et al. 2014,

337 Xu et al. 2015). The crystals obtained with both fertilisers were identical at the SEM – EDX

338 and XRD spectrum.

339 Finally, from these results, it can be concluded that almost all the Mg^{2+} that moved to the FS

340 during the filtration has reacted with the NH_4^+ and the PO_4^{3-} in the urine to form insoluble

341 struvite crystals. At 60% FS concertation, the RSF of Mg^{2+} was enough to recover 40% of the

342 PO_4^{3-} in the urine.
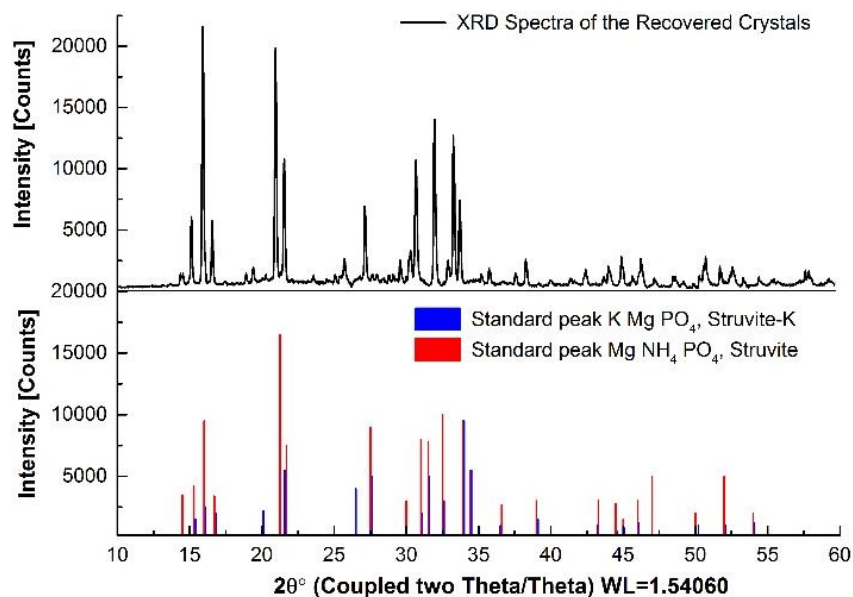
343

344 **Figure 5 XRD spectrum of the precipitates obtained from the concentrated FS after FO filtration. The**

345 **solution pH was further increased to 9.5 by addition 4 M NaOH. Continuous stirring was applied for two**

346 **h, and crystals were recovered and dried in a desiccator at room temperature.**

347
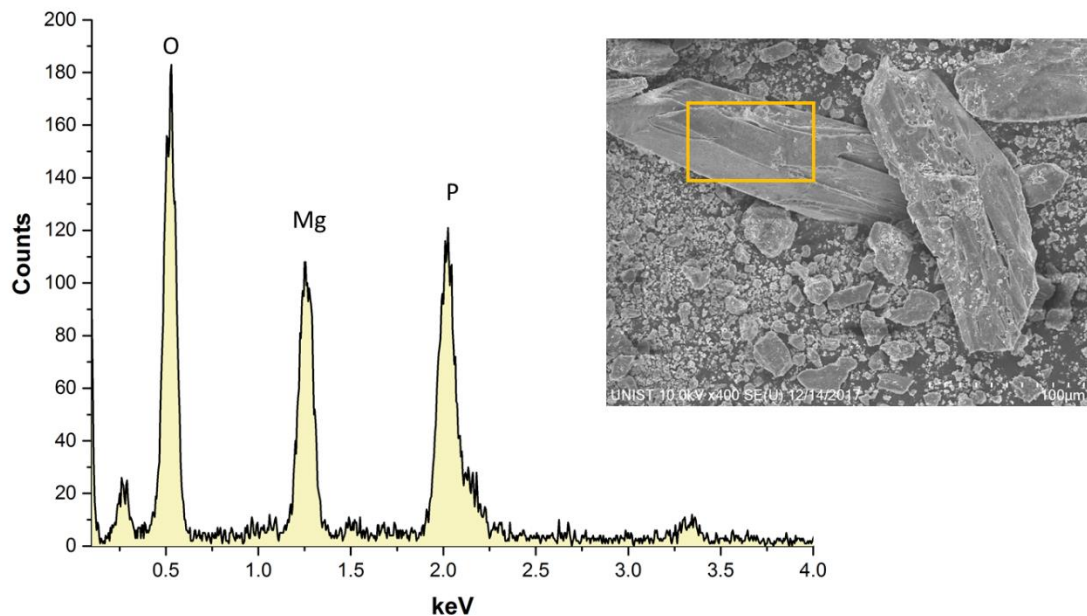
Figure 6 SEM picture and EDX spectrum of the precipitates obtained after the filtration of the concentrated urine.

3.4 Nitrogen recovery

Finally, during the experiments, the concentration of urea and NH_3 were measured in the DS while NO_3^- in the FS (when $Mg(NO_3)_2$ was used as DS). Given the absence of charge and the low molecular weight of urea, it was hypostatize that the FO membrane could not well reject it, thereby leading to an enrichment of the fertiliser DS with extra nitrogen (Cath et al. 2005).

The results, plotted in Figure 7, showed that this hypothesis was, at least partially, correct. In fact, at 60% FS concentration, up to 50% of the urea was recovered in the process. In particular, the flux of urea to the DS was found to be much higher than the RSF of NO_3^- when $Mg(NO_3)_2$ was used.

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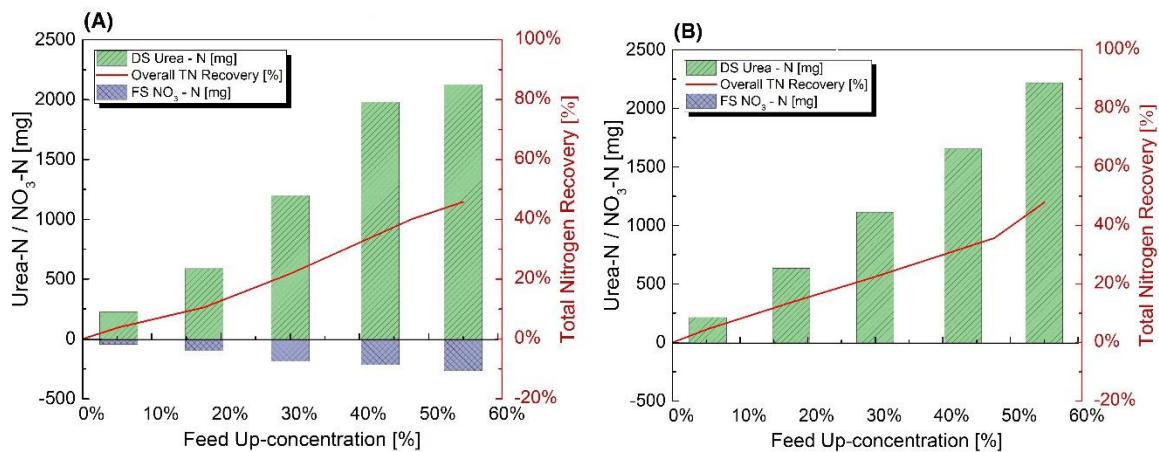
Figure 7 The histograms on the left y-axis show the total amount of urea-N "harvested" from the urine DS and the nitrate –N lost as reverse salt flux. On the right y-axis, the overall complete nitrogen recovery is plotted. Figure 7 (A) refers to the tests with 1 M Mg(NO$_3$)$_2$ and Figure 7 (B) to the ones with 2 M MgSO$_4$.

To conclude, at this stage, not all the P and N in the urine were recovered. However, the process still can be further optimised. For instance, the effect of transmembrane pressure (TMP) in the RSF and urea rejection could also be investigated. Additionally, the performances of real urine should be investigated as it will likely behave differently due to its very heterogeneous concentration. Nonetheless, the simplicity and low cost of the process could incentivise further investigations to reach higher P, N recovery.

4 Conclusions

This study investigated a novel application for FO to concentrate human urine while simultaneously recovering the phosphorous and nitrogen in it. Nitrogen recovery is achieved by urea transport over the FO membrane, enriching the fertiliser draw solution with urea. Simultaneously, phosphorous recovery is obtained on the feed side of the FO membrane by P-

376 precipitation as struvite due to the RSF of Mg^{2+}. In this process, the inherent limitations of FO

377 (i.e. RSF and poor urea/NH_3 rejection) are desirable and contribute to the simultaneous

378 recovery of P/N from the urine, while reducing its volume. Process modelling, as well as

379 experimental tests, were used to understand better and critically analyse the results. Two Mg^{2+}-

380 fertilisers (i.e., $MgSO_4$ and $Mg(NO_3)_2$) were identified as the most promising for this

381 application. Among the two $Mg(NO_3)_2$ displayed a much higher water flux and osmotic

382 pressure, achieving equal P and N recoveries as $MgSO_4$. Overall, the FDFO process enables to

383 obtain, simultaneously, the following outcomes:

384 • Reducing the volume of urine by more than 60% thereby possibly improving the

385 efficiency in downstream processes for N-recovery (e.g. ammonia stripping),

386 • Recovering 50% of the nitrogen in the urine,

387 • Recovering 40% of the phosphorous as struvite fertiliser.

388 To conclude, this low cost and robust treatment process enable a unique way to integrate urine

389 volume reduction and P and N recovery.   The economic feasibility of this technology, to

390 produce fertiliser for green walls, parks or urban farming applications, should be further

391 investigated in view of enhancing the sustainability of the urban water cycle.

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