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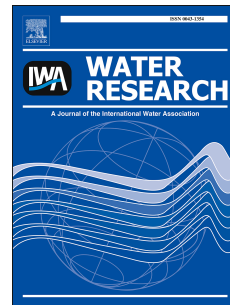
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Moving towards sustainable resources: recovery and fractionation of nutrients from dairy manure digestate using membranes

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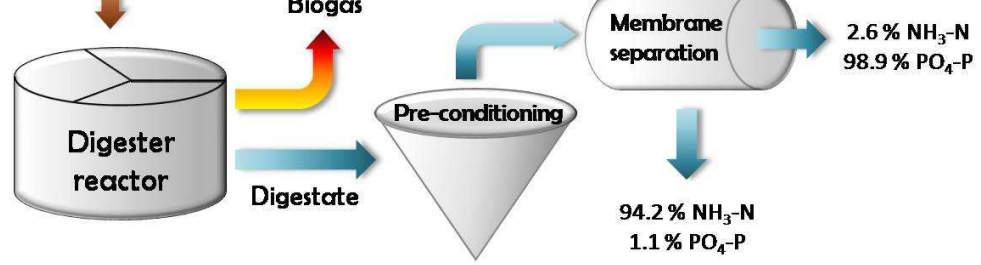
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ACCEPTED MANUSCRIPT

2 from dairy manure digestate using membranes
3
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17 **Abstract**

18 The fractionation of nitrogen (as ammonia/ammonium) and phosphorus (as phosphate ions)
19 present in the dairy manure digestate was investigated using a nanofiltration membrane
20 NF270. The filtration and separation efficiencies were correlated to pH across the range
21 $3 < \text{pH} < 11$. Filtration at pH 11 enabled higher permeate flux of 125-150 LMH at 20 bar,
22 however rejection of ammonia was high at 30-36 % and phosphate was 96.4-97.2 %. At pH 3
23 and pH 7, electrostatic charge effects led to higher permeation of ammonium and thus more
24 efficient separation of nitrogen.. The rejection of phosphorus was relatively constant at any

27 dependent on the charge of the membrane and ionic speciation. Solutions rich in nitrogen (as
28 ammonia/ammonium) were obtained with almost no phosphorus present (<1 ppm) whilst the
29 purification of the PO₄-P was achieved by series of diafiltration (DF) operations which
30 further separated the nitrogen. The separation of nutrients benefited from an advantageous
31 membrane process with potential added value for a wide range of industries. The analysis of
32 the process economics for a membrane based plant illustrates that the recovery of nutrients,
33 particularly NH₃-N, may be commercially feasible when compared to manufactured
34 anhydrous NH₃.

36 **Keywords**

37 Nutrient recovery, membrane filtration, digestate, process economics

39 **Abbreviations**

40 P – phosphorus

41 N – nitrogen

42 MF – microfiltration

43 DMDL – dairy manure digestate leachate

44 NF – nanofiltration

45 DF – diafiltration

46 **1. Introduction**

47 Fertilizers, including nitrogen and phosphorus, *i.e.* nutrients, have had a pivotal role in
48 sustaining the food supply to an increasing world population. However, the manufacture and
49 use of fertilisers is causing continuous environmental problems, such as the emission of

52 phosphorus (as phosphate) also carries a significant carbon footprint. Indeed, 1.5-2.6 tonnes
53 of CO₂ are produced per tonne of N (van Straaten 2008, Wood and Cowie 2004) and up to 1.0
54 tonnes of CO₂ per kg of P₂O₅ fertilizer (Oh-Ishi and Maeda 2002). The runoff of fertilisers
55 into watercourses also has a direct impact on human health, as well as the depletion of
56 oxygen supplies in the water leading to “dead zones”.

57 In recent times, agro-industrial wastes are being seen as a source of both energy and
58 resources. One particular example is that of manure waste being transformed into methane by
59 anaerobic digestion, whilst the nutrient-rich digestate is used as a replacement to
60 conventional fertilisers (Cornejo and Wilkie 2010, Desloover *et al.* 2012, Klavon *et al.*
61 2013). Nonetheless, there is only so much that can be applied to the soil without causing
62 nutrient excess and consequent damage to the environment. Also, nutrient run-offs owing to
63 rainfall and excess load may lead to the eutrophication of water courses (Smith and Schindler
64 2009, Smith *et al.* 1999). Indeed, the nitrate –directive (91/676/EEC nitrate) was created with
65 the purpose to protect ground water and lakes. According to the directive, the maximum
66 application of manure corresponds to 170 kg N/ha/year. However, during a transient period
67 up to 210 kg N/ha/year can be allowed (Commission 1991). Therefore, one of the greatest
68 engineering challenges of the 21st century is to develop strategies that help to control the
69 impact of agriculture on the environment.

70 Previous work has demonstrated the possibility of recovering nutrients in particle and
71 bacteria-free solutions from dairy manure digestate (Gerardo *et al.* 2013). Strategies such as
72 diafiltration (DF, i.e. addition of equal amounts of water for effective dialysis of solutes) and
73 acidification of the digestate showed to critically influence the leaching of soluble nitrogen
74 (NH₃-N), phosphorus (PO₄-P) and metals. When the digestate was acidified at pH 3, a nearly

77 separate streams of $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ are desirable and would potentially have a much higher
78 range of applications and market value. Fertilizer, textile, chemical and biotechnology
79 industries are heavily reliant on $\text{NH}_3\text{-N}$. Also, $\text{PO}_4\text{-P}$ is an essential element to all living cells
80 and has a crucial role in maintaining high crop yields (Beardsley 2011, Gaterell *et al.* 2000,
81 Tonini *et al.* 2013). In our recent work we have also suggested that separate streams of waste
82 derived $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ could allow optimal microalgae growing strategies associated to
83 biofuel production (Gerardo *et al.* 2014).

84 Membrane technology for the recovery and fractionation of nutrients from digestate is
85 preferential over alternative technologies such as precipitation, absorption and thermal
86 treatments. Ease of scaling up, chemical-free separations, low operating and maintenance
87 costs, compact and modular design and highly selective separations are some of the
88 advantages over their counter parts (Cheryan 1998, Strathmann 2011). Nanofiltration (NF)
89 membranes have been widely reported to selectively allow the passage or retention of solutes
90 based on both steric and electrostatic effects. Several NF membranes have been associated
91 with the retention of phosphorus, chloride, micropollutants and ammonia. Pronk *et al.* (2006)
92 compared three NF membranes (NF270, DS5 and N-30-F) and concluded that $\text{PO}_4\text{-P}$ and
93 NH_4 could be retained from synthetic urine at around 95 % and 45 %, respectively, using a
94 NF270 (polyamide) membrane (Pronk *et al.* 2006). Rejection of up to 98 % of PO_4 was
95 reported using a tailored made multilayer polyelectrolyte NF membrane (Hong *et al.*
96 2009). Phosphate anions, H_2PO_4^- and HPO_4^{2-} , were also demonstrated to be retained by
97 NF200 at 85 % and at 96 %, respectively (Ballet *et al.* 2007). Other authors have reported
98 that polyethersulphone membranes rejected up to nearly 70 % of $\text{NH}_3\text{-N}$ in solution (Ali *et al.*

101 phenomena are based on lab-grade synthetic solutions which do not mimic real separation
102 conditions.
103 The objective of this work was to investigate the fractionation of $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ derived
104 from dairy manure digestate using a NF270 membrane. Upon leaching nutrients by MF, the
105 influence of pH on the effective rejection of both $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ was discussed. Filtration
106 of up to 42 % of the feed volume allowed evaluating the dynamics of such process in relation
107 to the variation of the concentration of nutrients in the permeate stream. Diafiltration
108 strategies were investigated to enhance the separation and purification of nutrients. Finally,
109 capital expenditure and operational costs of a membrane filtration plant were determined.

110

111 **2. Materials and methods**

112 2.1. Preparation of the dairy manure digestate leachate (DMDL)

113 Dairy manure digestates were obtained from Fre-Energy dairy farm (Wrexham, Wales, UK).
114 Initial conditioning treatment consisted of adjustment to pH 3 with concentrated HCl (Fisher
115 Scientific, UK) and sedimentation for at least 1 hour. The supernatant was then collected and
116 screened through a 500 μm mesh. Nutrient rich leachates were produced by permeation
117 through a bench-top cross-flow filtration unit. The crossflow membrane filtration unit
118 consisted of an AGT Quix Stand benchtop system. This system featured a 1 L graduated
119 polysulfone reservoir, peristaltic pump and a polysulphone hollow fiber cartridge with 0.2
120 μm pore size and 0.042 m^2 surface area, all from AGT (now part of GE Healthcare). The
121 DMDL was analysed for nitrogen (as $\text{NH}_3\text{-N}$), phosphorus (as $\text{PO}_4\text{-P}$), metals and
122 conductivity. pH 3 was chosen because of the high recovery of phosphorus and metals, with
123 no influence on the recovery of nitrogen (Gerardo *et al.* 2013).

126 Paar GmbH -Austria) for pH range of 3-10. The dimension of the streaming channel were 74
127 mm × 10 mm × 0.3 mm (Oo & Ong, 2010). An electrolyte solution was pumped through the
128 cell and the pressure drop was measured by two pressure probes located up- and downstream
129 of the cell. The potential difference resulting from the accumulation of charge at one end, i.e.
130 streaming potential, was detected by two Ag/AgCl electrodes which provide information on
131 the electrostatic charge at the shear plane. Streaming potential can be determined
132 experimentally by plotting the voltage difference (ΔE) against various pressure drop (ΔP). A
133 linear relation was obtained and the gradient (streaming potential coefficient) was used to
134 calculate the zeta potential using Helmholtz–Smoluchowski equation (Ariza et al. 2001,
135 Chapman Wilbert et al. 1999, Huisman et al. 1998)

136

$$137 \quad \xi = \frac{dU}{dp} \frac{\eta}{\epsilon_r \epsilon_0} K_B \quad \text{(Equation 1)}$$

138

139 Where ξ is the zeta potential in mV, dU/dp is the slope of streaming potential versus
140 pressure (streaming coefficient) in mV/Pa, η the electrolyte viscosity in Pa.s, ϵ_r the relative
141 liquid permittivity (dielectric constant, dimensionless), ϵ_0 the vacuum permittivity (8.854×10^{-12}
142 $C^2 J^{-1} m^{-1}$ or $s m^{-1} \Omega^{-1}$), and K_B the specific conductivity of the bulk electrolyte solution
143 (Ohm). When ξ is zero the membrane is said to be isoelectric also known as isoelectric point
144 (IEP).

145 The membrane was characterised using KCl salt solutions at different concentrations
146 (0.001M, 0.01M and 0.025M KCl) and three diluted solutions of the DMDL. The dilution
147 factors are 100 (10ml of wastewater in 1000ml water), 50 (20ml of wastewater in 1000ml) and

150 in this study are summarised in Table 1.

151

152 2.3.Fractionation of nutrients – NF and DF

153 The high-pressure stirred cell was sourced from Membranology® (Membranology Ltd,
154 Swansea, UK) with a total volume capacity of 400 mL, maximum operational pressure
155 allowance of 100 bar and a membrane area of 32.17 cm². The system was pressurized with
156 nitrogen gas and controlled via valves and digital pressure gauges. The permeate line was
157 connected to a collecting vessel placed on a digital scale and the automated weight was
158 recorded via the RS232 (serial) port. A diagram of the NF setup is given in Figure 1. The
159 filtration was operated at 20 bar and 300 rpm (1.2 m/s) using a new and clean membrane for
160 every DMDL sample. Before introducing the DMDL sample, each membrane was flushed
161 and pressurized using deionised water at 20 bar.

162 Different aliquots of the DMDL were pH adjusted to pH 3, pH 7 and pH 11 with 0.1 M
163 NaOH (Fisher Scientific, UK) or 0.1 M HCl (Fisher Scientific, UK). Individual 250 mL
164 aliquots of DMDL at each respective pH were introduced into the high-pressure cell holding
165 the NF270 membrane. Permeate fractions were collected every 15 g (equivalent to 6 % of
166 initial feed volume) until 42 % of the feed volume was collected as permeate. Permeate flux
167 was continuously recorded for each pH value of the digestate leachate. All permeate fractions
168 were analysed for nitrogen (as NH₃-N) and phosphorus (as PO₄-P), conductivity and pH.
169 Retentate fractions were also analysed for metals.

170 DF using deionised water was also investigated to enhance the effective separation of
171 nutrients. Using a clean and pressurized membrane, 130 mL of DMDL at pH 7 was
172 introduced into the high pressure cell operating at 300 rpm and 20 bar. When half of the

175 Subsequently, when further 65 mL of permeate were collected another 65 mL of deionised
176 water were introduced into the high pressure cell and allowed to mix for 1 minute. These steps
177 were repeated until a total of four permeate samples and one retentate sample was collected.
178 All permeate samples were kept separate and analysed for nitrogen (as $\text{NH}_3\text{-N}$) and
179 phosphorus (as $\text{PO}_4\text{-P}$) only.

180

181 2.4. Chemical analysis

182 Nitrogen was analysed as $\text{NH}_3\text{-N}$ (or $\text{NH}_4\text{-N}$) using the phenate colourimetric method and
183 absorption was monitored using a spectrophotometer (UNICAM UV 300, Thermo Scientific,
184 UK) at 640 nm. Phosphorus was analysed as $\text{PO}_4\text{-P}$ using the vanadomolybdo-phosphoric acid
185 colourimetric method and absorption was monitored using a spectrophotometer (UNICAM
186 UV 300) at 470 nm, both analyses are according to *Standard Methods* (APHA 1998). The
187 elements Ca, Fe, Mn, Mg, K, Zn, Cr, Si and Cu were analysed using an Atomic Absorption
188 Spectrometer (PinAAcle 900F, PerkinElmer, UK) after dilution with 1 % nitric acid. The
189 calibration curves were performed using TraceCERT[®] AAS standard solutions (Sigma-
190 Aldrich, UK).

191

192 2.5. Rejection and selectivity of NF270

193 The degree of retention by the NF270 membrane is known as rejection which relates the
194 retention of each individual species relative to the concentration present in the feed. The
195 experimental rejection (R) is given by Equation 2 where C_{perm} and C_{feed} are the solute
196 concentrations in the permeate and feed, respectively. Membrane selectivity expresses the
197 relative preference to retain one solute over the other as a ratio of rejection between those two

200 $R = \left(1 - \frac{C_{perm}}{C_{feed}}\right) \times 100$ (Equation 2)

201 $S_{P/N} = 1 - \frac{R_{obs,N}}{R_{obs,P}}$ (Equation 3)(Hong *et al.*

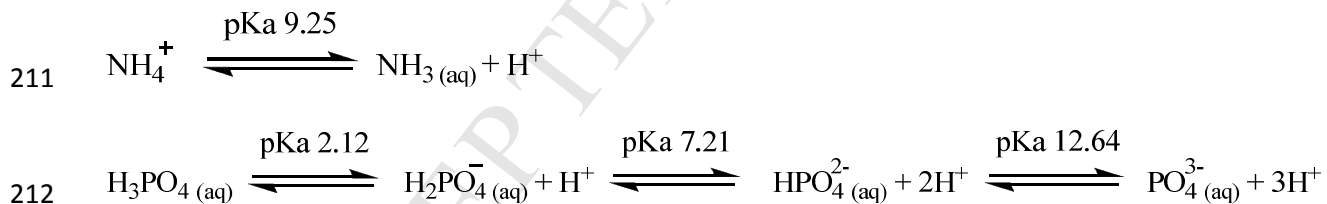
202 2009)

203

204 2.6. Nutrient speciation

205 Owing to the nature of NF systems, the chemical speciation of the targeted nutrients is
 206 important for the understanding of the fractionation of nitrogen from phosphorus. As a
 207 simplification, the soluble forms of nitrogen and phosphorus were represented as NH₃-N and
 208 PO₄-P, respectively. Nevertheless, the pH of the aqueous solution determines the speciation
 209 of each solute. The equilibrium reaction for each nutrient is given as:

210



214 Throughout this work, the pH was set at pH 3, pH 7 and pH 11. At pH 3, ionic species NH₄⁺
 215 and H₂PO₄⁻ were considered to be the dominant forms of the NH₃-N and PO₄-P respectively.
 216 At pH 7 this was NH₄⁺ and both H₂PO₄⁻/HPO₄²⁻ and at pH 11 NH₃ and HPO₄²⁻, respectively.
 217 Throughout this work, we assume that practically all nitrogen is present as ammonia and
 218 practically all phosphorus as phosphate.

219 **3. Results and discussion**

220 3.1. Electrokinetic properties of the NF270 membrane

223 *et al.* 2012). The electrokinetic properties of the membrane were also verified using the
224 DMDL solutions and showed very similar trends (Figure 2). The zeta potential curves for the
225 NF270membraneobtained in these experiments are characteristic of amphoteric surfaces with
226 both acidic and basic functional groups (Chiu and James 2007, Chun *et al.* 2003, Yang *et al.*
227 2003).The decrease of the negative surface charge observed with KCl salt from pH 10 (-35
228 mV) to pH 3 (~0 mV)is explained by the fact that cations interact with the membrane's
229 surface functional groups which counteract the negative charges(Szymczyk *et al.* 1997, Yang
230 *et al.* 2003). There was a significant difference of the membrane surface charge when
231 exposed to KCl salt in comparison to the DMDL, where the later resulted in "less negative"
232 surface charge throughout most of the pH range studied. This is more likely to do with the
233 increased presence of cations and ionic charge in the DMDL which form multivalent
234 chemical complexes with the membrane surface.

235

236

237 3.2. Recovery of nutrients from dairy manure digestate

238 Previous work reported on the success of MF in the recovery of nutrients from dairy manure
239 digestate (Gerardo *et al.* 2013). Improved recovery of phosphorus and metals in particle and
240 bacteria-free solutions was demonstrated at pH 3, with no influence on the recovery of
241 nitrogen. The same process to obtain nutrient leachate was used in this study. Table 2 gives
242 the concentration of the solutes of interest present in the DMDL at pH3 obtained in this
243 study. The concentration of nitrogen (as $\text{NH}_3\text{-N}$) was noted to be very high (1572.8 mg/L) in
244 contrast to that of phosphorus (as $\text{PO}_4\text{-P}$) (61.01 mg/L). Such recovery process is paramount
245 for the feasibility of nutrient fractionation using nanofiltration membranes. The MF process

248

249 3.3. Permeate flux and influence of pH

250 The influence of the feed pH on the flux and thus processing time was investigated and is
251 summarised in Figure 3. In each case the flux declined over the experimental period as a
252 result of membrane fouling. Operating at pH 11 allowed between 2- to 3-fold increase in the
253 permeate flux (permeate flux varied from the initial flux of 149.7 LMH to 125.4 LMH) when
254 compared to pH 3 (initial flux was 50.3 LMH and steadily declined to 22.2 LMH). After
255 processing 42 % of the feed volume at pH 11 the observed decline in flux was only 16 % of
256 the initial flux. Therefore, operation at pH 11 is recommended for optimal membrane flux
257 when filtering the DMDL.

258 Given the IEP of the NF270 is in the region of pH 3, the processing of the manure digestate at
259 pH 3 did not benefit from the (negative) charge effect typically present on the surface of this
260 membrane. In this case, solutes were being transported as neutral species and thus the mass
261 transfer of solutes through the membrane is solely due to size exclusion. As a result the
262 membrane is more prone to fouling resulting on lower permeate flux. On the other hand, at
263 high pH, e.g. pH 7 and pH 11, the increased charge on the membrane surface helps prevent
264 fouling leading to higher flux (Luo and Wan 2013, Nyström *et al.* 1995).

265 The permeation of ions is highlighted in Figure 4 in relation to conductivity of the permeate.
266 Conductivity of the permeate fractions obtained at pH 11 is consistent with the higher
267 permeation of solutes through the membrane.

268

269 3.4. Fractionation of nutrients by NF270 – rejection and selectivity

272 conditions. Rejection was calculated using Eq. 2 with the concentration of the feed being
273 corrected by mass balances for each permeate fraction collected.

274 At pH 3, the rejection of nitrogen was 30.3 %, however, a sharp decline in rejection to only
275 1.0 % was observed for the last permeate sample collected. A similar trend was observed at
276 pH 7 where initially the rejection of nitrogen was 23.9 % and declined to 4.6 %. This data
277 indicates that the rejection of nitrogen at pH 7 is less than at pH 3 which can be explained by
278 the fact that at pH 3 the membrane is isoelectric but negatively charged at pH 7. Thus, at pH
279 7, the electrostatic attraction of NH_4^+ is taking place and causing increased transport of the
280 species.

281 Contrary to this, at pH 11 the rejection of nitrogen was steady at around 30-33 % throughout
282 the course of the filtration experiment. This is explained by the fact that the nitrogen species
283 is now NH_3 and is neutral, which is not impacted by the membrane's negative charge. Luo *et*
284 *al.* (2013) also have reported that the retention of neutral solutes decreased with increasing pH
285 due to membrane swelling (i.e both membrane thickness and the pore size increased)(Luo and
286 Wan 2013).

287 The 30-33% retention of nitrogen at pH 11 was interesting since diffusion coefficients for
288 NH_3 and NH_4^+ are very similar, $1.80 \times 10^{-9} \text{ m}^2/\text{s}$ and $1.96 \times 10^{-9} \text{ m}^2/\text{s}$, respectively(Haynes
289 2011). This indicates that the size of both species in solution is similar (0.139 nm and 0.125
290 nm, respectively) and thus the phenomena observed is explained by electrostatic interactions
291 with the membrane surface. The negatively charged membrane acts as a charge screen
292 allowing positively charged ions through in detriment of neutral and negatively charged
293 species, therefore imposing the retention of nitrogen (as NH_3) at pH 11. The preferential

296 During the filtration experiment, a decline of the rejection of nitrogen was observed mostly at
297 pH 7 and pH 3. This phenomenon is explained by the fact that NH_4^+ is initially being rejected
298 at around 24-30 % and thus an accumulation of this ion takes place. As the concentration of
299 this species builds, the radii of the ionic charge cloud contracts due to charge proximity
300 which increases the potential for transport through the membrane(Oatley *et al.* 2012). This
301 inevitably leads to a reduction in the rejection of this species. At pH 11, the rejection of
302 nitrogen is typical of neutral species since rejection stayed constant throughout the filtration
303 experiment. The permeation of nitrogen at pH 3 and pH 7 is possibly determined by charge
304 effects which force NH_4^+ close to the negatively charged membrane surface and permeation
305 occurs through larger pores.

306 The rejection of phosphorus was steady throughout the filtration process regardless of the pH.
307 At pH 3 the observed rejection of phosphorus varied between 84.0-86.6 % and at pH 7 and
308 pH 11 the rejection was constant at around 97 %. Figure 5(b) illustrates that rejection of
309 phosphorus at pH 3 is always lower than observed at pH 7 and pH 11. To some extent,
310 this may be explained by the size of the ionic species in solution. At pH 3, H_2PO_4^- is the
311 dominant ionic species with a hydrodynamic radius of 0.27 nm, smaller than that of HPO_4^{2-}
312 with a radius of 0.32 nm and thus at pH 3 higher diffusion of H_2PO_4^- takes place leading to
313 lower rejection. Electrostatic effects on the membrane surface are also expected to define and
314 influence the underlying phenomena of such rejections. At pH 7 and pH 11, the natural
315 negative charge of the NF270 membrane is then present causing electrostatic repulsion of the
316 HPO_4^{2-} (and possibly PO_4^{3-}) leading to increased rejection. Moreover, at higher pH values the
317 valence of the phosphorus species is increased from 1- to 2- (and possibly 3-) which further
318 increases the electrostatic repulsion effect. Nonetheless, at pH 3 the observed rejection of

321 phosphorus and influence of pH are similar to that reported by Hong *et al.*(2009) with
322 standard solutions.

323 The fractionation of phosphorus from nitrogen, using NF has shown some interesting
324 phenomena. The NF270 membrane demonstrated effective rejection of phosphorus with a
325 minimum rejection of 84 %, however a maximum of 98 % rejection was attainable at and
326 above pH 7. Simultaneous to the retention of phosphorus, the permeation of nitrogen was
327 possible. At pH 11, nitrogen retention varied between 27-34 % and was considered high for
328 an effective nutrient fractionation. When operating at pH 7 and pH 3 the permeation of
329 nitrogen was much higher as charge effects dictated a lower rejection. Up to 6 % of volume
330 filtered, the rejection of nitrogen at these pH values was very similar at around 25 % and
331 declined significantly to around 2 %. Thus a more effective fractionation was taking place.

332 The results summarised in Table 3 highlight the differences in permeate flux, nutrient
333 rejection and P/N selectivity under different pH conditions throughout the experiment. For
334 the final permeate fraction collected, P/N selectivity was as high as 0.99 at pH 3 and 0.95 at
335 pH 7. Overall, the lowest P/N selectivity was observed at pH 11 yet much higher permeate
336 flux was possible.

337 3.5. Fate of metals after filtration with NF270

338 By analysis of the retentate fractions, total retention was calculated for Cu, Mn, Zn, Ca, Mg,
339 K, Cr and Fe in relation to that present in the feed solution. Table 4 summarises the rejection
340 of metals (and nutrients) for the filtration of DMDL under different pH conditions. In most
341 cases there is a slight decrease in rejection of most of the metal cations with increasing pH.

342 As previously explained, this is motivated by the membrane charge variation and
343 electrostatic/repulsion between ions and membrane. However, the rejection of Ca and K was

346 ions at acidic pH (> 90% for Ca^{2+} , Cu^{2+} , Mn^{2+} , Mg^{2+} , Cd^{2+} and Pb^{2+}) and a much lower
347 rejection at alkaline pH (Al-Rashdi *et al.* 2013, Luo and Wan 2013, Ozaki *et al.* 2002, Szoke
348 *et al.* 2003). Nonetheless, for a complex mixture of solutes such as DMDL, the ionic species
349 in solution are likely to significantly affect both retention and permeation of nutrients and
350 metals. As demonstrated by Al-Rashdi *et al.* 2013, multi-component mixtures of metals show
351 lower retention than that observed in single or two-component mixtures (Al-Rashdi *et al.*
352 2013). Moreover, the rejection of heavy metals also decreases with the increase in
353 concentration of the feed solution. This phenomena may be explained by the Donnan effect in
354 which positive ions in solution are able to permeate through the membrane also forcing
355 counter ions through so that electro-neutrality around the membrane is maintained (Luo and
356 Wan 2013). Indeed, the concentration of ions in the feed solution was high as illustrated by
357 the conductivity of 80 mS/cm (equivalent to around 5 % wt NaCl solution).

358 Metals such as Mn, Zn, Cr and Fe were highly retained by the NF270 with rejections above
359 70 %. Lowest retentions were observed for Cu and Mg which may have resulted from their
360 permeation as counter-acting ions. As a result of the rejection of metals, 25-86 % depending
361 on the metal and pH, the accumulation of metals in the retentate fractions was inevitable.

362 Overall, rejection of phosphorus and nitrogen at pH 7 seems to be the most effective means
363 of fractionating nutrients (Table 4). The N:P molar ratio of the permeates obtained varied
364 between 900-2868 against that in the feed solution of 57, representing a maximum of 50-fold
365 increase of nitrogen in solution obtained as permeate. On the other hand, the N:P ratio on the
366 retentate obtained after filtration at pH 7 was 24. Given that separate streams of nitrogen and
367 phosphorus are desirable, strategies such as DF may also help with further permeation of
368 nitrogen while phosphorus is retained.

371 means of NF using DF strategies as described in section 2.3. The principle of the
372 fractionation of the nutrients using the NF270 membrane follows the same underlying
373 phenomena as described in the sections above. From the series of filtration and DF steps,
374 each permeate was collected separately and analysed for nitrogen (as NH_3) and phosphorus
375 (as PO_4). Following a total of three DF steps, the retentate obtained was also analysed for
376 nitrogen and phosphorus. The results are summarised in Figure 6 and illustrate that nitrogen
377 and phosphorus can be nearly totally separated by a series of diafiltrations using the NF270
378 membrane. This approach allowed the separation of 94.2 % of nitrogen (as $\text{NH}_3/\text{NH}_4^+$)
379 present in the feed solution whereas only very small amounts of phosphorus (as ionic forms
380 of PO_4) were found in the permeate fractions. Simultaneously, 98.9 % of phosphorus present
381 in the feed solution was retained during the series of filtration and DF steps, in which only
382 2.6 % of nitrogen present in the DMDL remained with the retentate fraction. Further
383 purification of the phosphorus fraction may be attained by continuous DF. Such purification
384 step demonstrates the opportunity to obtain solutions of nitrogen with virtually no phosphorus
385 present in solution. On the other hand, the continuous retention of phosphorus increased the
386 concentration of phosphorus in the retentate with residual amounts of phosphorus still
387 present. The downside of this process was the increasingly diluted permeate stream which
388 resulted from the DF (addition of deionised water to the retentate stream on a 1:1 dilution
389 basis). While the first permeate fraction contained 1.54 g $\text{NH}_3\text{-N/L}$, the average concentration
390 of the permeate stream across all four permeate fractions collected was 0.74 g $\text{NH}_3\text{-N/L}$ and
391 0.07 mg $\text{PO}_4\text{-P/L}$.

392 The recovery and fractionation of nutrients from waste sludge is a vital step in the
393 valorisation of wastewater and waste sludge. In particular, dairy manure digestate contain

396 manure digestate (Fenton and Ó hUallacháin 2012, Rico *et al.* 2011). While the recovery of
397 nutrients will certainly represent a solution towards the minimisation of nutrient loading and
398 environmental damage, the fractionation of these nutrients in separate streams does
399 potentially increase their range of applications and market value. Nevertheless, an economy
400 based on sustainable resources relies on the feasibility, environmental concerns and on
401 nutrient availability, costs and health and safety considerations. Dairy manure digestate are
402 usually very rich in nutrients, however these fluids are typically complex and may potentially
403 contain pathogens (including viruses), prions and high concentration of toxic metals. The
404 methodology demonstrated here for the extraction and fractionation of nutrients benefits from
405 the attractive features of membrane technology. Particle and bacteria free leachate from
406 nutrient-rich dairy manure digestate was possible via sedimentation and MF which preceded
407 the nutrient fractionation step. Although the separation of any potential toxic metals from the
408 nutrient fractions is unlikely to be attainable via membrane separation, our previous work
409 with DMDL did not highlight an unusual concentration of toxic metals, e.g., Pb, As, Co, Cd
410 (Gerardo *et al.* 2013). The rejection of metals observed using the NF270 (Table 4) is likely to
411 lead to a built up to metals in the retentate fraction and thus limiting the use of the
412 phosphorus rich fraction in the wider context of commercial/industrial applications. In
413 addition, anions present in solution such as sulphate, chlorides and carbonate are likely to be
414 present and are expected to be found in the retentate fractions as a result of their negative
415 charge (Hong *et al.* 2007, Wang *et al.* 2005). Depending on the proposed applications of such
416 nutrients, further refining may be required to address the likely low purity of the fractions
417 obtained from dairy manure digestate.

418

421 by considering the process design and project evaluation. For that purpose, the process basis
422 here considered is a 200 m³ anaerobic digester for the treatment of dairy manure waste. If a
423 20 days residence time is given for the treatment of the manure waste, digestate flow would
424 be 10 m³/day. Figure 7 illustrates the process design for the extraction and fractionation of
425 nutrients from the digestate based on membrane filtration technology. The proposed process
426 design benefits from the acid treatment which increases the amount of phosphorus in the
427 soluble fraction (Gerardo *et al.* 2013).

428 Owing to the amount of solids present in the digestate, a solid-liquid separator was included
429 to prepare the digestate for the filtration steps. Mass balance to the solids is given as guidance
430 only since these may vary substantially depending on the feed stream. The solid-liquid
431 separator was considered to be able to separate around 85 % of the solids while 80 % of the
432 process flow would feed to the filtration units and consist mainly of solids with a particle size
433 below 1 µm at a range of 1-3 % total solids. A MF unit features a low pH tolerant membrane,
434 such as a ceramic membrane with a pore size of 0.2 µm. Around 125 LMH of virtually
435 sterilised permeate, i.e. absence of bacteria and virus, is adjusted in-line to pH 7 which
436 maximises the N/P separation using the NF system (Table 4). From Table 3 and Figure 6, the
437 NF operates at a 45-65 LMH with a separation efficiency of 50 % NH₃-N and nearly 100 %
438 PO₄-P retention. Further separation of NH₃-N is possible by DF, however these costs are
439 considered separately. From Figure 6, a total of four NF batch cycles are required for a
440 separation of 94.2 % NH₃-N as permeate and 98.9 % PO₄-P as retentate fractions.

441 Project evaluations can be very extensive, however for the purpose of nutrient extraction and
442 fractionation, simple estimates on equipment and operational requirements were carried
443 out (Table 5). Guideline prices for equipment were obtained from Axium Process Ltd

446 40 L/day, with an estimated bulk cost of \$ 100/ton (98 % H₂SO₄ from Guangzhou Baochu
447 Chemical Co., Ltd (China) and bulk 99% sodium hydroxide from Chengdu Hengyi Chemical
448 Industry Co., Ltd (China) as in November 2014). Finally, costs related with power usage were
449 estimated considering the pumping requirement based on flow and pressure (Fristam Pumpen
450 KG (GmbH & Co.), centrifugal pumps and multistage centrifugal pumps): 2.5 kW for solid-
451 liquid separator, 1.5 kW for MF and 5 kW for NF. The solid-liquid separator was estimated to
452 have a throughput of 2 m³/h giving a total of 5 hours/day operation and a daily power
453 consumption of 12.5 kWh. Using a 9 m² MF membrane, the throughput for a stabilised flux of
454 125 LMH would be 1.125 m³/h, with a total operating time of 5.33 hours/day and a power
455 consumption of 8 kWh/day in order to achieve 6 m³ permeate. Finally, the NF unit fitted with
456 a 30 m² membrane would have a throughput of 1.35 m³/h for a stabilised flux of 45 LMH.
457 This would lead to a 2.22 hours/day operating time and a power consumption of 11.11
458 kWh/day. If DF strategies are employed, which improve the separation of NH₃-N from PO₄-
459 P, energy consumption during the operation of NF would increase to 44.44 kWh/day. A total
460 of 64.9 kWh/day, 9 m³/day water and 40 L/day of chemicals are needed to support such
461 nutrient extraction plant. Thus, the daily operational cost is \$23.93/day or \$2.40/m³ with a
462 total output of 15 m³ resulting from the NF separation when including DF strategies.
463 Table 6 highlights the operational costs from the initial solid-liquid separator to fractionate
464 the nutrients by means of NF. These include power, water and chemicals as estimated in
465 Table 5. Single processing by NF has an estimated cost of \$1.12/m³ and achieves
466 considerable separation of NH₃-N at a cost of \$0.70/kg NH₃-N obtained in the 3 m³ permeate.
467 On the other hand, the retentate obtained still contains relatively high amounts of NH₃-N.
468 After the three DF steps, the remaining NH₃-N is separated at a cost of \$2.40/m³ or \$5.23/kg

471 permeate and 99 % of the $\text{PO}_4\text{-P}$ as retentate (Figure 6), can be accounted as the cost of
472 processing 3 m^3 by NF plus the 12 m^3 by NF-DF. Thus for a total amount of $8.89 \text{ kg NH}_3\text{-N}$
473 fractionated, the final cost is $\$3.62/\text{kg}$.

474 The value of any fractions obtained via membrane filtration is dependent upon the
475 concentration of the nutrients in the aqueous phase of the manure digestate. Such
476 concentration is highly variable and is certain to influence the feasibility of recovering
477 nutrients from manure digestate. Table 7 demonstrates how the composition in terms of
478 nutrients of the manure digestate affects the overall cost.

479 The estimations given above are taken as guidance only particularly since other costs such as
480 person-hours, taxes, maintenance, utilities, storage and transportation have not been
481 accounted for. In addition, savings may be achieved when scaling up and optimising such
482 processes. Nonetheless, the plan designed (Figure 7 and Table 5) to give 8 hour/day operation
483 using membrane filtration systems, NF permeates are produced at a cost of $\$1.12/\text{m}^3$ and
484 $\$2.40/\text{m}^3$ for one NF step or three DF steps, respectively.

485 The design process considered here is very general and capable of processing any given
486 sludge. Some dairy manure farms already employ solid-liquid separations of the digestate as
487 a means to reduce nutrient load onto the land. In addition, the level of phosphorus recovered
488 from the dairy manure sludge used in this work was particularly low and thus the
489 acidification-neutralisation treatments are likely to be deemed redundant and not suitable as
490 an economically feasible source of phosphorus. In such case scenario, the capital costs would
491 be reduced by 10 % with a processing cost of $\$0.41/\text{m}^3$ for one NF step or $\$1.69/\text{m}^3$ when
492 including DF steps.

495 respectively. Average (anhydrous) ammonia retail prices reported by the US Department of
496 Agriculture on the 13th November 2014 was \$725.83/ton (or \$0.73/kg NH₃, see Table 7 for
497 comparison). In contrast, cost estimates presented for the manure digestate used in this work
498 demonstrate that the recovery of NH₃-N may compete in the open market particularly for
499 digestate streams containing above 1.5 g NH₃-N/L. Considering the environmental impact of
500 producing NH₃ and the ever rising cost of energy, the recovery and recycling of NH₃ from
501 wastewater sources may become a viable option in the near future. Possible applications
502 include integration with other technologies such as reverse osmosis for concentration of the
503 dilute streams and consequent purification of water, air stripping of NH₃, hydroponics and
504 cultivation of microalgae.

505

506 **5. Conclusions**

507 The extraction and separation of nutrients from dairy manure digestate was demonstrated to
508 be possible by means of membrane filtration. pH was demonstrated to be instrumental in
509 maximizing the effective separation of nitrogen from phosphorus. Higher permeate
510 throughput was possible at pH 11, nonetheless separation of nitrogen from phosphorus was at
511 all times higher at pH 7 with 97-98% rejection of phosphorus and 5-23 % of ammonia.
512 Quantitative separation of nutrients was possible using DF, nonetheless processing costs were
513 substantially higher and led to dilute nitrogen fractions. The process economics highlighted
514 that the sustainable recovery of nutrients from dairy manure digestate is viable, however this
515 certainly depends on the concentration of the nutrients and on the process design adopted.
516 The use of chemicals to adjust pH was found to be costly and determinant in the process
517 economics.

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524

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620 dependent electroosmotic flow. *Journal of Membrane Science* 225(1–2), 155-164.
- 621
- 622

Table 1: Characteristics of the NF276 manufactured by Dow Liquid Separations

Surface material	Polyamide
Support material	Polysulphone
pH range (continuous operation)	3-11
Maximum operating pressure	41 bar
Maximum pressure drop	1.0 bar
Maximum operating temperature	45 °C
Stabilised salt rejection	
CaCl ₂	40-60 %
MgSO ₄	97 %
Clean water flux (López-Muñoz <i>et al.</i> 2009, Semião and Schäfer 2011)	13-18 LMH.bar
Pore size (diameter) (Oatley <i>et al.</i> 2012)	0.86 nm
MWCO (Da) (Pontié <i>et al.</i> 2008)	120

Element	Concentration (mg/L)
NH₃-N	1572.8
PO₄-P	61.01
Cu	44.5
Mn	27.5
Zn	58.0
Ca	744.0
Si	118.0
Mg	172.0
K	450.0
Cr	53.4
Fe	29.0

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pH	Flux (LMH)		% Rejection				P/N selectivity	
			NH ₃ -N		PO ₄ -P			
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
3.0	50.3	22.2	30.3	1.0	84.0	86.6	0.64	0.99
7.3	64.6	45.0	23.9	4.6	97.9	96.7	0.76	0.95
11.0	149.7	125.4	33.6	30.1	97.2	96.4	0.65	0.69

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Ion	Rejection (%)		
	pH 3	pH 7	pH 11
H₂PO₄⁻	83.4	96.8	-
HPO₄²⁻	-		95.3
NH₃	-	-	25.9
NH₄⁺	8.6	7.2	-
K⁺	63.3	61.0	50.2
Ca²⁺	66.2	56.7	33.2
Cu²⁺	47.3	46.7	46.3
Fe²⁺	75.9	70.6	69.0
Mg²⁺	26.8	26.3	24.6
Mn²⁺	77.0	74.7	73.2
Zn²⁺	83.9	80.9	77.7
Cr³⁺	74.3	72.3	71.0

prices obtained from Axium Process Ltd (Swansea, Wales, UK). ****Considers a 40 L/day of chemicals at a bulk cost of \$100/ton. \$0.142/kWh (UK prices from International Industrial Energy Prices. www.gov.uk) \$1.19/m³ water from Welsh Water rates for non-household.

	Quantity	Costs (\$)
Solid liquid separation		
Conditioning tank* (15 m ³)	1	6,000
Separator** (2.5 kW, 10 m ³ /day or 2 m ³ /h)	1	5,000
Nutrient extraction from the digestate		
MF, 9 m ² , 1.5 bar** (1.5 kW, 8 m ³ /day or 1 m ³ /h)	1	30,000
Nutrient fractionation		
NF unit, 30 m ² , 20 bar** (5 kW, 6 m ³ /d or 0.8 m ³ /h)	1	60,000
Operation		
Chemicals, L/day (acid and alkali***)	40	4
Energy, kWh/day	64.9	9.22
Water, m ³ /day (150 % of NF feed)	9	10.7

three consecutive DF steps, n.d. – not determined. *Cost per m³ is given as $\frac{\Sigma \text{Daily cost}}{\text{Input volume}}$.

**Accounts for 3 m³ from retentate of the previous NF step and a total of 9 m³ of water.

	Input volume (m ³)	Output volume (m ³)	Time of operation (h)	Energy (kWh)	Σ Daily cost (\$)	Σ Cost* (\$/m ³)	Nutrients extracted (kg)		
							NH ₃ -N	PO ₄ -P	
Separator	10	8	5.00	12.50	3.77	0.38	n.d.	n.d.	
MF	8	6	5.33	8.00	4.91	0.52	9.44	3.66	
NF	Ret.	6	3	2.22	11.11	8.49	1.12	4.68	3.65
	Perm.		3					4.76	0.02
NF-DF3	Ret.	12**	3	6.67	33.33	23.93	2.40	0.55	3.61
	Perm.		9					4.13	0.06

Table 6 using \$1.115/m³ for the NF and \$2.402/m³ for the NF-DF3. NF – one fractionation step using NF. NF-3DF – three DF steps subsequent to initial NF step.

Sludge composition		NF	NF-3DF	
NH ₃ -N (g/m ³)	PO ₄ -P (g/m ³)	\$/kg NH ₃ -N	\$/kg NH ₃ -N	\$/kg PO ₄ -P
250	70	4.43	32.91	17.42
400	150	2.77	20.57	8.13
750	300	1.48	10.97	4.07
1000	400	1.11	8.23	3.05
1250	500	0.89	6.58	2.44
1500	600	0.74	5.49	2.03
2000	750	0.55	4.11	1.63

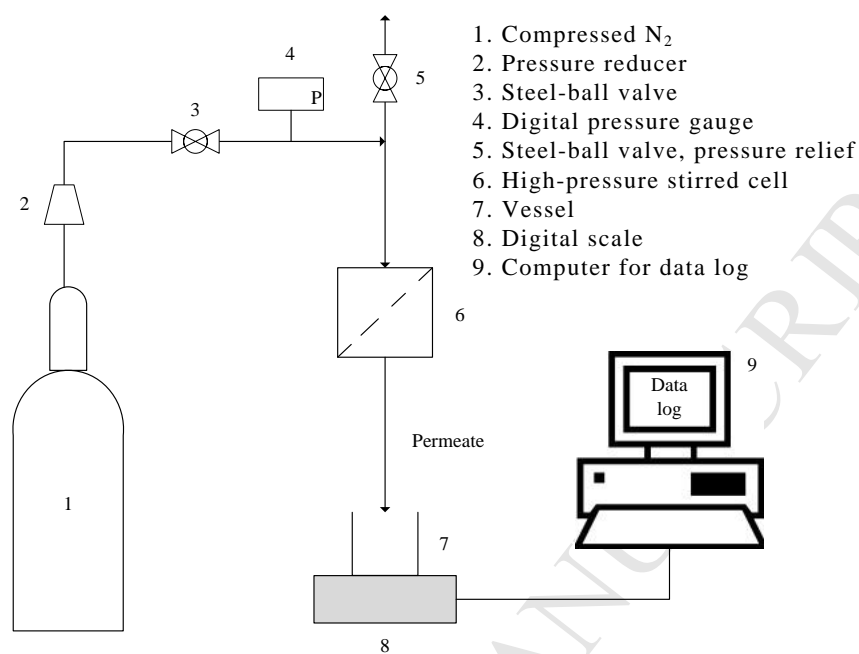


Figure 1. Experimental setup for the fractionation of DMDL by nanofiltration

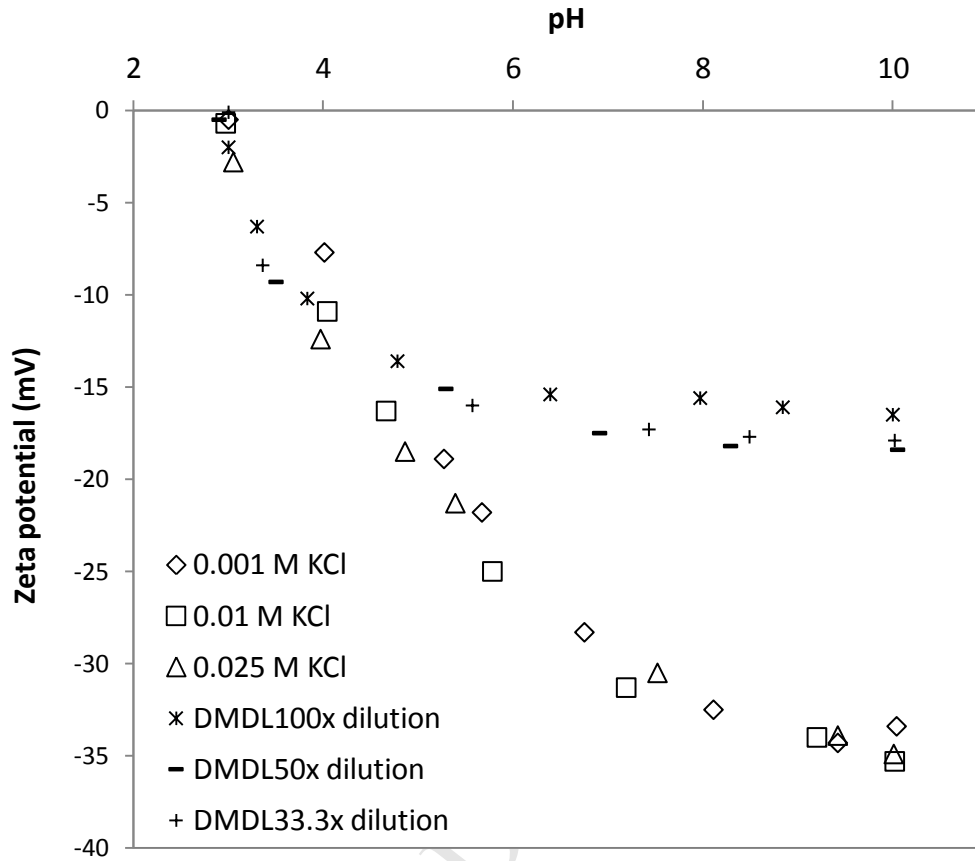


Figure 2. Zeta potential of the NF270 membrane in solutions of KCl salt and DMDL under different conditions of pH and concentration.

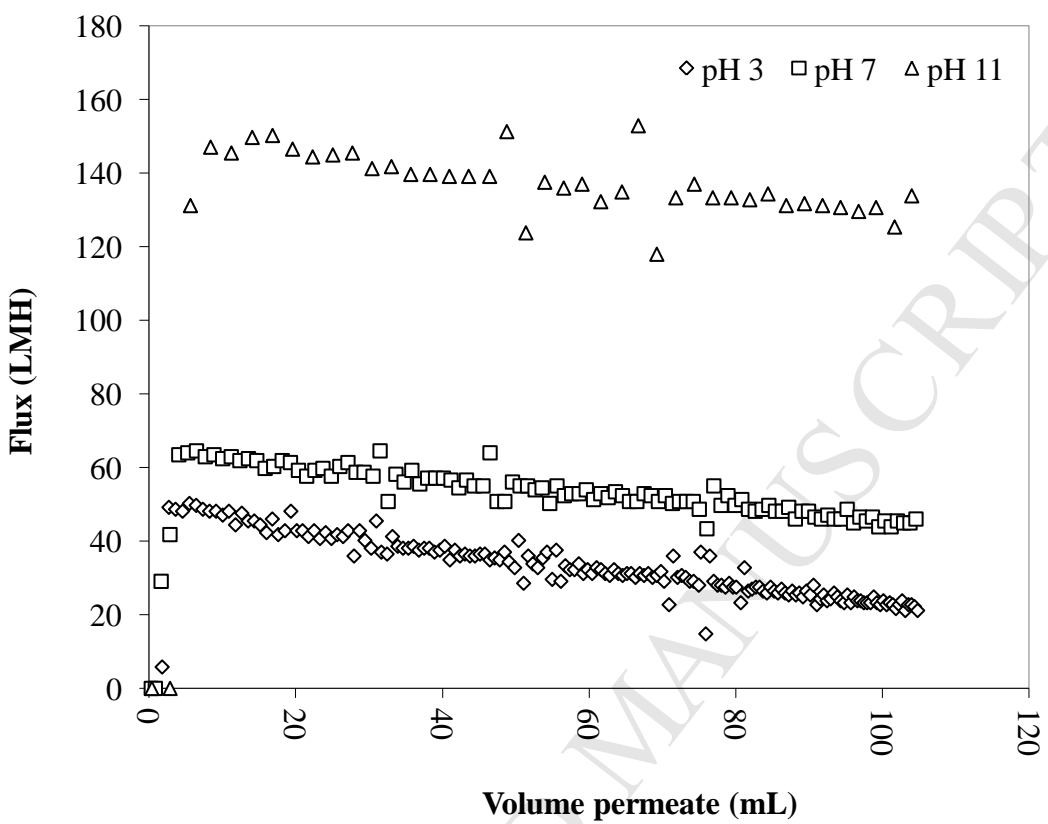


Figure 3. Influence of the feed solution pH on permeate flux at 20 bar.

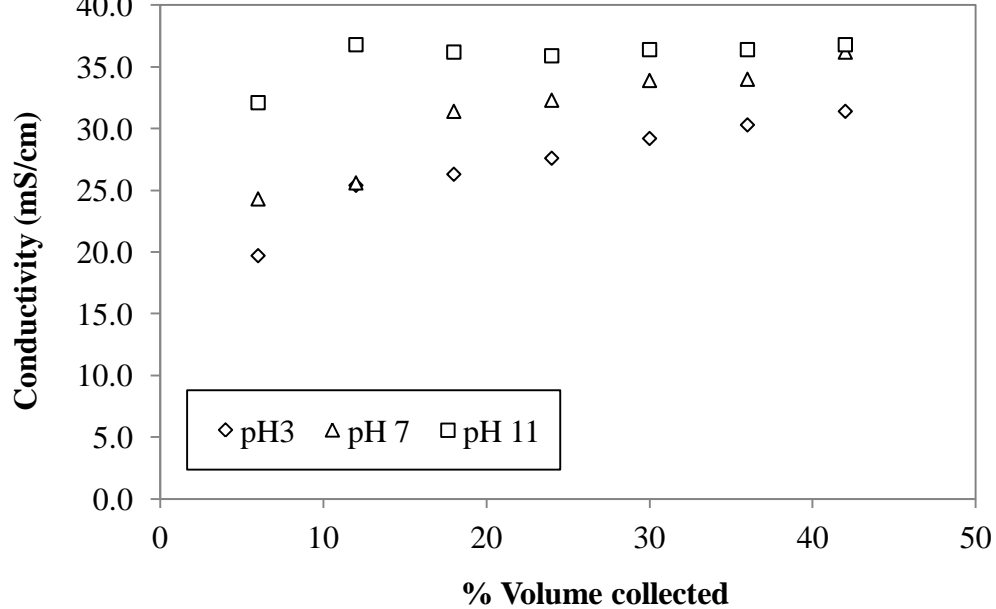


Figure 4. Influence of pH on the conductivity of the permeate during the nanofiltration of DMDL.

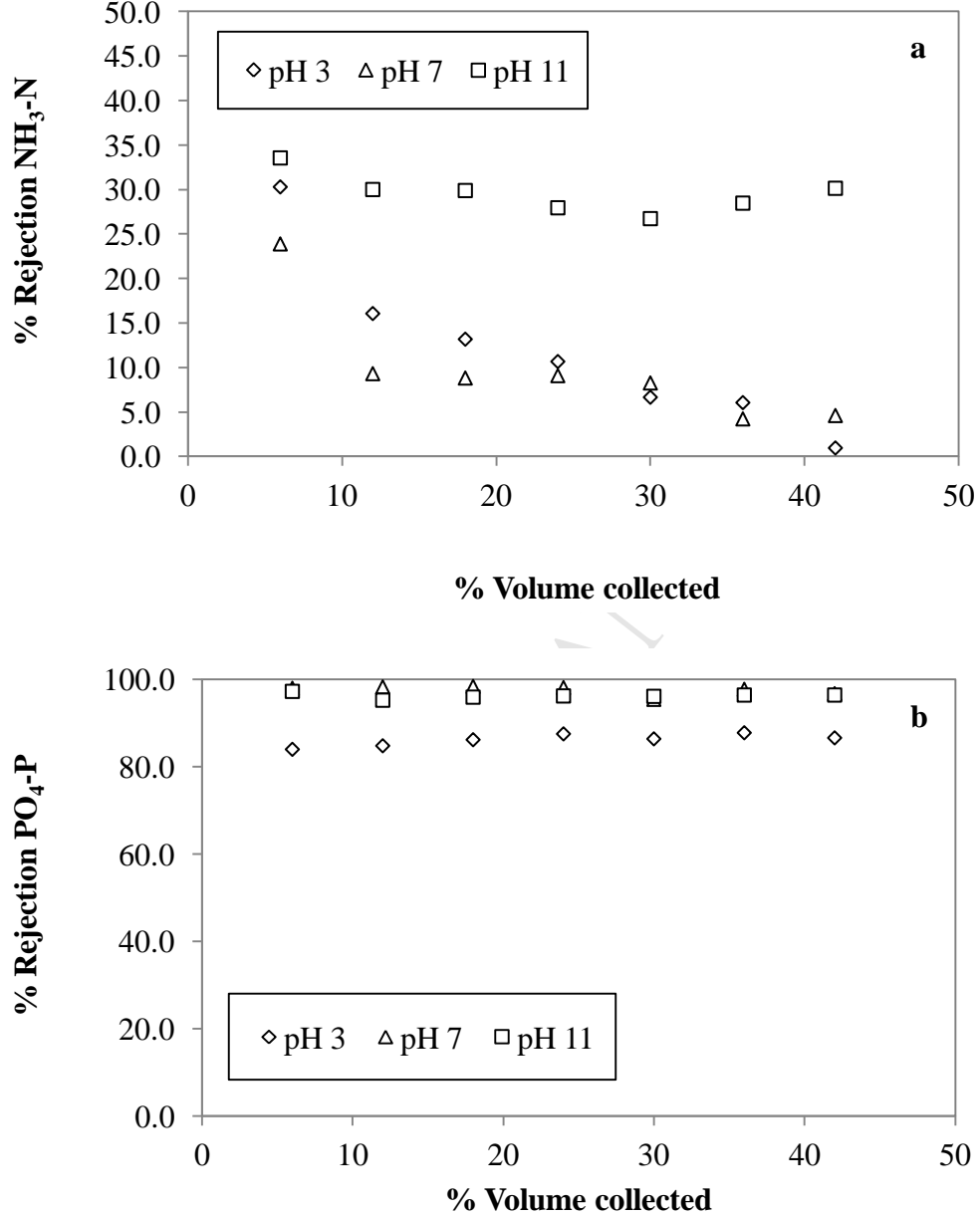


Figure 5. Influence of pH on the rejection of (a) NH₃-N and (b) PO₄-P during NF of DMDL with NF270 at 20 bar.

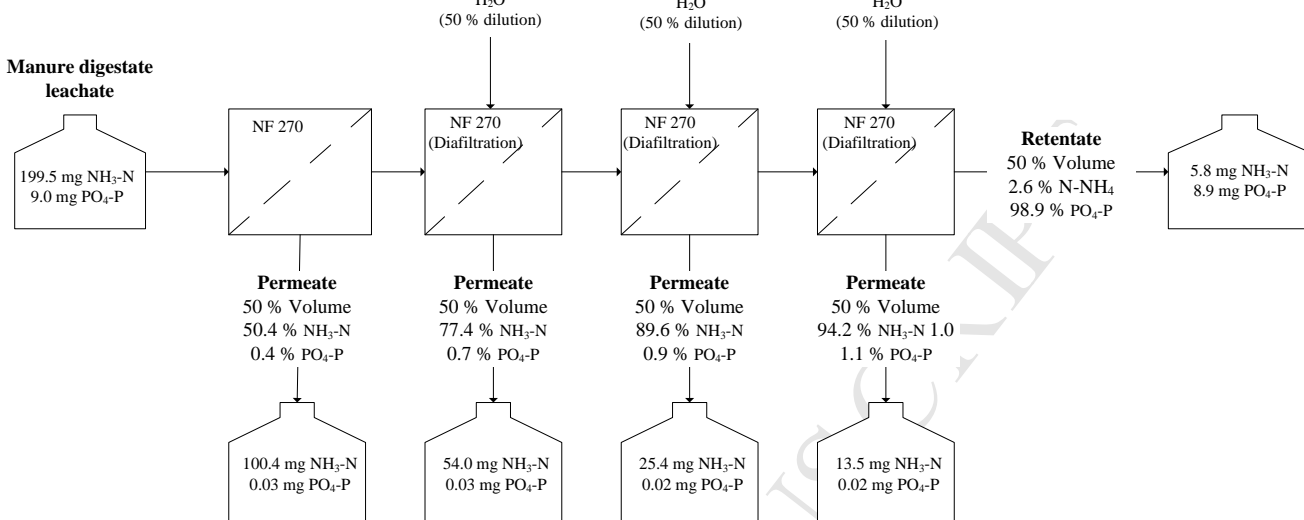


Figure 6. Further fractionation of nutrients from DMDL by consecutive filtration and DF steps using NF270 for high separation of NH₃-N and PO₄-P. Feed solutions was 130 mL of DMDL at pH 7.

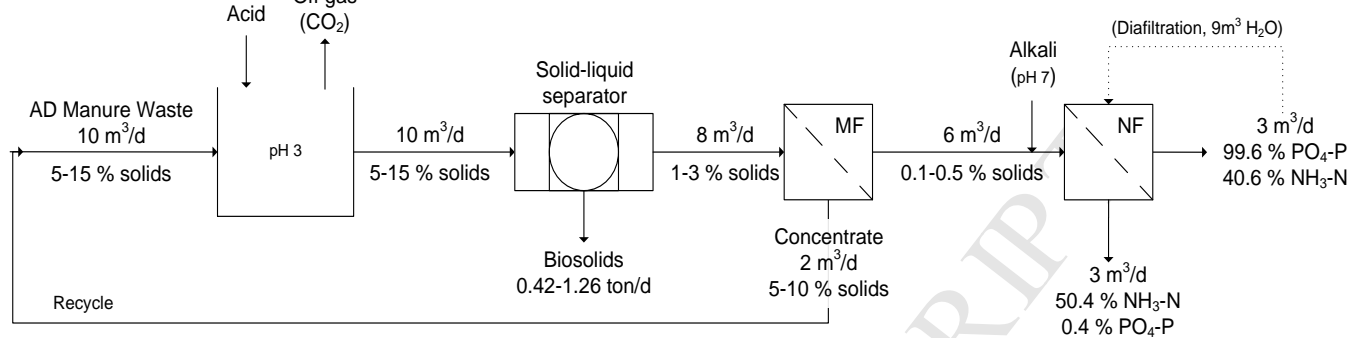


Figure 7. Process flow diagram for the extraction and fractionation of nutrients from dairy manure digestate using membrane filtration technology.

- NF270 membrane was used for the fractionation of nutrients from manure digestate.
- Membrane flux was highest at pH 11 but nutrient separation was more effective at pH 7.
 - P was mostly retained however the permeation of N was highly dependent on the pH.
 - 94.2 % of N was obtained as a series of permeates by DF strategies.
 - Nutrient recovery may be economically feasible under certain conditions.

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