

1 **Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration**
2 **of natural zeolites and hollow fibre membrane contactors**

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17 **ABSTRACT**

18 The integration of up-concentration processes to increase the efficiency of primary sedimentation,
19 as a solution to achieve energy neutral wastewater treatment plants, requires further post-treatment
20 due to the missing ammonium removal stage. This study evaluated the use of zeolites as a post-
21 treatment step, an alternative to the biological removal process. A natural granular clinoptilolite
22 zeolite was evaluated as a sorbent media to remove low levels (up to 100 mg-N/L) of ammonium
23 from treated wastewater using batch and fixed bed columns. After being activated to the Na-form
24 (Z-Na), the granular zeolite shown an ammonium exchange capacity of 29 ± 0.8 mg N-NH₄⁺/g in
25 single ammonium solutions and 23 ± 0.8 mg N-NH₄⁺/g in treated wastewater simulating up-

26 concentration effluent at pH=8. The equilibrium removal data were well described by the Langmuir
27 isotherm. The ammonium adsorption into zeolites is a very fast process when compared with
28 polymeric materials (zeolite particle diffusion coefficient around 3×10^{-12} m²/s). Column experiments
29 with solutions containing 100 mg N-NH₄⁺/L provide effective sorption and elution rates with
30 concentration factors between 20 and 30 in consecutive operation cycles. The loaded zeolite was
31 regenerated using 2 g NaOH/L solution and the rich ammonium/ammonia concentrates 2-3 g/L in
32 NaOH were used in a liquid-liquid membrane contactor system in a closed-loop configuration with
33 nitric and phosphoric acid as stripping solutions. The ammonia recovery ratio exceeded 98%.
34 Ammonia nitrate and di-ammonium phosphate concentrated solutions reached up to 2-5 % wt. of N.
35
36 **Keywords:** ammonia valorization; ion-exchange; natural clinoptilolite; liquid-liquid membrane
37 contactor; nitric acid; phosphoric acid; liquid fertilizers.

38

39 1. INTRODUCTION

40 The most common technology used in urban wastewater treatment is based on the conventional
41 activated sludge (CAS) process, which uses large amounts of energy for aeration and loses the
42 potential energy content of the organic load. Recently, it has been estimated that wastewaters
43 contains more chemical energy (as organic pollution load) than is needed for its treatment using
44 CAS. However, the low organic content (1 to 2 g/L) is the main barrier to overcome in order to use
45 this energy. Indeed, the energy balance of centralized sewage treatment can be improved by up-
46 concentrating sewage to achieve energy positive wastewater treatment plants, thus different pre-
47 concentration steps have been proposed (Verstraete et al., 2009; Jenicek et al., 2012; Meerburg et
48 al., 2015). In the implementation of up-concentration techniques (e.g., bio-flocculation) a high-load
49 organic stream is generated thus promoting the bio-methane production enhancement (Meerburg
50 et al., 2015). This solution increases the efficiency of primary sedimentation, eliminating the

51 chemical coagulant demand by recirculation of sewage sludge to the primary settler. However its
52 implementation as a mainstream sewage treatment process requires further post-treatment, due to
53 the missing ammonium removal approach and the relatively lower effluent quality. Most of the post-
54 treatment solutions for the novel up-concentration processes are focused on autotrophic nitrogen
55 removal (Lotti et al., 2015; Wett et al., 2015) or on membrane processes to ensure effluent
56 discharged standards (Diamantis et al., 2014), thus, the possibility to introduce ammonium recovery
57 solutions is a recently postulated alternative that needs further development (Gali et al., 2014).

58 Nitrogen is an essential nutrient for all living forms, however, an excessive growth of algae and the
59 consequently depletion of the dissolved oxygen is an effect of the nutrient overloading in surface
60 water receiving bodies (Blaas and Kroeze 2016). Therefore, the removal of ammonium from
61 wastewater to avoid the consequences of eutrophication processes has now become a challenge.
62 In order to reach the required low levels of N-NH_4^+ in the discharged effluents, which can be as low
63 as 1 mg NH_4^+/L (Salomon et al., 2016), a nitrogen treatment step is essential as part of the
64 wastewater treatment process. Moreover, nitrogen is a key component for fertilizer production and
65 indeed, it is critical to agricultural uses.

66 Nitrogen removal is commonly achieved by means of a biological nitrification–denitrification
67 process, where ammonium is transformed to nitrogen gas (Zhang et al., 2011). In addition to
68 incoming wastewaters, recycled streams within the WWTPs may also contribute to the nitrogen
69 load applied to the biological nitrogen removal process. Side streams arising from dewatering of
70 digested sludge (typically 500–1000 mg NH_4^+/L) are recirculated to the water line, increasing the
71 nitrogen loading on the WWTPs (Wirthensohn et al., 2009). Although representing only a small
72 fraction of the overall flow-rate (<2%), the high concentration of side streams could contribute up to
73 25% of the total nitrogen load. Anaerobic ammonium oxidation (Anammox) appears as a promising
74 alternative to the conventional process due to the low energy consumption and the suppression of
75 the necessity of an external carbon source (typically methanol) to denitrify (Ali and Okabe 2015; Ma

76 et al., 2016). However, the Anammox technology still present relevant limitations such as long start-
77 up periods, strong sensitivity to operation conditions variation and a high susceptibility to reactor
78 threats (Jin et al., 2012; Tian et al., 2015). Additionally, it is expected that in the future these
79 biological processes may not be able to sustain the nitrogen removal ratios required to meet the
80 regulated discharge values. Moreover, ammonium is at present increasingly considered a resource,
81 and not only a compound that has to be removed from wastewater (Batstone et al., 2015).
82 Consequently, there has been a renewed interest to recover nutrients from waste streams as a
83 synergy of economic, energy and environmental considerations (Sareer et al., 2016).

84 Physicochemical methods have been widely used for the removal and recovery of ammonium
85 species from waste streams in a usable form to supplement existing ammonia production. Inorganic
86 cation exchange materials, such as zeolites are suitable for the selective removal of ammonium.
87 Zeolites provide a framework structure with micro- and meso-pores (Hedström, 2001) with better
88 performance than polymeric ion-exchange resins due their higher selectivity to ammonium ions in
89 the presence of common competing cations (e.g., sodium, potassium, calcium and magnesium)
90 (Bashir et al., 2010). Both, natural and synthetic zeolites have been widely evaluated for
91 ammonium removal due to its high cation exchange capacity (Thornton et al., 2007a) and they have
92 been identified as suitable sorbents for wastewaters taking benefit of their properties (e.g.,
93 mechanical and thermal, cation-exchange capacity, easy operation and maintenance, low
94 treatment costs, high selectivity and the release of non-toxic exchangeable cations (K^+ , Na^+ , Ca^{2+}
95 and Mg^{2+}) (Millar et al., 2016; Thornton et al., 2007b; Jorgensen and Weatherley 2003).

96 Regeneration of loaded ammonium zeolites generates rich ammonium/ammonia concentrates (2-6
97 g NH_3/L) in NaCl, NaOH or NaOH/NaCl solutions. As the ion exchange concentration step involves
98 pre-treatment for particulate matter removal by sand filters or membrane ultrafiltration, the ammonia
99 concentrates quality is suitable for the integration of hollow fibre liquid-liquid membrane contactors
100 (HFMCs) (Lauterböck et al., 2013) as separation and concentration step.

101 This process has been used as a polishing step to remove low levels of ammonia/ammonium from
102 industrial effluents (up to 200 mgNH₄⁺/L) (Hedström, 2001; Klaassen et al., 2008; Mandowara and
103 Bhattacharya 2011; Tan et al., 2006). HFMCs using polyvinylidene fluoride (PVDF) and
104 polypropylene (PP) have shown high ammonia removal efficiencies dependent on the feed pH and
105 independent on the feed ammonia concentration using strong acids as stripping phase (e.g.,
106 sulfuric and hydrochloric acids) (Ashrafizadeh and Khorasani 2010). Compared to conventional
107 scrubbers, liquid-liquid membrane contactors have a much larger specific surface area, thus foot-
108 print and capital costs are reduced (Licon et al., 2014; Mandowara and Bhattacharya 2011). The
109 aim of this study is to evaluate the integration of a natural zeolite for the selective extraction of
110 ammonium from treated wastewater simulating up-concentration effluents and the subsequent
111 ammonium concentration and purification step using hollow fibre membrane contactors by
112 producing NH₄NO₃ and (NH₄)₂(HPO₄) for potential use as a liquid fertilizer.

113

114 **2. MATERIALS AND METHODS**

115 **2.1 Modification of natural clinoptilolite (Z) zeolite to sodium form (Z-Na)**

116 A natural zeolite (Z) from Slovakian Republic (Zeocem Co) was used. Zeolites particles below 200
117 µm were used for batch experiments and 800 – 1200 µm particles were used for column
118 experiments. A dried zeolite sample (30 g) was treated with 250 mL of NaCl (6 g/L) under reflux
119 conditions for 4 hours in two consecutive cycles to obtain the sodium form (Z-Na).

120 **2.2 Equilibrium and kinetic evaluation of ammonium removal by using batch experiments**

121 *Ammonium sorption equilibrium:* Z-Na samples (0.2 g) were equilibrated with 15 mL of solutions
122 containing 25 mgN-NH₄⁺/L (with pH ranging from 2 to 11). Experiments were replicated with a
123 treated effluent from the Sant Feliu WWTP (Barcelona – Spain) at pH of 7.7. The average
124 composition of the treated wastewater samples used is shown in Table 1.

125 *Ammonium sorption kinetics*: 10 g of Z-Na were equilibrated in 1L of the Sant Feliu WWTP treated
 126 effluent (Table 1) at pH 7.7±0.4. Experiments were performed at room temperature (22±1 °C).
 127 Samples were collected at given times to quantify the ammonium concentration. Assays were
 128 performed in triplicate and reported data are average values.

129

	Na ⁺	Ca ²⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Al(III)	Fe _i (III)
Cationic species (mg/L)	260	130	35	41	39	0,12	0.06
	SO ₄ ²⁺	HPO ₄ ²⁻	NO ₃ ⁻	Cl ⁻			
Anionic species (mg/L)	95	12	47	541			

130

131 Table 1. Chemical composition of Sant Feliu WWTP (Barcelona, Spain) treated water used for
 132 equilibrium and kinetic studies.

133

134 **2.3 Ammonium removal by using column experiments**

135 Z-Na samples (800 – 1200 µm particles) were packed in a glass column (10 cm length and 1.5 cm
 136 inner diameter and). The feed composition was defined taking as reference the characterization of
 137 the treated effluent of a high rate activated sludge effluent. The test solution was pumped in
 138 counter-current through the column. Samples were collected from the outlet of the column by a
 139 fraction collector (Gilson FC204) at given time intervals. After column saturation, the loaded zeolite
 140 was washed with deionized water and then regenerated with a 2 g NaOH/L solution.

141

142 **2.4 Ammonium recovery as ammonium nitrate and di-ammonium phosphate using liquid- 143 liquid hollow fibre membrane contactors**

144 Feed NH₃/NaOH solutions simulating the composition of the zeolites regeneration concentrates
 145 were used. Also ammonia solutions obtained in the regeneration of ammonium loaded zeolite

146 columns (2 g/L NaOH and pH>12) were used. Stripping solutions were prepared from 98% (w/w)
147 H₃PO₄ or 65% (w/w) HNO₃. A Hollow Fibre Liquid-Liquid Contactor (HFLLC) module was used. The
148 propylene HFMC module used was a Liquid-Cel 2.5x8" Extra Flow X30HF from Membrane-
149 Charlotte (3M, USA). Two tanks, one for the NH₃/NaOH feed solution and other for phosphoric or
150 nitric acid stripping solution, were used.

151 Deionized water was passed through the module circuits to flush out solutions from previous
152 experiments. NH₃/NaOH feed solutions were pumped through the HFMC lumen side at different
153 flow rates, while the stripping acid solution was pumped in a counter current mode into the shell
154 side by means of two peristaltic pumps. The feed and stripping volumes were 20 and 2 L,
155 respectively. At given times, samples were taken from the feed circuit for pH and total ammonia
156 concentration analysis. The solution pH and the acid concentration were also monitored. The lumen
157 and shell flows were stopped and membrane pores stability was tested when finishing the
158 experiment. Tests were carried out at room temperature (22±1 °C).

159

160 **2.5 Analytical methodologies**

161 Ammonium/ammonia analyses were carried-out by Ion-selective electrode method (4500-NH₃ D)
162 and ionic species concentration were determined by Ionic Chromatograph (Dionex ICS-1100 and
163 ICS-1000). The non-purgeable organic carbon (NPOC), total carbon (TC), total organic carbon
164 (TOC), inorganic carbon (IC) and total nitrogen (TN) were determined in an organic carbon
165 analyser (Shimadzu, TOC-V_{CPH}). Finally, trace species analysis of treated effluents was carried out
166 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

167

168 **2.6 Physicochemical characterization of sodium zeolites (Z-Na)**

169 Zeolite samples from sorption and desorption trials were washed with deionized water and then
170 oven-dried at 60°C for analysis. The chemical composition and morphology were determined by a

171 Field Emission Scanning Electron Microscope (JEOL JSM-7001F) coupled to an Energy Dispersive
172 Spectroscopy system (Oxford Instruments X-Max). The infrared absorption spectra (4000 – 550 cm⁻¹)
173 were recorded with a Fourier Transform FTIR 4100 (Jasco) spectrometer. The N₂(g) adsorption
174 method was used to measure the zeolites specific surface area (Micrometrics analyser). A powder
175 X-ray Diffractometer (D8 Advance A25 Bruker) was used for X-ray diffraction (XRD)
176 characterization. Measurements were replicated three times for each sample.
177 Samples of Z-Na zeolite were equilibrated in three different ionic strengths (25 mL of deionized
178 water; 0.01, 0.05 and 0.1 M NaCl) at 21±1°C. The pH drift method was used for point of zero
179 charge (PZC) determination in the range of pH 2 to 11 (Guaya et al., 2015a). Experiments were
180 carried out in triplicate and average values are reported.

181

182 **2.7 Data treatment methodologies: ammonium extraction equilibrium and kinetic evaluation** 183 **and ammonia transport in hollow fiber liquid contactors.**

184 The extraction of ammonium (q_e) was calculated by Eq.1.

$$185 \quad q_e = (C_o - C_e) \times \frac{v}{w} \quad (1)$$

186 where C_o (mg/L) and C_e (mg/L) are the total initial and the equilibrium concentrations, respectively;
187 v (L) is the solution volume, and w (g) is the zeolite mass.

188 The ammonium sorption was described by using the Langmuir isotherm (Eq. 2).

$$189 \quad q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)$$

190 where q_m (mg/g) is the maximum ammonium sorption capacity and K_L (L/mg) is the Langmuir
191 equilibrium constant.

192 Fractional attainment of equilibrium values ($X(t)$) were calculated by using Eq. 3:

193
$$X(t) = \frac{q_t}{q_e} \tag{3}$$

194 where q_t and q_e are zeolite ammonium loadings at time t and at equilibrium (mg/g), respectively.

195 The Shell Progressive Model (SPM) was used to describe the ammonium extraction kinetics (Liberti
 196 et al., 1986; Schmuckler and Golstein 1981). The extraction process involves diffusion of
 197 ammonium from the solution to the zeolite phase through a number of resistances. Ammonium ions
 198 originally in solution must diffuse across the fluid film surrounding the zeolite particle, transfer
 199 across the zeolite interface, diffuse into the zeolite particle and possibly react with the zeolite
 200 charged sites. The ammonium extraction rate controlling the different steps on the Na-zeolite
 201 particles leads to Equations 4 to 6:

202 a) Liquid film diffusion control:
$$X(t) = \frac{3C_{N(s)}K_F}{a_s C_{N(z)}} t \tag{4}$$

203 b) Particle diffusion control:
$$\left[3 - 3(1 - X(t))^{\frac{2}{3}} - 2X(t) \right] = \frac{6D_e C_{N(a)}}{a_s^2 C_{N(z)}} t \tag{5}$$

204 c) Ion-exchange control:
$$\left[1 - (1 - X(t))^{1/3} \right] = \frac{K_s C_{N(s)}}{r} t \tag{6}$$

205 where D_e is the ammonium diffusion coefficient in the Na-zeolite(m²/s); r is the Z-Na radius (m);
 206 $C_{N(s)}$ and $C_{N(z)}$ are the ammonium concentrations in solution and in the zeolite unreacted core,
 207 respectively (mg/L); a_s is the ion exchange coefficient, and k_s (m²/s) is the ion-exchange reaction
 208 constant.

209 Extraction kinetic data were analysed graphically by using the fractional attainment of equilibrium
 210 equations ($F(X) = f(t)$) (Eq. 4-6) and the kinetic parameters were estimated by regression analysis.

211 3. RESULTS AND DISCUSSION

212 3.1 Ammonium removal capacity of the sodium-zeolite: equilibrium characterization

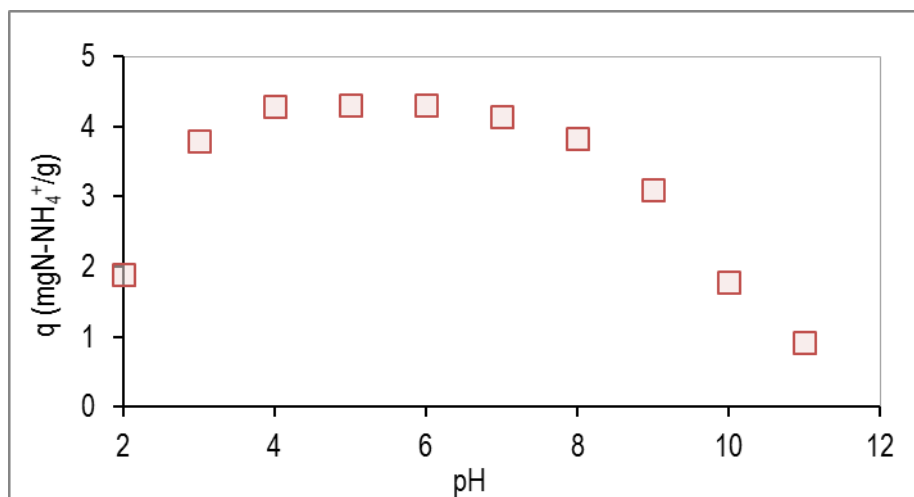
213 Chemical composition of tested zeolite sample (wt %) is shown in Table 2. EDX analyses of natural
 214 (Z) and the zeolite in the sodium form (Z-Na) revealed the presence of Al, Si, O, Fe, Na, Mg, K and
 215 Ca as the main elements (Table 2). In raw zeolite, K and Ca are the principal exchangeable
 216 cations. The conversion into the Na form is an effective process as the Na increases up to 1.6%,
 217 while K and Ca content was reduced up to a 50%.

Element	Z	Z-Na
Si	29.4 ± 1.9	29.3 ± 1.8
O	56.9 ± 2.4	59.2 ± 1.7
Al	5.2 ± 0.2	5.4 ± 0.3
Fe	1.7 ± 0.3	0.8 ± 0.2
Na	0.3 ± 0.1	1.6 ± 0.3
K	3.0 ± 0.6	1.7 ± 0.4
Ca	2.0 ± 0.4	1.1 ± 0.2

218 Table 2. Chemical composition (wt. %) of zeolite samples: raw natural zeolite (Z) and sodium
 219 zeolite form (Z-Na).

220 Mineralogical analysis showed that clinoptilolite is the main mineral phase for both natural and
 221 sodium-activated zeolites and small percentages of quartz and albite were also detected. The
 222 zeolite specific surface area was slightly reduced from 20 ± 0.5 to 19 ± 0.5 m²/g after conversión to
 223 the sodium form as reported by Sprynskyy et al. (2005b) for a a natural zeolite (Transcarpathia
 224 clinoptilolite). FSEM showed crystal clusters with homogeneous crystal size distribution and
 225 characteristics plate-like crystals and large entries and cavities to the zeolite framework channels
 226 for both zeolites. The presence of small particles covering the surface and lamellar-like crystals in
 227 the activated sodium form confirms the partial surface modification of clinoptilolite.

228 The ammonium sorption capacity on Z-Na zeolite showed pH dependence in solutions of
229 ammonium with competing ions (Figure 1) simulating the expected conditions of treated domestic
230 wastewater effluent incorporating a high rate activated sludge stage (pH 7 to 8.5) and during
231 regeneration cycles (acid and basic pH values).
232



233
234

235 Figure 1. Effect of pH on ammonium removal for the sodium-zeolite form (Z-Na) using batch
236 experiments.

237

238 The ammonium/sodium exchange process reaches its maximum at the pH range between 4 and 6.
239 According to the zeolite acid - base properties with a pH_{PZC} of 4.9 ± 0.3 (Z-Na), repulsion of
240 ammonium ions with the surface protonated ion exchange sites was observed below the pH_{pzc}
241 (e.g., in the acid range from pH 2 to pH 3). Sprynskyy et al. (2005b) studied the effect of acidic
242 conditions (e.g., in hydrochloric acid) on a natural clinoptilolite. Na^+ , Ca^{2+} and K^+ were removed
243 from the zeolite by exchange with H^+ ions and subsequent zeolite analysis shown the destruction of
244 the clinoptilolite structure by mineral dissolution processes as demonstrated the presence of Al and
245 Si in solution.

246 Then, the maximum ammonium sorption capacity values were measured in the pH range of 4 to 7
247 and a progressive reduction of sorption capacity was observed at pH above 7 due to the decrease
248 of the NH_4^+ concentration and the conversion to the neutral form (NH_3) (Mackinnon et al., 2003).
249 Then, the acid-base equilibria play a major role and the ammonium sorption can be described by
250 the combination of two reactions:

251 i) ion-exchange with sodium ions (Eq. 7):



253 ii) acid-base equilibrium (Eq. 8):



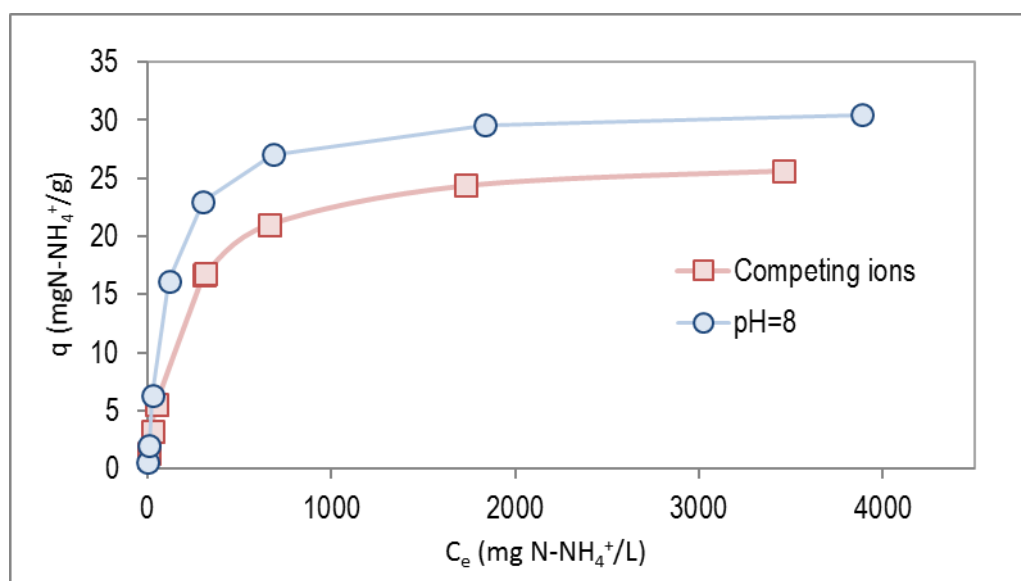
255 where Z- represents the ionogenic groups of the zeolite structure.

256 According to Eq. 8, ammonium sorption is pH-dependent and it stands that only ions can be
257 removed from solution by ion exchange with sodium ions. At pH 8 and below, ammonium is present
258 in the cationic form; therefore, these acidity conditions favour the removal process. Above pH 8 the
259 equilibrium shifts towards the NH_3 form and more basic conditions become increasingly less
260 favourable. Thorton et al. (2007b) described a reduction of ammonium capacity of mesolite from 49
261 mg N-NH_4^+ /g at pH 6-7 to 37 mg N-NH_4^+ /g at pH 8.3 and to 29 mg N-NH_4^+ /g at pH 10. This reduction
262 of ammonium removal is used to promote zeolite regeneration and the increase of pH above 11 by
263 using NaOH solutions is adequate to displace reaction 7 to the conversion to the sodium form.

264 The FTIR spectra shown peaks between 798 cm^{-1} and 547 cm^{-1} assigned to deformation vibration
265 modes of OH, Al-O-Si and Si-O-Si groups. A band at 1100 cm^{-1} is attributed to the stretching
266 vibration mode of Si-O groups and the band at 1630 cm^{-1} was assigned to the deformation
267 vibration mode of O-H groups of water molecules. Bands in the range from 3700 cm^{-1} to 3100 cm^{-1}
268 have been associated to the O-H groups of the zeolitic structure (Inglezakis et al., 2005). The small
269 differences in the spectra of both zeolites are consistent with the exchange between cations of the
270 same valence.

271 Ammonium sorption isotherms (in single ammonium solutions and in solutions simulating treated
 272 wastewater effluents) at constant pH of 8.0 ± 0.2 are shown in Figure 2. The Langmuir isotherm
 273 provided a good description of the ammonium sorption ($R^2 \geq 0.99$) at pH 8, where more than 95%
 274 of the total ammonium is present as NH_4^+ (e.g., 5% as NH_3). Results indicated that sorption
 275 process although mainly driven by an ion exchange, can be described by a solid with a
 276 homogeneous monolayer with ion-exchange of equal availability affinity. The maximum ammonium
 277 sorption capacity was 23.4 ± 0.8 mg N- NH_4^+ /g in single ammonium solutions, compared with
 278 18.7 ± 0.9 mg N- NH_4^+ /g for solutions simulating treated wastewater effluents. Higher values were
 279 reported by Guaya et al. (2015a and 2015b) working with solutions at pH range from 5 to 6, with
 280 more than 99% of the total ammonium present as NH_4^+ .

281



282

283

284 Figure 2. Ammonium loading isotherms on Z-Na zeolite in single ammonium solutions and in
 285 wastewater effluents containing competing cations at pH 8.

286

287 The ion-exchange selectivity of the exchange process is considered mainly affected by the ionic
 288 radius and the ionic charge. The Na^+ ion Stokes hydration ionic radius is higher than NH_4^+ ion

289 providing selectivity differences for the exchange of $\text{Na}^+/\text{NH}_4^+$ that ensure high ammonium removal
290 efficiency (Moussavi et al., 2011; Sprynskyy, 2005a).

291 Measured ammonium sorption capacities are comparable to those reported by Thornton et al.
292 (2007a), using mesolite for the removal of ammonium from digested sludge dewatering liquors
293 (e.g., 200–700 $\text{mgN-NH}_4^+/\text{L}$) with values between 27–36 $\text{mgN-NH}_4^+/\text{g}$. Similar, capacity was
294 reported for a large number of studies using clinoptilolite rich natural zeolites. Farkas et al. (2005),
295 using a Croatian clinoptilolite measured total maximum capacity of 7 $\text{mgN-NH}_4^+/\text{g}$ and an
296 operational capacity at breakthrough of 4 $\text{mgN-NH}_4^+/\text{g}$. Guaya et al. (2015a and 2015b) reported
297 capacities of 30 $\text{mgN-NH}_4^+/\text{g}$ also for metal hydrated oxide modified clinoptilolite. Thornton et al.
298 (2007b) described higher operational capacities of 39 $\text{mgN-NH}_4^+/\text{g}$ of mesolite in experiments
299 carried out under optimal conditions (e.g., during the first operation cycles). Wang and Peng (2010),
300 in a comprehensive review on ammonium removal by natural zeolites, concluded that adsorption
301 capacity of clinoptilolite ranges between 2 and 30 mgNH_4^+/g . Some chemical pre-treatments of
302 clinoptilolite may increase its sorption capacity. The ion-exchange order for ammonium, alkali and
303 alkaline earth metals follows: $\text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$. However, other ionic species such as
304 transition metal ions and organic solutes could decrease ammonium sorption capacity due to
305 competitive sorption.

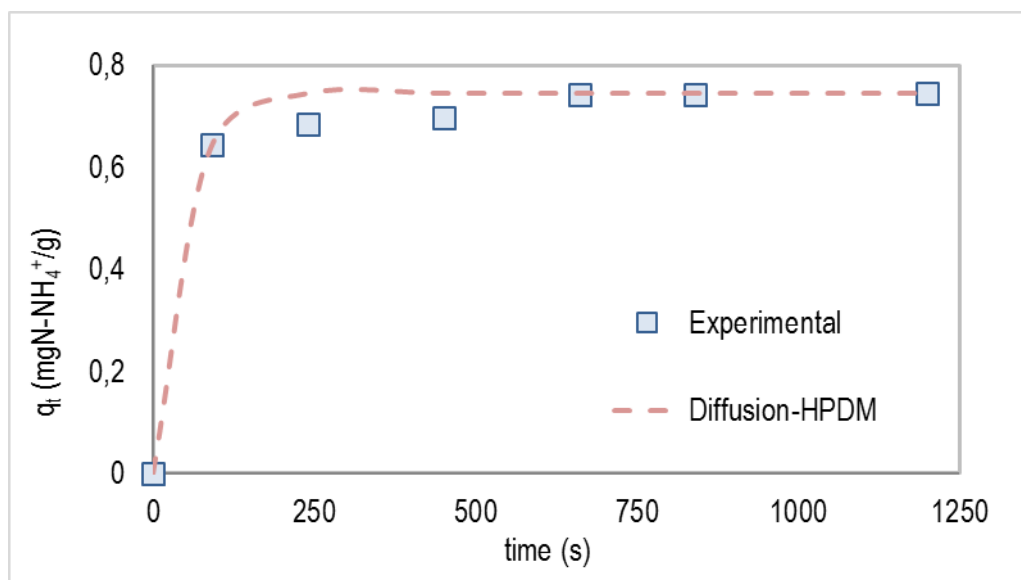
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307 **3.2 Ammonium sorption kinetics by Z-Na.**

308 Ammonium sorption of Z-Na zeolite (q_t) over time is shown in Figure 3. The ammonium sorption
309 rates are comparable with other natural and synthetic zeolites reaching the equilibrium in less than
310 10 minutes (Hedström, 2001; Inglezakis and Grigoropoulou 2001). These sorption rates are much
311 faster than the sorption kinetics of ammonium using polymeric ion-exchange resins. This behaviour
312 is attributed to the fact that the ion exchange reaction ($\text{NH}_4^+/\text{Na}^+$) is favoured due to the higher

313 affinity of ammonium ions to the negative sites than sodium ions as has been described by
314 Ashrafizadeh et al. (2008) using an Iranian natural clinoptilolite.

315



316

317

318 Figure 3. Variation of ammonium removal as a function of contact time for single ammonium
319 solutions at pH 8. Points represent experimental data and the trend line is the predicted values
320 assuming particle diffusion control for the Z-Na.

321 Analysis of the fractional equilibrium attainment functions ($F(X) = f(t)$) (Eqs. 4-6) indicated that
322 sorption rate control of ammonium ions is particle diffusion. A first stage of NH_4^+ diffusion from the
323 solution to the external zeolite surface is followed by a sorption stage along the zeolite internal
324 surface. The linear regression coefficients (R^2) values are closer to 1 for Eq. 5 considering particle
325 diffusion as rate determining step and the diffusion coefficients calculated ranged from 1.1 to
326 $3.4 \times 10^{-12} \text{ m}^2/\text{s}$. These values are consistent with the results reported for ammonium sorption on
327 natural clinoptilolite impregnated with metal hydrated oxides (Guaya et al., 2015a; 2015b) at low
328 initial ammonium concentrations and with diffusion coefficients determined on the removal of heavy
329 metals by natural zeolites (Farkas et al., 2005; Inglezakis and Grigoropoulou 2001). Measured

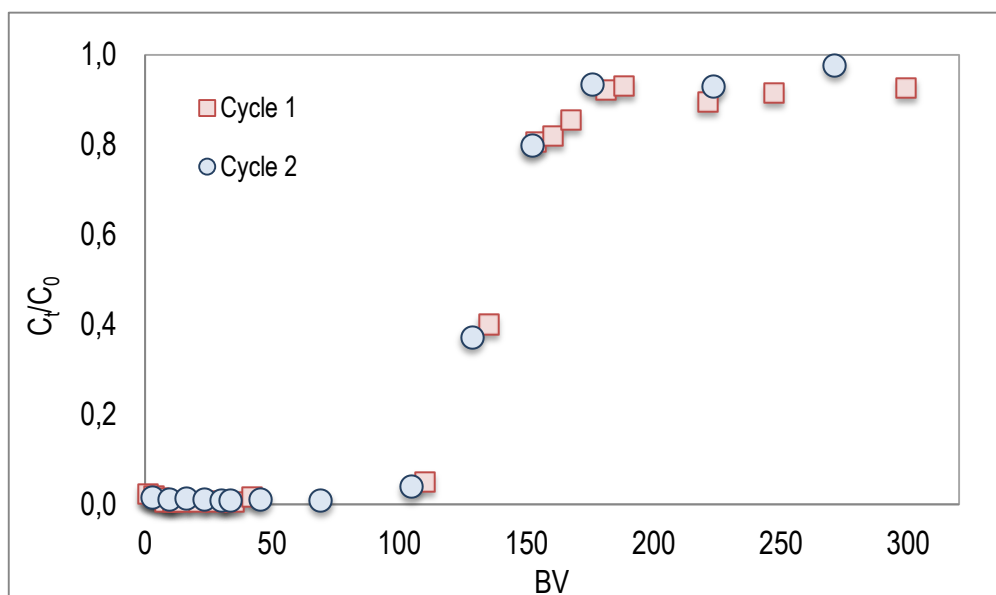
330 kinetic parameters were also comparable with synthetic powder zeolites produced from coal
331 combustion fly ash (Hermassi, 2016).

332

333 3.3 Removal of ammonium in fixed bed column tests

334 The ammonium breakthrough curves for two consecutive cycles are shown in Figure 4. The
335 ammonium sorption capacity at 120 BV was 21 mgN-NH₄⁺/g in the first cycle compared with 20
336 mgN-NH₄⁺/g in the second cycle. Dynamic ammonium sorption capacity is comparable with the
337 effect reported for other zeolites (Hedström, 2001; Inglezakis and Grigoropoulou 2001). More
338 limited capacity (below 2 mgN-NH₄⁺/g) was measured for the raw zeolite without being converted to
339 the sodium form (data not shown) and only when zeolites are regenerated by concentrated NaOH
340 solutions, the sorption capacity was improved in the following cycles when values of ca. 20 mgN-
341 NH₄⁺/g were reached.

342



343

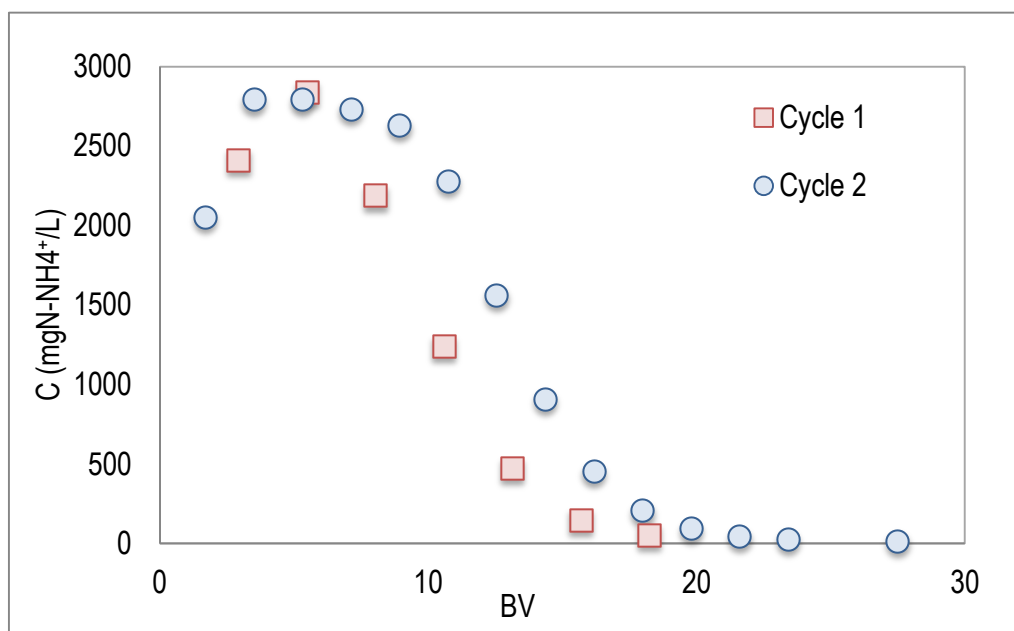
344 Figure 4. Breakthrough curves of ammonium sorption by the granular zeolite in the sodium form (Z-
345 Na). Treated solution contained 115±3 mgN-NH₄⁺/g pumped at a flow rate of 1.5 mL/min.

346

347 Sprynskyy et al. (2005b) studied NH_4^+ removal from synthetic solutions onto natural and pre-treated
348 forms of a natural clinoptilolite under dynamic conditions. Sodium ions were easily exchanged with
349 ammonium ions, however, the role of Ca^{2+} ions increased with zeolite saturation by NH_4^+ ions. The
350 maximum ammonium sorption capacity estimated under dynamic conditions was significantly
351 higher than that measured under static conditions. Thermal or chemical (e.g., acid, base and
352 sodium salts) pre-treatment of the raw zeolite confirmed the importance of the ion-exchange
353 mechanism. NaCl pre-treatments showed the most efficient improvement of ammonium removal
354 over other treatments.

355 Ammonium desorption from loaded Z-Na was performed using 0.05 NaOH solution, as shown in
356 Figure 5. The highest ammonium concentration achieved in the regeneration solution was 2900
357 mg-N/L. The 95% of the eluted ammonium was found at 3 BV representing an enrichment factor of
358 30.

359



360

361 Figure 5. Column desorption profile of ammonium from granular loaded Z-Na (breakthrough curves
362 of Figure 4) using 2 gNaOH/L.

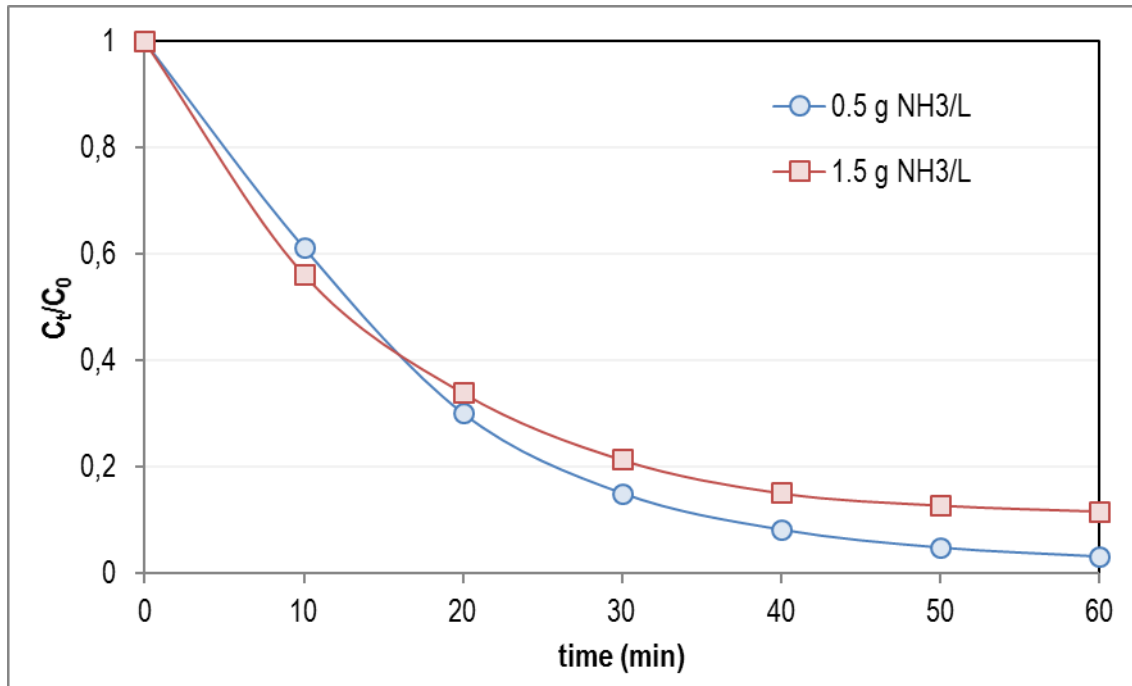
363 NaCl or NaOH solutions are the most commonly used regeneration solutions for loaded zeolites.
364 Rahmani et al. (2004) described constant regeneration ratios of 95–98% after three loading-
365 regeneration cycles of natural Chinese clinoptilolite, by using a solution of NaCl and without loss of
366 ammonium sorption capacity. Hlavay et al. (1982) also reported regeneration ratios of 98–99% of a
367 Chinese clinoptilolite using a 20 g/L NaCl solution at pH = 12.3. Malovanyy et al. (2011) evaluated
368 the concentration of ammonium from domestic WWTP mainstream before biological treatment with
369 an ion exchange process. The two-stage treatment line, referred as Ion Exchange assisted CANON
370 (IE-CANON) process showed that using strong-acid cation (SAC) resin and NaCl as regenerant
371 leads to the best results in terms of ammonium concentration and regeneration. However, it should
372 be noted that this study was performed using synthetic wastewater solutions and it is unknown if
373 the ammonium concentration step from real wastewater streams will proceed the same as when
374 synthetic wastewater is used since content of other ions and pH can influence the process.
375 Moreover, since not only ammonium but also other cations are concentrated, it is unknown if these
376 ions will not inhibit the biological process.

377

378 **3.4 Ammonium recovery from zeolites regeneration concentrates by using Hollow Fiber** 379 **Membrane Contactors (HFMC)**

380 The ammonium zeolite regeneration concentrates was used as input stream to a liquid-liquid
381 membrane contactor unit to recover and concentrate ammonium solutions. The influence of
382 operation parameters (flow rate, initial ammonia concentration and stripping acid concentration)
383 was evaluated using a closed-loop configuration. The reduction of the ammonia concentration ratio
384 (C_t/C_0) on the feed tank as a function of time for feed solutions of 0.5 and 1.5 gNH₃/L is shown in
385 Figure 6.

386

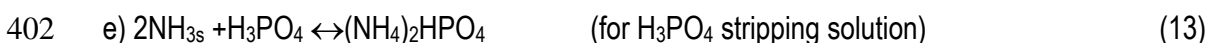
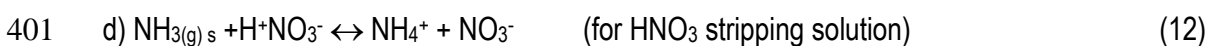


387

388 Figure 6. Variation of the ammonia concentration ratio (C_t/C_0) as a function of time for experiments
 389 at 1.2 g/L NaOH concentrates at flow rates of 9 and 11 cm³/s and using nitric acid (0.5%) as
 390 stripping solution.

391 The closed-loop set-up allowed ammonia recovery ratios higher than 98%, and ammonia residual
 392 concentration values below 150 mg/L, if the required free acid concentration in the stripping phase
 393 is maintained constant along the filtration experiment.

394 The ammonia mechanism transport from the feed stream (zeolites regeneration concentrates at pH
 395 11-12) in a hollow fibre membrane contactor involves the transfer from the feed to the stripping
 396 phase driven by the differences of ammonia partial pressure between both sides and conversion to
 397 ammonium nitrate and di-ammonium phosphate as described by Eq. 9-13:



403 where the subscript index f represents feed stream and s represents stripping stream.

404 Reactions 12 or 13, depending on the acid used as stripping solution, ensure the highest difference
405 in ammonia partial pressure between both sides of the membrane and thus provides the chemical
406 potential which drives the separation process.

407 The NH_3 transport process (Eqs. 9-12) is a very fast step and in less than 30 minutes more than
408 80% was removed. The ammonia flux decreases as membrane filtration time increases due to the
409 reduction in the ammonia concentration in the feed side, and accordingly the ammonia partial
410 pressure. The total ammonia removal efficiency was 85% for 1.5 g/L and 98% for 0.5 g/L within 60
411 min, respectively. Figure 6 shows the ammonia concentration ratio (C/C_0) decrease with a typical
412 exponential decay behaviour. In the first step of the removal process, the ammonia gas form
413 ($\text{NH}_{3(g)}$) diffuses from the bulk of the feed stream to the feed–membrane interface (Eq. 9). Then,
414 $\text{NH}_{3(g)}$ volatilizes through the feed–membrane interface, and diffuses across the air-filled pore of
415 the polypropylene membrane (Eqs.10-11). Finally, it reacts at the membrane-strip interface of the
416 shell side with phosphoric or nitric acid (Eqs. 12-13). This reaction is thermodynamically favoured
417 as it involves the neutralization of ammonia with a strong acid.

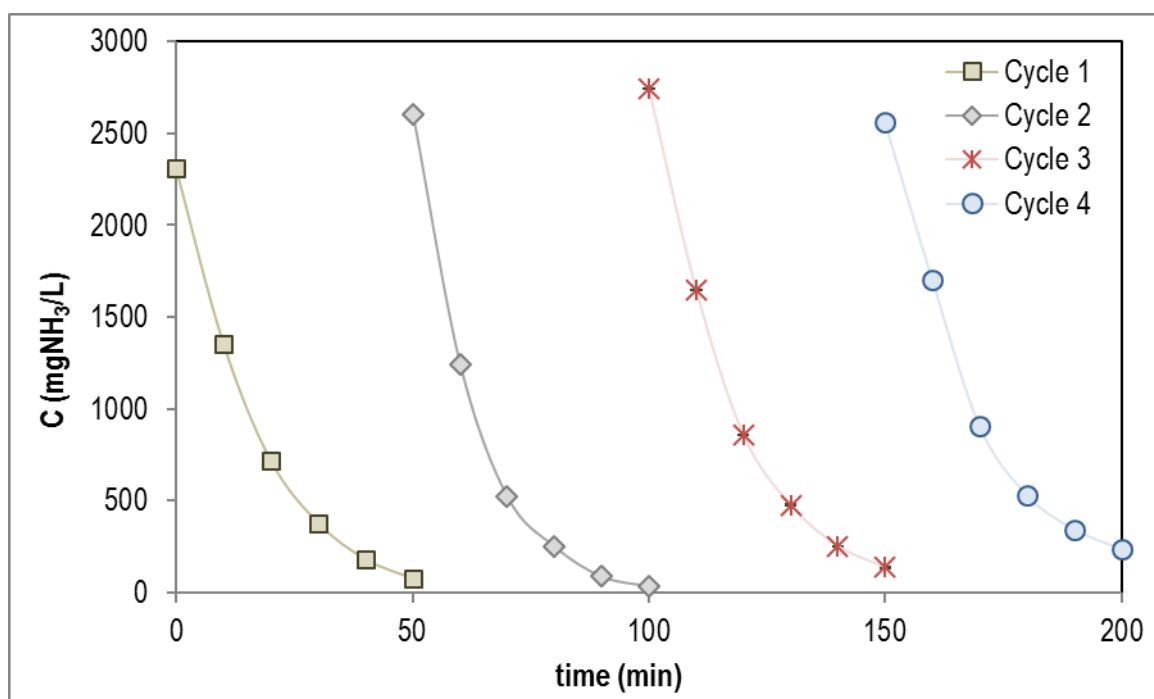
418 A critical point of the operational mode for hollow fiber membrane contactors is the presence of
419 $\text{NH}_{3(g)}$, which can traverse the pores in the polypropylene hydrophobic membrane. Consequently,
420 application of this HFMC technology for wastewater can only be feasible if the treated aqueous
421 stream is alkaline. In principle the pH should be above the pK_a ($\text{NH}_4^+/\text{NH}_3$)=9.3. Under basic
422 conditions (pH 11 to 12), where more than 99,9% of ammonium is present as NH_3 , mass transfer of
423 NH_{3f} is only controlled by the free acid concentration in the stripping side and controlled by the
424 neutralization reactions (Eqs.12, 13). Thus, free acid concentration in the stripping compartment is
425 the main driving force enhancing ammonia extraction from the feed solution.

426 The pH (12.2 ± 0.3) of the feed stream (data not shown) was kept constant along the experiment as
427 the buffer capacity of the background NaOH solution (1.2 g/L NaOH) is buffering any potential

428 change of pH due to the transfer of NH_3 from the feed to the stripping side. Measured values along
429 the extraction tests were below 0.2 pH units. The treated solutions containing residual ammonia
430 concentrations, between 15 and 150 mgNH_3/L , could be suitable for re-use as regeneration
431 solutions of zeolites columns.

432 The membrane contactors performance for ammonia recovery using phosphoric acid was
433 evaluated ensuring an excess of acid in the stripping side. Solutions were obtained from elution of
434 ammonium-saturated zeolites loaded using treated effluents from Sant Feliu WWTP and using 2
435 g/L NaOH solutions. Concentrated solutions of ammonia from four cycles ranged from 2.1 to 2.7
436 $\text{g NH}_3/\text{L}$ were fed in the close loop configuration reporting recoveries between 95 to 98% as could be
437 seen in Figure 7. The transported ammonia was converted to di-ammonium phosphate solution in
438 the stripping phase reaching concentrations up to 9-11 $\text{g NH}_4^+/\text{L}$.

439



440

441 Figure 7. NH_3 concentration profile in the feed phase as a function of time for four consecutive
442 cycles using concentrates (2.1 - 2.7 g/L NH_3 and 2 g/L NaOH) at flow rates of 0.5 L/min with an
443 initial phosphoric acid concentration of 0.4 M as stripping phase.

444 Similar results were obtained using a 0.4 M HNO₃ as stripping stream (data not shown). After four
445 cycles, a solution of 17 g/L of ammonium nitrate was obtained. The quality of the by-products
446 (incorporated in the zeolites adsorption-elution step) is high as the transport of metal ions on the
447 HFMC is restricted by the hydrophobic membrane properties. The exhausted NH₃/NaOH streams,
448 once NH₃ is removed, can be re-used for regeneration of the ammonium-loaded zeolites. The
449 quality of the ammonium phosphate product obtained and its market analysis need to be also
450 evaluated. Garcia-González and Vanotti (2015) reported that hydrophobic membranes reject
451 undesirable species to fertilizer product stream, but other considerations as the fertilizer
452 concentration range which is useful and achievable must be considered. In relation to the value
453 proposition for the fertilizer product, factors such as the risks associated with losses of fertilizer by
454 evaporation and the transport costs should also be incorporated in the economic assessment.

455

456 **4. CONCLUSIONS**

457 The implementation of up-concentration techniques for achieving energy neutral sewage
458 treatments increases the efficiency of primary sedimentation; however its implementation as a
459 mainstream sewage treatment requires further post-treatment, due to the missing ammonium
460 removal. This study evaluated the use of zeolite sorption process as a post-treatment for the novel
461 up-concentration processes. The use of natural zeolites as precursor of a selective sorbent of
462 ammonium from treated effluents was evaluated in batch and fixed bed experiments. Equilibrium
463 and kinetic parameters were improved after the conversion of the natural zeolite to the sodium
464 form. Results obtained shown promising performance when compared with available data in
465 literature for natural clinoptilolite zeolite in terms of selectivity, regeneration and reusability. Higher
466 enrichment factors allowed to obtain NH₃/NaOH concentrates that can be used to produce potential
467 liquid fertilizers by using liquid-liquid membrane contactors.

468 Trials with nitric and phosphoric acids in hollow fibre membrane contactors demonstrated a total
469 nitrogen recovery capacity above 95% if an excess of free acid is present in the stripping stream.
470 This solution avoids the use of low cost common acids (e.g., H₂SO₄ and HCl) as ammonia
471 collectors, providing rich ammonium nitrate and di-ammonium phosphate with high added value as
472 fertilizers.

473 The quality of ammonium nitrate and di-ammonium phosphates by-products, in terms of absence of
474 transition metal and non-metal ions or organic micro pollutants (e.g., potentially incorporated in the
475 zeolites sorption-elution step) is high, as their transport on the hydrophobic hollow fibre membrane
476 contactors is restricted by the membrane properties only supporting solutes in gas phases. The
477 exhausted NH₃/NaOH streams once NH₃ is removed can be re-used for regeneration of the
478 ammonium exhausted zeolites filters.

479 Taking into account the results obtained in the present work, the use of conventional stripping
480 process (e.g., air-stripping) for the regeneration of zeolites is seen as a waste of energy and
481 chemicals and moreover, the process involves the generation of a secondary pollution that requires
482 further treatment. Then, the validated solution integrating a liquid-liquid contactor provides an
483 environmental friendly (less energy intensive) alternative solution.

484

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493

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