

1 Removing ammonia from wastewater using natural 2 and synthetic zeolites: A batch experiment

3
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9 10 **Abstract**

11 Ion exchange based processes for the removal of ammonium from wastewater using
12 zeolites could be an attractive additional or potentially complementary treatment
13 option for conditions that pose a challenge for biological processes, such as variable
14 load or low temperatures. A range of natural and synthetic zeolites have been studied
15 for removing ammonium from wastewater. However, the relatively low capacity of
16 zeolites and challenges regarding regeneration have so far complicated efforts in this
17 research direction. Here, we compare the most commonly used natural zeolites US-
18 Clinoptilolite, UK-Clinoptilolite, Mordenite and Chabazite (using Na- and Ca- as main
19 cation exchanger) as well as a thermally modified US-Clinoptilolite and a synthetic
20 zeolite MesoLite in terms of their capacity and regeneration efficiency to determine
21 whether a synthetic zeolite like MesoLite can address the aforementioned problems
22 related to capacity and regeneration efficiency. This investigation was performed as a
23 series of batch experiments on synthetic and real wastewater solutions. When
24 zeolites were pre-saturated with sodium ions, we found the overall highest capacity of

25 4.6 meq g⁻¹ for the synthetic zeolite MesoLite, relative to a range between 1.1 and 2.1
26 meq g⁻¹ for the natural zeolites. Ammonium adsorption capacity of MesoLite with real
27 wastewater ranged between 74 and 97 % of what was observed for a synthetically
28 generated mono component solution set at approximately the same ionic load. Our
29 results indicate that MesoLite could be an appropriate media for ion-exchange based
30 tertiary treatment of wastewater.

31

32 **Keywords:** Ammonium removal, ion exchange, zeolite, capacity, selectivity

33

34 **1. Introduction**

35 Ammonium removal is a key component of most wastewater treatment works with
36 anticipated new pollution targets requiring a large number of sites to meet discharge
37 consents between 1 and 3 mg NH₄⁺ L⁻¹. Whilst this is commonly achieved in
38 biological systems such as the activated sludge process, it comes with a substantial
39 energy cost which can account for 50 % of the total energy demand of the process
40 (Canfield *et al.*, 2010; McAdam *et al.*, 2011) as well as potentially emitting the
41 greenhouse gas nitrous oxide which is 310 times more potent than carbon dioxide
42 (Huijie and Chandran, 2010). On smaller sites, especially those based on low energy
43 biological processes such as trickling filters, resilient compliance to the new
44 standards is thought to be challenging due to limitations related to controlling even
45 distribution and mass transfer (Miladinovic and Weatherley, 2008).

46 Under the normal pH range of wastewater, the ammonia exists predominantly in its
47 reactive ionic form (ammonium) NH_4^+ . Accordingly, it can be removed by ion
48 exchange processes where the wastewater is contacted with an ion exchange
49 material that is pre-saturated with an alternative cation, typically Na^+ . The ion
50 exchange material has a thermodynamic preference for the ammonium ion such that
51 it exchanges with the Na^+ ion and is removed. Once the media becomes saturated it
52 can be regenerated and the captured ammonia recovered (Mackinnon *et.al.*, 2010;
53 Thornton *et.al.*, 2007). The process works for all available cations and so there is
54 competition with the other constituents within the wastewater, mainly Ca^{2+} and Mg^{2+} .
55 A variety of materials can be used in such an ion exchange process, including
56 polymer ion exchange resin as well as natural and synthetic zeolites. All these
57 materials exhibit different capacities and selectivities towards the target ion and so
58 selection of the most appropriate media is important.

59 The capacity and selectivity of the different zeolites is influenced by a combination of
60 the internal pore sizes of the lattice structure, the ratio of Si:Al and the distribution of
61 Al within the lattice frame (Inglezakis, 2005; Malovanyy *et al.*, 2013; Wang *et al.*,
62 2006). The properties can be modified by pre-treatment with different cations,
63 activation agents (KOH and NaOH), temperature or microwave techniques (Barrer
64 and Meier, 1959; Klieve and Semmens, 1980; Lei *et al.*, 2008; Mackinnon *et al.*,
65 2010; Querol *et al.*, 2002; Shoumkova and Stoyanova, 2013). Zeolites can be natural
66 or synthetic. Natural zeolites are formed across the world by interaction of volcanic
67 rocks and ash with alkaline underground water (Shoumkova and Stoyanova, 2013).

68 For these natural zeolites, the purity, chemical composition, crystal size, porosity,
69 pore diameters vary and this influences their efficacy for wastewater treatment in
70 terms of their capacity and selectivity towards ammonium (Table 1). Modern synthetic
71 zeolites are made by alkali treatment of raw materials rich in silica and alumina such
72 as clays like montmorillonite and kaolinite (Basaldella *et al.*, 1998).

73 Experiments that compare different zeolite types, are typically conducted as
74 equilibrium batch trials to assess capacity and selectivity in synthetic and real
75 systems (Table 1). A wide range of materials have been previously tested for
76 ammonium removal using natural zeolites with most studies investigating
77 Clinoptilolite due to its high relative selectivity towards ammonia and wide spread
78 availability. In fact, full scale Clinoptilolite filters were used in California from 1978 to
79 1993 (Svetich, 1993). Comparisons with synthetic zeolites are less common and are
80 often based on synthetic zeolite not intended for ammonia removal such as zeolite A,
81 which is applied as a builder in detergent powders and tablets for water softening
82 (Aarts *et al.*, 2004; Dyer, 1998; Milton, 1959). Consequently, such studies tend to find
83 better efficacy for natural zeolites (Fletcher and Townsend, 1982; Hankins *et al.*,
84 2004; Weatherley and Miladinovic, 2004). However, Mackinon (2010) has also shown
85 the benefits of MesoLite or zeolite N, a synthetic zeolite made from Kaolinite
86 (Kingwhite 65 and Kingwhite 80) dissolved with potassium or sodium reagents heated
87 to between 65 and 100°C.

88 To the authors knowledge no study has conducted a direct comparison of MesoLite
89 with natural zeolites (both parent and modified) for the removal of ammonia. Here, we

90 investigate, adsorption, desorption, selectivity, cation exchange capacity (CEC) and
 91 performance of six natural zeolites (US-Clinoptilolite, UK-Clinoptilolite, thermally
 92 modified US-Clinoptilolite, Mordenite, Ca-Chabazite and Na-Chabazite) and the
 93 synthetic zeolite MesoLite in mono and multicomponent systems in order to evaluate
 94 the use of zeolites for removing ammonia from wastewater.

95 **Table 1: Batch equilibrium capacities for mono and multicomponent waters.**

Equilibrium capacity (meq g ⁻¹)			
Zeolite	Initial Concentration (mg NH ₄ ⁺ L ⁻¹)	Mono-component: NH ₄ ⁺ synthetic solution – Equilibrium capacity (meq g ⁻¹)	Reference
Clinoptilolite	200	0.22	(Hankins <i>et al.</i> , 2004)
Clinoptilolite	10	0.04	(Erdoğan and Ülkü, 2011)
Clinoptilolite	25 - 150	0.05 – 0.25	(Karadag <i>et al.</i> , 2006)
Clinoptilolite	10-200	0.07 – 0.66	(Weatherley and Miladinovic, 2004)
Mordenite		0.07 – 0.80	
Clinoptilolite	50	0.30	(Lei <i>et al.</i> , 2008)
Clinoptilolite	1000	0.95	(Lin <i>et al.</i> , 2012),
MesoLite	1000	4	(Thornton <i>et al.</i> , 2007)

96

97 **2. Materials and methods**

98 Natural UK Clinoptilolite (RS Minerals, UK), Mordenite (Newstone International,
 99 Japan), synthetic MesoLite (Nanochem Pty Ltd., Australia), US Clinoptilolite,
 100 Chabazite (in sodium and calcium forms), and thermally modified US Clinoptilolite
 101 (St. Cloud, NM, USA) were sieved to achieve uniform media size (1 to 1.7 mm) and

102 washed in distilled water to remove particulate impurities. The zeolites were
103 preconditioned prior to testing using 1 M NaCl and 1 M CaCl₂ (stated purity >99 %;
104 Fisher Scientific, UK) dissolved into de-ionised (DI) water (15 MΩ cm⁻¹). The test
105 solution was prepared using ammonium chloride (NH₄Cl) (stated purity > 99 %;
106 Fisher Scientific, UK) dissolved into DI water.

107 **2.1. Batch equilibrium experiment**

108 Experiments were conducted in batch using 250 mL Erlenmeyer flasks for each of the
109 zeolites. Different amounts of the zeolites (from 0.1 to 0.5 g) were contacted with
110 100 mL of the test solution. The synthetic ammonium solution was set at a
111 concentration of 16 mg NH₄⁺ L⁻¹ (0.89 meq NH₄⁺ L⁻¹, pH between 7 and 8) for the
112 mono component experiments and compared to real wastewater from Cranfield
113 University's sewage work with an average ammonium concentration of 16 mg NH₄⁺ L⁻¹
114 ¹. The sample of real wastewater was taken post biological treatment (trickling filter)
115 and then filtered through a 0.2 μm filter to remove solids. The tested concentration in
116 the real wastewater varied between 11.9 and 16.2 mg NH₄⁺ L⁻¹ at a pH of 7
117 corresponding to 0.9 and 0.66 meq NH₄⁺ L⁻¹. The flasks were then agitated at
118 125 rpm for up to 48 hours with samples taken at 0, 20 and 40 minutes as well as 1,
119 2, 4, 6, 8, 12, 24 and 48 hours. Equilibrium was reached for all zeolite types within
120 24 hours.

121 Equilibrium data for each of the zeolites was then compared to both Freundlich and
122 Langmuir isotherm models (Almutairi *et al.*, 2015; Karadag *et al.*, 2006; McAdam *et*

123 *al.*, 2011). The ammonium concentration was determined spectrometrically by cell
124 test (Merck, Germany) using a spectrophotometer (Merck, Spectroquant Nova 60,
125 Germany). With this method there is no interference by other dissolved species (e.g.
126 cations, anions) in the liquid phase. The concentration of Na⁺, Ca²⁺, K⁺ and Mg²⁺
127 were analysed by atomic absorption spectroscopy (AAS) (AAnalyst 800, PerkinElmer,
128 UK). The concentration of ions in the solid phase was calculated using the following
129 mass balance equation (Jorgensen *et al.*, 1976). The experiments were conducted in
130 duplicate.

$$Q_e = \frac{(C_o - C_e)V}{M} \quad \text{Equation 1}$$

131 where Q_e is the amount of ions in the solid phase (mg g⁻¹) or [meq g⁻¹], C_o is the initial
132 ion concentration in solution (mg L⁻¹) [meq L⁻¹], C_e is the ion concentration remaining
133 in solution at equilibrium (mg L⁻¹) [meq L⁻¹], V is the solution volume (L) and M is the
134 mass of zeolite media introduced (g).

135 **2.2. Regeneration**

136 Following the adsorption process, the zeolites were contacted with 1 M NaCl for 24 h
137 and the amount of ammonium released into solution was measured. The recovered
138 capacity was then determined for both synthetic and real wastewater solution
139 throughout an adsorption phase of 24 h to assess the new capacity. That value was
140 then compared to the capacity obtained on the previous adsorption experiment when
141 non-pretreated zeolite was used.

142 **2.3. Saturation capacity**

143 The saturation capacity of the test zeolite was established through a fed-batch
144 experiment using 0.3 g of zeolite (Cooney, 1999). The zeolites were prepared in
145 100 mL test solution that contained NH₄Cl at a concentration of 600 mg L⁻¹ and were
146 then agitated for 24 h. After this time, 50 mL of the solution was withdrawn and
147 replaced with a fresh 50 mL of test solution. These steps were repeated until no more
148 exchange of NH₄⁺ was measured.

149 **2.4. Cation exchange capacity (CEC)**

150 The CEC was evaluated for the following ions: Ca²⁺, Na⁺, K⁺ and Mg²⁺ following the
151 ammonium acetate method number 16 of the MAFF Reference Book RB427. For that
152 method, 20 ml of 1 M ammonium acetate solution (stated purity > 99 %, Fisher
153 Scientific, UK) was contacted with 5 g of zeolites sieved to a size between 1 and
154 1.7 mm after being pre-conditioned with NaCl. After 24 h of contact, the solution was
155 filtered and the zeolite was leached with 1 M ammonium acetate until 250 ml were
156 collected (Faithful ,1986).

157 To determine the CEC of Ca²⁺ and Mg²⁺, 2.5 mL of strontium chloride (stated purity
158 > 99 %; Fisher Scientific, UK) were added to a volumetric flask of 100 mL. The
159 volume was increased up to 25 mL using 1 M of ammonium acetate. The capacity for
160 Ca²⁺ and Mg²⁺ of each zeolite was calculated through the equations below:

$$meq Ca/100g = \frac{(Ca_s - Ca_b) \times 6.25}{v} \quad \text{Equation 2}$$

$$meq\ Mg/100g = \frac{(Mg_s - Mg_b) \times 10.3}{v} \quad \text{Equation 3}$$

161 where Ca_s is the concentration of calcium in the sample extract ($\mu\text{g mL}^{-1}$), Ca_b is the
162 concentration of calcium in the blank extract ($\mu\text{g mL}^{-1}$), Mg_s is the concentration of
163 magnesium in the sample extract ($\mu\text{g mL}^{-1}$), Mg_b is the concentration of magnesium in
164 the blank extract ($\mu\text{g mL}^{-1}$) and v is the aliquot volume (mL).

165 To determine the CEC of Na^+ and K^+ 10 ml of the extract were diluted to 25 ml using
166 1 M ammonium acetate. Equation 5 and 6 were used to calculate the capacity for Na^+
167 and K^+ for each zeolite respectively

$$meq\ Na/100g = \frac{(Na_s - Na_b) \times 5.4375}{v} \quad \text{Equation 4}$$

$$meq\ K/100g = \frac{(K_s - K_b) \times 3.2}{v} \quad \text{Equation 5}$$

168 where Na_s is the concentration of sodium in the sample extract ($\mu\text{g mL}^{-1}$), Na_b is the
169 concentration of sodium in the blank extract ($\mu\text{g mL}^{-1}$), K_s is the concentration of
170 potassium in the sample extract ($\mu\text{g mL}^{-1}$), K_b is the concentration of potassium in the
171 blank extract ($\mu\text{g mL}^{-1}$) and v is the aliquot volume in mL, of the sample used.

172 **2.5. Isotherm modelling**

173 Batch equilibrium data is commonly analysed with respect to empirical isotherm
174 models such as the *Langmuir* or *Freundlich* models. Both were originally developed
175 for gas adsorption in mono component systems but are now widely applied to liquid

176 adsorption, and particularly also ion exchange in mono-, binary- and multicomponent
177 systems (Karadag *et al.*, 2006; Mohan and Singh 2002; Thornton *et al.*, 2007).

178 *The Langmuir model* is based on the concept of constant site energy that assumes
179 one solute molecule per site and constant cation capacity for each exchangeable site
180 (monolayer adsorption), (Wang *et al.*, 2007; Mohan and Singh, 2002) and is
181 expressed as

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \quad \text{Non-linear form,} \quad \text{Equation 6}$$

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}b}\right) + \left(\frac{1}{q_{max}}\right)C_e \quad \text{Linear form,} \quad \text{Equation 7}$$

182 where q_e is the amount of solute adsorbed per unit of weight of adsorbent (mg g^{-1}),
183 C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), q_{max} is the
184 monolayer adsorption capacity (mg g^{-1}) and b is the constant related to the free
185 energy of adsorption ($b \sim e^{-\Delta G/RT}$). It is reciprocal to the concentration at which half the
186 saturation of the adsorbent is attained.

187 *The Freundlich model* describes a logarithmic relationship between solid and solution
188 concentration assuming that the adsorbent has a heterogeneous surface with non-
189 uniform distribution of adsorption sites (Mohan and Singh, 2002; Lin *et al.*, 2012). The
190 Freundlich equation can be written as

$$q_e = K_F C_e^{1/n} \quad \text{Non-linear form,} \quad \text{Equation 8}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Linear form,} \quad \text{Equation 9}$$

191 where q_e is the amount of solute adsorbed per unit of weight of adsorbent (mg g^{-1}),
192 C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), K_F is the
193 constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and
194 $1/n$ is the constant indicative of the intensity of the adsorption (Mohan and Singh,
195 2002). Strictly speaking, the models should only be applied to mono component
196 systems and when used beyond that, it is customary to compare the model constant
197 as an indication of the impact of competing species rather than for prediction.

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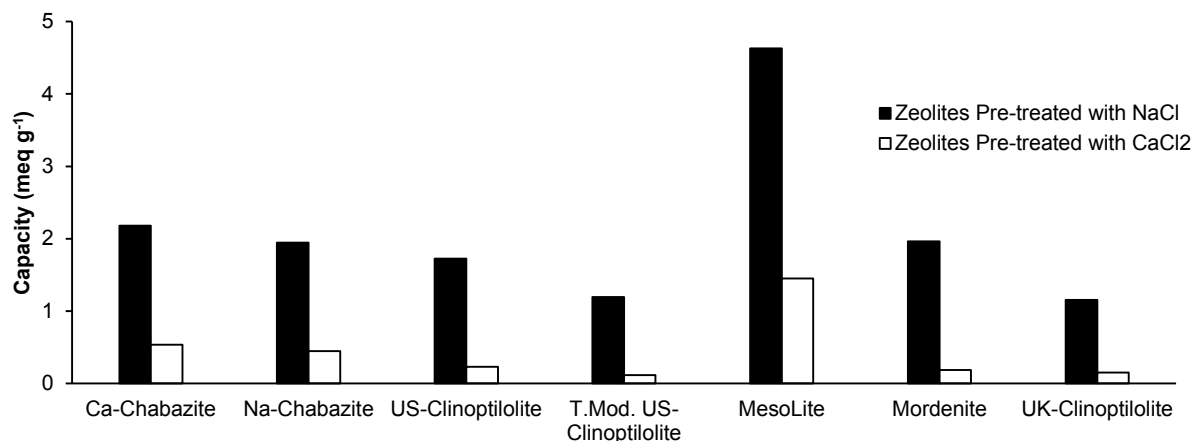
199 **3. Results and discussion**

200 **3.1. Comparison of capacity in mono component solution**

201 The equilibrium capacity of the different zeolites ranged from 1.15 to 4.6 meq
202 $\text{NH}_4^+ \text{g}^{-1}$ when in the sodium (Na^+) form and 0.15 to 1.45 meq $\text{NH}_4^+ \text{g}^{-1}$ when in the
203 calcium (Ca^{2+}) form with an initial NH_4Cl of 600 mg $\text{NH}_4^+ \text{L}^{-1}$ (33.3 meq $\text{NH}_4^+ \text{L}^{-1}$)
204 (Fig.1). Importantly, the synthetic zeolite, MesoLite, showed a higher equilibrium
205 capacity and selectivity than all the natural zeolites regardless of which pre-treatment
206 was used. This difference due to pre-treatment (Na^+ or Ca^{2+}) in all zeolites is in
207 accordance with previous studies of both natural and synthetic zeolites (Metropoulos
208 *et al.*, 1993; Lei *et al.*, 2008). The capacity reduction associated with calcium pre-

209 treatment is sensible given the known selectivity coefficient for the zeolites of 5.37 for
210 $\alpha_{\text{NH}_4^+, \text{Na}^+}$, 2.2 for $\alpha_{\text{NH}_4^+, \text{Ca}^{2+}}$ and 1.97 for $\alpha_{\text{Na}^+, \text{Ca}^{2+}}$ (Hankins *et al.*, 2004; Jama and
211 Yocel, 1989; Watanabe *et al.*, 2004). The results highlight the significance of the
212 presaturant ion initially associated with the zeolite and aligns with simulations that
213 have shown that Na^+ yields a lower energy state within the lattice than Ca^{2+}
214 (Channon *et al.*, 1998).

215 The thermally modified US-Clinoptilolite and Mordenite were affected most negatively
216 by pre-treatment with Ca^{2+} , with a reduction in capacity of 91 and 88 % respectively,
217 compared to pre-treatment with Na^+ . In comparison, the capacity of MesoLite
218 reduced by 68 % indicating a slightly higher resilience in terms of selectivity towards
219 ammonium ions. Interestingly, the three Clinoptilolite materials in the sodium form,
220 showed a variation of 35 % with regard to capacity; 1.72, 1.19 and 1.15 meq $\text{NH}_4^+ \text{g}^{-1}$
221 for the US, thermally modified US and the UK samples respectively. This confirms
222 previous reports about the potential variability in the properties of natural zeolites
223 such that capacities need to be confirmed when switching the origin of the material
224 (Almutairi *et al.*, 2015; Erdoğan and Ülkü, 2011).



226 **Fig. 1: Equilibrium batch saturation capacity against a synthetic mono component**
 227 **solution (125 rpm; $C_0 = 600 \text{ mg L}^{-1}$ (33.3 meq L^{-1}) during 5 cycles to ensure complete**
 228 **saturation; pH = 7) using 1 M of NaCl and CaCl₂ as a pre-treatment for seven different**
 229 **zeolites (1 g of zeolite).**

230 Comparison to the base properties of the different zeolites indicates that the Si:Al
 231 ratio may account for the difference between the observed capacity of MesoLite and
 232 the natural zeolites. To illustrate, the Si:Al ratio is > 4:1, 4:1, 4:1, 5:1 and 1:1 for
 233 Clinoptilolite, Na-Chabazite, Ca-Chabazite, Mordenite and MesoLite respectively.
 234 Whereas the effective window size was 4.6, 7.4, 7.4, 6.7 and 5.7 Å respectively for
 235 these zeolites. The hydrated size of the ions are 4.12, 3.58, 3.31 and 3.31 for Ca²⁺,
 236 Na⁺, K⁺ and NH₄⁺ respectively such that size exclusion is unlikely to be significantly
 237 different between the zeolites (Hankins *et al.*, 2004). Instead the much lower Si:Al
 238 ratio leads to a lattice structure with more exchange sites and hence an increased
 239 overall capacity (Armbruster and Gunter, 2001; Channon *et al.*, 1998; Ruiz-Salvador
 240 *et al.*, 1998).

241 **3.2. Capacity with real wastewater**

242 The seven zeolites were compared in terms of their equilibrium capacity when
 243 treating real wastewater effluent. Two different samples were required to test the full
 244 range of zeolites and the properties of the wastewater changed between the two
 245 samples (Table 2). The effluent was sourced post a trickling filter with a pH of 7.2 for
 246 the first sample and 7.3 for the second sample indicating that ammonium ions are
 247 likely to predominate. The actual concentration of ammonium ions within the sample
 248 was 16.2 and 11.7 mg NH₄⁺ L⁻¹ (0.9 and 0.65 meq NH₄⁺ L⁻¹) compared to calcium
 249 concentrations of 62.8 and 51.4 mg NH₄⁺ L⁻¹ (3.14 and 2.57 meq NH₄⁺ L⁻¹) and
 250 sodium of 100 and 67.16 mg NH₄⁺ L⁻¹ (4.37 and 2.92 meq NH₄⁺ L⁻¹). To adequately
 251 compare capacity for the real wastewater, a synthetic solution was created using the
 252 average NH₄-N concentration of the secondary effluent of 16 mg NH₄⁺ L⁻¹ (0.8 meq
 253 NH₄⁺ L⁻¹).

254 **Table 2: Characterization of the real effluent.**

Aerobic effluent	Zeolites	Total (meq L ⁻¹)	NH ₄ ⁺ (meq L ⁻¹)	Ca ²⁺ (meq L ⁻¹)	Na ⁺ (meq L ⁻¹)	K ⁺ (meq L ⁻¹)	Mg ²⁺ (meq L ⁻¹)
Day 1	MesoLite, US-Clinoptilolite, Na and Ca-Chabazite	9.96	0.90	3.1	4.4	0.47	0.74
Day 3	T. Mod. US-Clinoptilolite, Mordenite and UK-Clinoptilolite	7.44	0.66	2.6	3	0.46	0.71

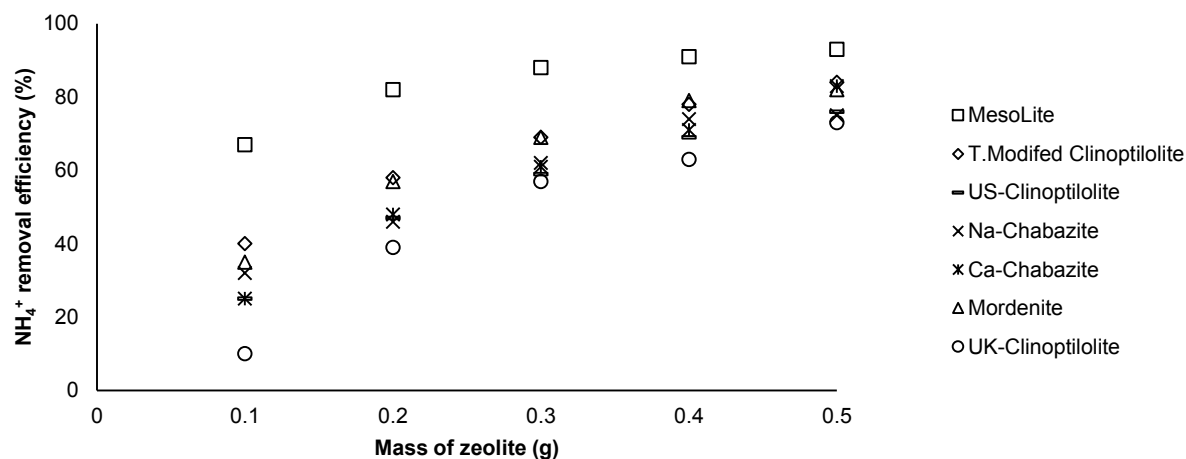
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256 A comparison of the zeolites revealed that for all zeolite masses tested, MesoLite
257 was able to remove more ammonium than the other zeolites. To illustrate, the
258 removal efficiency of ammonium with MesoLite increased by 67 to 93 % when the
259 mass of zeolite added increased from 0.1 to 0.5 g (Fig. 2). In comparison, the worst
260 performing zeolite was UK Clinoptilolite where the removal efficiency increased by 10
261 to 73 % for the same increase in zeolite mass. The best performing zeolite in this
262 aspect was the thermally modified Clinoptilolite where removal efficiency increased
263 by 36 to 84 % over the range of added masses that were tested. Whilst removal
264 increased with the added mass, the capacity decreased with MesoLite, which was the
265 most affected in terms of absolute capacity. In fact, the capacity of UK Clinoptilolite
266 did not vary much with added mass with capacities between 0.115 and
267 0.166 meq NH₄⁺ g⁻¹ compared to MesoLite where the capacity varied between 0.16
268 and 0.78 meq NH₄⁺ g⁻¹ for 0.5 g and 0.1 g of zeolite respectively (Fig. 3).

269 Overall, MesoLite demonstrated the highest capacity for ammonium and the least
270 relative reduction in ammonium capacity in presence of competing species. For
271 instance, the reduction in capacity from switching from the mono component system
272 to the real wastewater ranged from 3 to 26 % for 0.5 g to 0.1 g of zeolite. In
273 comparison, a greater impact as a result of competition was observed for the natural
274 zeolites ranging between 40 and 80 % for 0.1 g of zeolite and between 16 and 50 %
275 for 0.5 g of zeolite (Fig. 3). Therefore, the higher capacity numbers are associated
276 with the smaller masses of added zeolite where there are less total available
277 exchange sites. This occurs when the actual levels of ammonium removal are low

278 with values ranging between 10 and 40 % (Fig. 2). Increasing the removal efficiency
279 by adding more zeolite then reduces the percentage of the capacity associated with
280 ammonium reflecting an inefficiency which is much less pronounced in the case of
281 MesoLite.

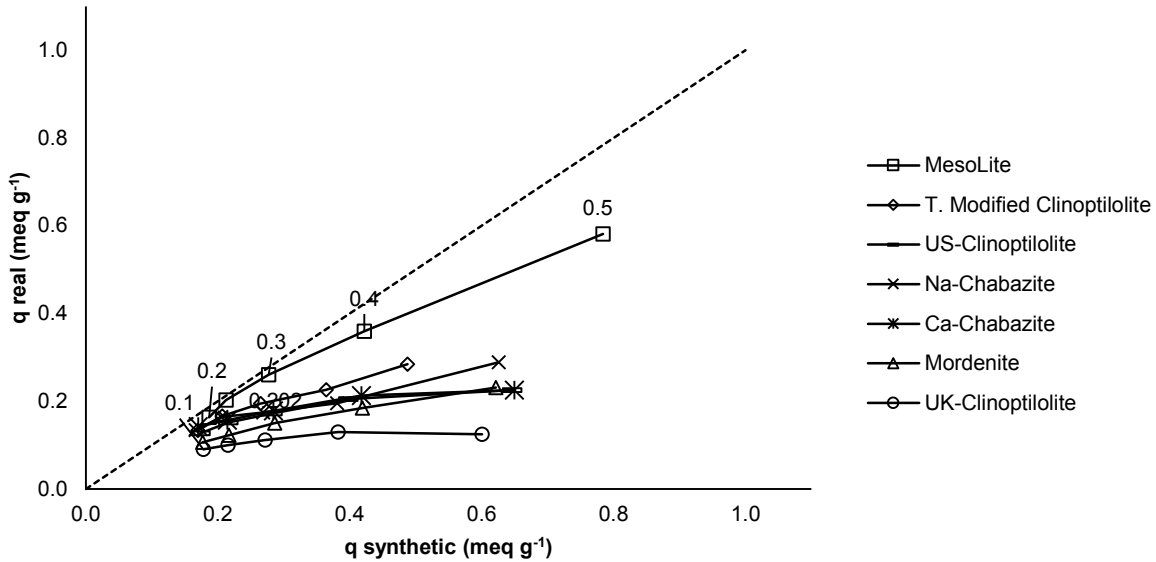
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284 **Fig. 2: Removal efficiency of ammonium for different masses of adsorbent in real**
285 **wastewater effluent.**

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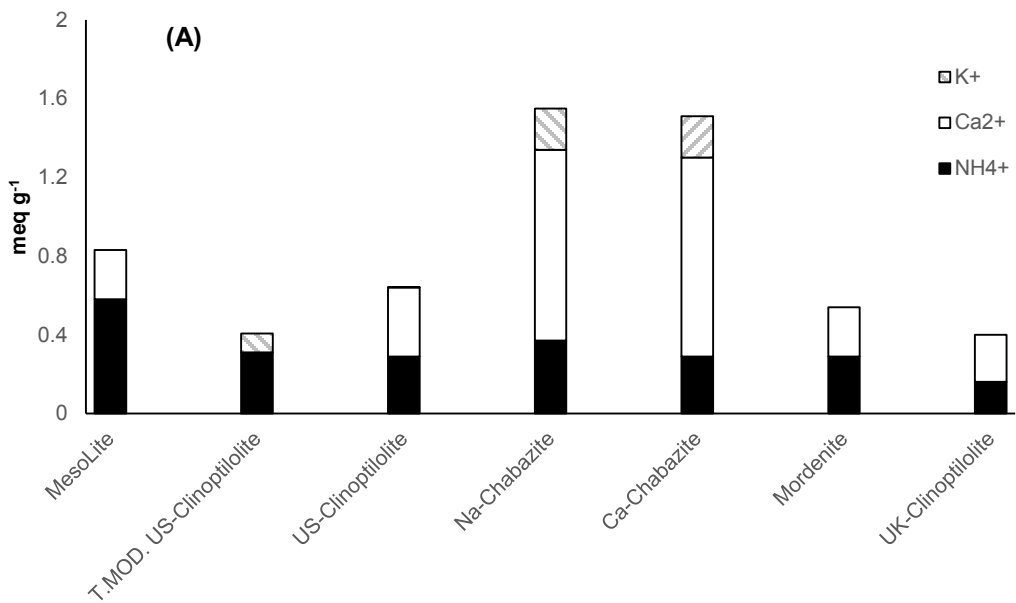
288 **Fig. 3: Comparison of batch capacity in real and synthetic effluents at five different**
 289 **zeolite masses (0.1 to 0.5 g). [125 rpm; $C_o = 16 \text{ mg L}^{-1}$ ($0.8 \text{ meq NH}_4^+ \text{ L}^{-1}$); pH=7].**

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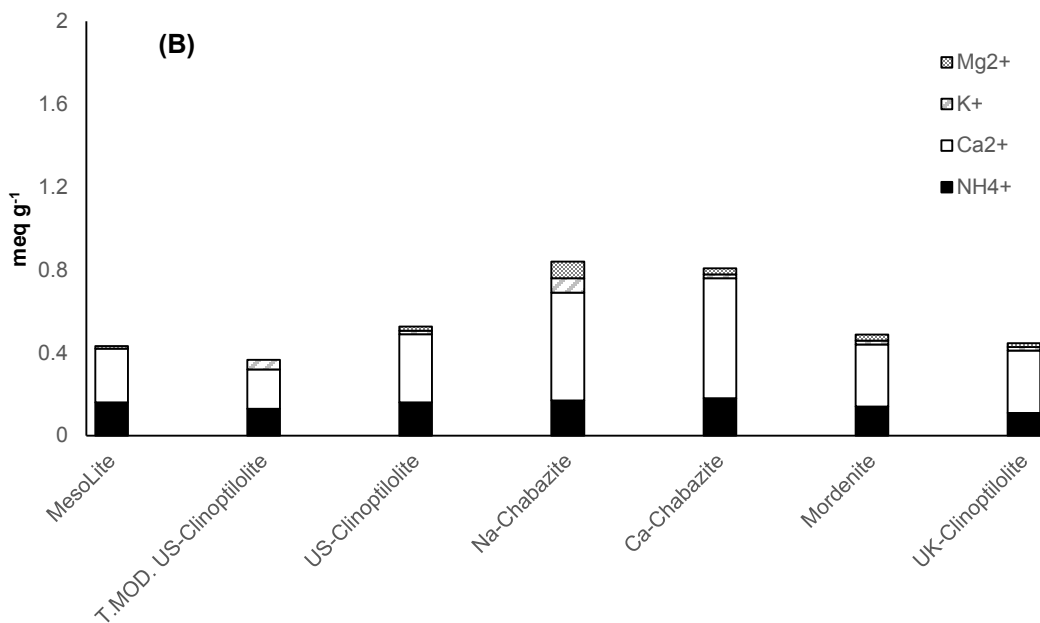
291 Further analysis of the removal of the different ions from the real wastewater revealed
 292 substantial uptake of Ca^{2+} with additional removal of K^+ and Mg^{2+} for some of the
 293 natural zeolites (Fig. 4). To illustrate: When adding 0.1 g of zeolite the capacity with
 294 respect to Ca^{2+} was 0.25, 0, 0.35, 0.97, 1.01, 0.25 and 0.24 meq g^{-1} for MesoLite,
 295 thermally modified US Clinoptilolite, US Clinoptilolite, Na-Chabazite, Ca-Chabazite,
 296 Mordenite and UK Clinoptilolite respectively. This represented 30 %, 0 %, 55 %, 55 %, 72 %, 78 %, 46 % and 60 % of the total uptake. Even though the thermally modified
 297 Clinoptilolite does not adsorb any Ca^{2+} , MesoLite has better capacity and selectivity
 298 towards ammonium (Fig.4 (A)). When increasing the mass of zeolite to 0.5 g, five
 300 times as many exchange sites were available. This decreased overall capacity,

301 indicating that a significant number of sites were still available, which made it possible
302 for other ions to be captured. For instance, it was observed that there was an
303 additional capacity for K^+ for all natural zeolites, in comparison to just for thermally
304 modified US Clinoptilolite, Na-Chabazite and Ca-Chabazite when only 0.1 g of zeolite
305 was added. Further, when the higher mass of 0.5 g of zeolite was added, Mg^{2+} was
306 also taken up by all the zeolites with the exception of thermally modified US
307 Clinoptilolite (Fig. 4 (B)). The corresponding percentage of the capacity associated
308 with ammonium was 38 % for MesoLite which removed 93 % of the available
309 ammonium from the water. The equivalent percentage of the uptake associated with
310 ammonium was lower for all the natural zeolites and ranged between 24 and 40 %.
311 The fact that when using 0.5 g of zeolite, the reduction in ammonium capacity (14 to
312 39 %) and the percentage of the total capacity associated with ammonium (41 to
313 25 %) were different, indicates, that the systems are not utilising all the available
314 sites. For instance, the overall saturation CEC of MesoLite for NH_4^+ is $4.6 \text{ meq } NH_4^+g^{-1}$,
315 thus indicating that the experiments conducted here were utilising around 13 and
316 3.5 % of the totally available active sites for 0.1 and 0.5 g respectively.

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Fig. 4: Comparison of adsorbance of competing cations (Ca²⁺, Mg²⁺ and K⁺) with the adsorbance of NH₄⁺ for (A) 0.1 g of zeolite and (B) 0.5 g of zeolite.

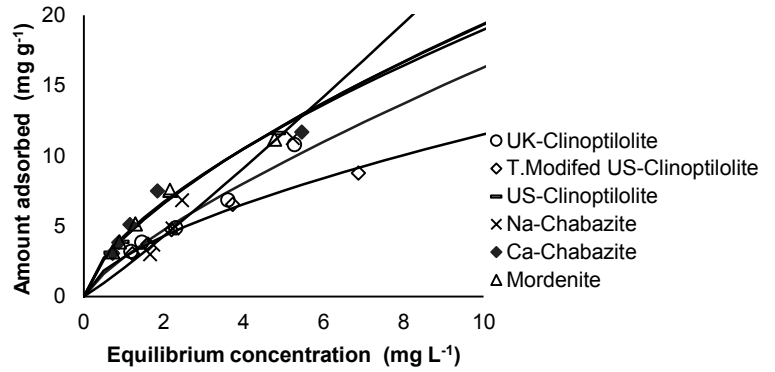
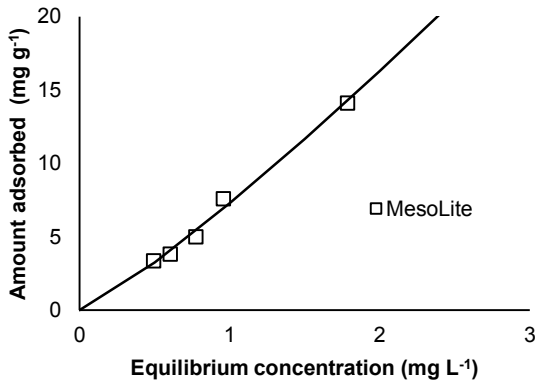
322 This outcome supports previous results with Clinoptilolite, where a selectivity
323 sequence of $\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ was reported during synthetic trials (Metropoulos *et al.*,
324 1993; Weatherley and Miladinovic, 2004). This was extended to include ammonium
325 with a sequence of $\text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+}$ during investigation into the use of Clinoptilolite
326 for the treatment of landfill leachate (Hankins *et al.*, 2004). However, it has been
327 previously suggested that calcium would not adversely affect uptake of most metallic
328 ions onto Clinoptilolite and Chabazite when the concentration is below 10 meq L^{-1}
329 with a dramatic reduction in ammonium removal expected once the Ca^{2+}
330 concentration exceeds 25 meq L^{-1} (Ouki and Kavannagh, 1997). In the present study
331 Ca^{2+} concentrations were lower than 25 meq L^{-1} and showed a substantial impact.
332 This is similar to previous work on landfill leachate where an addition of calcium
333 reduced ammonium capacity by 21 % in a 0.16 N ionic solution (Hankins *et al.*,
334 2004).

335 The relative impact of competing ions on the uptake of ammonium for the different
336 zeolites reflects a combination of the different concentrations of each component and
337 the differences in the ion (size and energy of hydration) and zeolite (aluminium
338 distribution and Si:Al ratio) properties (Channon *et al.*, 1998). The fact that uptake of
339 calcium was maximised for the zeolite Chabazite is in line with this idea, as the
340 zeolite has a relatively low charge in the framework (Si:Al = 4) and the largest
341 effective window size of the tested zeolites at 7.37 \AA compared to 5.97 \AA , 6.7 \AA and
342 5.7 \AA for Clinoptilolite, Mordenite and MesoLite respectively. The other feature is the
343 properties of the ions themselves in relation to the free energy of hydration. If all other

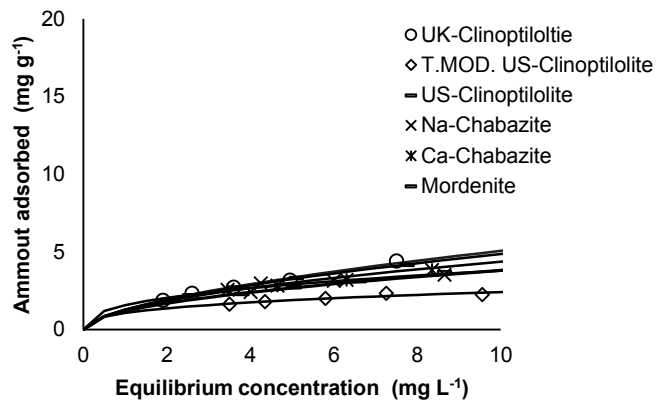
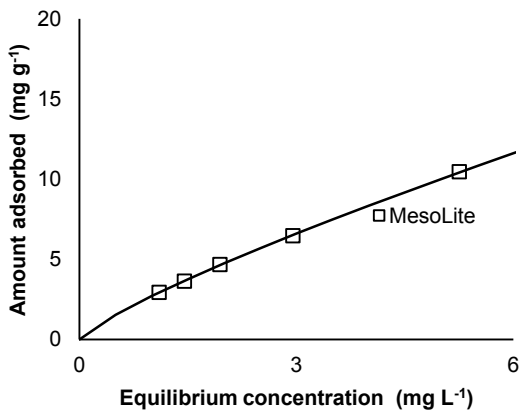
344 features are fixed, the selectivity sequence in low concentration systems is reported
345 to mirror the free energy of hydration with lower free energies reducing preference
346 (Kantiranis *et al.*, 2011a). This is because ions with higher free energy of hydration
347 are more likely to shed water molecules and form inner sphere complexes with the
348 zeolite structure (Kantiranis *et al.*, 2011b). Further, uptake of Mg^{2+} and K^+ became
349 significant only when the total number of sites was increased, reflecting their position
350 further down the selectivity sequence which is consistent with their lower free energy
351 of hydration and their larger effective ionic size (Eisenman, 1962; Sherry, 1966).

352 **3.3. Isotherm models**

353 Both isotherm models appropriately represented the equilibrium data although in the
354 cases of UK Clinoptilolite and Na-Chabazite, the Freundlich model was found to be a
355 more representative fit to the data since this model assumes non-distribution of
356 adsorption and it assumes a heterogeneous surface. The Freundlich constant (K_f) for
357 MesoLite decreased from $7.2 \text{ mg NH}_4^+ \text{ g}^{-1}$ in the mono component system to 2.7 mg
358 $\text{NH}_4^+ \text{ g}^{-1}$ in the multicomponent batch test (Fig. 5 and Fig. 6). The equivalent
359 decrease in K_f for the natural zeolites were 70, 69, 61, 64, 40, and 50 % for US-
360 Clinoptilolite, Mordenite, UK-Clinoptilolite, Ca-Chabazite, Na-Chabazite and thermally
361 modified US-Clinoptilolite respectively. Comparison to previously reported values for
362 Clinoptilolite show a large range of values (Table 3) reflecting the limitation of the
363 models for comparison between studies. Accordingly, Inglezakis (2005) suggests that
364 the isotherm coefficients are only true for the specific experimental conditions used,
365 such that comparison across different studies should be done very carefully.



366 Fig. 5: Comparison of the isotherm curves for the different zeolites fitted with a
 367 Freundlich model when treating a mono-component synthetic solution at an initial
 368 concentration of $16 \text{ mg NH}_4^+ \text{ L}^{-1}$ and a pH of 7.5. (A) For MesoLite and (B) for the
 369 natural zeolites.



370 Fig. 6: Comparison of the isotherm curves for the different zeolites fitted with a
 371 Freundlich model when treating a multi-component real wastewater at an initial
 372 concentration of $11.7 \text{ to } 11.2 \text{ mg NH}_4^+ \text{ L}^{-1}$ and a pH of 7. (A) For MesoLite and (B) for the
 373 natural zeolites.

374

375 **Table 3: Langmuir (q_m) and Freundlich (K_F) constants for different experimental**
 376 **setups.**

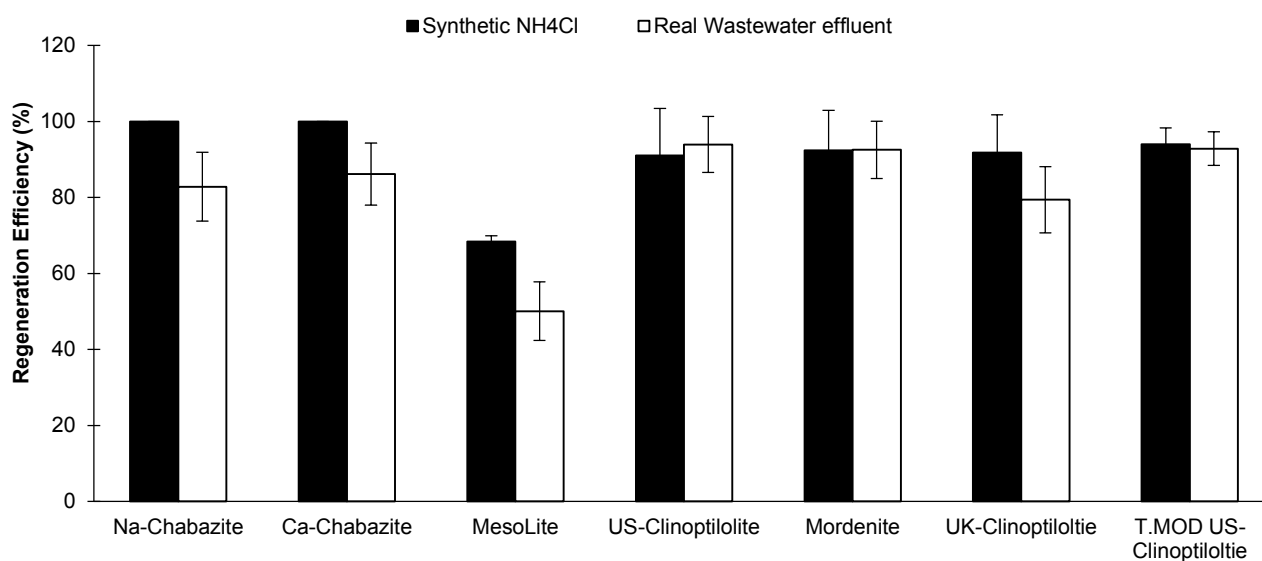
Material	Experimental conditions	q_m	K_F	Reference
Clinoptilolite	Concentration range of NH_4^+ (23 to 113 mg L^{-1}) in three different particle sizes	2.128	0.428	(Wang <i>et al.</i> , 2006)
		2.375	0.596	
		2.469	0.432	
Clinoptilolite and modified Zeolite	Concentration range (50 to 250 mg L^{-1})	11.2	2.71	(Wang <i>at al.</i> 2007)
		22.64	3.639	
Natural Clinoptilolite	Three temperatures (25, 40 and 55°C) Concentration range (25 to 150 mg L^{-1})	6.05	6.62	(Karadag <i>at al.</i> , 2006)
		4.75	5.50	
		3.76	4.01	
Clinoptilolite	Concentration range (0 to 200 mg L^{-1})	6.54	10.66	(Weatherley and Miladinovic, 2004)

377

378 3.3. Regeneration studies

379 The regeneration efficiency of the natural zeolites was higher than that for the
 380 synthetic zeolite, MesoLite (Fig. 7). For instance, the regeneration efficiency of
 381 MesoLite was 68 % during the synthetic trials and 50 % during the real wastewater
 382 trials. In comparison, the regeneration efficiency of the natural zeolites ranged from
 383 90 to 100 %. As such, whilst MesoLite provided a higher operational capacity, the
 384 ability to utilise the available capacity over prolonged periods may be a challenge. An
 385 explanation for this could be the strong Ca^{2+} binding with MesoLite as a consequence

386 of MesoLite's much lower Si:Al ratio. The higher proportion of Al substitution within
387 the lattice structure enables the Ca^{2+} ion to potentially bind with two Al ions and form
388 a stable inner sphere complex that is difficult to exchange (Ruiz-Salvador *et al.*,
389 1998). Thus, regeneration for MesoLite needs to be optimised to ensure that the
390 improved capacity can be maintained over multiple cycles so that the material can be
391 usable in practice.



393 **Fig. 7 Comparison of the average regeneration efficiency over a five cycle sequence**
394 **for the seven different zeolites treating synthetic and real wastewater.**

395

396 **4. Conclusion**

397 The synthetic zeolite MesoLite showed higher capacity and higher removal efficiency
398 than the natural zeolites, reaching a saturation capacity of 4.6 meq NH₄⁺ g⁻¹ relative
399 to an average of 1.5 meq NH₄⁺ g⁻¹ for the natural zeolites. Overall, the capacity of all
400 zeolites was significantly reduced when pre-treated into the calcium form with
401 Chabazite being most heavily impacted. The natural zeolites were more effectively
402 regenerated with a 1 M NaCl solution with restricted regeneration efficiency observed
403 for MesoLite. The Freundlich model adjusted to the experimental data better than the
404 Langmuir model, with MesoLite scoring the highest coefficient K_F of 7.28.

405

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410

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