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Fate and Impacts of Triclosan, Sulfamethoxazole, and 17 β -estradiol during Nutrient Recovery via ion Exchange and Struvite Precipitation

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16 Fate and Impacts of Triclosan,

17 Sulfamethoxazole, and 17 β -Estradiol

18 during Nutrient Recovery via Ion

19 Exchange and Struvite Precipitation

20

21

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27 Abstract

28 Increasing emphasis on resource recovery from wastewater highlights the importance of
29 capturing valuable products, e.g., nutrients such as nitrogen and phosphorus, while
30 removing contaminants, e.g., organic micropollutants. The objective of this research was
31 to evaluate the fate of the micropollutants triclosan (present as a mixture of neutral and
32 anionic species at neutral pH), 17 β -estradiol (neutral at neutral pH), and
33 sulfamethoxazole (anionic at neutral pH) during nutrient recovery using ion exchange-
34 precipitation. Adsorption of the three micropollutants to the phosphate-selective ion
35 exchange resins LayneRT and DOW-HFO-Cu ranged from 54% to 88%. The
36 micropollutants did not sorb to the ammonium-selective resin, clinoptilolite. The
37 presence of the micropollutants reduced kinetics of nutrient exchange rates onto ion
38 exchangers. However, the micropollutants did not interfere with nutrient capacity on
39 the ion exchangers, likely due to the low concentration of micropollutants and
40 potentially different mechanisms of adsorption (i.e., coulombic and non-coulombic
41 attractions for micropollutants) compared to the target ions. Less than half of the
42 micropollutants that sorbed to the phosphate exchangers were released with phosphate
43 ions during regeneration. Concentrations of NaOH and NaCl in regeneration solutions
44 did not statistically correlate with the amount of desorbed micropollutants, which may
45 be attributed to the complexity of micropollutants' binding mechanisms with ion
46 exchangers. Triclosan, the most hydrophobic of the three micropollutants studied,
47 adsorbed to the resins to the greatest extent and demonstrated the lowest desorption
48 rates during regeneration. Batch struvite precipitation tests revealed that the
49 micropollutants were not enmeshed in precipitated struvite crystals nor sorbed during
50 crystallization, indicating that the struvite product was free of triclosan, 17 β -estradiol,
51 and sulfamethoxazole.

52 Introduction

53 Water resource recovery facilities (WRRFs) are inextricably linked to the food, energy,
54 and water nexus as they provide a centralized opportunity to recover energy, e.g., as
55 methane; produce high-quality treated water; and recover valuable products, e.g., for
56 use as agricultural fertilizers or soil amendments¹. Anaerobic treatments such as
57 anaerobic membrane bioreactors (AnMBRs) for secondary treatment and anaerobic
58 digestion (AD) for solids treatment produce methane, which can offset some energy
59 requirements for WRRFs. Furthermore, AnMBRs do not require aeration and could be a
60 more sustainable alternative to conventional activated sludge processes²⁻⁵.
61 Additionally, anaerobic processes offer an opportunity for downstream nutrient
62 recovery and thus an option to produce and recover a valuable product instead of using
63 energy to convert nutrients to a wasted product (e.g., as an off-gas).

64
65 The effluent from anaerobic processes usually contains high ammonia nitrogen (NH₄-N)
66 and inorganic phosphate (PO₄-P)^{2,4}. Accordingly, additional nutrient removal
67 technologies may be needed to treat anaerobic effluent to meet increasingly stringent
68 nutrient discharge regulations⁶. While excess phosphorus and nitrogen in
69 environmental waters causes eutrophication⁷, insufficient nutrient availability is also a
70 concern for agriculture⁸. Depleting reserves of mined phosphate, together with the
71 energy-intensive nature of Haber-Bosch nitrogen fixation, could limit global food
72 production^{9,10}. Anaerobic effluent, as a reservoir of nutrients, is a resource from which
73 to recover nitrogen and phosphorus in the form of a solid fertilizer product that can help
74 to close anthropogenic nutrient loops by supplementing nonrenewable phosphate
75 mining and energy-intensive atmospheric nitrogen fixation¹¹.

76
77 Wastewater contains a host of inherently valuable constituents including energy and
78 nutrients, but it also contains a mixture of micropollutants that pose potential adverse
79 ecological health impacts¹². For example, triclosan (TCS) is an antimicrobial agent used
80 in a variety of consumer products, and can select for antibiotic resistance in engineered
81 and natural systems¹³⁻¹⁶. 17β-estradiol (E2) is a natural hormone that is linked to fish
82 feminization near treatment plant outfalls¹⁷. Sulfamethoxazole (SMX) is one of the most
83 popularly prescribed sulfonamide antibiotics and can affect nutrient cycling in microbial
84 communities^{18,19}. WRRFs were not specifically designed to remove micropollutants, and
85 anaerobic processes are often worse at removing micropollutants compared to aerobic
86 processes. For instance, Samaras et al. (2013) reported approximately 20±35% removal
87 of TCS via biotransformation using AD²⁰. Studies on endocrine disruptors such as
88 estrone (E1), E2 and 17α-ethynylestradiol (EE2) revealed that AD and AnMBRs offered
89 poor biotransformation of these compounds²¹⁻²³. SMX had variable biological

90 transformation in AD and AnMBR systems, ranging from 41.9% to 99%²³⁻²⁵. If valuable
91 products such as treated water and nutrients are to be recovered from anaerobic
92 effluents, it is important to understand the fate of micropollutants to ensure that they
93 are not enriched in the WRRF products. This study focused on the impact and fate of
94 TCS, E2 and SMX during nutrient recovery because of the potential presence of these
95 micropollutants in anaerobic effluent and their different physicochemical properties
96 (molecular details of which are included in the Supplemental Information [SI], S1).

97

98 One option for removing and recovering nutrients is ion exchange-precipitation. In this
99 process, nutrient-selective materials are used to extract and concentrate nitrogen and
100 phosphorus via ion exchange and subsequent regeneration followed by precipitation of
101 nutrient-rich solid fertilizer products, e.g., struvite (MgNH_4PO_4). Clinoptilolite is a natural
102 zeolite that effectively exchanges ammonium ions²⁶. In wastewater, phosphorus is most
103 commonly present in the HPO_4^{2-} and H_2PO_4^- forms²⁷. These orthophosphate species can
104 exhibit strong ligand sorption to polyvalent metals such as Fe(III) and Cu(II) by forming
105 inner-sphere complexes^{28,29}. Therefore, polymeric anion exchangers are usually
106 impregnated with metal salts to selectively exchange orthophosphate. After removal,
107 nutrients are concentrated during ion exchange regeneration, thereby facilitating
108 precipitation of nutrient-rich solids that can be used as fertilizer. Controlled struvite
109 precipitation has been studied in mainstream and side-stream wastewater (direct
110 precipitation)³⁰⁻³² and in membrane-concentrated streams and ion exchange
111 regeneration brines (indirect precipitation)^{31,33}. Compared to direct precipitation,
112 indirect precipitation is more favorable for producing a high purity mineral and easier
113 operational control³¹. However, organic micropollutants such as tetracycline and
114 quinolones have been detected in struvite produced from digester filtrate and urine
115^{34,35}. Thus, if valuable fertilizer is recovered from anaerobic effluents, it is essential to
116 thoroughly assess the potential for co-concentration of residual micropollutants along
117 with nutrients.

118

119 The objective of this work was to evaluate the fate of the micropollutants TCS, E2, and
120 SMX during ammonium and phosphate ion exchange-regeneration and struvite
121 precipitation. Batch experiments were conducted to specifically determine: a) the
122 impact of micropollutants on nutrient exchange reaction rates, capacities and
123 desorption, b) the fate of the micropollutants during ion exchange-regeneration-
124 precipitation, and c) micropollutants' impact and fate during ion exchange-regeneration
125 in actual anaerobic filtrate.

126 Materials and Methods

127 Ion exchangers

128 LayneRT and DOW-HFO-Cu were evaluated as phosphate-selective ion exchangers^{29,36}.
129 LayneRT (Layne Christensen, The Woodlands, TX) is a 300 - 1200 μm particle size ready-
130 to-purchase hybrid anion exchange resin consisting of hydrated ferric oxide (HFO)
131 nanoparticles impregnated in a strong base anion exchange polymer²⁹. DOWEX M4195
132 (DOW Chemical Company, Midland, MI) was used as the base resin for producing
133 functional DOW-HFO-Cu resin by immobilizing Cu(II) and HFO, which provide ligand
134 bonding with HPO_4^{2-} and H_2PO_4^- , onto the 300 - 850 μm particle size polymer, in
135 accordance with Sengupta and Pandit's protocol²⁹. Clinoptilolite, a natural zeolite, was
136 used as a selective ammonium exchanger (420 – 1410 μm particle size). Clinoptilolite
137 (St. Cloud Mining, Winston, NM, 14X40 mesh) was pre-conditioned with 1% NaCl
138 solution and rinsed with de-ionized water.

139

140 Ion exchanger characterization

141 Characterization of ion exchangers was performed to better elucidate the interactions
142 between the dissolved chemicals and the ion exchangers. Ion exchanger surface area
143 and pore size were measured using a Brunauer–Emmett–Teller (BET) surface analysis
144 instrument (NOVA 4200e, Quantachrome Instruments, Boynton Beach, FL). The surface
145 charge of the materials was determined using a Malvern Zetasizer Nano S (Malvern
146 Instruments Ltd, Malvern, UK). The ion exchangers' surface element composition was
147 observed via JEOL JSM-6510LV SEM (JEOL USA, Inc., Peabody, MA) with an energy-
148 dispersive X-ray (EDX) detector at an accelerating voltage of 10 kV.

149

150 Ion exchange and regeneration batch experiments

151 Batch ion exchange tests were conducted to determine if micropollutants would be co-
152 captured with nutrient ions. These tests were performed in feed water with 40 mg-N/L
153 as NH_4Cl and 5 mg-P/L as K_2HPO_4 ³³ to mimic plausible nutrient levels in anaerobic
154 effluents². The feed water was prepared by dissolving 300 ± 50 $\mu\text{g/L}$ each of TCS, E2 and
155 SMX in HPLC-grade methanol. The volumetric ratio of methanol stock to water was
156 below 0.5% to negate co-solvent effects³⁷. The spiked micropollutant concentrations
157 were higher than in actual anaerobic effluents^{23,24} so that reaction rates and adsorption
158 capacities could be determined via liquid chromatography-mass spectrometry (LC-MS;
159 detection limits were in the low $\mu\text{g/L}$ range). The pH of feed water was adjusted to 7
160 with NaOH.

161

162 For ion exchange tests, 50 mL feed water was added to 60 mL serum bottles. Each bottle
163 contained either 0.25 g clinoptilolite, 0.05 g LayneRT, or 0.05 g DOW-HFO-Cu resin

164 (higher levels of clinoptilolite were added based on higher ammonium concentrations).
165 The bottles were mixed on a rotating tumbler for 4 days as preliminary tests
166 demonstrated this time was sufficient time to achieve equilibrium. For kinetic tests,
167 periodic samples were collected for four days, as shown in Figures 1 and 2. Nutrient
168 exchange typically achieved equilibrium in less than one day and micropollutants
169 adsorption typically achieved equilibrium within two days (<5% change in
170 concentrations).

171

172 Ion exchange isotherm tests were conducted to assess potential interference with
173 nutrient capture caused by micropollutants. For these tests, 50 mL of feed water were
174 added to 60 mL serum bottles. The amount of ion exchanger in each bottle varied: 0.01,
175 0.02, 0.03, 0.04, or 0.05 g DOW-HFO-Cu or LayneRT; 0.01, 0.05, 0.1, 0.2, or 0.5 g
176 clinoptilolite. Samples were analyzed at time zero and after 4 days.

177

178 Ion exchange regeneration tests were conducted to determine if the micropollutants
179 that were adsorbed on the ion exchangers would be released during subsequent
180 regeneration. All ion exchangers were regenerated using brine solutions with high levels
181 of Na^+ , Cl^- and OH^- ^{33,38}. For clinoptilolite, the regeneration brine was fixed at 8% NaCl ³³.
182 The concentrations of NaCl and NaOH in phosphate exchanger regeneration brine were
183 varied to study their impact on phosphate and micropollutant recovery (S2, Tables S2-
184 S5). Differences in recoveries as a function of regeneration solution could enable
185 process optimization to elicit greater desorption of nutrients and less desorption of
186 micropollutants. The regeneration brine for LayneRT ranged from 0 to 2% NaCl and 0 to
187 2% NaOH. The regeneration brine for DOW-HFO-Cu ranged from 0 to 2.5% NaCl and 0 to
188 2% NaOH ³⁹. The pH of all regeneration brines was 12 to 14. Ion exchange tests were
189 initially performed in 250 mL water in 500 mL Erlenmeyer flasks. The amount of ion
190 exchanger added to each flask was fixed at 1.25 g clinoptilolite or 0.25 g DOW or
191 LayneRT resin. After completing the 4-day ion exchange period, the flasks were
192 decanted and 150 mL NaCl+NaOH regeneration solution was added. Regeneration
193 lasted for 4 hours, in accordance with previous equilibrium tests ³³. Samples were
194 collected for nutrient and micropollutant analysis from the feed water, after ion
195 exchange, and after regeneration.

196

197 Tests in actual anaerobic wastewater filtrate

198 A filtrate sample from a belt filter press used to dewater anaerobically digested sludge
199 from Jones Island Water Reclamation Facility, Milwaukee, WI, was acquired to test the
200 impact of a complex anaerobic wastewater matrix on the fate and impact of TCS, E2 and
201 SMX during ion exchange-regeneration. Water quality parameters including pH,
202 chemical oxygen demand (COD), total organic carbon (TOC), and total suspended solids

203 (TSS) were measured in accordance with standard methods ⁴⁰, results of which are
204 provided in SI 13. Ammonium-N content in the filtrate was approximately 110 mg/L; no
205 additional N was added. Phosphate-P content in the effluent was approximately 1.4
206 mg/L; additional P was added for a final P concentration of 8 mg/L. Approximately 300
207 µg/L each of TCS, E2 and SMX stock solution was added to the anaerobic effluent
208 (background concentrations were below detection). Each bottle was dosed with 5 g/L of
209 clinoptilolite, 1 g/ of LayneRT, or 1 g/L of DOW-HFO-Cu, as described for the batch
210 experiments. Controls were performed using no ion exchangers to investigate the
211 adsorption of micropollutants to the organic carbon in the wastewater matrix. Samples
212 were analyzed after four days to determine the extent of removal and desorption from
213 the ion exchangers.

214

215 Struvite precipitation in the presence of micropollutants

216 Batch tests were conducted to determine the fate of micropollutants during struvite
217 precipitation in Milli-Q water. A molar ratio of P:N:Mg=1:1:1 was targeted by mixing
218 Na₂HPO₄•7H₂O (165 mL, 4.26 g/L), NH₄Cl (15 mL, 9.33 g/L), MgCl₂•6 H₂O (20 mL, 26.65
219 g/L). Approximately 300 µg/L each of TCS, E2, and SMX was added. To mimic the
220 regeneration brine, the pH was adjusted to 9 using NaOH and 2% NaCl was added. The
221 solution was mixed on a shaker table at 180 rpm for 40 min and allowed to settle for 10
222 min ³³. Filtrate was collected before and after the precipitation reaction for
223 quantification of micropollutants and nutrients.

224 Analytical methods

225 The standard phenate and ascorbic acid methods were used to quantify NH₄-N and PO₄-
226 P, respectively ⁴⁰. Micropollutants were quantified via online solid-phase extraction
227 (SPE, to eliminate interferences with micropollutant detection from background ions)
228 with single quadrupole liquid chromatograph-mass spectrometry (LC-MS). An online SPE
229 cartridge (Phenomenex, Torrance, CA, USA) was incorporated in the LC-MS system (LC-
230 MS 2020, Shimadzu, Columbia, MD, USA). All samples were filtered through 0.45 µm
231 PTFE filters. 13C-TCS, estrone (E1) and 13C-SMX were added as internal standards
232 before SPE. Details of the SPE-LC-MS method are provided in the SI (S3). Method
233 detection limits were 8 µg/L TCS, 8 µg/L E2, and 9 µg/L SMX. Recovery of TCS, E2, and
234 SMX was between 70 – 130% ⁴¹.

235

236 Data analysis

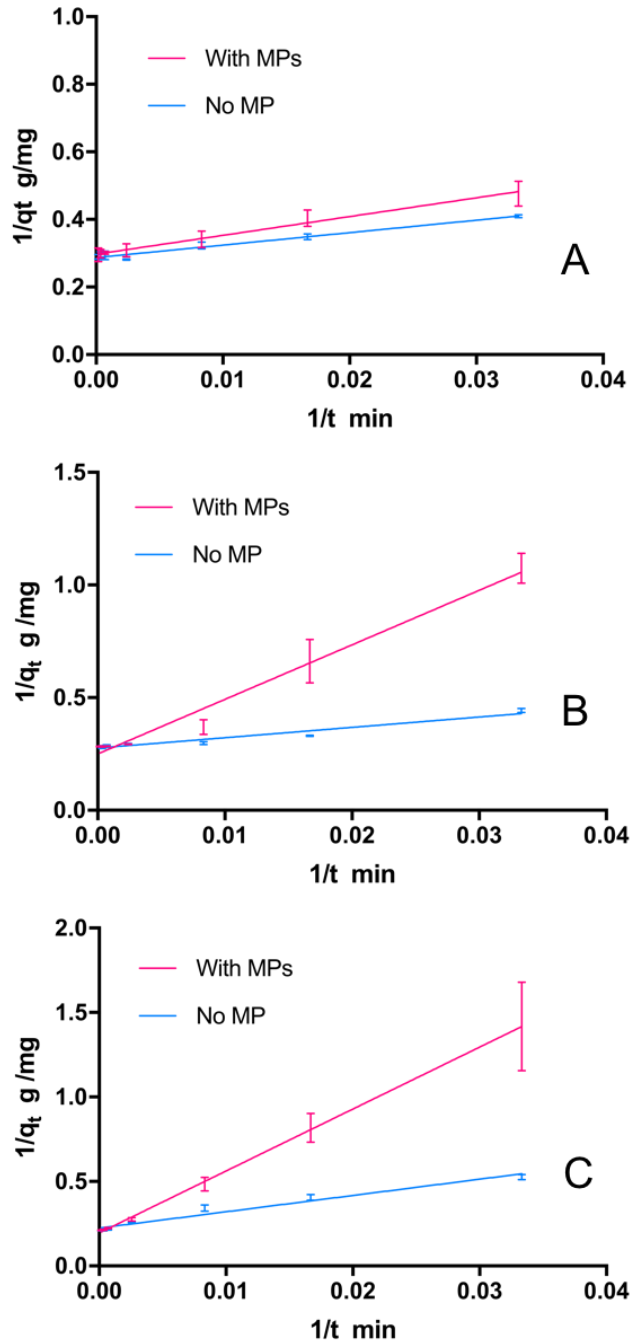
237 Adsorption capacity from batch ion exchange tests and percent recovery from
238 exchange-regeneration tests were calculated as described in the SI, Section S4. Nutrient
239 removal kinetics were modelled as pseudo-second order reactions (which demonstrated
240 the best fit for the data), as described in the SI (S5).

241

242 Isotherm modeling and statistical analysis (t-test, α level = 5%) were conducted using
243 GraphPad Prism 6 (Graphpad Software, Inc., La Jolla, CA). To determine the relative
244 influence of NaOH and NaCl on the recovery of $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$, or micropollutants during
245 regeneration, response surface methodology (RSM) was used in R (S6) ⁴².

246 Results and Discussion

247 The impact of micropollutants on nutrient ion exchange reaction kinetics
248 The reaction rate of nutrient ion exchange with and without micropollutants was
249 determined in batch studies. The nutrient ion exchange kinetics (Figure 1) were modeled
250 as pseudo-second order reactions ^{43,44}, which provided the best fit (average fitting
251 parameters of linearized nutrient exchange kinetic curves are shown in Table S7 and
252 equilibrium curves are shown in Figure S2). The presence of micropollutants significantly
253 decreased ammonium and phosphate exchange reaction rate constants (Table 1,
254 calculated using Eq. S5). When micropollutants were present in the water, the reaction
255 rate constants for clinoptilolite, LayneRT and DOW-HFO-Cu decreased by 32%, 85% and
256 80%, respectively (S7, Figure S2).



257

258 **Figure 1:** Linearized second order nutrient removal kinetics curves, plotted as the
 259 reciprocal of total adsorbed amount per unit mass of exchanger ($1/q_t$, g/mg) versus the
 260 reciprocal of time ($1/t$, 1/min). The plots show nutrient removal kinetics with and
 261 without micropollutants (MPs) for: A) $\text{NH}_4\text{-N}$ removal by clinoptilolite, B) $\text{PO}_4\text{-P}$ removal
 262 by LayneRT, and C) $\text{PO}_4\text{-P}$ removal by DOW-HFO-Cu. The data points represent averages
 263 and error bars represent ± 1 standard deviation of triplicate experiments.

264

265 **Table 1:** Pseudo-second order reaction rate constants for nutrient ion exchange
 266 reactions with and without micropollutants

Nutrient	Ion Exchanger	Rate Constant (L/mg/min)		p-value
		With Micropollutants	Without Micropollutants	
Ammonium	Clinoptilolite	0.015	0.022	0.0002
Phosphate	LayneRT	0.003	0.020	<0.0001
Phosphate	DOW-HFO-Cu	0.001	0.005	<0.0001

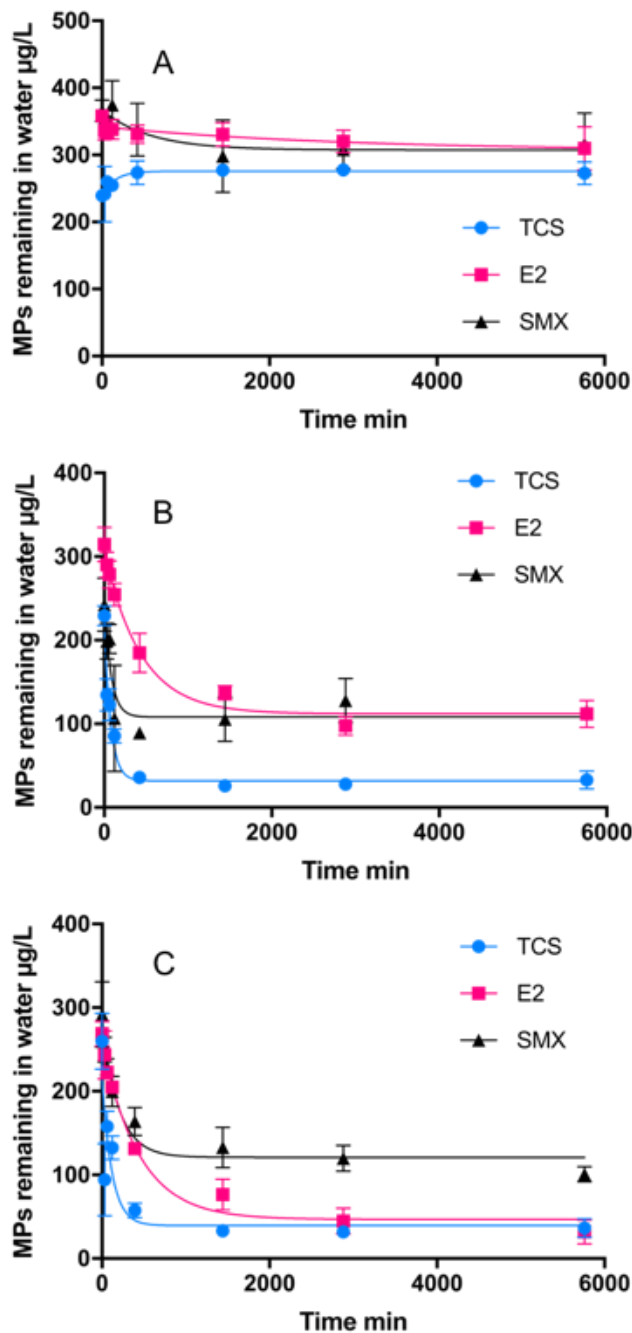
267

268 According to Planzinski et al. (2013), the pseudo-second order reaction model for
 269 spherical sorbent particles can be well interpreted in terms of an intraparticle diffusion
 270 model. This model assumes that the overall sorption reaction rate is controlled by the
 271 rate of sorbate diffusion across the sorbate/solution interface within pores⁴⁵. In terms
 272 of nutrient exchange in this study, reductions in reaction rates in the presence of
 273 micropollutants may have been caused by the micropollutants interfering with nutrient
 274 diffusion from the aqueous phase to the solid surface of the adsorbent^{46,47}. Although
 275 micropollutants significantly decreased nutrient ion exchange reaction rates,
 276 micropollutants did not impact the total amount of nutrients sorbed at equilibrium
 277 (Figure S2). The long-term effect of micropollutants on the suppression of nutrient ion
 278 exchange rates could potentially hinder the removal of nutrients by reducing the
 279 number of bed volumes treated prior to regeneration.

280

281 Adsorption of micropollutants onto nutrient ion exchangers

282 Batch studies were conducted to track the fate of micropollutants during nutrient
 283 removal via ion exchange. The three micropollutants were adsorbed to varying extents,
 284 as shown in Figure 2. LayneRT adsorbed 85.6±4.5% TCS, 64.4%±4.1 E2, and 51.6±8.0%
 285 SMX. DOW-HFO-Cu adsorbed 86.2±2.3% TCS, 88.2±4.6% E2, and 65.1±5.1% SMX. The
 286 extent of micropollutants adsorbed on each resin was proportional to the
 287 micropollutant log D_{ow} values (Table S1), as the most hydrophobic micropollutant, TCS,
 288 exhibited the greatest adsorption, while the most hydrophilic micropollutant, SMX,
 289 exhibited the least adsorption. Using clinoptilolite to capture ammonium, TCS and E2
 290 were not readily adsorbed ($p=0.314$ for TCS and $p=0.067$ for E2), and the SMX
 291 concentration at the end of the equilibrium period did not differ significantly from the
 292 initial concentration ($p=0.154$), signifying that these micropollutants were not readily
 293 removed with clinoptilolite.



294

295 **Figure 2:** Micropollutant (MP) removal by three ion exchangers, A) clinoptilolite, B)
 296 LaynERT, and C) DOW-HFO-Cu, over time during batch tests. Feed water concentrations
 297 were $\sim 300 \pm 50 \mu\text{g/L}$ each for TCS, E2, and SMX. Initial nutrient concentrations were 40
 298 mg-N/L and 5 mg-P/L, with pH=7. The data points represent average results and error
 299 bars depict ± 1 standard deviation of triplicate experiments.

300

301 Clinoptilolite has a negative surface charge (S8, Figure S3), making it unlikely to adsorb
302 the negatively charged dissociated fractions of TCS, E2, or SMX through coulombic
303 attraction. Furthermore, according to pore size analysis, the mode pore width of
304 clinoptilolite is 10.2 Å (S9, Figure S4). According to 3D-structure measurements in
305 ChemDraw[®], TCS has a minor dimension of 7.9 Å and a major dimension of 13.7 Å. The
306 minor and major dimensions of E2 are 8.5 Å and 18 Å, respectively, while the minor and
307 major dimensions of SMX are 14 Å and 15 Å, respectively. As the molecular size of the
308 micropollutants is near or larger than the clinoptilolite pores, the likelihood for
309 adsorption of micropollutants due to transport into pores is low ⁴⁸. Poor adsorption of
310 SMX on clinoptilolite was also demonstrated previously ⁴⁹.

311

312 On the other hand, the phosphate-selective exchange resins, LayneRT and DOW-HFO-
313 Cu, readily sorbed TCS, E2, and SMX at neutral pH (Figures 2B and 2C, respectively). Gas
314 sorption tests indicated that LayneRT has a mode pore size of 20.2 Å, and DOW-HFO-Cu
315 has a mode pore size of 23.4 Å (Figure S4). Thus, the phosphate resins' pores are larger
316 (in comparison to clinoptilolite's mode pore size of 10.2 Å) and more accessible for
317 micropollutant adsorption.

318

319 There are two plausible means by which micropollutants could bind with phosphate-
320 selective ion exchange resins: i) coulombic attraction due to opposite charges, and ii)
321 non-coulombic attractions such as hydrophobic interactions, hydrogen bonding, and
322 aromatic system π stacking ⁵⁰⁻⁵². Further discussion on mechanisms of micropollutant-
323 ion exchanger interaction is provided in the *Potential mechanisms of micropollutant-ion*
324 *exchanger interaction* section.

325

326 The impact of micropollutants on nutrient ion exchange capacity
327 Nutrient ion exchange isotherm modeling was performed using data from batch tests
328 conducted with and without micropollutants in the feed water to assess
329 micropollutants' influence on nutrient exchange capacity and mechanisms. Exchange of
330 ammonium using clinoptilolite fit the empirical Langmuir isotherm model (Figure S5A),
331 which assumes one solute ion per adsorption site, forming a single layer on the sorbate
332 surface ⁵³. The ammonium exchange isotherms with and without micropollutants were
333 not significantly different ($p=0.756$).

334

335 An empirical sigmoidal isotherm (type D) ^{54,55}, provided the best fit for modeling
336 exchange of phosphate via LayneRT and DOW-HFO-Cu resins with and without
337 micropollutants in the feed water (Figures S5B and S5C). A sigmoidal isotherm often
338 occurs when using a homogenous adsorbent ⁵⁴, such as LayneRT and DOW-HFO-Cu
339 resins, which are manufactured under controlled conditions. Observation using a

340 scanning electron microscope (Figure S6) together with surface pore analysis indicated
341 that these phosphate ion exchangers were more homogeneous than clinoptilolite,
342 reaffirming the underlying basis for the best fit isotherm model behaviors. At near-
343 neutral pH, the predominant orthophosphate species, H_2PO_4^- and HPO_4^{2-} , are Lewis
344 bases (electron pair donors) that can exhibit strong ligand adsorption on the HFO in
345 LayneRT resin, as well as on both HFO and Cu^{2+} in the DOW-HFO-Cu resin, by forming
346 inner-sphere complexes through coordinate bonding. Sigmoidal isotherms provide good
347 representations of this type of phosphate exchange, according to previous reports
348 ^{29,36,56–58}. The inflection expected for a sigmoidal isotherm was not observed, likely due
349 to the small phosphorus range tested (less than 5 mg/L).

350

351 Similar to the case for clinoptilolite, there was no significant difference in exchange
352 capacity with and without micropollutants for the phosphate-selective resins (LayneRT
353 $p=0.768$ and DOW-HFO-Cu $p=0.796$, Figure S5). Although the presence of
354 micropollutants slowed the reaction rates of nutrient ion exchange, as described
355 previously, the amount (q_e) of phosphate or ammonium exchanged at equilibrium
356 remained similar with or without micropollutants, as did the shape of the isotherm. For
357 clinoptilolite, the ammonium isotherm was not expected to change since TCS, E2 and
358 SMX did not adsorb effectively (Figure 2A). For LayneRT and DOW-HFO-Cu, it is possible
359 that the low initial concentrations of micropollutants relative to nutrients and different
360 adsorption/exchange mechanisms contributed to the lack of observed change in the
361 nutrient exchange isotherms with and without micropollutants.

362

363 Potential mechanisms of micropollutant-ion exchanger interaction

364 In near-neutral pH feed water, TCS and E2 are predominantly in the neutral form (88.8%
365 neutral for TCS and 99.9% for E2, Figure S1). Therefore, the non-coulombic mechanisms
366 for TCS and E2 adsorption by LayneRT and DOW-HFO-Cu differ from the electrostatic
367 mechanism that controls phosphate exchange. The aromatic pyridyl group in the bis-
368 picolylamine attached to the DOWEX M4195 polymer matrix, and the benzene ring of
369 LayneRT's backbone structure, are able to form π stacking with the benzene rings on
370 TCS and E2 molecules ^{39,59}.

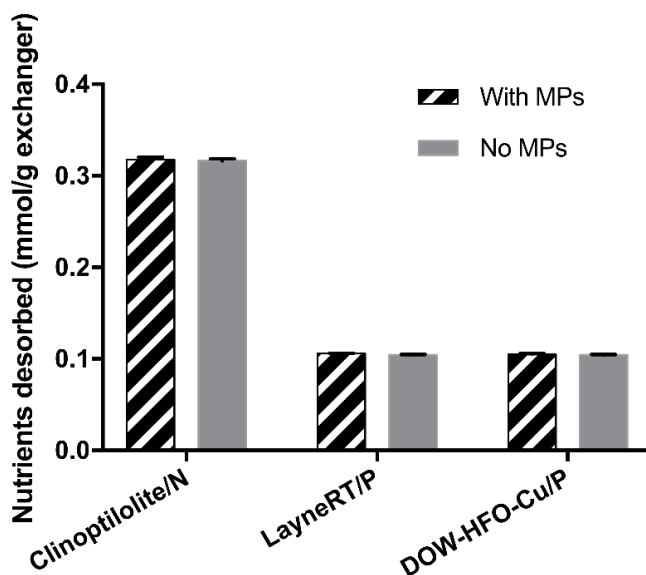
371

372 Negatively charged dissociated SMX is more likely to adsorb to LayneRT and DOW-HFO-
373 Cu via coulombic attraction with positively charged moieties that are dissociated while
374 in water (Figure S3). At pH 7, the majority of SMX molecules are anionic (98.0%) (Figure
375 S1), implying that the adsorption onto phosphate exchangers is likely due to coulombic
376 attraction. Ionic SMX may be adsorbed to the quaternary ammonium groups (R_4N^+) on
377 LayneRT's surface via coulombic attraction. The removal of ionic SMX by DOW-HFO-Cu
378 may be attributed to the coulombic attraction between the ions and chelated HFO or

379 Cu^{2+} that forms outer sphere complexes ³⁶. Additionally, the π -electron rich moiety in
380 SMX's structure may form π stacking with the ion exchanger surface, which may play a
381 minor role. Alternately, phosphate prefers ligand adsorption by forming inner sphere
382 complexes via both coulombic and Lewis acid-base attraction with HFO ^{36,60}. In
383 accordance with these potentially different adsorption mechanisms and low
384 micropollutant loadings, ionic SMX is unlikely to compete with phosphate for exchange
385 sites on LayneRT and DOW-HFO-Cu resins. However, the absence of an inflection point
386 in the phosphate exchange isotherm indicates that the functional HFO and Cu^{2+} sites are
387 far from saturation. Considering the initial concentrations of TCS, E2 and SMX
388 (approximately 0.0012 mM, whereas phosphate was 0.16 mM), the availability of
389 binding sites on the resins was sufficient for phosphate adsorption.

390

391 The impact and fate of micropollutants during ion exchange regeneration
392 Ion exchange regeneration was performed to investigate the fate of the micropollutants
393 adsorbed on the ion exchangers, and their potential effect on nutrient desorption
394 during regeneration. Following ion exchange, regeneration brine containing varying
395 concentrations of NaCl and NaOH was used to increase adsorption capacity of
396 exhausted clinoptilolite, LayneRT, and DOW-HFO-Cu ⁶¹. Micropollutants that were
397 adsorbed onto phosphate exchangers did not impact nutrient desorption, as shown in
398 Figure 3 ($p=0.058$ for LayneRT and $p=0.699$ for DOW-HFO-Cu). Since micropollutants
399 were not adsorbed by clinoptilolite during the ion exchange stage, micropollutants did
400 not have a significant impact on the desorption of ammonium ($p=0.57$). Therefore,
401 clinoptilolite was not considered in further studies of micropollutant desorption during
402 regeneration.



403

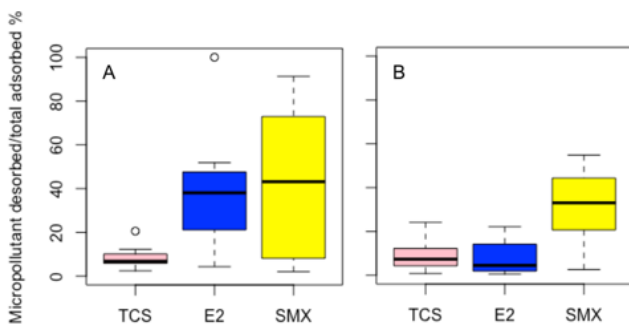
404 **Figure 3.** Nutrient desorption per mass of ion exchanger during ion exchange-
405 regeneration batch tests, with and without micropollutants (MPs, ~300 µg/L each TCS,
406 E2, and SMX, in the pH=7 ion exchange feed waters). The regeneration brine for
407 phosphate exchangers was 2% NaOH + 2% NaCl and was 8% NaCl for clinoptilolite. The
408 data represent average results and error bars show ± 1 standard deviation of triplicate
409 experiments.

410

411 To explore the impact of NaCl and NaOH on micropollutant desorption from LayneRT
412 and DOW-HFO-Cu resins, concentrations of NaCl and NaOH in the regenerant were
413 varied, as listed in Tables S2-S5. There was no significant correlation between
414 regeneration brine constituents and micropollutant desorption ($p > 0.05$), except for
415 NaOH, which yielded significant positive linear correlations with SMX ($p = 0.05$, $\beta_1 = 26.95$)
416 and TCS ($p = 0.032$, $\beta_1 = 12.31$) for desorption from DOW-HFO-Cu. Under the tested
417 conditions, micropollutant desorption from LayneRT or DOW-HFO-Cu cannot be
418 accurately predicted using the concentration of constituents in the regeneration brine,
419 nor is it easy to control desorption by varying brine concentration, possibly due to the
420 complexity of micropollutants' binding with ion exchangers. Therefore, the potential
421 desorption of micropollutants is unlikely to influence the selection of regeneration brine
422 in real-life operations. Instead, impacts on nutrient ion exchange capacity and operation
423 costs will be the most important criteria when selecting a regenerant ⁶².

424

425 Although there was no significant correlation between regeneration brine concentration
426 and micropollutant desorption, the extent of desorption (based on percent mass
427 desorbed relative to initial mass sorbed) varied among the micropollutants (Figure 4).
428 The variations in the extent of SMX desorption indicate that the main mechanisms of
429 SMX adhesion to ion exchangers may be coulombic attraction, which is more easily
430 disturbed by high ionic strength solution compared to non-coulombic attractions.
431 Comparing data in Figures 2 and 4, micropollutant desorption was inversely related with
432 the degree of adsorption, where compounds that poorly adsorbed were better
433 desorbed (i.e., SMX). For TCS, the extent of adsorption (Fig. 2) and desorption (Fig. 4)
434 onto the two phosphate exchangers was similar. For E2, adsorption using LayneRT was
435 lower than for DOW-HFO-Cu (Figure 2), and desorption was generally higher than DOW-
436 HFO-Cu (Figure 4), which indicates that E2 has stronger binding with LayneRT than
437 DOW-HFO-Cu.



438

439 **Figure 4.** Micropollutant desorption relative to total adsorption for batch ion exchange-
 440 regeneration tests with varying NaCl and NaOH regenerant compositions using A)
 441 LayneRT and B) DOW-HFO-Cu resin (n = 11 for each exchanger). Clinoptilolite is not
 442 shown because no significant adsorption was observed. The horizontal bold line
 443 indicates the median. The boxes represent the first and third quartile of the data set.
 444 The whiskers above and below the boxes show the locations of the minimum and
 445 maximum. The hollow circles signify outliers.

446

447 Phosphate readily desorbed from each phosphate exchanger under the regeneration
 448 conditions tested, but desorption did not correlate to NaCl or NaOH concentration
 449 ($p=0.791$ for LayneRT and $p=0.380$ for DOW-HFO-Cu, first order linear regression model;
 450 Tables S2 and S4). Phosphate desorption was 3.50 ± 0.19 mg-P/g LayneRT ($94.5\pm5.54\%$ of
 451 the portion captured was released) and 3.69 ± 0.30 mg-P/g DOW-HFO-Cu ($74.35\pm5.31\%$).
 452 The mass of phosphate desorbed from LayneRT was not significantly different from that
 453 desorbed from DOW-HFO-Cu ($p=0.12$). However, DOW-HFO-Cu resin generally
 454 demonstrated greater total mass removal of phosphate, possibly indicating stronger
 455 binding.

456

457 Phosphate ions are exchanged by forming inner-sphere complexes with HFO and Cu^{2+} on
 458 the exchangers via coulombic and Lewis acid-base interactions, while adsorption of SMX
 459 in pH 7 feed water was possibly due to non-selective coulombic attraction forming outer
 460 sphere complexes³⁶. Thus, the attachment of both phosphate and SMX to phosphate
 461 exchange resins was likely due to electrostatic attractions, which would be easily
 462 disrupted by the concentrated Cl^- and OH^- in the regeneration brine⁶⁰. As noted
 463 previously, adsorption of TCS and E2 to the two phosphate exchange resins was not
 464 likely due to coulombic attraction, indicating that the presence of strong counter ions
 465 would not significantly affect desorption⁶⁰.

466

467 Desorption of TCS, E2, and SMX (median <50%) was much lower than phosphorus
 468 desorption (>90%). These results indicate that the majority of the micropollutants

469 tended to irreversibly adsorb to the ion exchangers, regardless of the interactions
470 between micropollutants and exchangers (e.g., coulombic or non-coulombic). Landry
471 and Boyer⁶⁰ also reported low desorption of diclofenac sorbed on polymeric strong-
472 base anion exchange resins (24% using 4% NaCl brine). Even though coulombic forces
473 played a major role for diclofenac (pKa= 4.7) attaching to the polystyrene resin in fresh
474 urine (pH = 6), high strength regeneration brine could not disrupt the interaction
475 between the dissociated diclofenac and the resin⁶⁰. Previous studies have also shown
476 favorable adsorption of chlorinated phenols and aromatic micropollutant anions on
477 polymeric exchangers, with a preference for these contaminants over inorganic chloride
478 ions present in either feed water or regeneration solutions^{63,64}. This was attributed to
479 the non-polar moiety of the aromatic ions leading to simultaneous hydrophobic
480 interactions and coulombic attractions⁶⁵.

481

482 The low desorption to adsorption ratio of micropollutants from ion exchangers
483 potentially introduces additional concerns for flow-through reactor operation. Based on
484 the lack of effective micropollutant desorption during regeneration, over time, ion
485 exchangers may become saturated with adsorbed micropollutants. Consequently,
486 micropollutants in the influent may eventually bypass the ion exchange bed, and be
487 carried into the ion exchange effluent. During WRRF operation, the ion exchange
488 effluent would either be recycled to the head of the WRRF or discharged to receiving
489 water, depending on whether the ion exchange feed water was from an AD or AnMBR .
490 Moreover, it is unknown if a buildup of micropollutants on ion exchangers due to
491 inefficient desorption would eventually block nutrient exchange sites. In this study, the
492 adsorption of micropollutants (present at low concentrations in the feed water) on ion
493 exchangers had negligible impact on nutrient removal, but long-term performance is
494 uncertain.

495

496 The impact and fate of TCS, E2 and SMX during nutrient ion exchange-
497 regeneration in actual anaerobic filtrate

498 Ion exchangers were tested in anaerobic filtrate supplemented with 300 µg/L each TCS,
499 E2, and SMX to investigate the impact of micropollutants on nutrient exchange in a real
500 wastewater matrix containing organic carbon (water quality parameters are listed in SI,
501 Table S9). The presence of micropollutants in actual anaerobic wastewater did not
502 impact nutrient removal or regeneration (all t-test p-values were greater than 0.05;
503 Table 2), this finding was similar to the finding from Milli-Q water tests. Compared to
504 other constituents in real anaerobic filtrate, such as organic carbon and ions,
505 micropollutants were in much lower levels, and therefore, they less likely had
506 substantial impact on nutrient removal.

507

508 **Table 2:** Nutrient removal and regeneration by ion exchangers in anaerobic effluent,
 509 with and without the presence of micropollutants. All tests were conducted in triplicate,
 510 and values shown indicate means \pm 1 standard deviation.

Ion exchanger	Nutrient mole		No MP	With MPs	p-value
Clinoptilolite	NH ₄ -N mmol/g exchanger	removed	0.69 \pm 0.07	0.58 \pm 0.15	0.31
		regenerated	0.69 \pm 0.07	0.48 \pm 0.08	0.31
LayneRT	PO ₄ -P mmol/g exchanger	removed	0.13 \pm 0.00	0.13 \pm 0.00	0.97
		regenerated	0.11 \pm 0.00	0.10 \pm 0.00	0.10
DOW-HFO-Cu		removed	0.13 \pm 0.00	0.12 \pm 0.00	0.09
		regenerated	0.11 \pm 0.01	0.11 \pm 0.00	0.09

511
 512 The adsorption and desorption of micropollutants during nutrient ion exchange-
 513 regeneration was changed in complex wastewater matrix compared to pure water tests.
 514 In control experiments without ion-exchangers, approximately 44% of TCS (the most
 515 hydrophobic compound) was lost to the wastewater matrix, and approximately 26% of
 516 E2 was lost to the matrix. The most hydrophilic compound tested, SMX, was not lost to
 517 the wastewater matrix. Therefore, when calculating percent removal by ion exchangers,
 518 the compound lost in control tests was considered. In experiments conducted with ion
 519 exchangers, as shown in Table 3, the extent of SMX adsorption onto phosphate
 520 exchangers from anaerobic filtrate was 57%, which was similar to the results from MilliQ
 521 water tests, indicating suspended solids and organic matter did not interfere with SMX
 522 adsorption. However, SMX percent desorption decreased in real effluent tests. TCS and
 523 E2 adsorption onto ion exchangers from real anaerobic filtrate decreased in the complex
 524 matrix compared with previous pure water tests, which could be attributed to
 525 adsorption onto suspended solids and competition from organic carbon with these
 526 neutral micropollutant molecules. The extent of TCS and E2 desorption were much
 527 higher in the anaerobic filtrate than in pure water tests. These results indicate that
 528 constituents in real anaerobic wastewater would hinder TCS and E2 adsorption and
 529 desorption with phosphate exchangers.

530
 531

532 **Table 3:** TCS, E2 and SMX removal and regeneration by ion exchangers in anaerobic
 533 effluent.

	Clinoptilolite		LayneRT		DOW-HFO-Cu	
	% removal	% regeneration	% removal	% regeneration	% removal	% regeneration
TCS	NA	NA	50	74	54	68
E2	NA	NA	59	55	66	68
SMX	NA	NA	57	3	71	4

534

535 The fate of micropollutants during struvite precipitation

536 The concentrations of TCS, E2 and SMX in the aqueous solution did not decrease during
 537 struvite precipitation (Table S8), indicating that these micropollutants were not able to
 538 adsorb on, or assimilate into, struvite crystals. The distribution coefficient D_{ow} (Table S1)
 539 shows that, at pH 9, which was used for struvite precipitation, the majority of TCS and
 540 E2 molecules were still hydrophobic, whereas SMX was mostly dissociated and
 541 hydrophilic. Previous reports suggested that the accumulation of micropollutants in
 542 struvite cannot be fully explained by hydrophobicity since relatively hydrophilic
 543 compounds tetracycline ($\log K_{ow} = -1.37$) and quinolones ($\log K_{ow} = 0.89$) were observed
 544 in struvite crystals^{34,35}.

545

546 In previous studies, the majority of tetracycline accumulation in struvite was considered
 547 to be due to spontaneous assimilation into struvite's structure during formation, rather
 548 than being adsorbed onto the surface of pre-formed struvite^{34,35}. This finding was
 549 explained by tetracycline's potential as a ligand, wherein the molecule's β -hydroxyl
 550 ketone moiety can donate electron pairs to form stable complexes with Mg^{2+} or Ca^{2+}
 551 ^{35,66-68}. Thus, the partitioning of E2, TCS, and SMX to the aqueous phase observed in this
 552 study may be explained by the compounds' inability to form coordination complexes
 553 with Mg^{2+} in struvite. According to the pKa value, more than 98% of E2 was in neutral
 554 form at pH 9, clearly preventing it from participating in Lewis acid-base reactions with
 555 metal ions. For TCS, the charged fractions dominate at pH 9. The dissociated phenolic
 556 group on TCS (Table S1) is affected by resonance due to the presence of benzene. The
 557 resonance phenomenon makes non-bonded electron pairs of oxygen form double bonds
 558 with benzene carbon, turning the dissociated phenolic group into more acidic forms,
 559 which can result in difficulty forming a coordinate bond between TCS and Mg^{2+} ^{37,69}.
 560 Dissociated SMX also dominates at pH 9. The charged fraction of SMX can form
 561 coordinate complexes with first and second row transition metals such as Cr, Mn(II),
 562 Zn(II), Cd(II), and Co(II).^{70,71} However, as negligible removal of SMX was observed during
 563 struvite precipitation, SMX may not be able to form complexes with metals such as

564 Mg(II). According to hard soft acid bases rules ⁷², Mg is a hard acid that is relatively
565 nonpolarizable; therefore, it is easier for Mg to form stable complexes with hard bases
566 such as OH⁻, which is present in tetracyclines. However, it is more difficult for Mg to
567 form stable complexes with the soft base functional groups in SMX such as sulfonamide
568 nitrogen, amino nitrogen, and sulfonyl oxygen. Thus, micropollutants that cannot form
569 coordinate complexes with the metal in struvite are unlikely to be present in
570 precipitated struvite.

571 Conclusions

572 This research demonstrated that ion exchange-precipitation can effectively recover
573 nutrients from nutrient-rich waters (both lab-grade and actual anaerobic effluent),
574 regardless of the presence of TCS, E2 and SMX. The extent of nutrient sorption and
575 desorption was not influenced by the presence of these micropollutants, but the
576 reaction rate of nutrient exchange decreased when TCS, E2, and SMX were present.
577 These neutral and anionic micropollutants were able to co-adsorb to phosphate
578 exchangers while orthophosphate was exchanged and were desorbed during ion
579 exchanger regeneration. However, these micropollutants did not partition to
580 precipitated struvite, so they do not pose risks in the final solid fertilizer product.

581
582 The findings from this research have real-world implications. Specifically, the
583 adsorption/desorption behaviors indicated that micropollutants could accumulate on
584 ion exchangers, which may eventually lead to saturation of the ion exchangers, causing
585 bypass of micropollutants into the ion exchange effluent that would put additional
586 stress on mainstream treatment or receiving natural waters, depending on whether ion
587 exchange feed water is from AnMBRs or AD belt filter filtrate. When the micropollutants
588 were present in actual anaerobic wastewater, they did not interfere with nutrient
589 removal and recovery; however, the complex matrix of anaerobic wastewater tended to
590 decrease co-adsorption and increase desorption of TCS and E2 from phosphate-specific
591 exchangers. There could also be greater chances for these neutral compounds to be
592 present in the ion exchange bed effluent or regeneration solution. Therefore, other non-
593 selective adsorbents, such as biosolids-derived biochar, could be employed prior to ion
594 exchange to remove micropollutants before recovering nutrients ⁵².

595
596 The fate of micropollutants through ion exchange-precipitation process is closely related
597 to the physical and chemical properties of both micropollutants, ion exchangers and
598 struvite. For example, clinoptilolite did not sorb selected micropollutants, likely on the
599 basis of surface charge and molecular size disparities, and the ability of micropollutants
600 to form coordinate complexes with the metal ions in struvite crystals appears to be the
601 key factor that determines partitioning of micropollutants between the aqueous phase

602 and the precipitated struvite product. Future research extending these results to
603 cationic and zwitterionic micropollutants can help to derive more universal conclusions
604 related to the impact and fate of micropollutants during nutrient recovery.

605 Supporting Information

606 The Supporting Information (SI) is available free of charge on the RSC Publishing Home
607 website. The SI includes additional information related the micropollutant structure and
608 properties, desorption datasets, LC-MS operation and analysis, calculation details of
609 adsorption capacities and recoveries, kinetic modeling approach, response surface
610 methodology, kinetic datasets, activity coefficient calculations, zeta potential and pore
611 size analyses, nutrient isotherms, SEM images, and struvite data.

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