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# Ion Exchange-Precipitation for Nutrient Recovery from Dilute Wastewater

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## Ion Exchange-precipitation for Nutrient Recovery from Dilute Wastewater

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**Abstract:** Regulated phosphorus (P) and nitrogen (N) discharges and the cost of fertilizer provide economic drivers for nutrient removal and recovery from wastewater. This study used ion exchange (IX) in dilute (domestic) wastewater to concentrate nutrients with subsequent recovery by struvite precipitation. This is the first tertiary wastewater treatment study directly comparing P removal using a range of Fe, Cu, and Al-based media followed by clinoptilolite IX columns for N removal and precipitation using the combined regenerants. Phosphate removal prior to breakthrough was 0.5–2.0 g P L<sub>media</sub><sup>-1</sup>, providing effluent concentrations <0.1 mg L<sup>-1</sup> PO<sub>4</sub>-P and <0.2 mg L<sup>-1</sup> NH<sub>4</sub>-N for ≥80 bed volumes. Dow-FeCu resin provided effective P removal, efficient neutral pH regeneration and 560 mg P L<sup>-1</sup> in the regeneration eluate (≥100× concentration factor). Exchange capacity of clinoptilolite in column mode was 3.9–6.1 g N L<sub>media</sub><sup>-1</sup> prior to breakthrough. Precipitation using the combined cation and anion regenerants resulted in a maximum of 74% P removal using Dow-FeCu. Precipitates contained impurities, including Al<sup>3+</sup>, Ca<sup>2+</sup>, and Fe. Overall, the IX-precipitation recovery process removed ≥98% P and 95% N and precipitates contained 13% P and 1.6% N. This sequential process can

satisfy increasingly stringent wastewater standards and offers an effective alternative to traditional treatment technologies that simply remove nutrients. Approximately 84% of total P and 97% of total Kjeldahl N entering a treatment plant can be captured (accounting for primary clarifier removal), whereas most existing technologies target side streams that typically contain only 20–30% of influent P and 15–20% of influent N.

## Water impact

Wastewater treatment targets removal of nitrogen (N) and phosphorus (P). Productive agriculture also depends on N and P, where P is a nonrenewable resource, diminishing reserves of which encourage not only removal from wastewater, but also recovery for fertilizer use. This research advances sustainable, economic approaches to domestic wastewater treatment through recovery of clean water and valuable nutrient fertilizers.

## Introduction

The macronutrients nitrogen (N) and phosphorus (P) are commonly applied to improve agricultural yields.<sup>1</sup> Currently, the Haber–Bosch process produces 500 million tons per year of N fertilizer, accounting for 1% of the world's energy consumption.<sup>2.3</sup> Phosphate (PO<sub>4</sub><sup>3–</sup>) rock is mined to produce PO<sub>4</sub><sup>3–</sup> fertilizer, and depletion of available reserves is possible within the next 60–240 years.<sup>4</sup> A substantial portion of P fertilizer demand ( $\approx$ 15%) could be satisfied by municipal wastewater facilities.<sup>1.5.6</sup> To comply with effluent permits, municipalities commonly remove N through nitrification/denitrification,<sup>7</sup> while P is removed in the biosolids through precipitation and biological uptake.<sup>6</sup> Although these processes successfully remove nutrients from wastewater, agricultural reuse of biosolids is commonly regulated and P bioavailability can be inhibited by Fe and Al binding.<sup>6.8</sup> A more sustainable approach is to recover the N and P removed to satisfy discharge permits and recycle it as a valuable fertilizer product.

Ion exchange (IX), or the exchange of ions of similar charge between liquid and solid phases, is a promising method of concentrating nutrients for subsequent recovery.<sup>9–11</sup> Ammonium (NH<sub>4</sub>+) and PO<sub>4</sub><sup>3–</sup> are removed using cationic and anionic IX media, respectively. Clinoptilolite is a natural zeolite that preferentially exchanges NH<sub>4</sub>+.<sup>12</sup> Synthetic PO<sub>4</sub><sup>3–</sup>-selective media have been developed, including: Dow-Cu, Dow-HFO-Cu, LayneRT<sup>M</sup> and others.<sup>9,13–15</sup> Yet, improved selectivity of PO<sub>4</sub><sup>3–</sup> remains a critical need to facilitate use in full-scale applications.<sup>11,16</sup> Small-scale column tests of polymeric ligand exchangers indicate that improved selectivity of PO<sub>4</sub><sup>3–</sup> sorption and controlled release to recover the PO<sub>4</sub><sup>3–</sup> can be achieved using hydrated ferric oxide and/or Cu<sup>2+</sup> loading.<sup>9,14,17–19</sup> Upon exhaustion of surface exchange sites, the media is regenerated with brine solution,

producing concentrated P or N eluate. Subsequent treatment processes, such as struvite precipitation, can recover concentrated P and N from the eluate in a readily reusable form.<sup>20,21</sup>

Clinoptilolite's NH<sub>4</sub>-N removal and recovery capacity is well-defined<sup>22,23</sup> and previous work has determined that high pH regenerants improve desorption;<sup>24</sup> however, excessive pH can negatively impact subsequent NH<sub>4</sub>-N capacity.<sup>25</sup> In the current work, optimal regenerant NaCl concentration and pH were identified through multiple cycles of IX batch tests. Additionally, the concentration of cations and the pH of the regeneration eluate were analyzed as these have not previously been well-defined and these characteristics affect downstream processes (e.g., precipitation). This study also evaluated the mass of P exchanged (g  $P_{removed} L_{media^{-1}}$ ) and effluent PO<sub>4</sub>-P concentration using a range of Fe, Cu, or Albased media, direct wastewater comparisons of which have not been reported. The pH and concentrations of PO<sub>4</sub>-P and metals of the regeneration eluate were analyzed.

Struvite (MgNH<sub>4</sub>PO<sub>4</sub>) precipitation has previously been tested in anion exchange regeneration eluates<sup>9.26</sup> and using select combinations of cation and anion regeneration eluates.<sup>16,21,27,28</sup> The present study directly compared performance of cation eluate combined with a range of P-specific anion regeneration eluates to precipitate N and P from dilute wastewater. Nutrient recovery and purity of the fertilizer were evaluated as these parameters directly influence process economics. Results of this work advance practical application of nutrient recovery by improving upon existing treatment options to design economical nutrient recovery processes for dilute wastewaters. This recovery scheme can produce effluent which satisfies nutrient discharge limits while recovering a valuable fertilizer product. Furthermore, the IX-precipitation nutrient recovery process can facilitate implementation of more sustainable treatment trains such as those utilizing anaerobic membrane bioreactors, which avoid the costs of aerobic-driven nutrient removal.

## Materials and methods

Anion exchange tests were conducted with PO<sub>4<sup>3-</sup></sub>-selective media. Three commercially available IX resins were purchased ready-to-use: LayneRT<sup>™</sup> (Layne Christensen Co., The Woodlands, TX) and a neutral and basic activated alumina (AA, Sigma Aldrich, Milwaukee, WI). Four anionic media were prepared in the lab using the base resin Dowex<sup>™</sup> M4195 (Dow Chemical Co., Midland, MI). Dow-Cu was prepared in accordance with Zhao and Sengupta (1996).<sup>14</sup> Preparation of Dow-NAB-Cu followed the same process excluding the acid and base pretreatment steps. The hydrated ferric oxide (HFO) resin, Dow-HFO, was produced as described by Sengupta and Pandit (2011).<sup>9</sup> The

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Dow-HFO and Dow-Cu preparation methods were conducted sequentially to produce a resin loaded with iron and copper, denoted as Dow-FeCu in this work, similar to Dow-HFO-Cu described by Sengupta and Pandit (2011).<sup>9</sup>

Clinoptilolite (St. Cloud Zeolite, Tucson, AZ) in the sodium aluminosilicate form was utilized for NH<sub>4</sub>-N exchange. The exchange sites were saturated with Na<sup>+</sup> by adding 25 g of zeolite to a 0.5 L bottle and rinsing  $3 \times$  with deionized (DI) water to remove fine particles, similar to the method described by Weatherley and Miladinovic (2004).<sup>29</sup> Next, 0.5 L of 1% NaCl was added and the mixture was placed on a shaker table at 150 rpm for 2 d. The solution was discarded and the media was rinsed  $2 \times$  with DI water and dried at 103 °C for 24 h.

#### **Batch IX studies**

To determine the effect of various regenerants on subsequent IX capacity, zeolite batch testing was conducted using a shaker table at room temperature. Two sets of zeolite experiments were conducted in triplicate: zeolite with NH<sub>4</sub>-N solution and zeolite with mixed cations. Bottles containing zeolite and 40 mg L<sup>-1</sup> NH<sub>4</sub>-N solution were evaluated using varying regenerant solutions, as listed in Table 2. Initial kinetic tests demonstrated that sorption equilibrium was achieved within 4 days. Thus, all tests were conducted under the following conditions: 128 mL solution, 4 d IX duration, 2 h regeneration duration, and 150 rpm rotation speed. IX and regeneration were conducted for 3 cycles; zeolite was rinsed with DI water 2× after each regeneration cycle. The concentration of NH<sub>4</sub>-N in the final IX and regeneration solutions was analyzed to determine removal and desorption, respectively. A mixed cation solution (representative of a typical dilute wastewater) containing 40 mg NH<sub>4</sub>-N L<sup>-1</sup>, 35 mg Ca<sup>2+</sup> L<sup>-1</sup>, 10 mg K<sup>+</sup> L<sup>-1</sup>, 22 mg Mg<sup>2+</sup> L<sup>-1</sup>, and 140 mg Na<sup>+</sup> L<sup>-1</sup> was used to determine competitive uptake and the optimal regenerant solution for zeolite.

To determine the capacity of each anion exchange media,  $PO_4$ -P batch testing was conducted using 100 mg L<sup>-1</sup> PO<sub>4</sub>-P in DI water. One IX cycle followed by one regeneration cycle was conducted for each media to determine percent P removal and desorption. All media/regenerant pairs tested are shown in <u>Table 1</u>.

 Table 1 Phosphate removal and desorption in batch tests using anionic IX resin

Resin	% removalª	Regenerant <sup>b</sup>	% desorptionª
DOW-Cu	$76 \pm 0.1$	6% NaCl, pH = 4.3	$60 \pm 5.4$
DOW-FeCu	$64 \pm 1.4$	6% NaCl, pH = 8	65 <u>±</u> 3.2
LayneRT™	60 ± 1.6	2% NaCl + 2% NaOH, pH > 14	49 <u>+</u> 3.9

Resin	% removalª	Regenerant <sup>b</sup>	% desorptionª
Dow-NAB- Cu	53 ± 1.0	6% NaCl, pH = 4.3	38 ± 2.9
DOW-HFO	$52 \pm 0.4$	6% NaCl, pH = 8	8 ± 1.9
AA neutral	32 <u>±</u> 1.4	6% NaCl, pH = 7.5	31 ± 4.0
AA basic	$28 \pm 1.1$	6% NaCl, pH = 9.5	$53 \pm 14$

a Average results of triplicate measures ±1 standard deviation. b pH of all regenerants is that at which the media was prepared, with the exception of LayneRT<sup>™</sup>, for which regenerant pH was based on Blaney et al. (2007).<sup>35</sup>

#### **Column IX studies**

To determine exchange capacity under more realistic operating conditions, the top three performing anion resins and zeolite were tested using rapid small-scale column tests, as illustrated in Fig. 1. Secondary wastewater effluent was passed through 1.5  $\mu$ m filters and used as column influent. This pre-filtration step was used to model realistic operating conditions for scenarios with low TSS due to tertiary filtration. As stricter regulatory compliance is required and water reuse becomes increasingly economical, membrane filtration, including membrane bioreactors, is being increasingly implemented, thereby providing excellent effluent for subsequent IX processes. Column effluent was collected every 2 h using a CF-1 Fraction Collector (Spectrum Chromatography, Houston, TX). Influent and effluent were analyzed as described in the Analytical Procedures section. Regression analysis was completed for the effluent PO<sub>4</sub>-P or NH<sub>4</sub>-N to determine P or N removal prior to breakthrough, defined as 0.1 mg L<sup>-1</sup> PO<sub>4</sub>-P and 1.5 mg L<sup>-1</sup> NH<sub>4</sub>-N based on Wisconsin's discharge limits.<sup>30,31</sup>

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Fig. 1 Schematic of rapid small-scale column testing system.

Columns were regenerated with brine solution (based on optimal batch-scale testing) following the IX cycle. Regenerant effluent samples were initially collected after every 5–20 mL of brine passed, and every 50–100 mL as testing progressed. Regression analysis was conducted to estimate PO<sub>4</sub>-P or NH<sub>4</sub>-N desorption over time. This enabled quantification of percent nutrient desorption and nutrient concentrations in regeneration eluate at a range of brine volumes. Adequate IX capacity during subsequent cycles (as a result of P or N desorption) and elevated nutrient concentrations improve cost effectiveness of the process.

#### Precipitation

Precipitation was conducted in Erlenmeyer flasks by combining one anion regeneration eluate, zeolite regeneration eluate, MgCl<sub>2</sub> solution and NaOH for pH adjustment. Solutions were mixed with a target Mg : P : N ratio of 1 : 1 : 1 and a pH of 10. The mixture was stirred at 150 rpm for 10 min and then allowed to settle for 30 min. Supernatant was analyzed for PO<sub>4</sub>-P, NH<sub>4</sub>-N and cations. Percent removal was calculated and solids composition was estimated using a mass balance approach. For further evaluation, predicted precipitants were modelled using MINEQL+ v.4.62.3 and MINTEQ v.3.1 chemical equilibrium software. Struvite was added to the MINEQL+ custom thermodynamics database using pK = 13.26.32

#### Analytical procedures

Standard analytical methods<sup>33</sup> were used, including: phenate method 4500-NH<sub>3</sub>-F for NH<sub>4</sub>-N; cadmium reduction method 4500-NO<sub>3</sub>-E for NO<sub>3</sub>-N; turbidimetric method for SO<sub>4</sub><sup>2–</sup>; and method 2320 B for alkalinity. Additional analyses included the ascorbic acid method<sup>34</sup> for PO<sub>4</sub>-P and the Hach mercuric thiocyanate method for Cl<sup>–</sup>. Absorbance was measured using a Thermo Scientific (Waltham, MA) Genesys 20 spectrophotometer. An ICP-MS (7700 Series, Agilent Technologies, Santa Clara, CA) was used to measure Ca, Mg, K, Na, Al, Fe, Cu, Be, Cr, Mn, Co, Ni, Zn, Se, As, Mo, Pb, Hg, Ag, and Cd. A Thermo Scientific Orion 4 STAR meter was used for pH.

## **Results and discussion**

#### Phosphate exchange capacity

Batch tests showed that ≥60% P removal was achieved using Dow-Cu, Dow-FeCu, and LayneRT<sup>™</sup>, as shown in <u>Table 1</u>. Elimination of the acid/base treatment step for Dow-Cu (Dow-NAB-Cu) decreased performance by almost 25%. Despite both Dow-HFO and LayneRT<sup>™</sup> media utilizing HFO particles, which predominantly remove PO<sub>4</sub><sup>3-</sup> by ligand exchange,<sup>35</sup> Dow-HFO underperformed LayneRT<sup>™</sup>. Both basic and neutral activated alumina performed poorly in comparison to other media. The three resins with the greatest P removal (Dow-Cu, Dow-FeCu, and LayneRT<sup>™</sup>) also provided the greatest P desorption (≥49%), suggesting that they offer the greatest potential for P recovery operations. These media were used for subsequent column testing. Greater phosphate removal potential of these media stems from their incorporation of transition metal cations Fe and Cu. Polyvalent metals such as these exhibit strong ligand adsorption of phosphate species through Lewis acid–base interactions, i.e., formation of inner-sphere complexes.<sup>17,36</sup>

Effluent PO<sub>4</sub>-P concentration during each column run is shown in Fig. 2a. All three media maintained effluent PO<sub>4</sub>-P <0.1 mg L<sup>-1</sup> for  $\geq$ 80 bed volumes (BV). Achieving this low concentration is a critical study outcome as it is sufficient to satisfy increasingly lower wastewater discharge limits which may not be feasible using conventional precipitation and biological treatment processes.<sup>18</sup> These results suggest that LayneRT<sup>M</sup> was the optimal media as it required no preparation and provided the longest bed life prior to breakthrough, thereby maximizing P removal.

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**Fig. 2** PO<sub>4</sub>-P concentrations from column testing of anionic media showing (a) phosphate breakthrough comparison of IX media and (b) desorption comparison showing regeneration eluate concentration.

#### Regeneration performance with anionic media

After exhaustion of the anion exchange columns, media was regenerated with brine solution, as identified in <u>Table 1</u>. Regeneration was conducted to determine total P desorption, volume of regenerant required, and characteristics of the regeneration eluate. Effluent PO<sub>4</sub>-P and percent desorption after 5 BV are shown in <u>Fig. 2b</u>. In order to achieve 80% P desorption, 3.5 BV of regenerant was needed for LayneRT<sup>M</sup>, 3 BV for Dow-FeCu and 1.1 BV for Dow-Cu. Based on regression analysis, the regeneration eluates contained approximately 400–550 mg PO<sub>4</sub>-P L<sup>-1</sup> at 80% desorption, thereby concentrating PO<sub>4</sub>-P  $\geq$ 100×. This was sufficient for effective precipitation as full-scale struvite precipitation reactors are typically applied to side streams with >150 mg L<sup>-1</sup> PO<sub>4</sub>-P.<u>37.38</u>

The pH of Dow-Cu and Dow-FeCu regeneration eluates was approximately 9.6–9.9, whereas LayneRT<sup>M</sup> eluate was 14. As optimal pH for struvite precipitation is 8–9,<sup>39</sup> significant pH adjustment would be required when using LayneRT<sup>M</sup> eluate to precipitate struvite. LayneRT<sup>M</sup> eluate contained 155 mg L<sup>-1</sup> Al<sup>3+</sup>, while 7 and 30 mg L<sup>-1</sup> Cu<sup>2+</sup> were measured in Dow-Cu and Dow-FeCu eluates, respectively. Due to the detection of high metal concentrations in the regeneration eluates, there is a significant risk for coprecipitation of metals with struvite, resulting in decreased fertilizer value. Based on the results, Dow-FeCu is the optimal media for P desorption as it provided the greatest concentration of P (550 mg L<sup>-1</sup>) and the regeneration eluate pH was closest to optimal precipitation conditions.

#### Optimization of zeolite regeneration

High pH improves N desorption from zeolite;<sup>24</sup> however, excessive pH can cause attrition.<sup>25</sup> Batch tests were conducted using NH<sub>4</sub>Cl solution to identify the optimal pH and the effect of increasing NaCl concentration on long-term NH<sub>4</sub>-N exchange capacity. As shown in <u>Table 2</u>, initial tests were performed using 7 alternative regenerants. Regeneration tests did not conclusively identify an optimal NaCl concentration with respect to NH<sub>4</sub>-N removal. Regeneration solutions with pH  $\geq$  13 negatively impacted NH<sub>4</sub>-N exchange after 3 cycles. Based on these results, zeolite was tested in a mixed cation solution using lower pH regenerants.

Table 2 Removal of NH<sub>4</sub>-N using varying zeolite regenerant solutions

	NH <sub>4</sub> -N-only solution after 3 cycles					Mixed ion solution after 5 cycles					
Regenerant	5% NaCl	8% NaCl	10% NaCl	7.5% NaCl + 0.5% NaOH	0.5% NaOH	2% NaOH	2% Ca(OH) <sub>2</sub>	0.1% Ca(OH) <sub>2</sub>	0.1% NaOH	8% NaCl	7.5% NaCl pH 12
a Average results of triplicate data $\pm 1$ standard deviation.											
рН	7.5	8	8.3	13	13	13.7	13.7	12	12	8	12
Total NH <sub>4</sub> - N removal <sup>a</sup> (%)	70 ± 6.3	85 ± 0.6	76 ± 4.2	55 ± 1.5	66 ± 8.2	44 <u>+</u> 4.2	$0 \pm 0$	40 ± 1.6	56 ± 3.8	70 ± 0.2	71 ± 4.6

As shown in <u>Table 2</u>, regeneration with 8% NaCl and 7.5% NaCl (pH = 12) resulted in similar NH<sub>4</sub>-N removal after 5 cycles. Regeneration with 0.1% NaOH or 0.1% Ca(OH)<sub>2</sub> was ineffective, likely due to the lower concentration of cations driving desorption of NH<sub>4</sub>-N. A

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pH of 12 did not negatively impact IX, whereas pH of 13 did negatively impact removal after repeated IX cycles. Additionally, the data suggests that NaCl concentration can be reduced without diminishing capacity, with 2% NaCl being sufficient.<sup>24</sup>

#### Zeolite IX performance and regeneration efficiency

Zeolite was tested in columns to determine the media's NH<sub>4</sub>-N removal capacity when treating anion exchange effluent. Two IX cycles were conducted to determine the change in capacity following regeneration, as shown in Fig. 3a. Breakthrough was defined as 1.5 mg L<sup>-1</sup> NH<sub>4</sub>-N, which falls within the waterbody nutrient criteria range of 0.2–5 mg L<sup>-1</sup> total nitrogen (TN) developed by some states.<sup>31</sup> The effluent remained below this concentration for  $\geq$ 100 BVs, and was less than 0.2 mg L<sup>-1</sup> throughout the first IX cycle. Total removal prior to breakthrough was 3.9 g N L<sub>BV</sub><sup>-1</sup> and 6.1 g N L<sub>BV</sub><sup>-1</sup> for the first and second cycles, respectively. The variability in zeolite capacity was likely due to differences in influent cations. Concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> in the influent during cycle 2 were lower, enabling greater NH<sub>4</sub>-N exchange. The N removal capacities are comparable to zeolite tests performed using similar wastewater.<sup>23,40</sup>



Fig. 3 Two cycles of column testing of  $NH_4$ -selective zeolite showing (a) ammonium IX breakthrough and (b) desorption showing regeneration eluate concentration.

Zeolite was regenerated to evaluate reuse of the media for IX and to determine the regeneration eluate characteristics. Based on batch testing, 6% NaCl (pH = 11) regenerant was used. As shown in Fig. 3b, 74% and 68% of N was desorbed during cycles 1 and 2, respectively. Regeneration may potentially be improved by raising the regenerant pH and reducing NaCl concentrations to improve N desorption.

The eluate characteristics of the first two BV of regenerant are shown in <u>Table 3</u>. The eluate contains substantial amounts of Ca<sup>2+</sup> and K<sup>+</sup>, which may precipitate along with struvite, thereby decreasing the purity of the product. A reduction in fertilizer quality will reduce the value of the product and therefore the revenue.<sup>41</sup>

Table 3 Zeolite regeneration eluate characteristics for column tests

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Regeneration cycle	pН	NH4-N	K+	Ca <sup>2+</sup>	Mg <sup>2+</sup>
1	8.7	600	660	350	23

1	0.7 000	000 330	23
2	7.7 740	320 390	24

#### Precipitation efficiency and solids composition

The overarching process goal is recovery of struvite, a slow release fertilizer that performs comparably to standard fertilizers.<sup>6</sup> Precipitation tests were conducted to determine P and N recovery as well as product purity. Precipitation was accomplished by combining cation and anion IX column regeneration eluates containing high concentrations of N and P, respectively, adding Mg<sup>2+</sup> and adjusting the pH to 10. After settling the solids, the supernatant was analyzed to determine the P, N and metals concentrations, as shown in <u>Table 4</u>. Greater than 70% P removal was achieved with LayneRT<sup>™</sup> and Dow-FeCu regeneration eluates. Precipitation ceased at P concentrations of approximately 60–80 mg L<sup>-1</sup>. This was likely due to limited multivalent cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup>; however, it has also been shown that greater Ca : Mg ratios reduce P removal efficiency.<sup>42</sup> The majority of Al<sup>3+</sup>, Ca<sup>2+</sup> and Fe present in the initial concentrated regeneration solutions precipitated, which impacts product quality, and would necessitate additional testing to determine the precipitated product's potential as a fertilizer. This is a substantial issue for the LayneRT<sup>™</sup> regeneration eluate as the Al<sup>3+</sup> concentration exceeds 100 mg L<sup>-1</sup>.

**Table 4** Initial ion concentration and percent removal for precipitation of combined anion and zeoliteregeneration eluates

LayneRT™		DOW-	Cu	DOW-FeCu			
Initial (mg L <sup>-1</sup> )	% removalª	Initial (mg L <sup>-1</sup> )	% removalª	Initial (mg L <sup>-1</sup> )	% removalª		
a Average results of triplicate data $\pm 1$ standard deviation. b No result due to analytical error.							
270	$71 \pm 1.6$	120	$28\pm1.0$	230	$74 \pm 1.7$		
120	$19 \pm 1.8$	53	$16\pm0.9$	100	$22 \pm 1.6$		
170	$96 \pm 0.8$	84	$66 \pm 2.5$	270	$62 \pm 2.7$		
71	$81 \pm 4.0$	31	$45 \pm 0.2$	65	$98 \pm 0.6$		
78	$92 \pm 0.2$	0.28	$58 \pm 16$	0.15			
5.8	$76 \pm 0.2$	7.3	$79\pm0.3$	5.2	$100 \pm 0.0$		
0.28	59 ± 3.5	22	$9.5\pm0.3$	12	$14 \pm 0.5$		
130	$6.5 \pm 1.5$	58	$12 \pm 2.5$	111			
	Layne Initial (mg L <sup>-1</sup> ) ults of t ie to an 270 120 170 71 78 5.8 0.28 130	LayneRT <sup>™</sup> Initial (mg % L <sup>-1</sup> ) removal <sup>2</sup> ults of triplicate of the to analytical er 270 71 ± 1.6 120 19 ± 1.8 170 96 ± 0.8 71 81 ± 4.0 78 92 ± 0.2 5.8 76 ± 0.2 0.28 59 ± 3.5 130 $6.5 \pm 1.5$	Layne RT™       DOW-1         Initial       Initial         (mg       %       (mg         L <sup>-1</sup> )       removal # L <sup>-1</sup> )         uts of triplicate data ±1       triplicate data ±1         te to analytical error.       120         120       19 ± 1.6       120         120       19 ± 1.8       53         170       96 ± 0.8       84         71       81 ± 4.0       31         78       92 ± 0.2       0.28         5.8       76 ± 0.2       7.3         0.28       59 ± 3.5       22         130       6.5 ± 1.5       58	Layne $\mathbb{T}^{m}$ DOW- $\mathbb{U}$ Initial       Initial         (mg       %       (mg       %         L^-1)       removal $\mathbb{Z}$ L^-1)       removal $\mathbb{Z}$ uts of $\mathbb{T}^{r}$ picture $\mathbb{Z}$ $\mathbb{Z}^{-1}$ zandard         270 $71 \pm 1.6$ 120 $28 \pm 1.0$ 120 $99 \pm 1.8$ 53 $16 \pm 0.9$ 170 $96 \pm 0.8$ 84 $66 \pm 2.5$ 71 $81 \pm 4.0$ $31$ $45 \pm 0.2$ 78 $92 \pm 0.2$ $0.28$ $58 \pm 16$ 5.8 $76 \pm 0.2$ $7.3$ $79 \pm 0.3$ $0.28$ $59 \pm 3.5$ $22$ $9.5 \pm 0.3$ $130$ $6.5 \pm 1.5$ $58$ $12 \pm 2.5$	Layne T <sup>m</sup> DOW-U       DOW-I         Initial       Initial       Initial       Initial         (mg       %       (mg       %       (mg $(mg)$ %       (mg       %       (mg $(mf)$ %       (mg       %       (mg $(1^{-1})$ 12 $(1^{-1})$ 12 $(1^{-1})$ $(1^{2})$ $(1^{2} \pm 1.6)$ 120 $(2^{3} \pm 1.6)$ 100 $(120)$ $(1^{2} \pm 1.6)$ $(170)$ $96 \pm 0.8$ $84$ $66 \pm 2.5$ $(2^{-1} \pm 1.6)$ $(1^{-1} \pm$		

Removal of N was less than 25% in all precipitation tests, whereas 100% was targeted. P was likely being precipitated as calcium phosphates in addition to struvite and therefore N removal was lower than expected. Chemical equilibrium modeling confirmed that under these conditions Ca and Mg-based species such as hydroxyapatite, calcium phosphates, and magnesium phosphates were likely outcompeting struvite precipitation. Improved precipitate purity may be obtained by decreasing the pH to 8.7<sup>43</sup> (compared to 10, as in this study). Additionally, a reactor seeded with struvite pellets can be operated at a lower pH, such as 7.3, and achieve high P removal.<sup>44</sup> Therefore, future testing should be conducted with struvite seeding at neutral pH to minimize chemical requirements and reduce Ca<sup>2+</sup> precipitation while maximizing P and N removal.

A mass balance analysis was performed to estimate solids composition in order to assess fertilizer quality. The precipitates formed after combining LayneRT<sup>™</sup> and zeolite regeneration eluate contained: 13% P, 1.6% N, 11% Mg, 3.9% Ca, 0.6% K, 0.3% Fe, and 5.3% Al. In comparison, pure struvite should contain 13% P, 5.7% N, and 10% Mg. The amount of P and Mg in the precipitate from the lab test is similar to pure struvite; however, the N content is low, as discussed previously. Additionally, there are significant amounts of Ca<sup>2+</sup> and Al<sup>3+</sup>, which could negatively impact the fertilizer value of the precipitated product.

### Conclusions

The ultimate goal of nutrient recovery is to produce a marketable nutrient-rich product in addition to meeting nutrient discharge limits for the treated water. The IX-precipitation process evaluated here concentrated and precipitated P and N to accomplish this objective using dilute wastewater. A range of Fe, Cu, or Al-based media were used for direct performance comparison in wastewater. Using the top-performing  $PO_{4^{3-}}$ -selective resins, removal prior to column breakthrough was 0.5–2.0 g P  $L_{media}^{-1}$ , which provided effluent concentrations <0.1 mg  $L^{-1}$  PO<sub>4</sub>-P for  $\geq$ 80 BV and <0.2 mg  $L^{-1}$ NH<sub>4</sub>-N for  $\geq$ 100 BV. Dow-FeCu provided the most effective P removal, efficient neutral pH regeneration and 560 mg L<sup>-1</sup> P in the regeneration eluate (concentration factor  $\geq$  100). Greater than 98% PO<sub>4</sub>-P and 97% NH<sub>4</sub>-N were removed using combined anionic and cationic column regenerants for precipitation. The regenerant streams also contained substantial levels of Al, Cu, Ca, and/or K, which may diminish the value of the recovered product. Recommended future tests include continued testing of anion exchange media to determine the most economical media considering cost of preparation, P removal and selectivity, P desorption, chemical requirements and minimal metal leaching. Furthermore, the precipitation method can be adjusted to improve struvite purity and to evaluate the potential use of supernatant from precipitation as a recycled regenerant. Overall economics of the IX-precipitation process is of key interest for larger-scale implementation, and evaluation of chemical and energy costs, regenerant reuse, and price point of the recovered fertilizer product must be considered together in future assessments.

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