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## PAPER

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# Evaluating the use of chemically modified clinoptilolite zeolite for the simultaneous recovery of ammonium and phosphate from blackwater†

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Natural clinoptilolite zeolite (CZ) was chemically modified with sodium (Na), calcium (Ca), or magnesium (Mg) to recover ammonium and phosphate from simulated blackwater. Chemical modification of CZ with Na, Ca, and Mg was able to increase the mass of each metal by a factor of 2.2, 2.7, and 1.8, respectively. The removal performance of ammonium and phosphate by each chemically modified CZ under concentrations relevant to onsite wastewater treatment systems was evaluated. Initially, single ion isotherm tests were conducted to quantify phosphate and ammonium removal without the presence of the opposite nutrient. Without ammonium present, phosphate removal with Na and Mg modified CZ was marginal, observing sorption capacities of $0.06 \pm 0.19$ and $0.17 \pm 0.12$ g P g$^{-1}$, respectively, at a starting concentration of 95 mg P L$^{-1}$. At the same starting concentration, Ca modified CZ observed the highest phosphate sorption of $0.45 \pm 0.08$ g P g$^{-1}$. Phosphate removal was enhanced by the presence of ammonium in solution for Na, Mg and Ca modified CZ, achieving sorption capacities up to $0.38 \pm 0.06$, $0.98 \pm 0.02$ and $2.92 \pm 0.01$ mg P g$^{-1}$, respectively, at a starting phosphate concentration of 120 mg P L$^{-1}$. These removal capacities were associated with phosphate removal rates of $9.5 \pm 1.4\%$, $24.4 \pm 0.6\%$ and $72.7 \pm 0.4\%$ for Na, Mg and Ca modified CZ. The removal of ammonium remained consistent across a range of phosphate concentrations. The Langmuir isotherm model best predicted the phosphate sorption behavior to Mg and Ca modified CZ when ammonium was not present. When both nutrients were present in solution together, the Freundlich isotherm model best depicted the phosphate sorption behavior to Mg and Ca modified CZ. This change in isotherm behavior was due to a shift in surface reactions from primarily adsorption to primarily complexation. In both cases, phosphorus was recovered onto the zeolite surface as calcium phosphate precipitates. This supports the idea that the Ca content of the CZ, regardless of which metal was used for chemical modification, dictated the phosphate removal performance. X-ray fluorescence revealed that the zeolite granules retained nitrogen, phosphorus, and potassium at a molar ratio of 5.3 : 1 : 13.4 which can be used as a complete fertilizer or as an amendment for incomplete fertilizers.

### Water impact

Onsite and decentralized wastewater treatment systems experience high nutrient loading, yet effective and affordable treatment options are still limited to large-scale treatment facilities. Passive and low-oversight treatment options may assist in meeting increasingly stringent effluent standards. This study shows that calcium modified clinoptilolite zeolite is an effective material option for immobilizing phosphate while unaffecting the ammonium sorption capacity of clinoptilolite zeolite, exemplifying the versatility of zeolites as a sustainable dual nutrient recovery option.

## 1. Introduction

Nitrogen and phosphorus are necessary nutrients in the production of agricultural crops that maintain global food supplies. However, the discharge of anthropogenic nitrogen and phosphorus into local waterways have detrimental impacts on aquatic ecosystems as well as human health.[1] Onsite wastewater treatment systems (OWTS) have only recently been directly recognized as major contributors to nutrient pollution.[2] Nitrogen and phosphorus removal is minimal in conventional septic systems, with 10–30% nitrogen and 0–7% phosphorus removal by sludge settling being common performance values.[2,3] In the state of Florida, OWTS account for the third highest nitrogen loading to local water bodies, behind only atmospheric deposition and reclaimed water discharge.[4,5] Advance secondary OWTS technologies exist that can enable significant reductions in

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nitrogen by facilitating biological nitrification and denitrification processes and discharging nitrogen as nitrate. Yet, they do not always achieve effluent levels that meet local regulations consistently. In several New England coastal counties considered critical resource areas, studies have shown than advanced secondary OWTS targeted to meet the local standard of 19 mg N L$^{-1}$ do so 0–78% of the time, with their treatment effectiveness heavily dependent on the treatment train of the applied commercial technology and the daily nitrogen loading rates.[6–8] Meanwhile, achieving phosphorus reductions is left to natural attenuation in drainfields or requires an additional secondary or tertiary treatment step.[9] Drainfields with high clay content soils do well at removing phosphorus due to their high iron and aluminum content while sandy soils with limited metal oxides do poorly.[10] However, phosphate (PO$_4$) can inevitably desorb from soils and reach groundwater sources. Groundwater near OWTS, particularly near aged cesspools and conventional septic systems, has been associated with high phosphorus discharge to nearby lakes which has led to eutrophication.[11] When targeted phosphorus removal is desired, chemical dosing of iron (Fe) or aluminum (Al) salts or media adsorption are the primary methods for removal. Treatment units that use Fe-rich media are commercially available, but their adoption and implementation has been slow. Combining nitrogen and phosphorus removal into a single secondary treatment step using sorption media for nutrients management is a promising approach for managing the variable nutrient loading rates inherent to OWTS and to reduce the footprint of secondary and tertiary treatment needed to treat both nutrients separately.

A variety of natural, engineered, or industrial waste by-products have been investigated as a sorption media for phosphorus removal.[12] Natural materials include mineral apatite, dolomite, bauxite, and calcite, with studies reporting a wide range of sorption capacities, but on average below 5 mg P g$^{-1}$.[12–15] Dolomite, apatite, and calcite are calcium (Ca)-bearing minerals while bauxite is a mineral used as a rich source of aluminum. Industrial by-products tend to yield the highest sorption capacities, with fly ash exhibiting capacities upwards of 260–420 mg P g$^{-1}$.[16,17] For most sorption materials evaluated in the literature, a high CaO content is correlated with improved phosphorus sorption capacities.[12] At a pH between 6 and 7, minerals with high Ca content sorb phosphorus through the formation of Ca-PO$_4$ precipitates, such as amorphous calcium phosphate (ACP), dibasic calcium phosphate (DCP), and hydroxyapatite (HAP).[18]

For nitrogen removal, bentonites, zeolites, biochar, and other clay materials have been widely used for ammonium (NH$_4$) removal in wastewater due to their low cost.[19] Zeolites are an attractive material for nitrogen removal because of their high affinity for NH$_4$ uptake and ability to be regenerated and reused over many cycles.[20–22] Zeolite is a negatively charged aluminosilicate mineral that can exchange its extra framework cation with NH$_4$. Zeolites have an order or ionic preference of K$^+$ > NH$_4^+$ > Na$^+$ > Ca$^{2+}$ > Mg$^{2+}$

making them attractive for nitrogen removal and recovery from wastewater.[23] While zeolite is used exclusively as a cationic exchange material, it is also capable of phosphorus uptake, particularly orthophosphate.[24–27] Orthophosphates can be retained by strong interactions with the loosely bound extra framework cation or with Brønsted acid sites within the zeolite cavities.[28,29] There is evidence that phosphates complex with metal framework cations and are retained within the zeolite structure as NaH$_2$PO$_4$, NaHPO$_4$, and followed by H$_2$PO$_4$, with CaHPO$_4$ and MgHPO$_4$ at a much lower presence.[29]

Recently, using zeolites for the simultaneous removal of nitrogen and phosphorus has gained significant interest. Promising PO$_4$ sorption capacities have been reported for natural (clinoptilolite), chemically altered, thermally altered, and synthesized zeolites but the range of removal is quite variable (0.4–40 mg P g$^{-1}$) and heavily dependent on the initial concentrations of both PO$_4$ and NH$_4$ and the metal used as the extra framework cation.[27,30–32] For clinoptilolite zeolites (CZs) chemically modified with metals such as sodium (Na), Ca, magnesium (Mg), Fe, or aluminum (Al) the concentration of NH$_4$ dictates the level of PO$_4$ removal, however, the maximum capacities are commonly reported but are not achievable in practice. It is not clear how the sorption capacities for both NH$_4$ and PO$_4$ will be influenced by different ratios of NH$_4$ to PO$_4$ that are directly observed in practice and the impact the removal of both ions will have on the effluent quality with regards to dissolved metals. At high nitrogen to phosphorus (N/P) ratios as observed in OWTS (3–40), NH$_4$ can exchange readily with extra framework metals attached to natural zeolites and allow for such metals to complex with PO$_4$, removing both ions from water simultaneously and efficiently.

Therefore, this study aims to identify the sorption performance of chemically modified CZ to remove NH$_4$ and PO$_4$ at concentrations and N/P ratios relevant to onsite wastewater. The objectives are to (1) quantify the sorption performance of chemically modified CZ with three distinct metal cations (Na, Mg, and Ca) for removing both nitrogen and phosphorus in a single reactor; (2) characterize the cation composition of the effluent post sorption; (3) apply sorption isotherm models, including Langmuir and Freundlich, to give insight into the sorption mechanisms; and (4) evaluate the elemental and surface compositional changes of zeolite. We further discuss the implications of using CZ as a treatment method for OWTS and reusing nutrient loaded CZ for agricultural applications.

## 2. Materials and methods

### 2.1. Clinoptilolite zeolite pre-treatment

Granular natural CZ composed of hydrous sodium aluminosilicate was used as the primary zeolite source and had a chemical formula of Na$_6$(Al$_6$Si$_{30}$O$_{72}$)H$_2$O (KMI Zeolite, Amargoza Valley, NV). This material was chosen due to its low cost and ability to uptake both NH$_4$ and PO$_4$ (see Fig. S1 and Table S1 in ESI† section Material selection). The CZ was

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sieved and had on average a diameter of 0.85–1 mm. Prior to any testing, the CZ was first rinsed three times with deionized water (DI) and then dried at 105 °C for 24 hours. Three metal cations were selected, Na, Ca, and Mg, to pre-treat CZ for testing. Potassium (K) was initially evaluated as well but did not observe any phosphate removal after contact with 500 or 5000 mg P L$^{-1}$ in preliminary test and was therefore not used (Table S2†). From here on, each pre-treated CZ is denoted as Na-PT CZ, Mg-PT CZ, or Ca-PT CZ to distinguish between the three metal ions used for pre-treatment. A total of 50 g of washed zeolite was soaked in 500 mL of either 2 M NaCl, CaCl$_2$, or MgCl$_2$ for Na, Ca, or Mg pre-treatment, respectively. The CZ was shaken continuously in an orbital shaker at 150 RPM and allowed to soak in solution for 48 h. Samples of the soaking solution were collected before and after 48 h to verify the mass adsorption of each cation onto the CZ. The granules were then rinsed with ultrapure water and dried at 105 °C for 24 hours and stored in a desiccator.

### 2.2. Single nutrient sorption characterization

The sorption dynamics of NH$_4$ onto zeolite has been heavily documented by previous literature. However, sorption isotherms with only NH$_4$ present were conducted as a control to understand the effects of PO$_4$ presence on the NH$_4$ sorption capacity of the pre-treated CZ used in this study. A total of five NH$_4$ concentrations relevant to the nutrient composition of blackwater were assessed for each pre-treated CZ: 100, 200, 300, 400, and 500 mg NH$_4$–N per liter using NH$_4$Cl in DI water. These concentrations fell within the range of NH$_4$ that has been observed in the permeate of an AnMBR used as an OWTS.[20] For each flask, 3 g of Na, Ca, or Mg pre-treated CZ was added into 100 mL of the described NH$_4$ solutions and shaken for 48 h. Liquid samples were taken from the five stock solutions before testing began and from each experiment flask after the 48 h period. All samples were centrifuged and filtered with 0.45 μm filters before processing. The remaining granules were dried for 24 h at 105 °C and stored in an airtight container.

A similar procedure was taken for determining the removal capacity of CZ with phosphorus as the main nutrient present. Batch experiments used 0.51 g K$_2$HPO$_4$ and 4.0 g KH$_2$PO$_4$ to yield a phosphate buffer stock solution of 32 mM (1000 mg PO$_4$–P per liter) and was diluted with DI water to yield stock concentrations of 10, 25, 50, 100, and 500 mg PO$_4$–P per liter with an average starting pH of 6.02 ± 0.07. A volume of 100 mL for each concentration was added to a flask containing 3 g of Na, Ca, or Mg pre-treated CZ. All flasks were shaken for 48 h and liquid samples before and after mixing were collected as previously described.

### 2.3. Ammonium and phosphate sorption characterization

The simultaneous removal of NH$_4$ and PO$_4$ was evaluated under 15 different scenarios. The first ten tests were conducted to develop the sorption models for PO$_4$ and NH$_4$, respectively, while maintaining one nutrient concentration constant and varying the nutrient of interest. The final five tests (11–15) were used to validate whether the sorption capacities were influenced by the presence of the opposite nutrient ion. All tests were conducted similarly to the previously described sorption tests. In five scenarios, the starting NH$_4$ concentration of the solution remained constant near 340 mg N L$^{-1}$ while the concentration of PO$_4$–P added was varied between 10, 30, 50, 70, and 100 mg P L$^{-1}$. The next five scenarios varied the NH$_4$ concentration between 100, 200, 300, 400, and 500 mg N L$^{-1}$ while the concentration of PO$_4$ remained constant near 65 mg P L$^{-1}$. The constant concentrations of NH$_4$ and PO$_4$ were both selected based on the average concentrations observed previously from a field tested OWTS.[33] The last five tests varied both in NH$_4$ and PO$_4$ concentrations, each containing an initial $N_o/P_o$ ratio within the range 3.7–31. Two stocks solutions were prepared where one contained 10.01 g NH$_4$Cl and the other contained 2.98 g (NH$_4$)$_2$HPO$_4$ per liter, thus, eliminating the presence of any competing cation. The pH of the final solutions varied slightly due to the variations of NH$_4$ concentration, but all remained between pH 7–8. The stock solutions were diluted and mixed to reach the desired concentrations of NH$_4$ and PO$_4$. Samples of the soaking solution were collected before and after 48 h to verify the removal of nutrients and the composition of the bulk liquid.

### 2.4. Chemical analysis

Reactive PO$_4$ was measured using the phosphorus molybdovanadate Test 'N Tube method (HACH method 8114) while NH$_4$ was measured using the nitrogen–ammonia salicylate Test 'N Tube method (HACH method 10031). All samples were filtered with 0.45 μm filters and processed immediately. During analysis, all procedures were followed as outlined by the manufacturer. The pH of all samples was also measured immediately after sample collection. Relevant cations, such as Na, NH$_4$, K, Ca, and Mg were measured using ion chromatography (Metrohm 930 Compact IC Flex). The ions Na, NH$_4$, and K had a detection limit of 0.2 mg L$^{-1}$ while the limit was 1.0 mg L$^{-1}$ for Mg and Ca.

### 2.5. Characterization of material composition

At the end of each 48 hour sorption test, the CZ and liquid mixture were filtered through a 0.45 μm glass fiber filter. The liquid portion was collected for water quality analysis while the solids were rinsed with ultrapure water and dried at 105 °C for 24 hours and stored in a desiccator for downstream microscopy imaging and elemental identification. Eight samples of clinoptilolite zeolite were processed for elemental analysis using X-ray fluorescence (XRF) spectrometry (Bruker S2 PUMA series 2) equipped with a Hisense detector. Six samples were selected from the experimental tests for analyses, including: raw CZ, Na-PT CZ, Ca-PT CZ, Mg-PT CZ, Mg-PT CZ after contact with 0.066 g P L$^{-1}$ and 0.43 g N L$^{-1}$, and Ca-PT CZ after contact with 0.067 g P L$^{-1}$ and 0.32 g N

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$L^{-1}$. Additionally, two Ca-PT CZ samples soaked in either 0.5 g P $L^{-1}$ or 5.0 g P $L^{-1}$ were also analyzed. Prior to XRF analysis, the granule samples were first ground into fine powders. For six of the eight zeolite samples, the masses of specimen powder processed were 2.135 ± 0.375 g, while 8.0 g and 10.3 g of specimen mass were used for detection of zeolite from the 0.5 g P $L^{-1}$ and 5.0 g P $L^{-1}$ experiments, respectively. All detections were performed under helium. Elemental quantification was performed using the SPECTRA. ELEMENTS software.

In addition to XRF analysis, microscopic imaging was accomplished using a dual-beam Focused Ion Beam – Scanning Electron Microscope (FIB-SEM) (Quanta 200 3D) with a gallium ion source. All images were captured at a high acceleration voltage of 30 kV and current of 0.35 nA. An IXRF 550i digitizer, along with Iridium Ultra software (version 2.4L) were used for image acquisition, EDS mapping, and spectral analysis.

### 2.6. Data analysis & calculations

**2.6.1. Sorption by clinoptilolite zeolite.** To determine the sorption of either $NH_4$ or $PO_4$ during the reaction period, the following equation was applied:

$$q_e = \frac{(C_o - C_e) \times V}{m_z} \quad (1)$$

Where $C_o$ is the initial concentration of the sorbate (mg $L^{-1}$), $C_e$ is the concentration of the sorbate in the solution at equilibrium (mg $L^{-1}$), $V$ was the volume of the solution in liters and $m_z$ was the initial dry mass of the clinoptilolite zeolite (sorbent) in grams. All liquid samples were analyzed in triplicates and the standard deviation across the replicates was reported. Percent removals, $R$, were determined by:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

**2.6.2. Sorption isotherms.** Two adsorption isotherm models, Langmuir and Freundlich, were evaluated to describe the sorption mechanism of $NH_4$ and $PO_4$ removal using the R package PUPAIM.[34] The Langmuir isotherm model assumes that a continuous monolayer of sorbate molecules forms on a homogeneous sorbent surface and that binding sites are identical.[35,36] The Freundlich model is entirely empirically derived, but it assumes that a multilayer of sorbate molecules form onto a heterogeneous sorbate surface and that surface sorption is not uniform. Freundlich is only valid for low concentrations where the relationship between mass sorbed and the mass in the bulk liquid is linear. In this context, the Langmuir model's Goodness-of-Fit is indicative of dominance in ion-exchange mechanism while the Freundlich isotherm corresponds more closely to adsorption and complexation reactions taking place on the sorbent surface.[37] The non-linear Langmuir isotherm model was used to describe chemical adsorption at equilibrium:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where $q_e$ is the sorption capacity at equilibrium (mg $g^{-1}$), $q_m$ is the maximum sorption capacity (mg $g^{-1}$), and $K_L$ is the ratio of adsorption rate to desorption rate (L $mg^{-1}$).[38] Once the ratio of adsorption to desorption rate is known, the separation factor, $R_L$, can also be determined by:

$$R_L = \frac{1}{1 + K_L C_o} \quad (4)$$

The separation factor indicates whether sorption is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), and irreversible ($R_L = 0$).[39] The empirically derived non-linear Freundlich isotherm model was also evaluated to describe physical adsorption:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where $K_F$ is the Freundlich constant and is comparable to the sorption capacity of the adsorbent and $n$ is a constant that represents the heterogeneity of the adsorbent surface.[40] The constant $1/n$ indicates whether sorption is unfavorable ($1/n > 1$), linear ($1/n = 1$), favorable ($0 < 1/n < 1$), and irreversible ($1/n = 0$). For each model, the standard error (SE) for each constant, the adjusted $R^2$, the $p$-value ($\alpha = 0.05$), and residual standard error (RSE) are reported.

## 3. Results

### 3.1. Ammonium and phosphorus removal *via* zeolite sorption

A total of ten different tests containing a variation of $NH_4$ and $PO_4$ concentrations were conducted to determine the equilibrium sorption capacities of CZ pre-treated with either Na, Ca, or Mg. The tests were divided into two groups where tests 1–5 began with $PO_4$ concentrations of 66.5 ± 0.6 P mg $L^{-1}$ and a range of $NH_4$ concentration spanning 100–550 mg N $L^{-1}$ (Table 1). The second set of five tests (tests 6–10) began with similar $NH_4$ concentrations of 344 ± 14 mg N $L^{-1}$ but with variable $PO_4$ concentrations ranging from 10.5 to 121 mg P $L^{-1}$. Two sets of control tests were conducted with only a single nutrient present, phosphorus or nitrogen, within the ranges previously mentioned.

Without the presence of nitrogen, the $PO_4$ sorption capacity of all pre-treated CZ was low and dependent on the pre-treatment cation used. Na-PT CZ showed little to no removal of $PO_4$ (Fig. 1A and B). The $PO_4$ sorption capacity improved slightly for Mg-PT CZ and furthermore with Ca-PT CZ (Fig. 1C–F). Both Mg-PT CZ and Ca-PT CZ $PO_4$ sorption had a positive linear relationship with the initial concentrations, where CZ with higher initial $PO_4$ concentrations observed higher sorption capacities. At a starting concentration of 95 mg P $L^{-1}$, corresponding to the highest sorption capacities observed when there was no $NH_4$ present, the sorption capacities reached values of 0.06 ± 0.19,

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**Table 1** Summary of sorption test initial conditions for simultaneous nitrogen and phosphorus removal. All tests were conducted in contact with Na, Ca, or Mg-PTCZ for 48 hours

| Test | $N_o$ | $P_o$ | $N_o/P_o$ | $pH_o$ |
|---|---|---|---|---|
| Constant $PO_4$ and variable $NH_4$ | | | | |
| 1 | $103 \pm 7.8$ | $67.5 \pm 0.5$ | 1.5 | 7.83 |
| 2 | $206 \pm 11$ | $66.5 \pm 0.0$ | 3.1 | 7.65 |
| 3 | $318 \pm 4.2$ | $66.5 \pm 0.0$ | 4.8 | 7.55 |
| 4 | $425 \pm 8.5$ | $66.3 \pm 0.4$ | 6.4 | 7.46 |
| 5 | $549 \pm 24$ | $65.8 \pm 0.4$ | 8.3 | 7.42 |
| | | | | |
| Constant $NH_4$ and variable $PO_4$ | | | | |
| 6 | $328 \pm 4.2$ | $10.5 \pm 0.7$ | 31.2 | 7.14 |
| 7 | $332 \pm 1.4$ | $36.0 \pm 4.2$ | 9.2 | 7.59 |
| 8 | $348 \pm 4.9$ | $56.5 \pm 0.0$ | 6.2 | 7.65 |
| 9 | $348 \pm 0.7$ | $81.3 \pm 0.4$ | 4.3 | 7.90 |
| 10 | $362 \pm 0.7$ | $121 \pm 0.4$ | 3.0 | 7.94 |
| | | | | |
| Variable $NH_4$ and variable $PO_4$ | | | | |
| 11 | $266 \pm 2.5$ | $8.64 \pm 0.0$ | 30.9 | 6.96 |
| 12 | $286 \pm 15.2$ | $33.3 \pm 0.2$ | 8.59 | 7.42 |
| 13 | $333 \pm 6.4$ | $60.7 \pm 2.1$ | 5.46 | 7.57 |
| 14 | $360 \pm 4.2$ | $79.0 \pm 4.7$ | 4.56 | 7.64 |
| 15 | $402 \pm 5.7$ | $109 \pm 9.0$ | 3.69 | 7.72 |

$0.17 \pm 0.12$, and $0.45 \pm 0.08$ mg P g$^{-1}$ for Na, Mg, and Ca pre-treated CZ, respectively. The availability of K$^+$ in solution allowed for its exchange with Mg and Ca sorbed onto the CZ, thus, it is possible that higher removal capacities may have been observed had Mg and Ca remained on the CZ. Additional testing confirmed that $PO_4$ sorption capacities of Ca-PT CZ were below 0.10 mg P g$^{-1}$ for initial concentrations of 9.0, 40.0 and 92.0 mg P L$^{-1}$ when $PO_4$ was added as $H_3PO_4$

(Fig. S2†). Once $NH_4$ was in solution with $PO_4$, sorption capacities improved for Mg-PT CZ and Ca-PT CZ. There was no significant improvement in $PO_4$ sorption using Na-PT CZ with $NH_4$ presence (Fig. 1A and B). At a starting concentration of 120 mg P L$^{-1}$, the phosphorus sorption capacities were $0.38 \pm 0.06$, $0.98 \pm 0.02$, and $2.92 \pm 0.01$ mg P g$^{-1}$ for Na, Mg and Ca pre-treatment, which correlated to removal rates of $9.52 \pm 1.4\%$, $24.4 \pm 0.6\%$, and $72.7 \pm 0.4\%$. During these tests, the $NH_4$ removal remained consistently at $91.3 \pm 6.3\%$, $82.3 \pm 4.9\%$, and $84.3 \pm 6.8\%$ for Na, Mg, and Ca pre-treated CZ, respectively, and all with sorption capacities above 9 mg N g$^{-1}$ (Fig. 1G and H).

When phosphorus concentrations in the solution remained constant, the $NH_4$ removal and sorption capacity of all the pre-treated CZ remained consistent with respect to their controls when $PO_4$ was not present (Fig. 2A–F). This was a clear indication that the presence of $PO_4$ in solution had no effect on the sorption capacity of $NH_4$ by ion-exchange regardless of pre-treatment method. However, the presence of $NH_4$ did influence the $PO_4$ sorption capacities of Mg-PT CZ and Ca-PT CZ. As the initial $NH_4$ concentration increased (*i.e.* higher N/P), $PO_4$ removal percentages and sorption capacities increased at a decreasing rate, stabilizing at N/P greater than 6.4. Mg-PT CZ saw the largest improvement in $PO_4$ removal with increasing $NH_4$ presence, increasing from 10.4% (0.23 mg P g$^{-1}$) at N/P 1.5 to 30.8% (0.67 mg P g$^{-1}$) at N/P 8.4. In tests 11–15, where neither $NH_4$ nor $PO_4$ remained constant, $NH_4$ removal was consistent across a range of N/P ratios (Fig. 3). Phosphate removals also remained consistent for Na-PT CZ across a range of N/P ratios, where $PO_4$ sorption
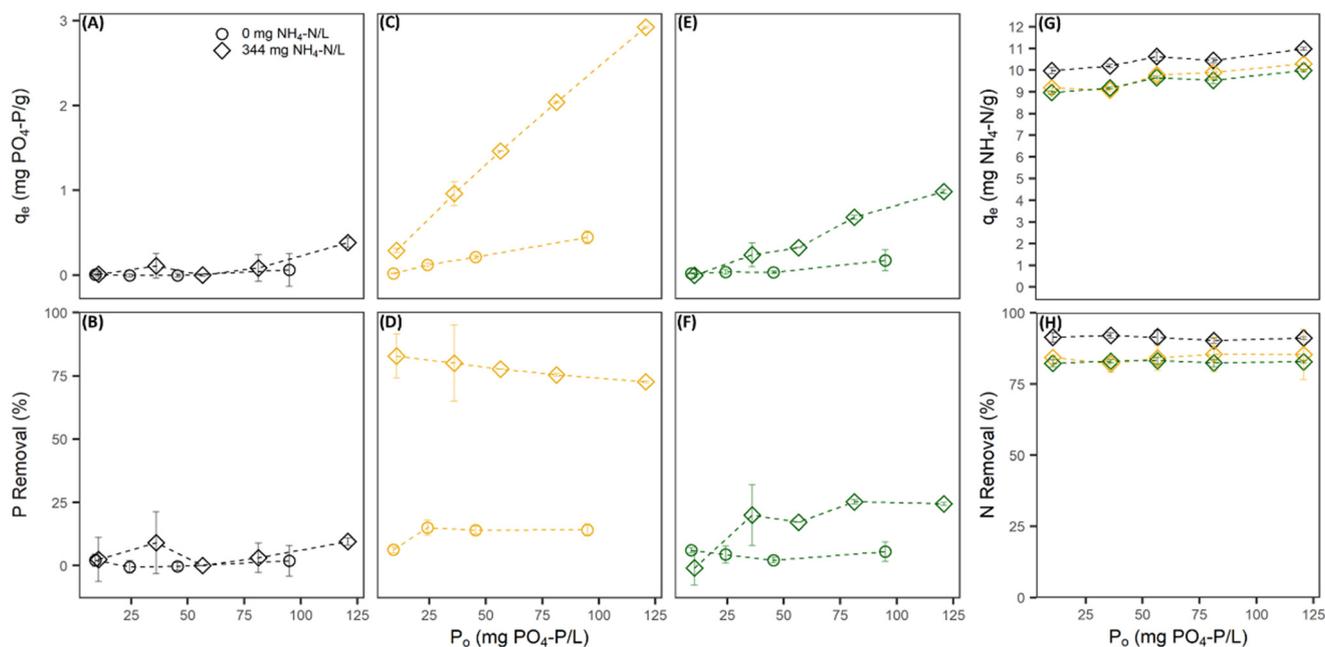


**Fig. 1** Equilibrium $PO_4$ sorption after contact with Na-PT CZ (A), Ca-PT CZ (C), and Mg-PT CZ (E) and their respective phosphorus removals (B, D and F). Contact with Na-PT CZ is shown in black, Ca-PT CZ is in yellow, and Mg-PT CZ is in green. Data is shown for two scenarios: without presence of $NH_4$ in bulk liquid (circle) and with an initial background $NH_4$ of $N_o = 344 \pm 14$ mg N L$^{-1}$ (diamond). The associated equilibrium sorption (G) and percent removal (H) of $NH_4$ after contact with Na-PT CZ, Ca-PT CZ, and Mg-PT CZ is also shown.
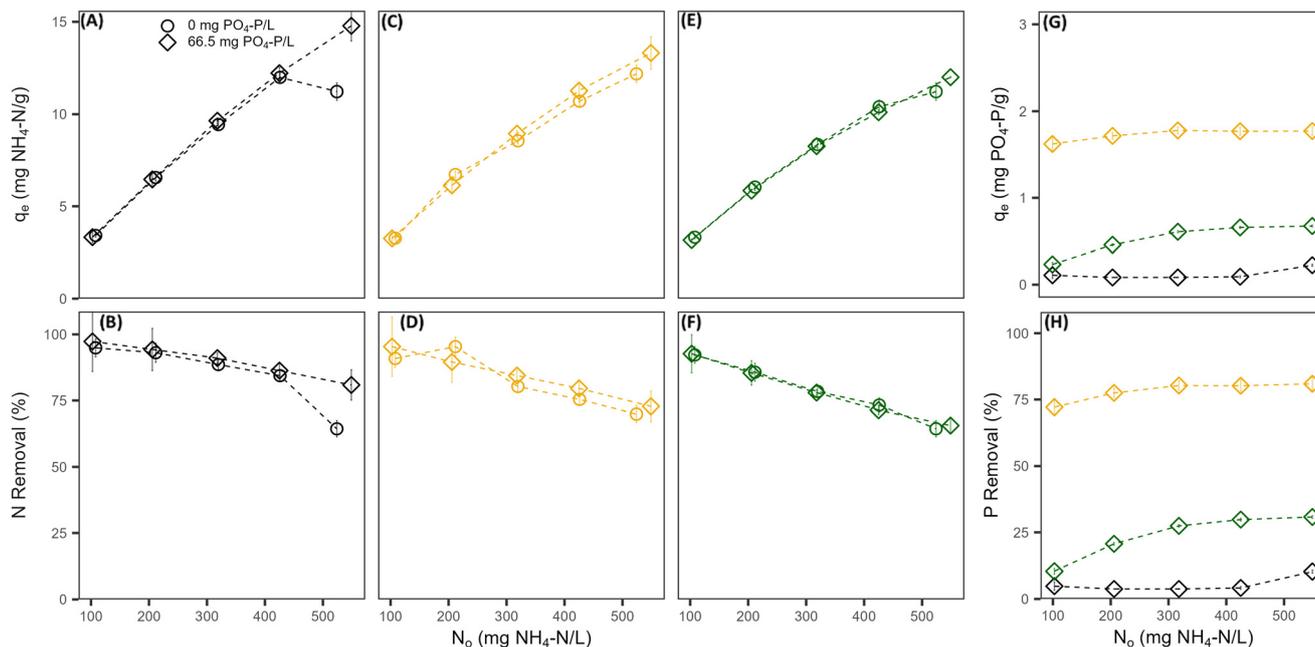
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**Fig. 2** Equilibrium $NH_4$ sorption after contact with Na–PT CZ (A), Ca–PT CZ (C), and Mg–PT CZ (E) and their respective $NH_4$ removals (B, D and F). Contact with Na–PT CZ is shown in black, Ca–PT CZ is in yellow, and Mg–PT CZ is in green. Data is shown for two scenarios: without presence of $PO_4$ in bulk liquid (circle) and with an initial background $PO_4$ of $P_o = 66.5 \pm 0.6$ P mg $L^{-1}$ (diamond). The associated equilibrium sorption (G) and percent removal (H) of $PO_4$ after contact with Na–PT CZ, Ca–PT CZ, and Mg–PT CZ is also shown.

decreased with Mg–PT CZ at higher N/P ratios and increased with Ca–PT CZ.

### 3.2. Ion composition in the bulk liquid

To quantify the ion exchange reactions during $PO_4$ removal, five major cations of interest including Na, $NH_4$, K, Ca, and Mg were measured at equilibrium for tests with $PO_4$ only and with $344 \pm 14$ mg N $L^{-1}$ in the background matrix. Phosphorus was the only nutrient present for all the $PO_4$ only tests. Potassium was also present since $PO_4$ was added as potassium phosphate salts (Fig. 4A). The presence of K during the sorption process allowed for the pre-treatment extra framework cations to exchange with K, as K has a stronger affinity for ion-exchange with CZ than Na, Ca, and Mg. After contact with all three pre-treated CZs, there was little to no K present in the bulk liquid at equilibrium (Fig. 4C, E and G). For Na–PT CZ, Na was the only major cation present in the bulk liquid. Similarly, for Ca–PT CZ, Ca was the major cation present in solution at equilibrium with small concentrations of Na present in all samples. For Mg–PT CZ, both Mg and Na were readily found in solution at near equal concentrations, with Ca presence increasing in samples as $PO_4$ concentrations increased. Overall, little $PO_4$ removal was observed while ion exchange occurred between K, Na, Ca, and Mg. However, the starting pH of all solutions began at 6 or less and increased significantly after contact with Na–PT CZ, and increased to a lesser extent when in contact with Ca–PT and Mg–PT CZ, respectively (Fig. 5A, C, E and G). The pH increase was likely to due to ion exchange between $Na^+$ on the CZ surface and $H^+$ in solution after K had exchanged with Na. As

phosphorus concentrations increased, and more $K^+$ was present in solution, the pH change was reduced.

When $PO_4$ was present with $344 \pm 14$ mg N $L^{-1}$ of $NH_4$ in the background matrix, $NH_4$ readily exchange with all the pre-treated clinoptilolite zeolites. With only $NH_4$ available for ion-exchange with the CZ extra framework cations (Fig. 4B), Na–PT CZ was able to readily exchange its Na for $NH_4$, however, small amounts of Ca and K were also present in the bulk liquid (Fig. 4D). Similar results were observed with Ca–PT CZ, where the majority of cation presence was as Ca followed by Na and a small amount of K (Fig. 4F). Interestingly, for Mg–PT CZ, Na was the most abundant cation, followed by Ca and small amounts of K in all the samples (Fig. 4H). Magnesium was only observed when the initial $PO_4$ concentration was 120 mg P $L^{-1}$.

The starting pH of all the solutions containing both $NH_4$ and $PO_4$ were between 7–8. Minor increases in final pHs were observed when low $PO_4$ concentrations were in contact with Na–PT and Mg–PT CZ due to the loss of $NH_4$ (Fig. 5B, D and H). In this case, $PO_4$ behaved as a buffer, diminishing the pH effects as $PO_4$ concentrations increased. When the solutions were in contact with Ca–PT CZ, the pH dropped below the starting pH for initial $PO_4$ concentrations greater than 10.5 mg P $L^{-1}$ as Ca–$PO_4$ precipitation is a base consuming reaction (Fig. 5F).

### 3.3. Sorption isotherms

The equilibrium results were fitted to both Freundlich and Langmuir isotherm models for $PO_4$ sorption without $NH_4$
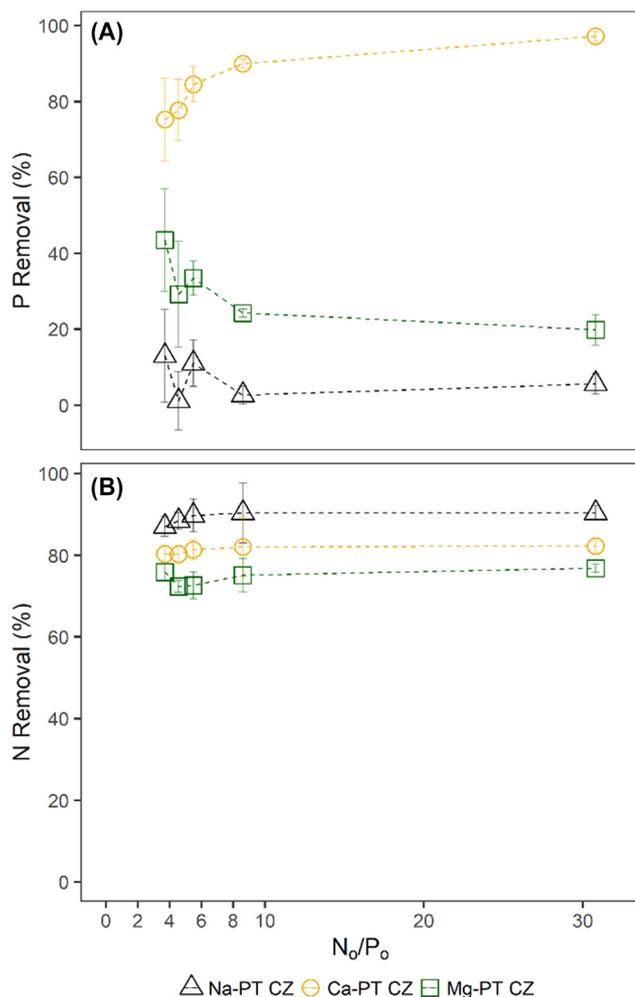
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**Fig. 3** $PO_4$ (A) and $NH_4$ (B) percent removal from tests 11–15 where the initial N/P ratios varied between 3.7–30.8.

addition, $NH_4$ sorption without $PO_4$ addition, $PO_4$ with 344 ± 14 mg N $L^{-1}$, and $NH_4$ with 66 ± 0.6 mg P $L^{-1}$ when each were in contact with Na-PT CZ, Mg-PT CZ, and Ca-PT (Table 2). For $PO_4$ only, the Langmuir model best described both $PO_4$ sorption to Mg-PT CZ and Ca-PT CZ (Fig. S3†), with $R^2$ values of 0.8938 and 0.9995 and exhibiting RSEs less than what was obtained with the Freundlich models in each scenario. Since Na-PT CZ did not readily adsorb $PO_4$, the data did not fit either model, with or without the presence of $NH_4$. When $NH_4$ was present in solution with $PO_4$, the inverse results were observed for $PO_4$ sorption to Mg and Ca pre-treated CZ, with the Freundlich model best describing the sorption behavior. Within the range of $PO_4$ concentrations tested, both Freundlich and Langmuir were able to describe the sorption onto Ca-PT CZ, while statistically Freundlich was a better fit. The $PO_4$ sorption data from tests 1–5 as well as additional sorption data when both $NH_4$ and $PO_4$ were varied (tests 11–15) were also plotted against the Freundlich and Langmuir models for Mg-PT CZ and Ca-PT CZ (Fig. 6). It can be observed that $PO_4$ sorption onto Ca-PT CZ was completely

independent of the background $NH_4$ concentration. However, $PO_4$ sorption using Mg-PT CZ was affected by the presence of $NH_4$.

For $NH_4$ sorption with and without $PO_4$ in the background matrix, both the Freundlich and Langmuir isotherm models fit the data well for the given concentrations tested, all having $R^2$ values well beyond 0.70. The Langmuir models had the best fit for sorption to Mg-PT CZ and Na-PT CZ without $PO_4$ presence, while the Freundlich model fit best for sorption to Ca-PT CZ. The Freundlich models best described $NH_4$ sorption to all three PT-CZs when $PO_4$ was present.

### 3.4. CZ material characterization

CZ samples prior to any treated and post cation treatment were analyzed for elemental composition using XRF (Table 3). Untreated CZ primarily contained K as the main extra framework cation followed by Ca, Fe, Na, and Mg. For all pre-treated CZ, the iron percent composition did not change, suggesting that while it was present on the CZ it did not play a significant role in ion-exchange with the pre-treatment cations. After CZ was pretreated with Na, the Na composition of CZ increased 2.2-fold, but K remained the main extra framework cation followed by Na and Ca while experiencing no change to the Mg content. After CZ was pretreated with Ca, the Ca composition increased 2.7-fold, increasing from 3.48% to 9.41%. Ca became the main extra framework cation followed closely by K. Both the Na and Mg presence was low within the CZ composition, accounting for less than 0.5% each. For Mg pre-treatment, the metal ion content increased 1.8-fold to 0.9%, however, this percent composition was low compared to other competing cations. K was the main extra framework cation, followed by Ca.

For natural CZ (untreated) and all pretreated CZs, there was no phosphorus detected within its elemental composition. The composition was also analyzed for Ca-PT CZ from Test 3 and Mg-PT CZ from Test 4 (Table 1), which each initially in contact with 0.067 g P $L^{-1}$ and 0.32 g N $L^{-1}$ and 0.066 g P $L^{-1}$ and 0.43 g N $L^{-1}$, respectively. Phosphorus was present on the surface of both CZ samples, with Ca-PT CZ able to retain nearly 4 times more phosphorus than Mg-PT CZ. Since Ca pretreatment observed the best $PO_4$ removal performance, two additional tests were conducted to observe the compositional changes of Ca-PT CZ soaked under 0.5 g P $L^{-1}$ and 5.0 g P $L^{-1}$ (Table S2†). Both Ca-PT CZ were able to retain 0.27% and 3.37% phosphorus, respectively. When $NH_4$ was also present in the initial solution with $PO_4$, the percent of phosphorus composition found within the Ca-PT CZ was higher (0.37%) than when $PO_4$ was initially present in solution alone (0.27%) at a much higher initial concentration (Table S3†). These results indicate that the presence of $NH_4$ can significantly enhance phosphorus sorption and recovery when compared to sorption of $PO_4$ alone by CZ.

Surface imaging of Ca-PT CZ soaked in 0.067 g P $L^{-1}$ and 0.32 g N $L^{-1}$ is shown in Fig. 7. The images reveal small granular aggregates attached to the surface of the CZ

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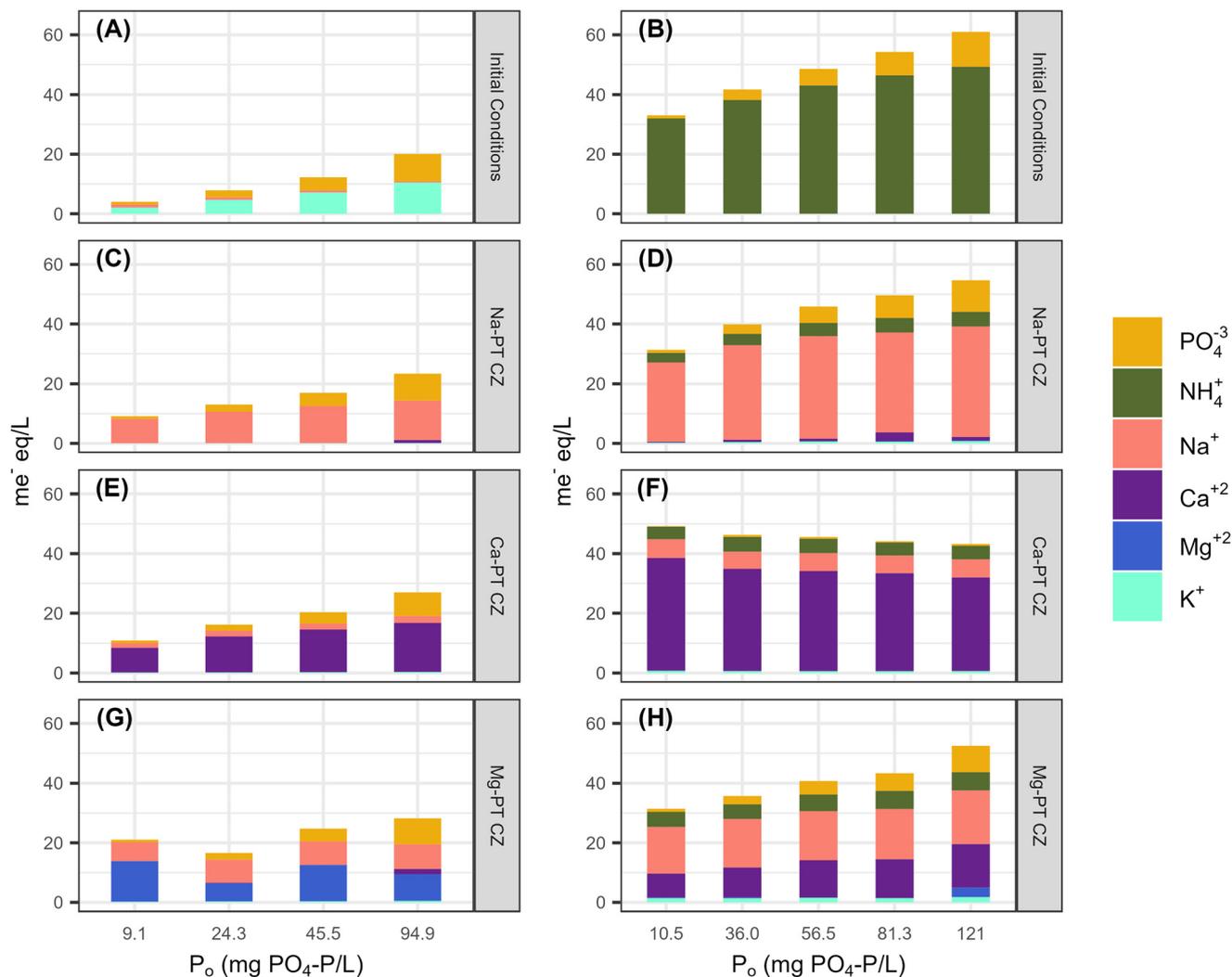This journal is © The Royal Society of Chemistry 2023

**Fig. 4** Concentration of major ions present in the bulk liquid before contact with adsorbent, and after contact with Na-PT CZ, Ca-PT CZ, and Mg-PT CZ across a range of initial phosphorus concentrations. (A) Initial ion composition where no initial $NH_4$ was present and after contact with (C) Na-PT CZ (E) Ca-PT CZ (G) Mg-PT CZ. (B) Initial ion composition when initial $NH_4$ was present at a background concentration of $N_o = 344 \pm 14$ mg N L$^{-1}$ and after contact with (D) Na-PT CZ (F) Ca-PT CZ (H) Mg-PT CZ.

(Fig. 7A), with an approximate diameter of 15 μm (Fig. 7D). Small sheath-like crystals can also be observed around the granular aggregates of approximately 1–2.5 μm in length. The elemental distribution of Ca and phosphorus overlapped consistently across the surface of the CZ (Fig. 7B and C). After further magnification onto one of the aggregates on the CZ, Ca and phosphorus are seen to be densely distributed across the same vector space as the aggregate, suggesting that the aggregate is a Ca–PO$_4$ composite. The spectral analysis on the individual aggregate revealed that the concentration by percent weight was primarily oxygen, accounting for 49%, followed by Ca at 27%, and phosphorus at 16%. Elemental nitrogen only comprised 2.5% of the aggregate. The ratio of Ca to phosphorus was 1.69, suggesting that the precipitate was hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, which also has a Ca to phosphorus ratio of 1.66.[41] Mg-PT CZ was also imaged after soaking in 0.066 g P and 0.32 g N L$^{-1}$. The surface of

Mg-PT CZ also showed, to a much lesser extent, small, localized aggregates of Ca–PO$_4$ precipitates (Fig. S4†).

## 4. Discussion

### 4.1. Phosphate removal by clinoptilolite zeolite is improved with the presence of ammonium

Three metal cations frequently found in wastewater sources (Na, Ca, and Mg) were chosen to modify the surface composition of natural CZ to evaluate the simultaneous removal effectiveness and sorption mechanism of $NH_4$ and $PO_4$ at a range of concentrations readily found in blackwater. The preference for $NH_4$ sorption followed the order Na > Mg > Ca while the opposite was true for $PO_4$ sorption, where the preferential order was Ca > Mg > Na. This distinction in cation preference allowed for a lower competition between $NH_4$ and $PO_4$ removal, having no effect on the overall $NH_4$
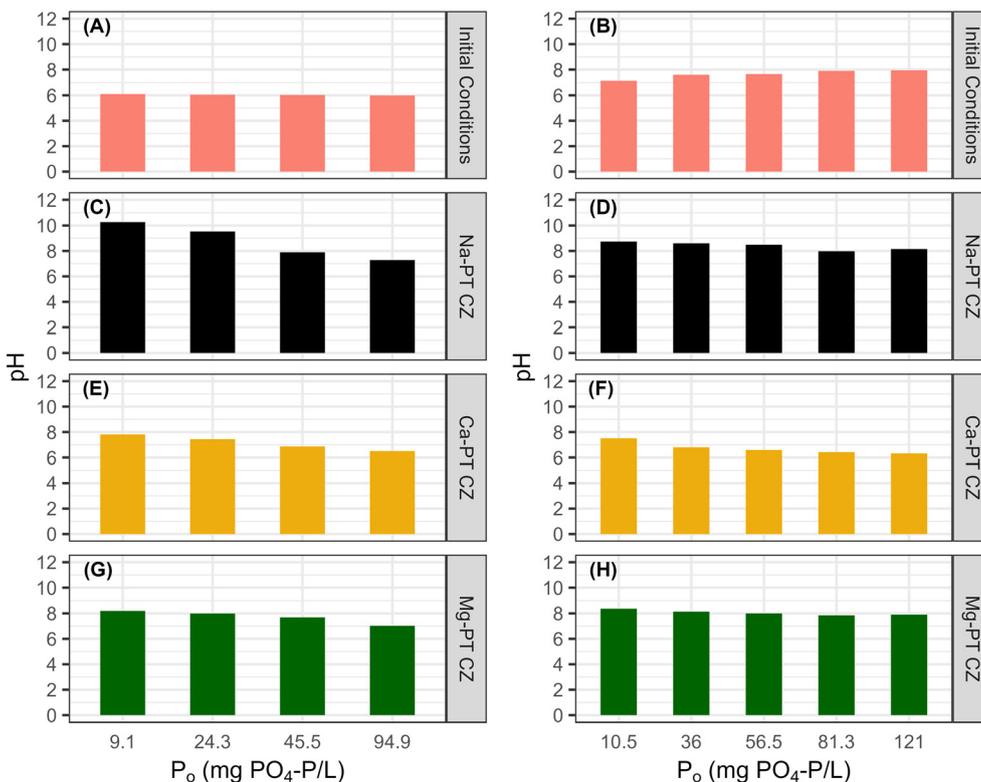
**Fig. 5** Bulk liquid pH before contact with pre-treated CZ, and after 48 h contact with Na-PT CZ, Ca-PT CZ, and Mg-PT CZ across a range of initial phosphorus concentrations. (A) Initial pHs when no $NH_4$ was present (C, E and G) and after contact with Na-PT CZ, Ca-PT CZ, and Mg-PT CZ, respectively. (B) Initial pH when $NH_4$ was present at a background concentration of $N_o$ = 344 ± 14 mg N $L^{-1}$ and (D, F and H) after contact with Na-PT CZ, Ca-PT CZ, and Mg-PT CZ, respectively.

**Table 2** Summary of Freundlich and Langmuir isotherm parameters obtained by non-linear fit for Mg-PT, Na-PT, and Ca-PT CZ when in contact with $PO_4$ with no $NH_4$ addition, $NH_4$ with no $PO_4$ addition, $PO_4$ with 344 ± 14 mg N $L^{-1}$ in background matrix, and $NH_4$ with 66 ± 0.6 mg P $L^{-1}$ in background matrix. Bolded values of RSE represent the best fit models between Freundlich and Langmuir in each of the Ca and Mg scenario where sorption occurred

| | | Mg-PT | | Na-PT | | Ca-PT | | Mg-PT | | Na-PT | | Ca-PT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Value | SE | Value | SE | Value | SE | Value | SE | Value | SE | Value | SE |
| | | $PO_4$ with 0 mg N $L^{-1}$ | | | | | | $PO_4$ with 344 ± 14 mg N $L^{-1}$ | | | | | |
| Freundlich | $K_f$ | 0.0096 | 0.009 | 0.0041 | 0.012 | 0.0095 | 0.002 | 0.0023 | 0.002 | $6.4 \times 10^{-7}$ | $3.9 \times 10^{-6}$ | 0.221 | 0.012 |
| | $n$ | 1.842 | 0.525 | 3.082 | 5.285 | 1.162 | 0.040 | 0.7411 | 0.125 | 0.3551 | 0.167 | 1.351 | 0.032 |
| | $R^2$ | 0.8331 | | −0.1300 | | 0.9988 | | 0.9530 | | 0.7749 | | 0.9990 | |
| | $p$ | 0.0196 | | 0.5157 | | $1.2 \times 10^{-5}$ | | 0.0028 | | 0.0311 | | $8.4 \times 10^{-6}$ | |
| | RSE | 0.0462 | | 0.0287 | | 0.0291 | | **0.0863** | | 0.0744 | | **0.0344** | |
| Langmuir | $q_{max}$ | 0.3664 | 0.087 | 0.0365 | 0.037 | 6.098 | 0.683 | 99.52 | 4589 | $1.2 \times 10^3$ | $9.6 \times 10^6$ | 7.274 | 0.598 |
| | $K_L$ | 0.0061 | 0.004 | 0.0164 | 0.047 | 0.0009 | 0.0001 | 0.0001 | 0.005 | $1.9 \times 10^{-6}$ | 0.0148 | 0.0201 | 0.002 |
| | $R^2$ | 0.8938 | | 0.0096 | | 0.9995 | | 0.9579 | | 0.451 | | 0.9987 | |
| | $p$ | 0.0098 | | 0.3832 | | $2.8 \times 10^{-6}$ | | 0.0024 | | 0.1302 | | $1.3 \times 10^{-5}$ | |
| | RSE | **0.0372** | | 0.0271 | | **0.0184** | | 0.1243 | | 0.1227 | | 0.0425 | |
| | | $NH_4$ with 0 mg P $L^{-1}$ | | | | | | $NH_4$ with 66 ± 0.6 mg P $L^{-1}$ | | | | | |
| Freundlich | $K_f$ | 1.706 | 1.311 | 3.397 | 1.311 | 2.334 | 0.881 | 1.490 | 0.069 | 2.549 | 0.233 | 1.847 | 0.156 |
| | $n$ | 2.708 | 1.402 | 3.956 | 1.402 | 3.080 | 0.797 | 2.505 | 0.062 | 2.619 | 0.153 | 2.508 | 0.119 |
| | $R^2$ | 0.9734 | | 0.7040 | | 0.8317 | | 0.9985 | | 0.9917 | | 0.9945 | |
| | $p$ | 0.0012 | | 0.0478 | | 0.0198 | | $1.6 \times 10^{-5}$ | | 0.0002 | | 0.0001 | |
| | RSE | 0.5357 | | 1.942 | | 1.433 | | **0.1369** | | **0.4245** | | **0.3003** | |
| Langmuir | $q_{max}$ | 13.04 | 0.784 | 12.96 | 0.937 | 12.39 | 1.705 | 13.79 | 1.271 | 16.70 | 1.305 | 15.61 | 1.466 |
| | $K_L$ | 0.0307 | 0.006 | 0.0738 | 0.020 | 0.0621 | 0.034 | 0.0253 | 0.007 | 0.0540 | 0.014 | 0.0314 | 0.009 |
| | $R^2$ | 0.9788 | | 0.9385 | | 0.7613 | | 0.9647 | | 0.9761 | | 0.9719 | |
| | $p$ | 0.0009 | | 0.0042 | | 0.0341 | | 0.0018 | | 0.0010 | | 0.0013 | |
| | RSE | **0.5207** | | **0.8876** | | 1.713 | | 0.7527 | | 0.8438 | | 0.8286 | |
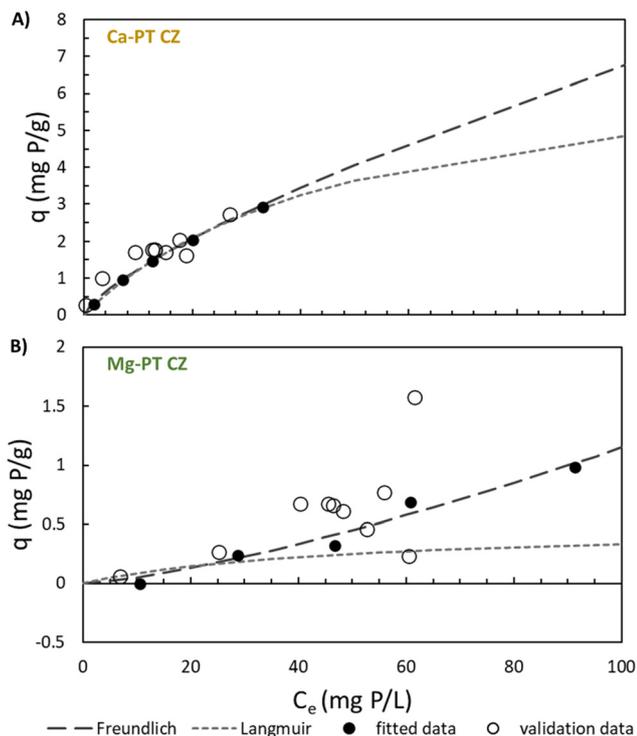
**Fig. 6** Langmuir and Freundlich isotherm models for $PO_4$ sorption onto Ca-PT CZ (A) and Mg-PT CZ (B) with a background $NH_4$ concentration of 344 ± 14 mg N L$^{-1}$. The black circles represent the fitted data use to develop the non-linear models (test 6–10) and the unfilled circles represent validation data from tests 1–5 and 11–15.

sorption capacities. The N/P ratio had a significant impact on the removal performance of Ca-PT CZ, increasing $PO_4$ removal rates from 75.2% at 3.7 N/P to 97.2% at 30.8 N/P. Typical values of N/P in blackwater may vary widely, but several studies that have quantified the nutrient concentrations of such wastewaters yield average values near 6–8.[33,42,43] This study observed $PO_4$ removal capacities of 1.46 mg P g$^{-1}$ (Test 8 at 6.2 N/P) and 1.77 mg P g$^{-1}$ (Test 4 at 6.4 N/P) with $NH_4$ removal capacities of 11.3 mg N g$^{-1}$ and 9.78 mg N g$^{-1}$ using Ca-PT CZ. By comparison, Stocker et al. maintained $NH_4$ constant at 780 mg N L$^{-1}$ and varied the $PO_4$ concentration from 160–820 mg P L$^{-1}$, which correlated to N/

P ratios of 0.95–47.7.[31] At a N/P ratio of 4.76 with a starting concentration of 163 mg P L$^{-1}$ and 777 mg N L$^{-1}$, $PO_4$ removal was near 2.0 mg P g$^{-1}$ of Ca modified CZ. The results indicate that under lower concentrations of both nutrients with similar N/P ratios, improved removal capacities can be achieved using Ca-PT CZ.

The XRD results revealed that even after modifying the CZ with 2 M of Na and Mg, the dominant extra framework cation remained as K. For Ca-PT CZ, the elemental composition of Ca was greater than K. While K concentration was on par with or higher than the pre-treatment cation, it did not contribute to $PO_4$ removal. This further highlights that the presence of Ca on each of the PT-CZ played a critical role in the direct removal of $PO_4$. The large increase in $PO_4$ removal using Ca-PT CZ when $NH_4$ was also present, and to a lesser extent for Mg-PT CZ, is largely due to several surface reactions occurring simultaneously: (1) ion exchange between $NH_4$ and the extra framework cations; (2) Brønsted–Lowry interactions between dihydrogen phosphate ($H_2PO_4^-$) and the CZ framework (3) the formation of hydrogen bonds between oxygen atoms on the CZ framework and hydroxyl groups of di- or monohydrogen phosphate ions ($HPO_4^{2-}$) sorbed to extra framework divalent cations (Ca or Mg) and (4) Ca–$PO_4$ complexation in the bulk liquid adsorbing to the CZ surface.[29,44] Phosphates are also able to complex with the hydroxyl groups of aluminum oxide, however, $PO_4$ removal could only be improved by increasing the aluminum oxide to silicon dioxide ratios. Guaya et al. observed that $PO_4$ removal could be enhanced by more than 10 times from 0.6 mg g$^{-1}$ using natural zeolite to 7.0 mg g$^{-1}$ using natural zeolite that was impregnated with aluminum oxides.[45] While other theories suggest that surface complexation to aluminum or iron oxides occurs first before the formation of Ca–$PO_4$ precipitates, this is highly dependent in the chemical composition of the CZ. Our study supports that Ca–$PO_4$ complexation is the primary $PO_4$ removal mechanisms using Ca-PT and Mg-PT CZ within the N/P range evaluated.[46]

The reaction required in removing $PO_4$ affect the ratio of weak acids and conjugate bases in the bulk liquid. To support this, an inverse linear correlation exists between the equilibrium pH and the $PO_4$ sorption capacity in order of Ca,

**Table 3** Elemental composition in percentage of natural zeolite, Na-PT CZ, Mg-PT CZ, Ca-PT CZ, and Ca-PT CZ soaked in a range of $PO_4$ solutions. The aggregate of all elements shown account for over 97% of the total composition and are on a mass-by-mass basis

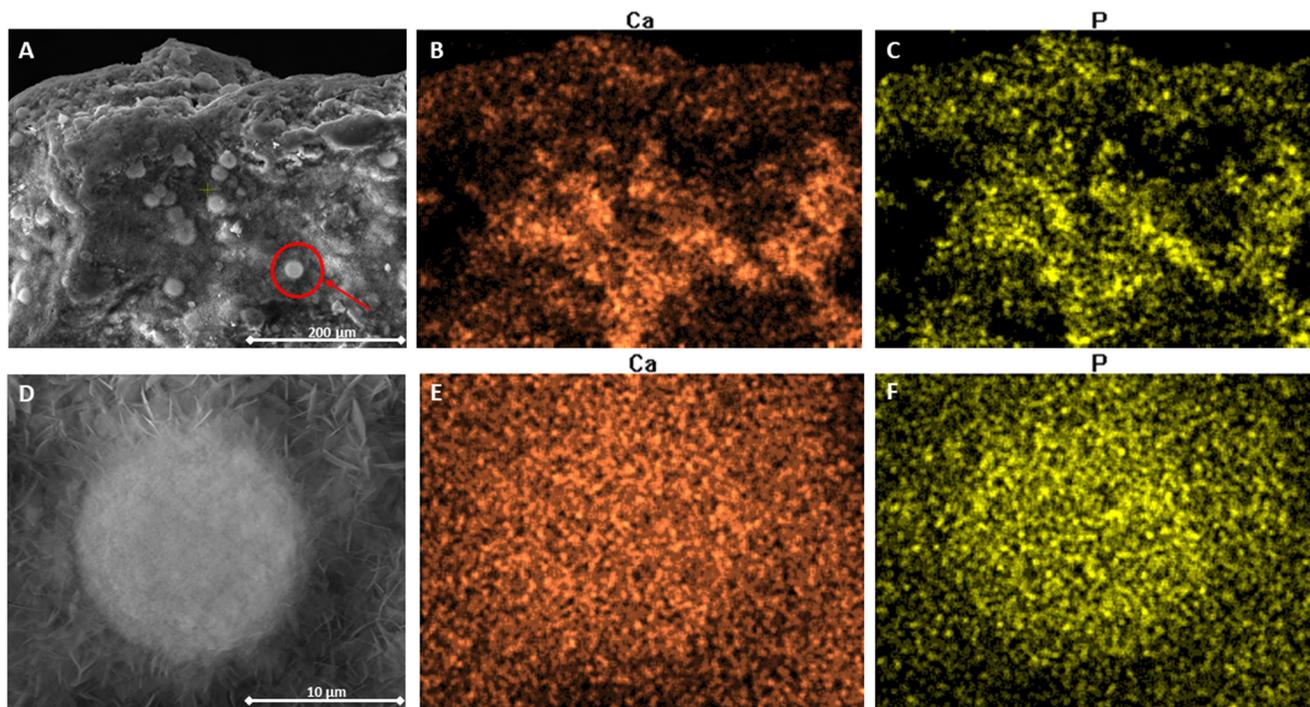| Element | Natural CZ | Na-PT CZ | Mg-PT CZ | Ca-PT CZ | Mg-PT CZ soaked in 0.066 g P L$^{-1}$ and 0.43 g N L$^{-1}$ | Ca-PT CZ soaked in 0.067 g P L$^{-1}$ and 0.32 g N L$^{-1}$ |
|---|---|---|---|---|---|---|
| P | BDL | BDL | BDL | BDL | 0.10 | 0.37 |
| Ca | 3.48 | 2.16 | 4.47 | 9.41 | 3.70 | 6.57 |
| K | 7.78 | 6.43 | 10.7 | 7.24 | 9.62 | 6.26 |
| Na | 1.54 | 3.31 | BDL | 0.38 | BDL | 0.11 |
| Al | 12.4 | 12.5 | 10.2 | 11.4 | 10.6 | 12.6 |
| Si | 69.7 | 70.2 | 67.3 | 65.1 | 69.6 | 68.9 |
| Mg | 0.50 | 0.42 | 0.90 | 0.49 | 1.11 | 0.58 |
| Fe | 3.07 | 2.97 | 2.94 | 3.28 | 3.07 | 3.08 |

BDL = below detection limit.

**Fig. 7** FIB-SEM EDS surface imaging of Ca pre-treated clinoptilolite zeolite after contact with 66.5 mg P L$^{-1}$ and 318 mg N L$^{-1}$ for 48 hours. The top images (A, B and C) were observed under 500× magnification, and the bottom images (D, E and F) were magnified 6000× onto the precipitate marked in image A. The elemental distribution of Ca (B and E) and phosphorus (C and F) onto the imaged surface (A and D) are shown.

Mg, and Na. As PO$_4$ removal increases, so does the consumption of hydroxides. The Ca-PT bulk liquid pH increased from 6.0 to only 6.5 but observed the highest PO$_4$ removal. The Mg-PT and Na-PT bulk liquid equilibrium pH increased to 7.02 and 7.28, respectively, indicating that the extent of pH increase was due to the removal of NH$_4$ from solution, raising the pH accordingly. The pHs of the effluent were well within the range desired for discharge (6–9), indicating that in practice no pH adjustments may be needed. Other P sorption materials, such as Polonite, has a high sorption capacity for phosphorus but effluent wastewater can have pHs of near 12 as hydroxides are released.[12,47]

From the EDS and XRD results of NH$_4$ and PO$_4$ loaded Ca-PT CZ and Mg-PT CZ, PO$_4$ is primarily removed by physical sorption and complexation of PO$_4$ and Ca onto the zeolite surface. Karapinar *et al.* (2009) observed that the addition of zeolite into a solution of Ca, PO$_4$, and NH$_4$, at any given pH between 7.5–10 did not affect the formation of Ca-PO$_4$ precipitates, further supporting that precipitation under this study's experimental conditions happens at the site of Ca.[44] While the phase composition of the precipitates on the CZ was not directly investigated, it is speculated that the precipitate is HAP based on the elemental composition of the aggregate, the drop in pH as PO$_4$ uptake occurred, and the EDS images depicting granule and crystal formation. Overall, the presence of NH$_4$ in solution allows for its exchange with Ca, enhancing the PO$_4$ removal by increasing the presence of Ca in the bulk liquid so that CZ can be used as a seed for

Ca–PO$_4$ precipitation onto the CZ surface. Increasing the Ca content of CZ composition yields improved PO$_4$ removal and further chemical modification to enhance Ca ion exchange to CZ should be explored. This study did show that significant residual Ca was present within the final effluent wastewater, which could prove to be a challenge in piped systems. Future work should focus on reactor configuration and contact time to optimize both nitrogen and phosphorus removal and minimize Ca losses.

### 4.2. Phosphate sorption mechanism is altered by ammonium presence

When PO$_4$ was in contact with Mg and Ca pretreated CZ, the PO$_4$ sorption mechanisms was unequivocally altered by the addition of NH$_4$ in solution. Isotherm models for PO$_4$ sorption by Mg-PT CZ and Ca-PT CZ showed that without the presence of NH$_4$, the Langmuir model best fits the resulting sorption. Sorption to both Mg-PT and Ca-PT CZ was favorable, with separation factors ranging between 0.94–0.58 and 0.99–0.90 (Fig. S5†), respectively, within the concentrations of 10–120 mg P L$^{-1}$ evaluated in this study. Once NH$_4$ was in solution, the sorption mechanism for both Mg-PT CZ and Ca-PT CZ changed due to the competitive nature of PO$_4$ and NH$_4$ for Ca active sites. The adsorption of Ca–PO$_4$ precipitates in the bulk liquid to the CZ surface leads to an increase in the overall size of CZ.[44] Therefore, the multilayer binding of Ca–PO$_4$ precipitates onto CZ changes the sorption behavior. How rapidly these complexes form in

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solution and adsorb to CZ is still to be investigated. The Freundlich model best depicted the change in sorption mechanism. Interestingly, the sorption behavior of $PO_4$ onto zeolite was independent of the concentration of $NH_4$ added (Fig. 5A) which has also been observed by recent studies.[31] The presence of $NH_4$ allows for ion-exchange with Ca ions, which then complex with $PO_4$ and bind to CZ. Phosphate sorption will be limited at lower concentrations of initial $NH_4$, beyond the N/P ratios evaluated, as there will be less Ca ions in the bulk liquid due to the limited ion-exchange activity. Future work should also consider the competition between $PO_4$ and other anions, such as sulfide, for complexation with Ca. Similarly, competition between $NH_4$ and other cations, particularly K which has a higher ionic affinity for ion exchange with CZ than $NH_4$, and its effect on $PO_4$ complexation should be explored.

### 4.3. Applications for nutrient recovery at the small-scale

Advance OWTS use biological processes downstream of the septic tank to primarily remove organic contaminants and facilitate partial nitrification and denitrification, but do not readily remove phosphorus. OWTS take advantage of natural attenuation in leach fields to uptake $PO_4$ before reaching discharge points. However, where land usage is limited, and soil types are inadequate, non-point nutrient discharge perpetuates. Natural CZ can be chemically modified more readily with Ca than it is with Na or Mg and while there are other competitive cations on the CZ surface, their presence aids in exchanging with $NH_4$, leaving Ca sites available for $PO_4$ and Ca–$PO_4$ precipitates. Additional tests (data not shown) revealed that with Ca-PT CZ, equilibrium removal of both nutrients was reached within 8 h of contact time. Septic systems typically have 1–3 days of hydraulic retention time before discharging into the drainfields, indicating that Ca-PT CZ would have sufficient time to achieve the results presented in this study. Mixtures of chemically modified CZ with other natural $PO_4$ removal media, including shale, sand, limestone, calcite, dolomite, or pumice, can be used to further enhance $PO_4$ removal by physical sorption.[48,49] Used as a single sorption material, CZ can be readily regenerated with alkali brine solutions to recover soluble nitrogen, while Ca–$PO_4$ has been marginally desorbed using bicarbonate as Ca–$PO_4$ bonds are irreversible.[20,46] However, rather than recovering soluble ions of $NH_4$ and $PO_4$, CZ loaded with these nutrients can be reutilized as a slow-released fertilizer for agricultural applications. For the Ca-PT CZ soaked in 0.067 g P $L^{-1}$ and 0.32 g N $L^{-1}$ in this study, the final sample was able to retain a molar ratio of $N:P:K$ of $5.3:1:13.4$, making the synthesized material a complete fertilizer. Within the last few years, hydroxyapatite nanoparticle (nHAP) production has been evaluated as a fertilizer for plant nutrition. Typically, fertilizers contain phosphorus in the form of soluble salts such as monoammonium phosphate (MAP), diammonium phosphate (DAP), and triple superphosphate (TSP) as they are readily available for uptake.[50,51] There is evidence that HAP,

both as a nanoparticle and as a bulk material, can be a source of slow-release phosphorus for P-deficient soils.[52,53] Further work is needed on the application of chemically modified CZ as a fertilizer, particularly to quantify the efficiency of phosphorus release to soils or by plant uptake. Beyond the removal of nutrients, the increase in ionic content, particularly sodium and calcium, in the effluent should be considered before discharge to nearby soils. The addition of a desalination and softening step may be required to reduce salinity and hardness.

## 5. Conclusion

The consistent treatment of both nitrogen and phosphorus by biological means has been a challenge for onsite wastewater treatment which is attributed to high and variable influent loading rates and limited applied technologies for phosphorus removal. One strategy to combat these challenges is to use sorption methods for the simultaneous removal and recovery of nitrogen and phosphorus in a single step. Natural CZ is a low-cost material that can be chemically modified with $CaCl_2$ to increase its Ca content, which readily exchanges with $NH_4$ and precipitates with $PO_4$. Phosphate removal is more complex, and is directly dependent on the extra framework cation composition of the CZ. The results from this study indicated that phosphorus was primarily removed by complexation of Ca–$PO_4$ onto the CZ surface regardless of pre-treatment method and was significantly enhaced when CZ was pre-treated with Ca. The final Ca-PT CZ product was able to retain nitrogen, phosphorus, and potassium, which are important nutrients for agricultural production. When using Ca-based pretreatment methods for nutrient recovery, the effluent wastewater will need further processing to reduce the resulting hardness and salinity. Further exploration is needed on reactor design and operation to minimize the negative impacts to the discharging soils.

## Author contributions

CJC: conceptualization, investigation, methodology, supervision, data curation, formal analysis, writing – original draft, writing – review & editing. HYS: investigation, methodology, writing – review & editing. BH: investigation, methodology, writing – review & editing. DHY: conceptualization, funding acquisition.

## Conflicts of interest

The authors declare no competing financial interest.

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zeolite samples for XRF, and FIB-SEM with EDS analysis. We also thank Robert Bair for assisting in reviewing and proofreading the manuscript.

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