Supplemental Information for

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

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Material Selection

Preliminary studies were conducted to identify sorption capacities of various commercially available phosphorus sorption materials. The initial materials selected were Polonite® (Ecofiltration; Wroclaw, Poland), AmberSep™ 21K XLT (Dupont; Wilmington, DE), DIAION™ (Mitsubishi; Tokyo, Japan), and Purolite® FerrIX™ A33E (Purolite; King of Prussia, PA). Clinoptilolite zeolite (CZ) (KMI Zeolites; Pahrump, Nevada) was also tested along with the four phosphate sorption materials as it is a commonly used sorbent for ammonium sorption and has been documented to also uptake phosphate, albeit, at significantly lower sorption capacities than ammonium (Drizio et al, 1999). Before any testing occurred, each material was triple rinsed with DI water and dried at 105°C for 24 hours. For each material, 3 g was soaked in 100 mL of 0.4 M PO_4-P solution, which was comprised of 0.278 M of Na_2HPO_4 and 0.126 KH_2PO_4. Phosphate concentrations were measured before sorption occurred, after 24 h, and after 48 h. Details on the sorption capacities of each material are presented in Figure S1, and commercial costs in Table S1. While CZ observed the lowest phosphate sorption compared to the four other commercial products, it showed promising results as a material that could recovery both nitrogen and phosphorus in a single reactor.

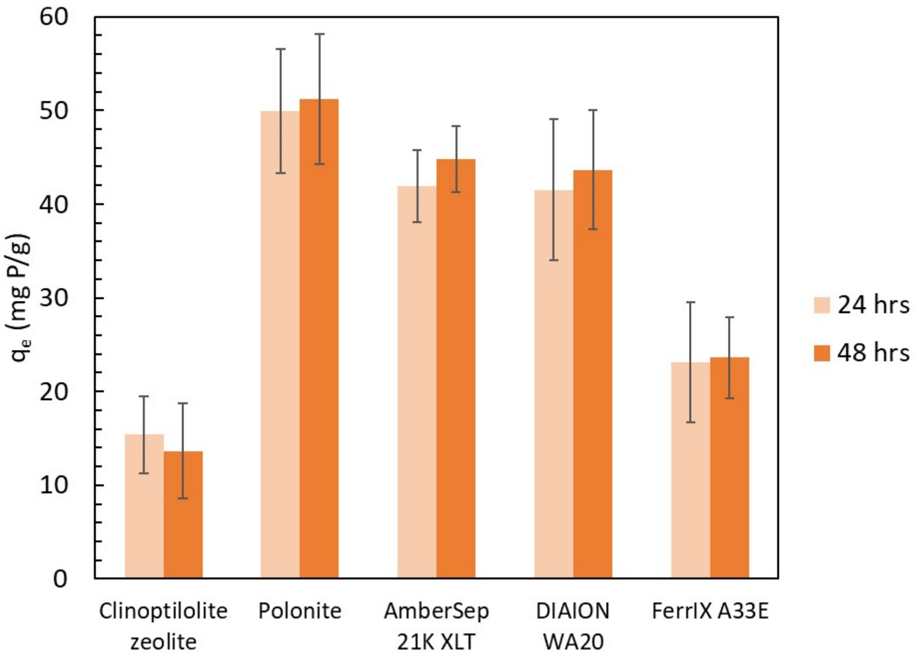

Figure S1. Phosphate sorption capacity for five commercial sorbent products after 24 hrs and 48hrs of soaking in a 0.4 M PO4-P solution

Table S1. Summary of sorbent materials tested with 0.4 M PO_4-P solution.

Material	Size (mm)	Sorption Capacity after 48 h (mg P/g)	Cost per kg (USD)[c]	Comments
Polonite®	0.85-1.0[b]	50.6 ± 6.8	0.78	Generates high pH (10-11)
AmberSep 21K LXT	0.575 ± 0.05[a]	43.3 ± 3.7	195.00	
DIAION W20	0.3-1.18[a]	42.6 ± 6.9	148.00	
FerrIX A33E	0.3-1.2[a]	23.4 ± 5.4	36.00	Generates a yellow discoloration
Clinoptilolite Zeolite	0.85-1.0[b]	14.5 ± 4.6	0.23	

[a] Size distribution information obtained directly from the manufacturer

[b] material sieved in lab

[c] cost not adjusted for economies of scale

Additional Sorption Results

Since potassium (K^+) is readily able to exchange with any of the pre-treatment cations, an additional experiment was conducted to validate any discrepancies in phosphate removal due to ion exchange of Ca^{+2} with a different cation, in this case H^+, since the Ca-PT scenario observed the best removal of phosphate. A solution of 85% (w/w) phosphoric acid was used to make solutions of 10, 50, and 100 mg PO4-P per liter. The same procedure was followed for the experiment as previously described but only for Ca-PT CZ. The results in Figure S2 show that no phosphorus was removed using H_3PO_4 as the source of phosphate and that the available of H+ did not promote ion exchange with cations to improve removal.

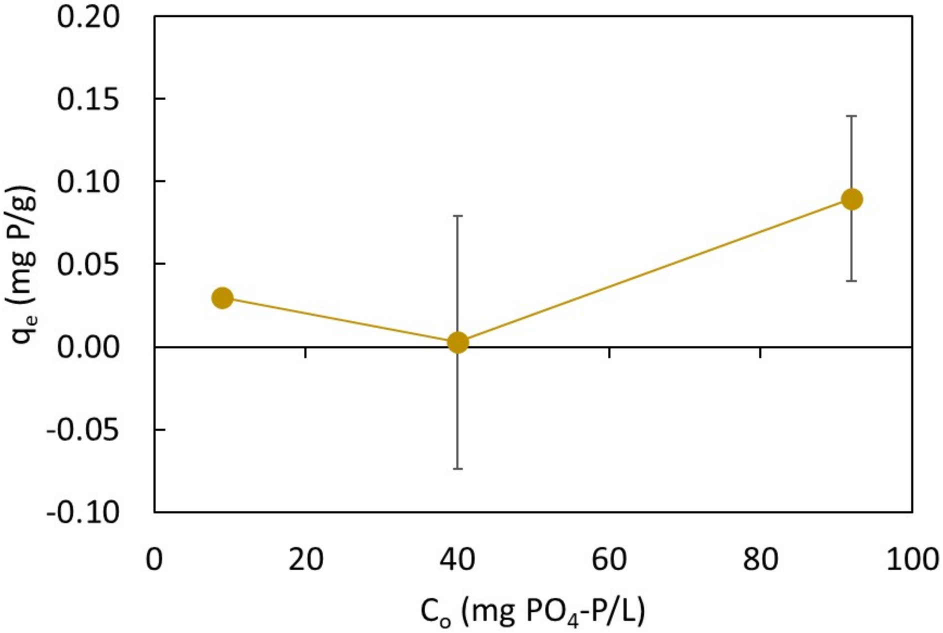

Figure S2. Phosphate sorption capacity of Ca-PT CZ in contact with 9.0, 40.0 and 92.0 mg PO_4-P/L at starting pHs of 3.27, 2.62, and 2.34, respectively. The source of phosphorus was H_3PO4.

Table S2. Phosphorus removal capabilities of potassium pre-treated clinoptilolite zeolite soaked under 500 and 5000 mg PO_4-P/L

	500 mg PO4-P/L		5000 mg PO4-P/L	
Time (hours)	0	48	0	48
mg PO_4-P/L	476.2 ± 2.94	489.6 ± 3.29	5064 ± 39.3	5081 ± 19.6

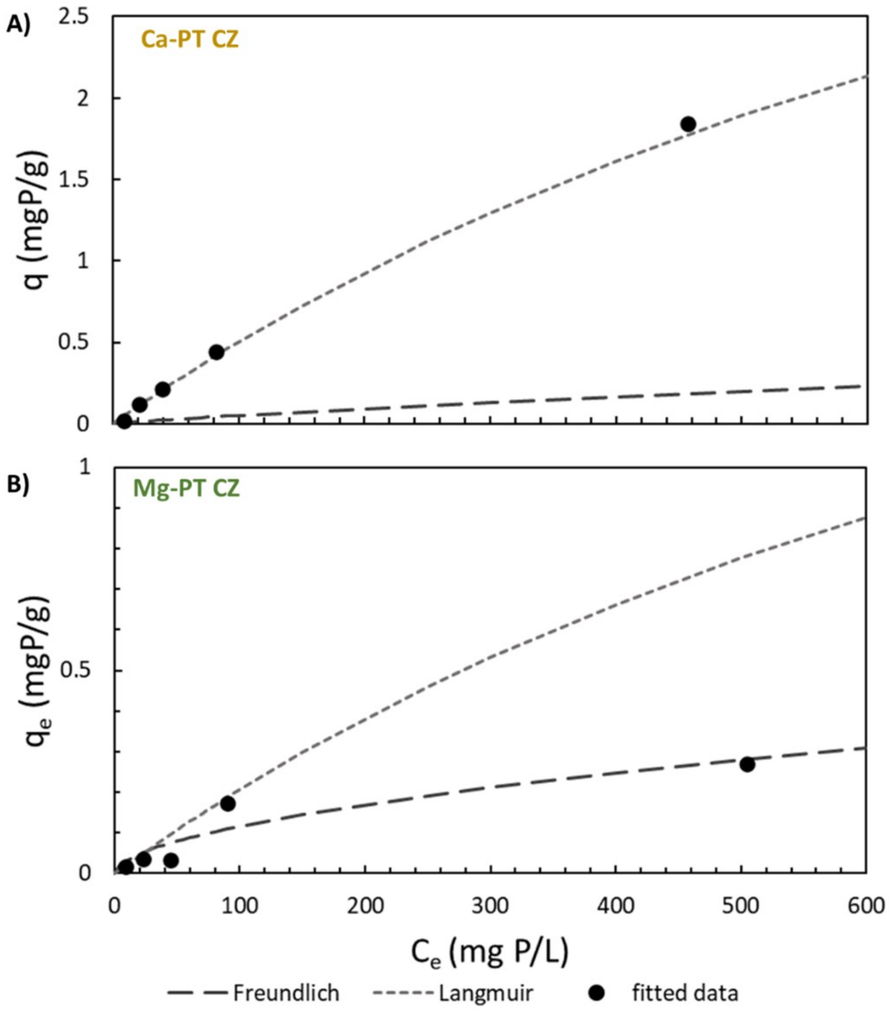

Figure S3. Langmuir and Freundlich isotherm models for phosphate sorption onto (A) Ca-PT CZ and (B) Mg-PT CZ with no ammonium present. The black circles represent data used to fit the non-linear models.

Table S3. Elemental Composition in percentage of Ca-PT CZ soaked in 0.5 g P/L and 5.0 g P/L. The aggregate of all elements shown account for over 97% of the total composition.

Element	Ca-PT CZ soaked in 0.5 g P/L	Ca-PT CZ soaked in 5 g P/L
P	0.27	3.37
Ca	6.54	6.36
K	10.7	15.4
Na	0.21	0.00
Al	12.3	11.3
Si	65.3	59.5
Mg	0.56	0.53
Fe	2.71	2.39

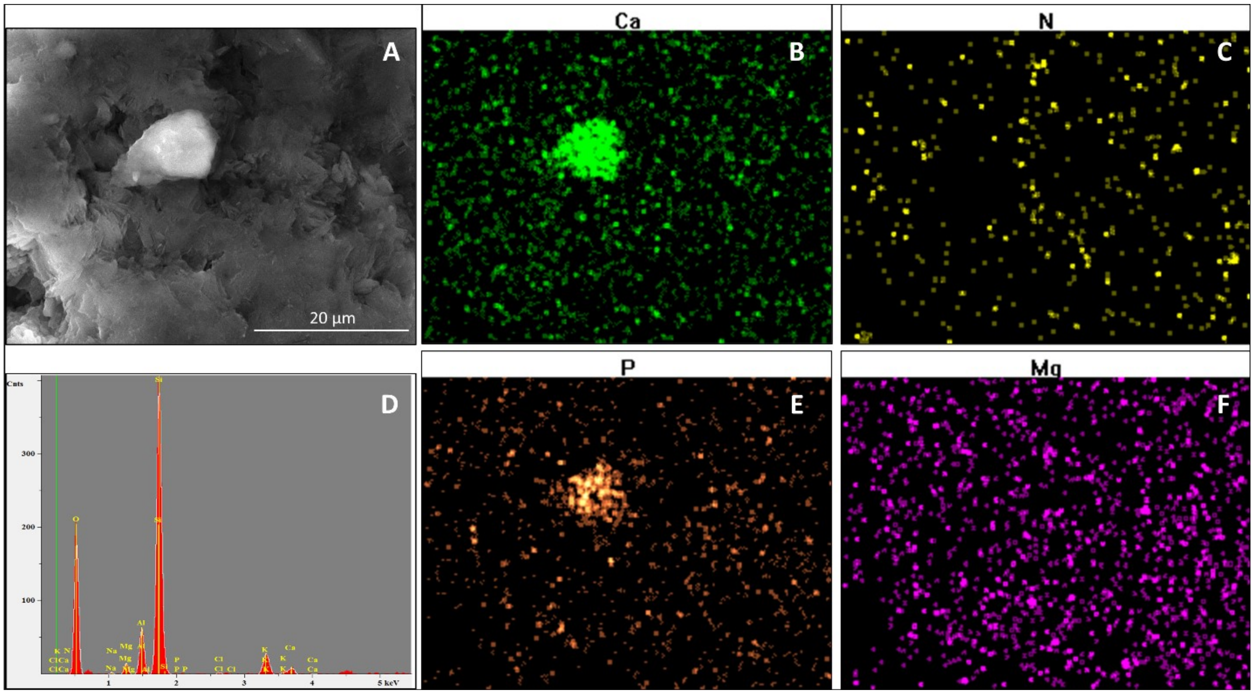

Figure S4. SEM-EDS surface imaging of magnesium pre-treated clinoptilolite zeolite contacted with 66.0 mg PO_4-P/L and 430 mg NH_4-N/L for 48 hours. A) surface imaging of Mg-PT CZ at 5000X magnification B-C) elemental distribution of calcium and nitrogen; (D) EDS spectrum; (E,F) elemental distribution of P and Mg.

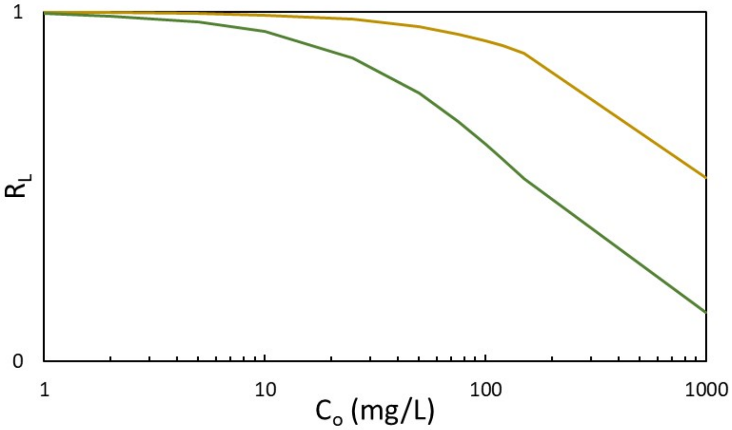

Figure S5. Langmuir separation factor for a range of initial phosphate concentrations when in contact with Mg-PT CZ (green) or Ca-PT CZ (yellow).