The development of cationized carboxymethyl rich sorbent materials for the removal of inorganic phosphate from water

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Acknowledgements

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1. Background – P_i as Fertilizer

Phosphorus is applied to crops as inorganic phosphate (P_i)

P_i is a non-renewable resource and the supply is dwindling

Shortages expected by the end of the century

Excess P_i leaches from fields and accumulates in aquatic ecosystems in a process called eutrophication

1. Background – P_i Drives Eutrophication

Eutrophication – the over abundance of nutrients (P_i and nitrate)

Leads to the proliferation of algae and formation of harmful algal blooms (HABs)

Produce toxins & deplete oxygen (by bacterial proliferation), prohibit recreational activities

Remediation prevents negative environmental outcomes and allows recovery of a limited, non-renewable resource

1. Background – Chemical Methods

The remediation of P_i using chemical methods is widely studied and includes precipitation, crystallization, and adsorption

Precipitation: Formation of insoluble metal-P_i salts including aluminum and iron

$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4$

Crystallization: Selective growth of insoluble Pi crystals such as struvite

$Mg^{2+} + HPO_4^{2-} + NH_4^{+} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H2O$

1. Background – Adsorption

Adsorption onto P_i sorbent materials (PSMs) allows for efficient, inexpensive removal

No continuous chemical inputs = decentralized application

High affinity allows efficacy to be retained at low concentrations

PSMs include natural materials (sand, gravel), industrial by products (metal slags), and agricultural by products

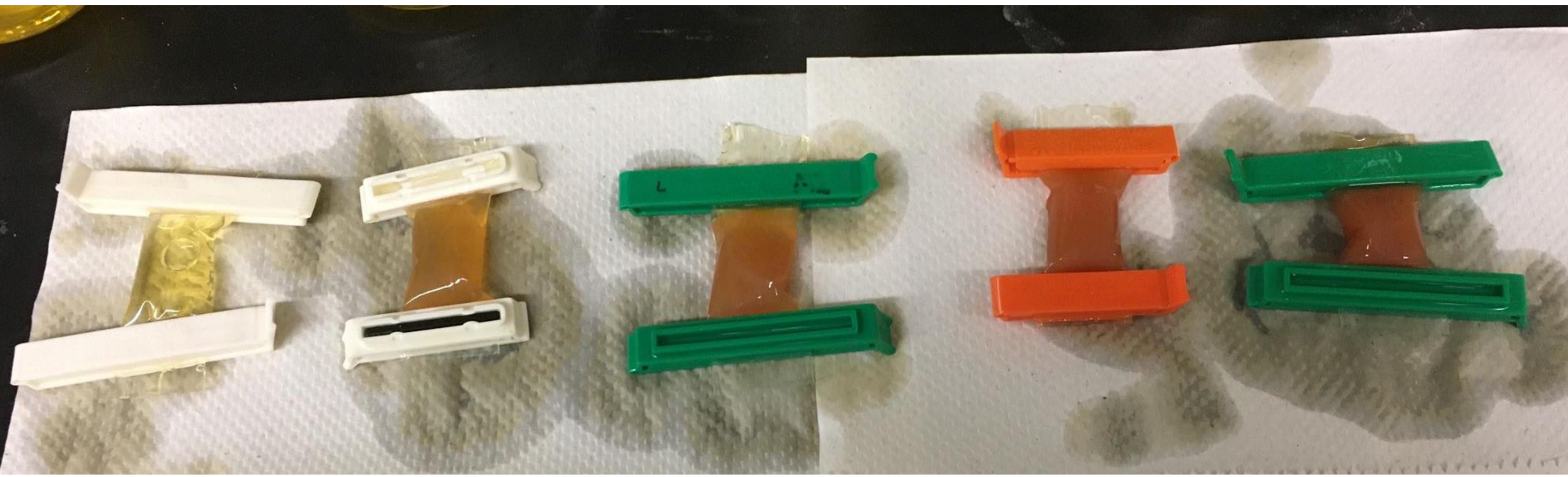
1. Background – Agricultural By Products as PSMs

Desirable PSM Characteristics

1. Inexpensive
2. Re-useable – through desorption of P_i (bonus if P_i is reusable)
3. High Affinity
4. High Capacity

2. CMC-Fe Hydrogel as a PSM

Objective: Create nanoporous iron-hydrogel (CMC-Fe) to remediate P_i from water



0.0 % CMC	0.25 % CMC	0.5 % CMC	1.0 % CMC	1.5 % CMC

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2. CMC-Fe Hydrogel as a PSM

Higher CMC concentrations led to the formation of stable hydrogels

3.0 % w/v CMC is the practical upper limit due to solution viscosity / time to dissolve

2. CMC-Fe Hydrogel as a PSM

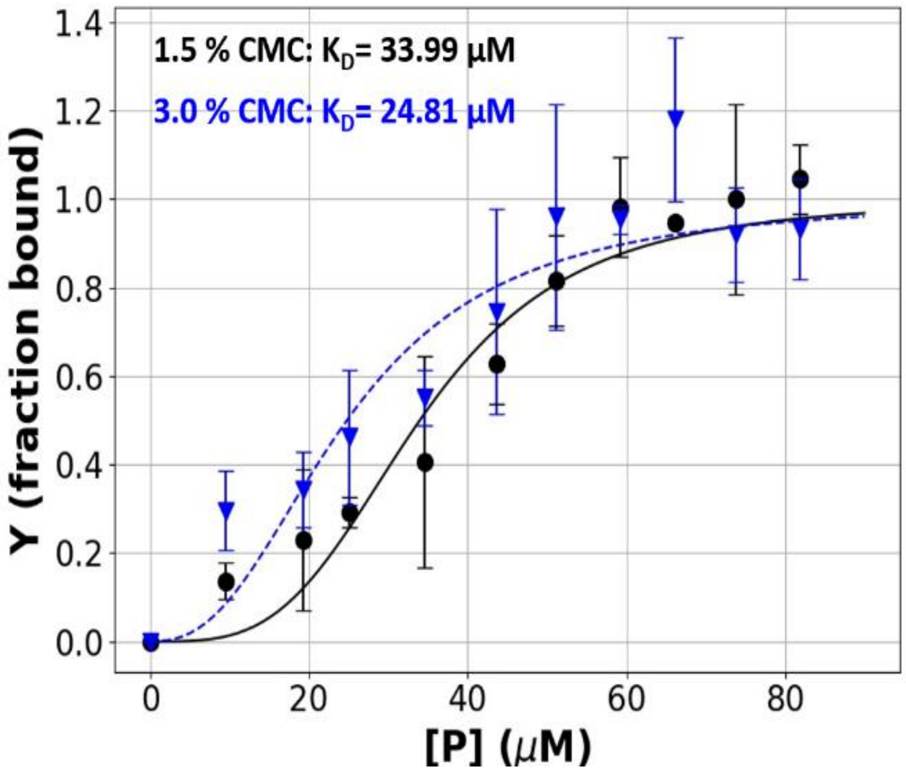
Two CMC concentrations studied (1.5 % and 3.0 %)

In general, the 3.0 % CMC-Fe hydrogel performed better in all experiments

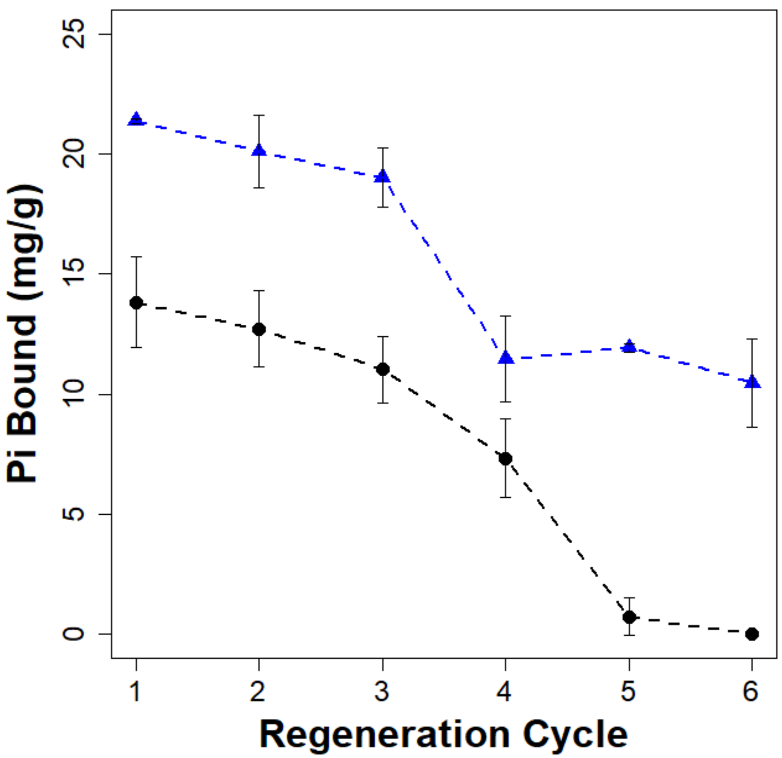
Type of CMC-Fe	Dehydrated PSC (mg/g)	Hydrated PSC (mg/g)
1.5 % CMC-Fe	13.91 ± 0.14	74.0 ± 3.06
3.0 % CMC-Fe	19.11 ± 0.51	91.4 ± 4.51

2. CMC-Fe Hydrogel as a PSM

Affinity of 1.5 % and 3.0 % CMC-Fe



Regeneration and reuse of CMC-Fe (1.5 % and 3.0 %)



2. CMC-Fe Hydrogel as a PSM

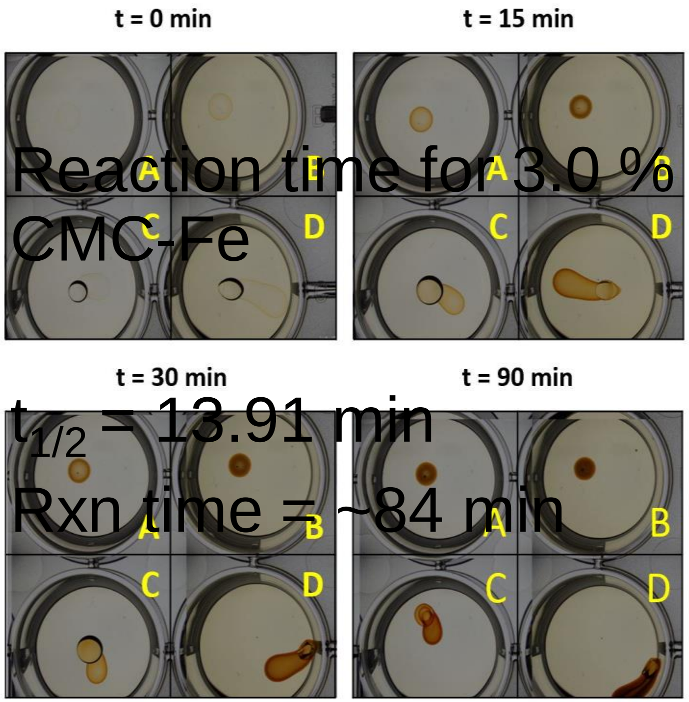
Metal permeation studied using time lapse images and bead opacity to optimize reaction time

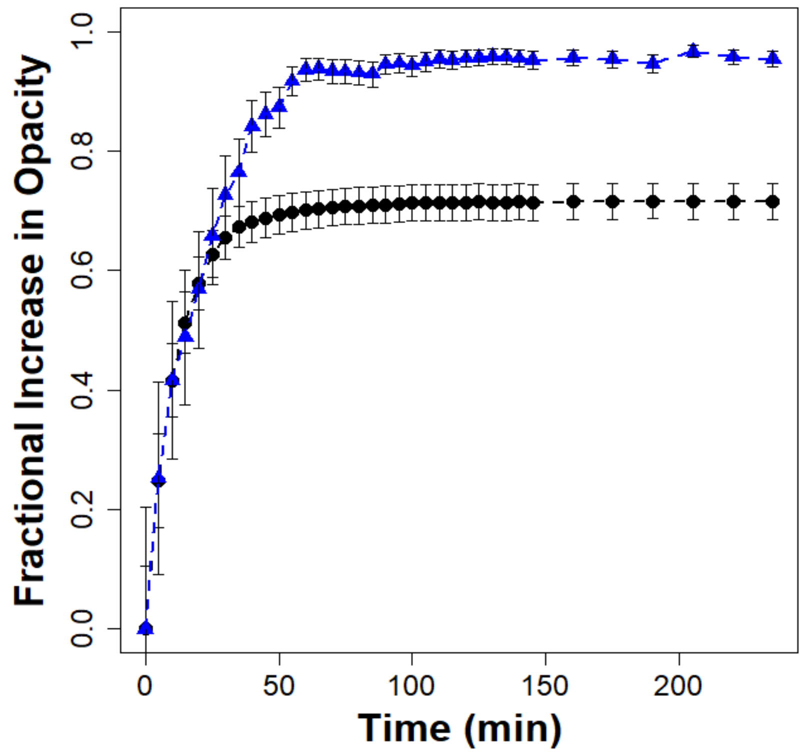
Fit to $t_{1/2} = \frac{0.693}{k}$ where k is rate constant and six half-lives = reaction time

Reaction time for 3.0 % CMC-Fe

$t_{1/2}$ = 13.91 min

Rxn time = ~84 min





3. Comparison of multimetal hydrogel composites

Objective: Create composite hydrogel PSMs with more desirable characteristics than CMC-Fe

Proposed Optimizations:

i) Vary polymer composition by incorporating alginate (ALG) with CMC to create hydrogel composites
ii) Test different metal cations for removal efficiency (aluminum, calcium, copper, iron, and lanthanum)
iii) Vary the ratio of metal cations in bimetallic composites

3. Comparison of multimetal hydrogel composites

Experimental Outline

1. Optimize the ratio of ALG:CMC with individual metal cations from pH 6.0 – 8.0 targeting high PSC at pH 7.0
2. Optimize the ratio of metal cations in bimetallic composites at appropriate ALG:CMC ratio
3. Detailed P_i binding studies on optimized bimetallic composites

Field studies from CMC-Fe field trials = only study dehydrated materials

3. Comparison of multimetal hydrogel composites

1. Optimized ALG:CMC Ratio

Four ratios of ALG:CMC studied with total w/v concentration of 3.0 % (ie. A0C3, A1C2, A2C1, A3C0)

Al and Fe perform best with pure 3.0 % CMC (A0C3)

Ca, Cu, and La perform best with 1.0 % ALG, 2.0 % CMC (A1C2)

Ca-CMC unstable below pH 9.0, La-CMC stable but efficacy is very low above pH 6.0

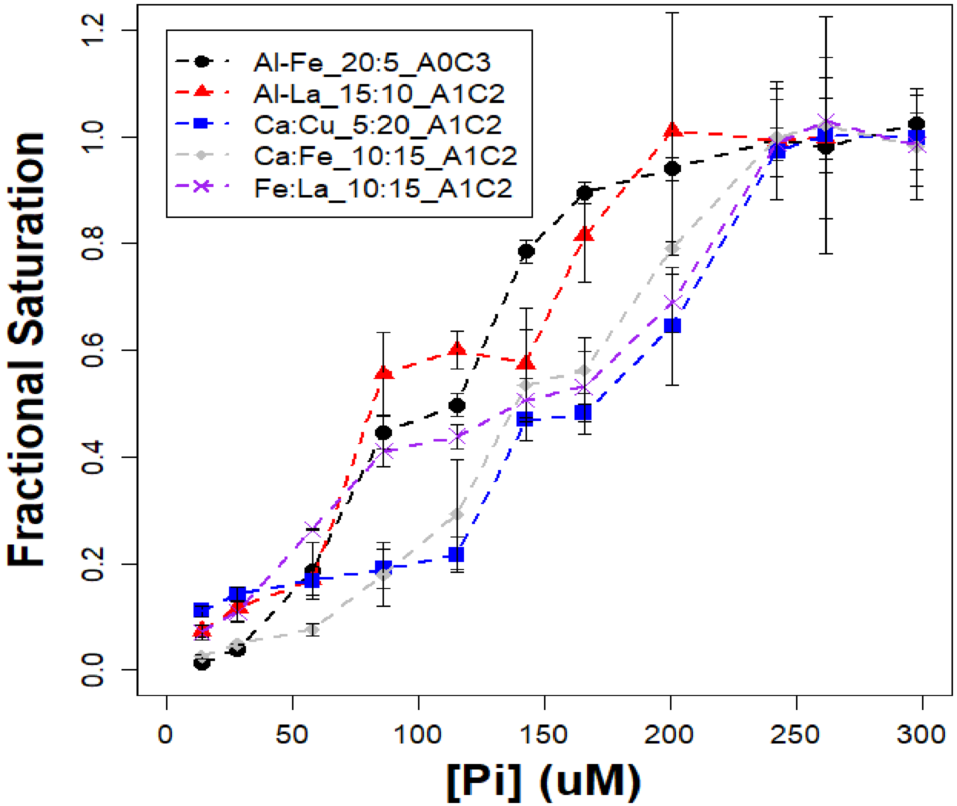
3. Comparison of multimetal hydrogel composites

Metal Pairing	Optimized Ratio	PSC (mg/g)
Al:Fe	20:5	50.96 ± 2.558
Al:La	15:10	45.37 ± 4.921
Ca:Cu	5:20	20.38 ± 7.989
Ca:Fe	10:15	24.93 ± 2.253
Fe:La	5:20	52.84 ± 1.473
Ca:La	NA	NA

Pure La^{3+} better than all Ca:La composites

3. Comparison of multimetal hydrogel composites

Saturation curves (0 to 300 µM P_i) show two distinct binding sites

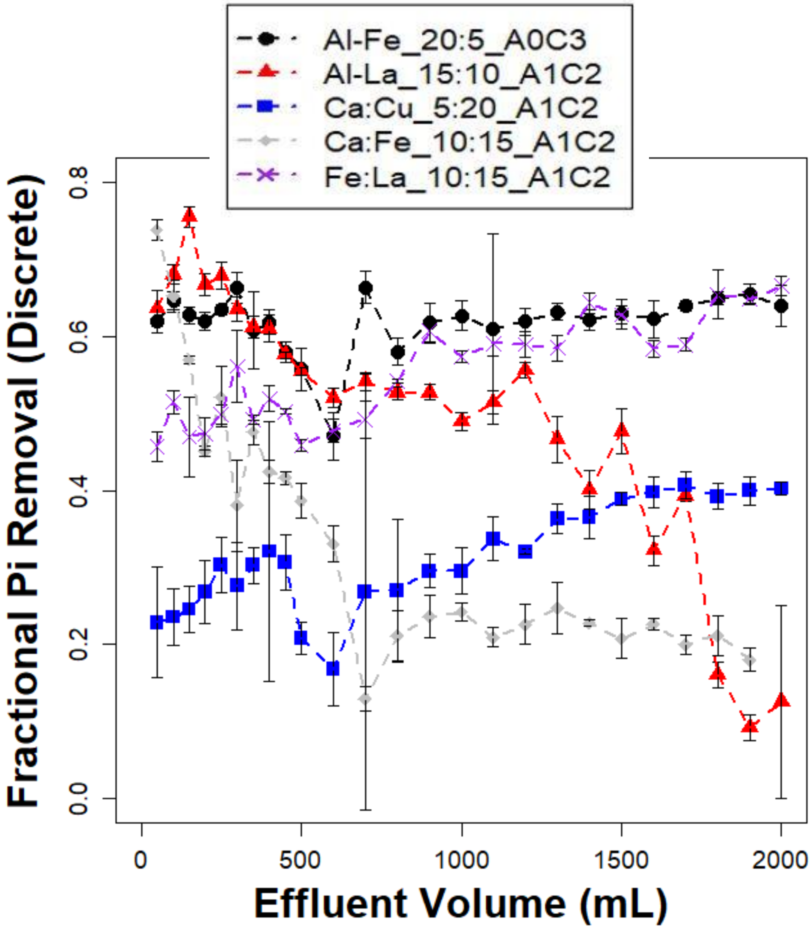


Hydrogel	$K_{D\ App1}$ (µM)	$K_{D\ App2}$ (µM)
Al:Fe_20:5_A0C3	66.51	102.14
Al:La_15:10_A1C2	90.01	132.78
Ca:Cu_5:20_A1C2	130.31	214.70
Ca:Fe_10:15_A1C2	143.05	204.10
Fe:La_10:15_A1C2	50.69	191.56

Data suggest that polymer composition influences $K_{D\ App}$ which agrees with work on the CMC-Fe hydrogel

3. Comparison of multimetal hydrogel composites

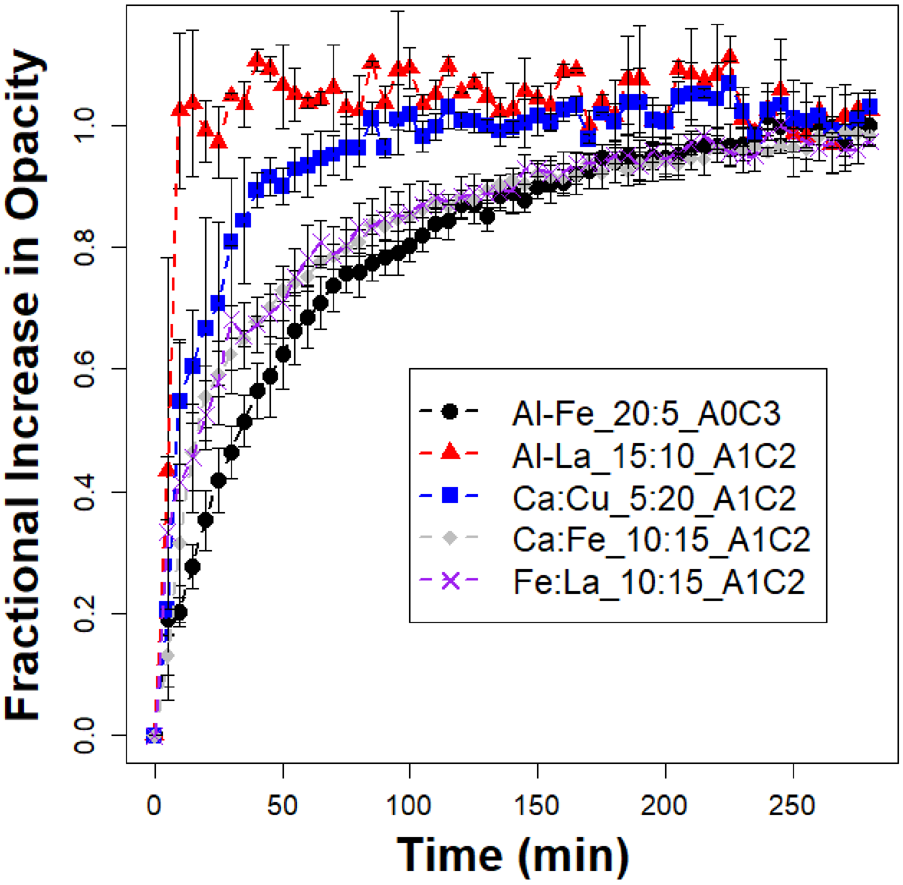
Removal of P_i (~1.7 mg/L) from a continuous flow filtration system with retention time = 1 min



Type of Hydrogel	Total % Removal
Al:Fe_20:5_A0C3	61.8
Al:La_15:10_A1C2	50.01
Ca:Cu_5:20_A1C2	31.1
Ca:Fe_10:15_A1C2	33.8
Fe:La_10:15_A1C2	55.3

3. Comparison of multimetal hydrogel composites

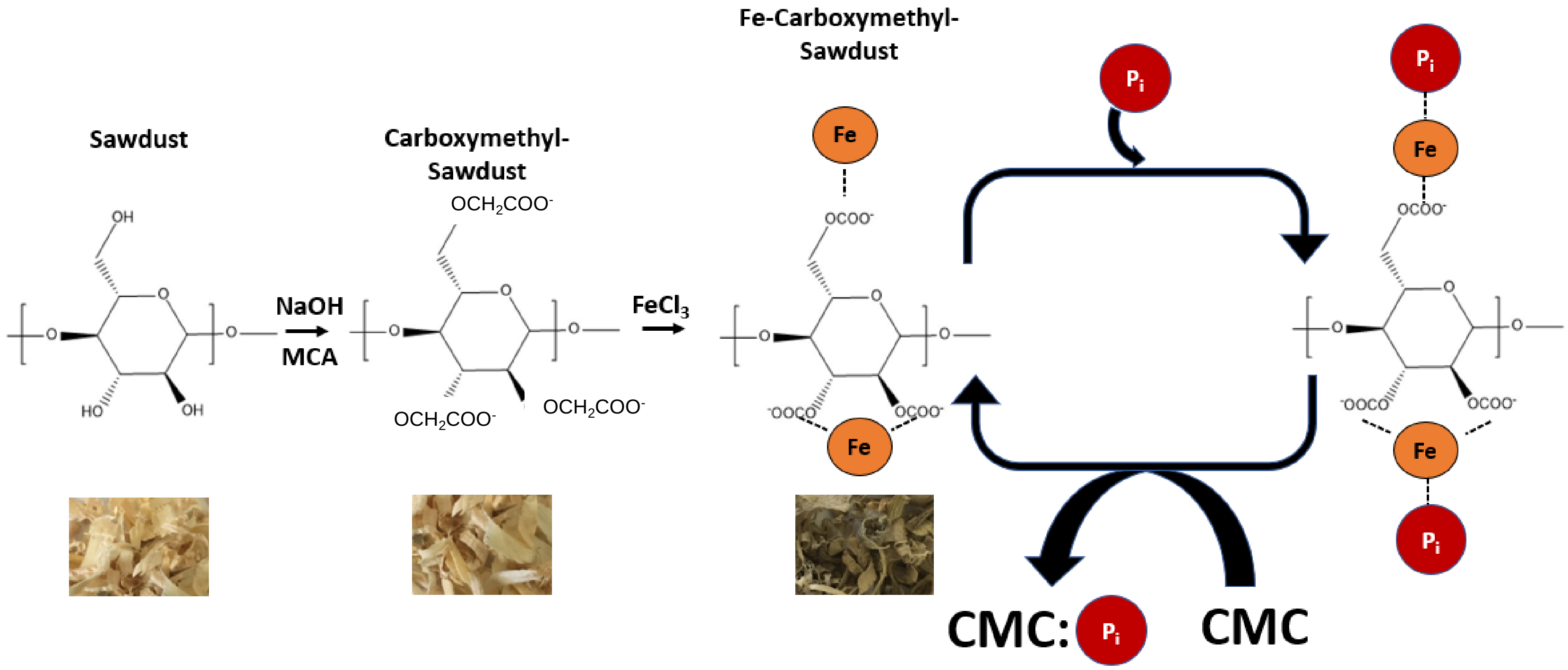
Compatibility with current manufacturing system



Hydrogel	$t_{1/2}$	~ Rxn Time
Al:Fe_20:5_A0C3	34.34 min	206 min
Al:La_15:10_A1C2	6.77 min	41 min
Ca:Cu_5:20_A1C2	12.68 min	76 min
Ca:Fe_10:15_A1C2	22.00 min	132 min
Fe:La_10:15_A1C2	16.70 min	101 min

4. Iron-carboxymethyl SD (Fe-CMSD) as a PSM

<u>Objective</u>: Directly functionalize SD with carboxymethyl (CM) groups and bind iron to confer PSC



4. Fe-CMSD as a PSM

<u>Background</u>: CMC is manufactured from SD by a Williamson etherification with monochloroacetic acid (MCA)

Tone reaction down to produce solid CMSD instead of CMC powder

Skipped three pre-treatment steps used to remove hemicellulose / lignin

Physical manipulation of SD during alkalization = breakdown

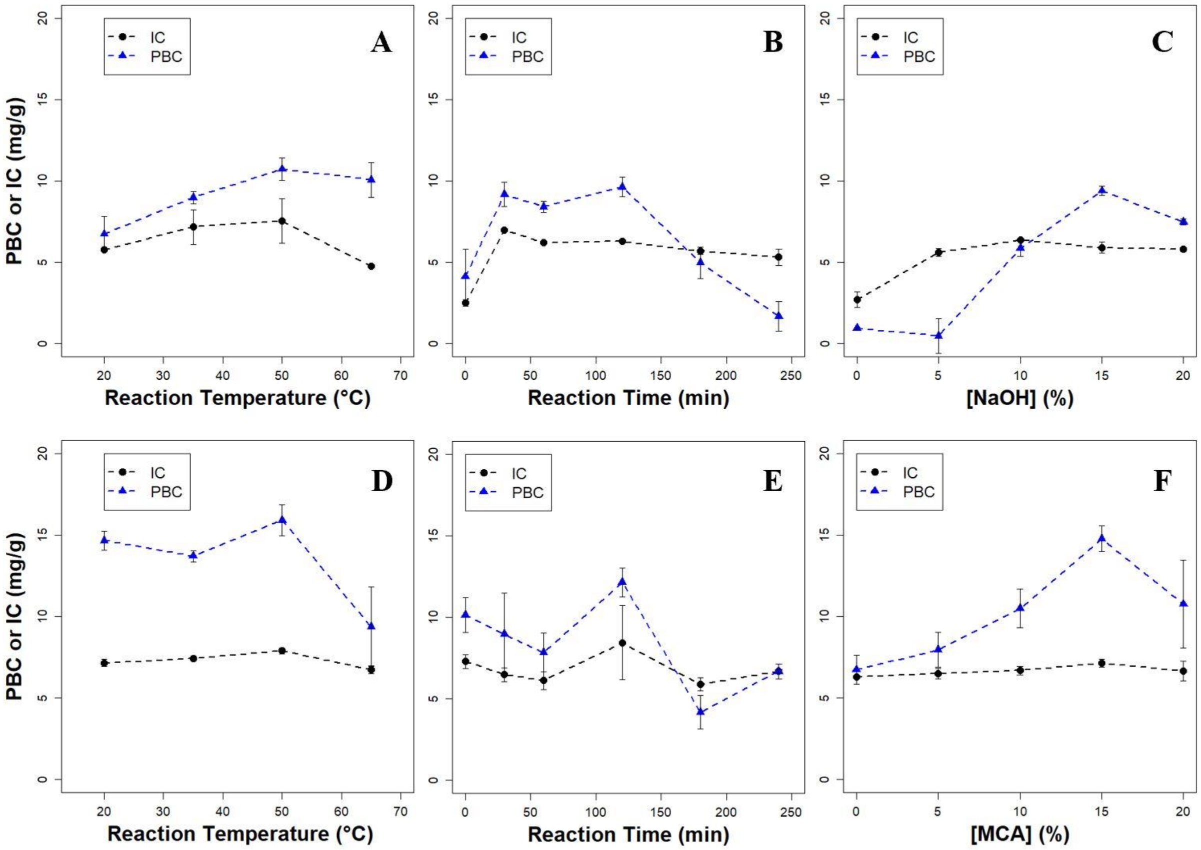
4. Fe-CMSD as a PSM

Experimental Approach

1. Optimize the two reactions (alkalization / CM'n) across time, temp and reactant concentration
2. Monitor the PSC and iron content (IC) of products
3. Further optimize using additives reported to enhance the DS (does not work… it actually makes it worse)
4. Take optimized material and conduct detailed P_i binding studies

4. Fe-CMSD as a PSM

Alkalization and CM'n optimizations using PSC (blue) and IC (black)



Optimized conditions: 120 min, 50 ºC, 15 % NaOH or MCA

Conditions are milder than those used for CMC production

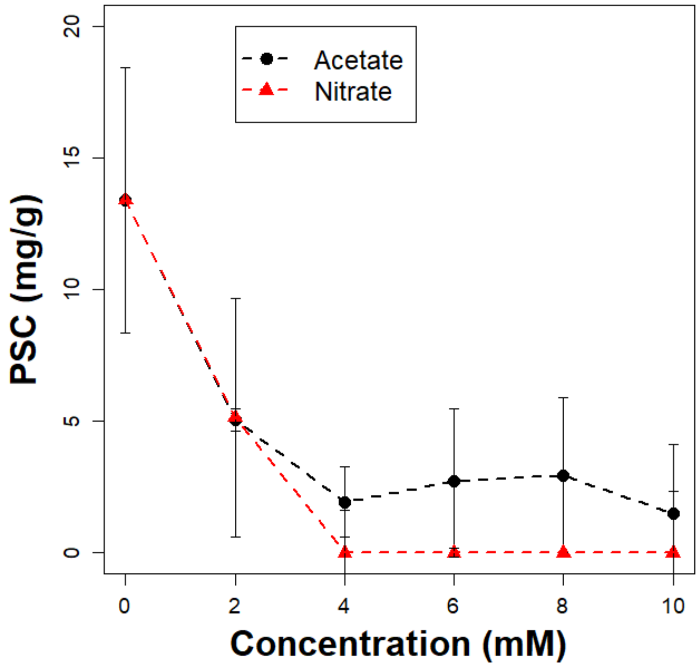
4. Fe-CMSD as a PSM

If rxn is too successful – cellulose chains dissolve off the material (recoverable as CMC powder)

Breaks in the cellulose chains at extreme conditions enhance loss of surface modification (ie. lower mw/viscosity CMC)

Literature shows acetate or nitrate as additives enhance the CM'n during CMC production (achieving DS > 1.0)

PSC reduced to zero, similar results with solvent modifications

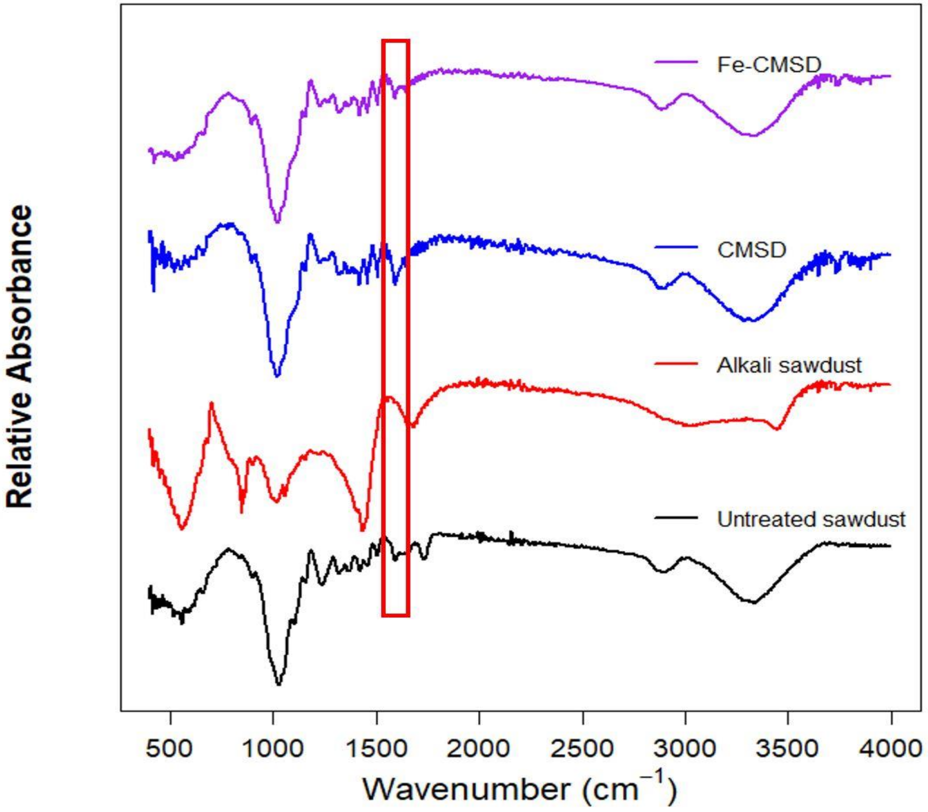


4. Fe-CMSD as a PSM

The PSC of the optimized material is 16.1 mg/g

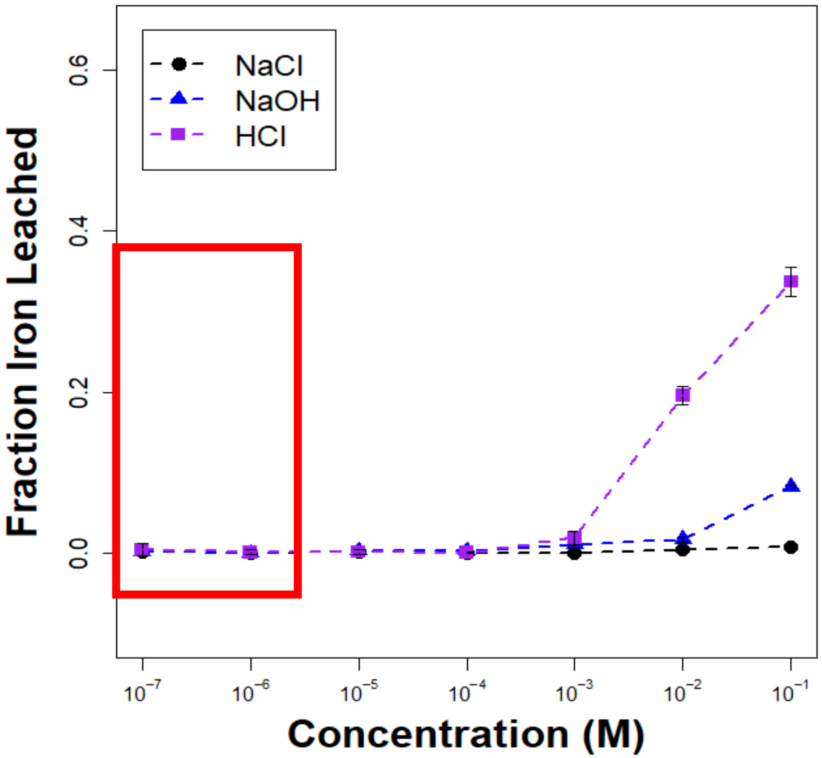
1593 cm^{-1} ATR-FTIR peak in CMSD confirms CM'n reaction

Iron binding = peak reduction – reduced carboxyl stretching

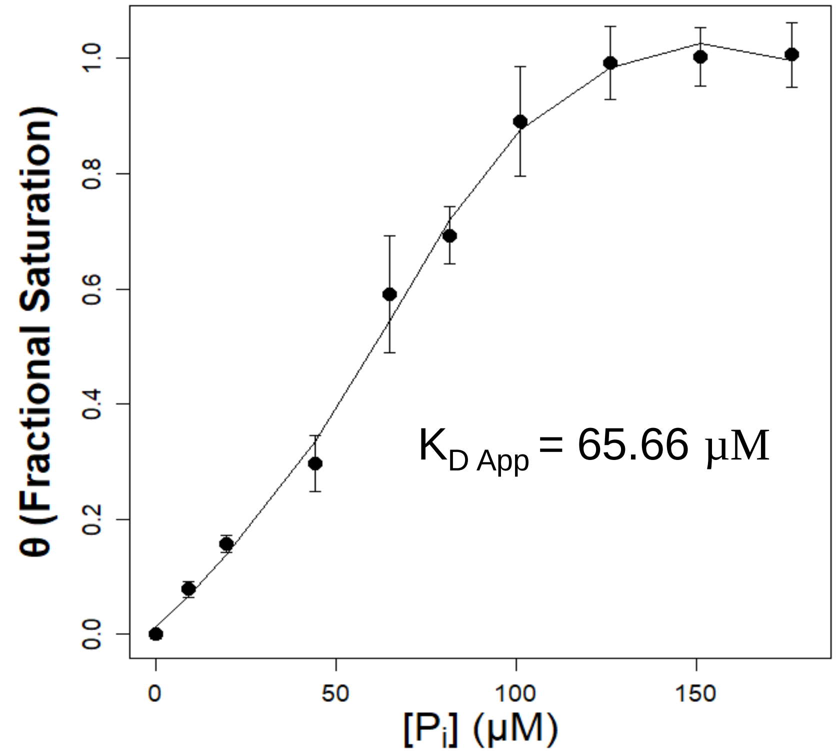


4. Fe-CMSD as a PSM

Iron leaching with increasing pH, pOH, ionic strength

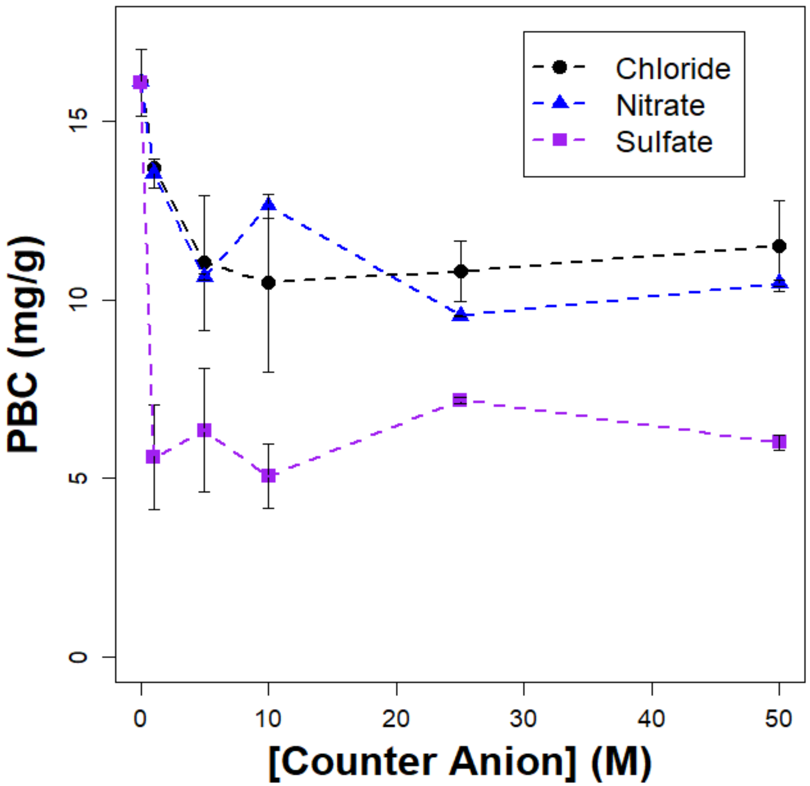


Affinity much higher than roots indicating potential efficacy at low concentrations

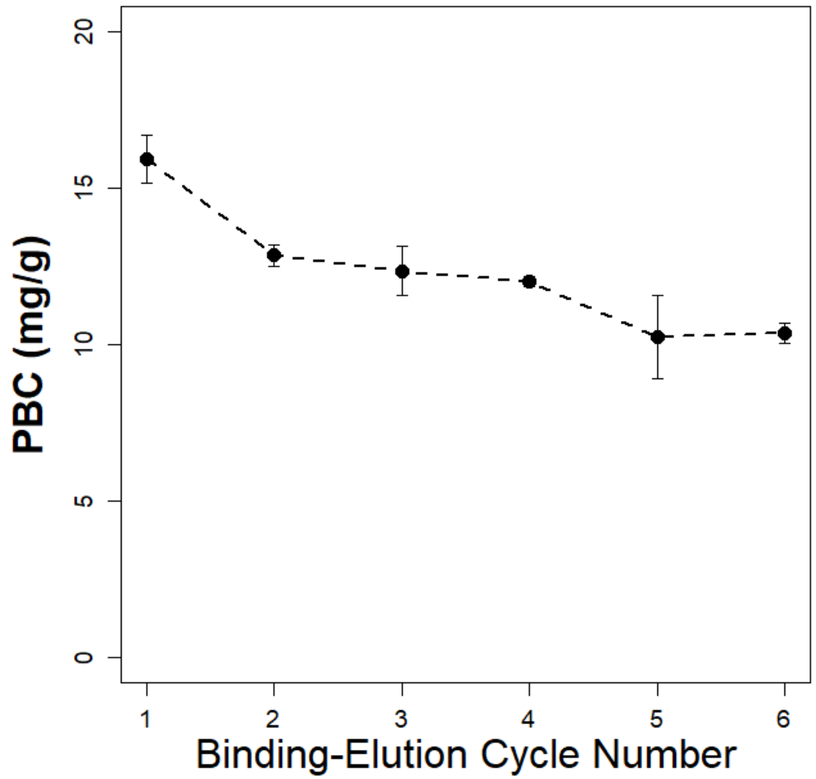


4. Fe-CMSD as a PSM

Impact of counter anions on PSC

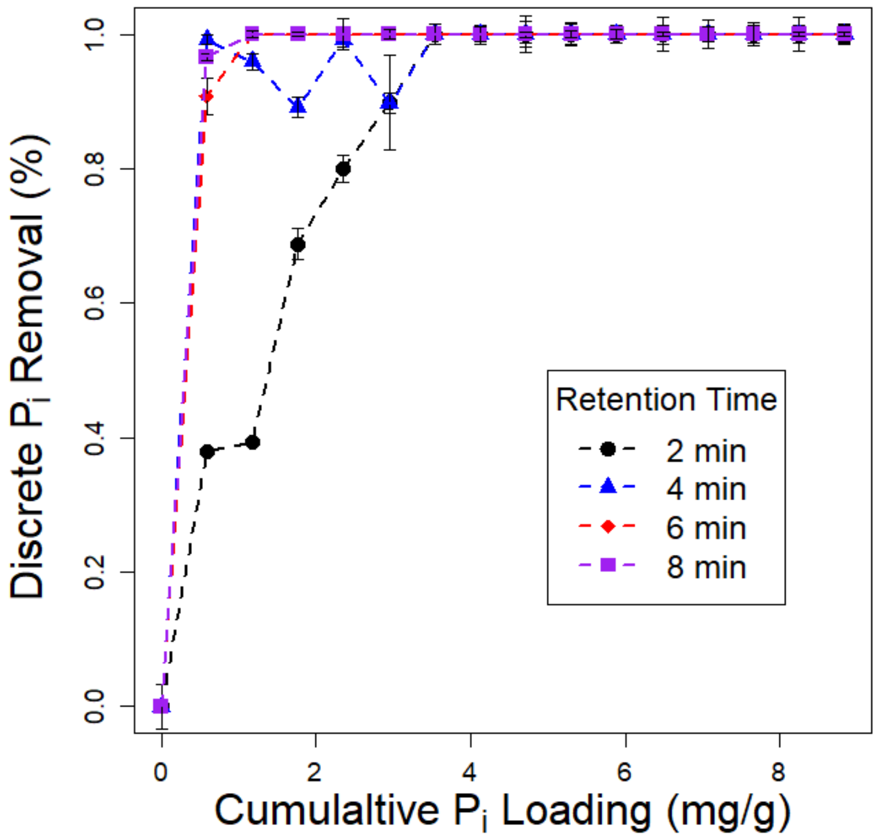


Regeneration and reuse of Fe-CMSD after CMC induced desorption of P_i



4. Fe-CMSD as a PSM

Removal efficiency with varied retention times in a flowing filtration system (influent $[P_i]$ = 589.3 µg/L)



Removal efficiency increases with retention time and with solvent saturation of the Fe-CMSD

Retention Time (min)	Total Removal
2	88.5
4	98.3
6	99.4
8	99.8

4. Fe-CMSD as a PSM

Conclusions: Fe-CMSD is an inexpensive and effective PSM

Largest drawback is the disruption of P_i binding by sulfate

Still useful as an early stage PSM in a multistage filtration system

Future Work:

i) Alternative routes to introduce multiple acid groups to a single site (ie. citric acid instead of MCA)

ii) Test alternative anionic groups for metal binding (ie. sulfonic acids)

iii) Test alternative metal cations (ie. Al^{3+}, Cu^{2+}, La^{3+})

Thank you very much for listening

Questions?