Enhancing transport and delivery of ferrihydrite nanoparticles via polymer encapsulation in PFAS-contaminated sediments to stimulate PFAS defluorination by *Acidimicrobium* sp. Strain A6

Utilizing Innovative Materials Science Approaches to Enhance Bioremediation
Session I - Per- and Polyfluoroalkyl Substances
NIEHS Superfund Research Program

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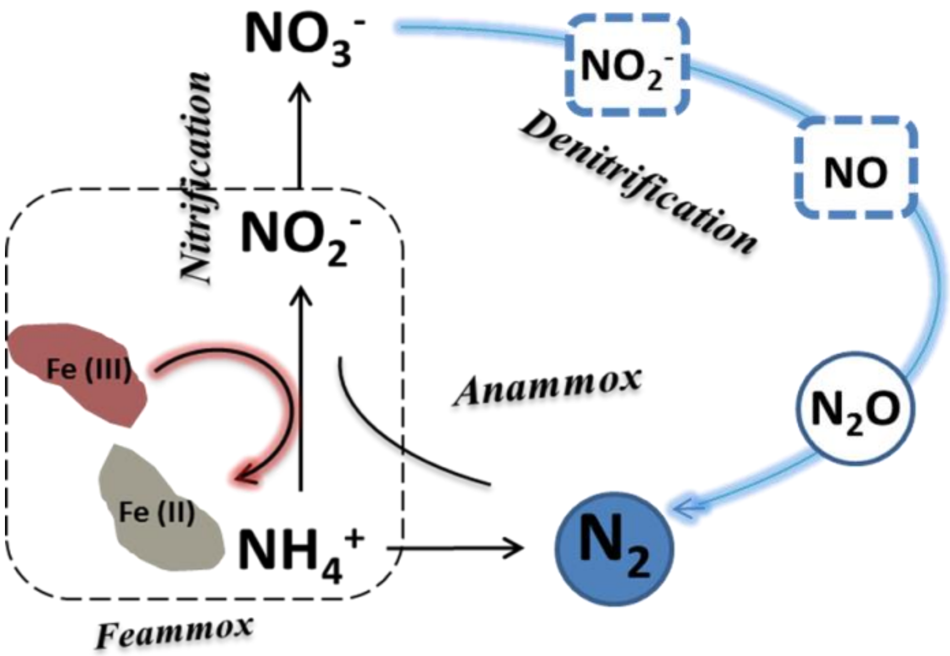
Oxidation of NH_4^+ under Fe reducing conditions (Feammox)



$$3Fe_2O_3 \cdot 0.5H_2O + 10H^+ + NH_4^+ \rightarrow 6Fe^{2+} + 8.5H_2O + NO_2^-$$

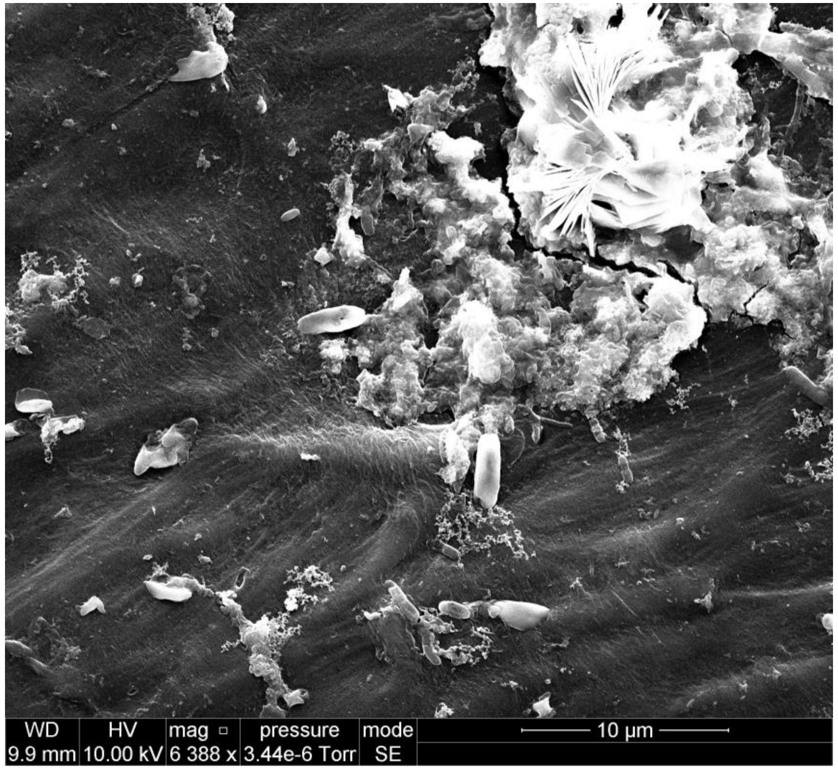
anaerobic
autotrophic

$$\Delta G_r \leq -145.08\,kJ\ mol^{-1}$$

Clement *et al*. (2005); Shrestha *et al.* (2009), Sawayama (2006); Yang *et al*. (2012), many recent papers on Feammox …

Acidimicrobium sp. Strain A6 (referred to here as A6)

(ATCC, PTA-122488)



A6 can also use NH_4^+ and H_2 as electron donor
A6 is an autotroph
A6's doubling time ~ 10 – 14 days
A6 is electrogenic

Not a "domesticated" organism. Difficult to grow. Does not take off in many incubations…

Cells are rod-shaped, 1.5–3 μm long by 0.5 μm wide. **Gram-positive**.

As far as we know it only uses solid Fe(III) phases as electron acceptor.

Needs to be recultured ~ every 2 to 3 months.

After growing on H_2, A6 no longer oxidizes NH_4^+.

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RESEARCH ARTICLE

Isolation and characterization of an ammonium-oxidizing iron reducer: *Acidimicrobiaceae* sp. A6

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Genes for dehalogenases identified in the genome of A6

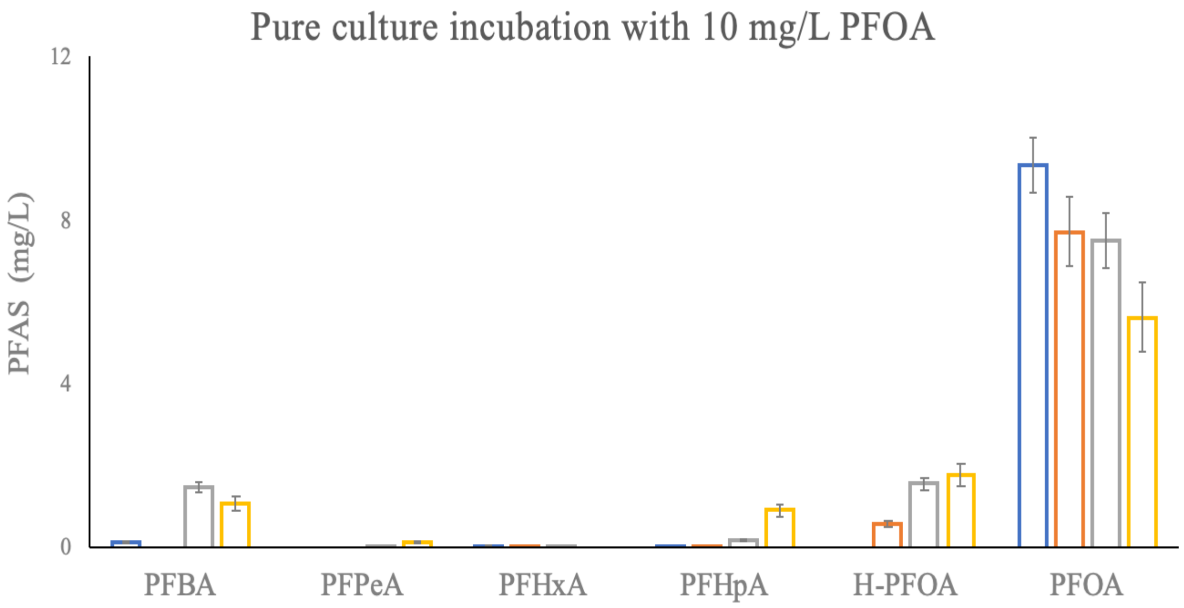
Acidimicrobium sp. Strain A6 s genome contains multiple dehalogenase genes (GenBank accession numbers MK358459-MK358462), including a gene for a:

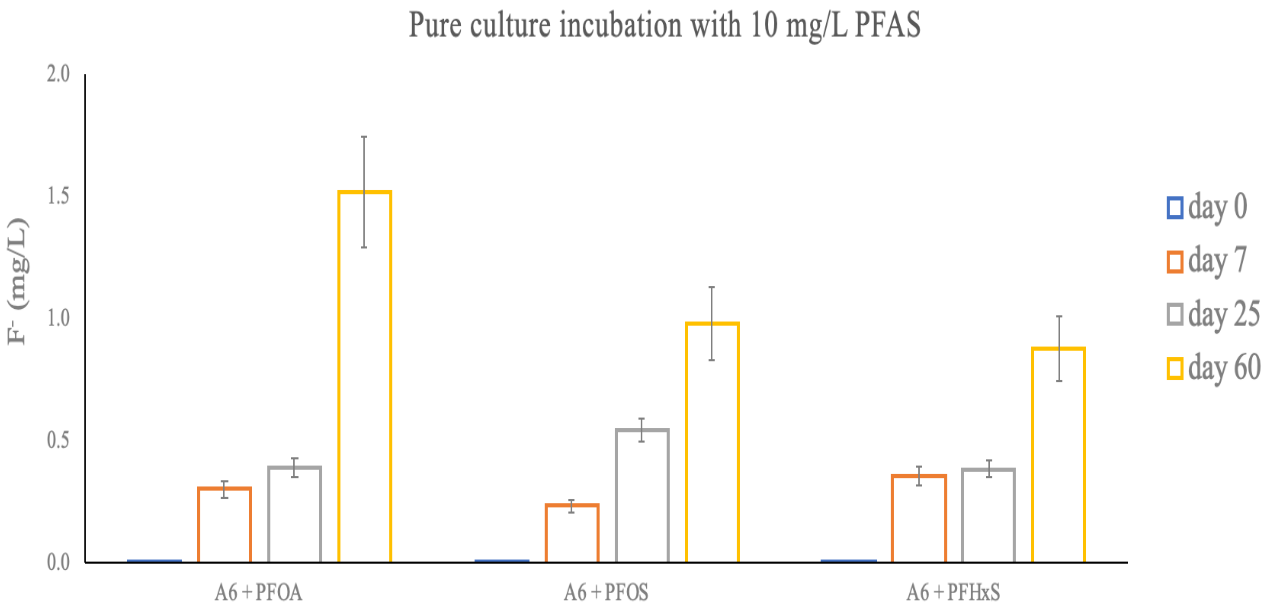
Reductive dehalogenase homolog (***rdhA***),

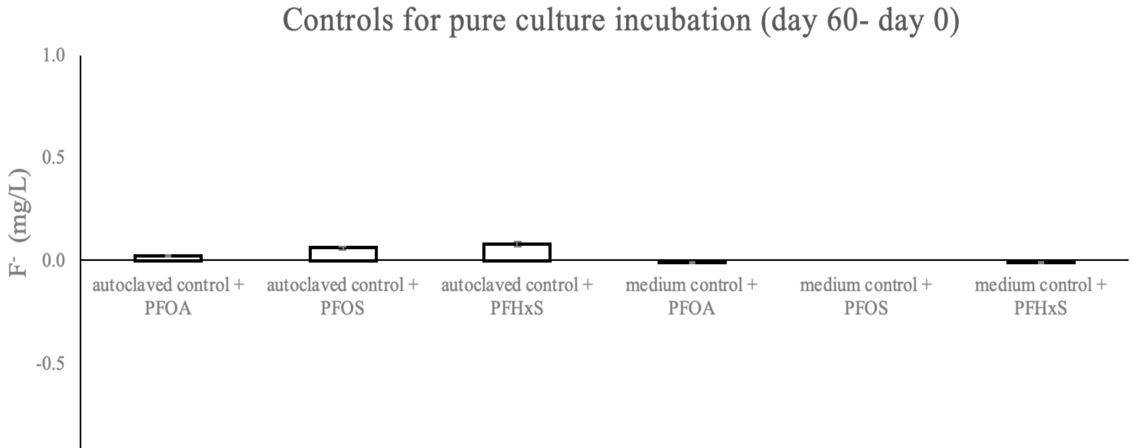
Fluoroacetate dehalogenase homolog (***FceA***),

Two putative haloacid dehalogenase genes (***dhl_1* and *dhl_2***).

Pure A6 culture incubations augmented with 10 mg/l PFOA

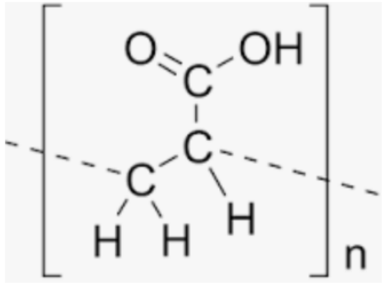






Problem and motivation

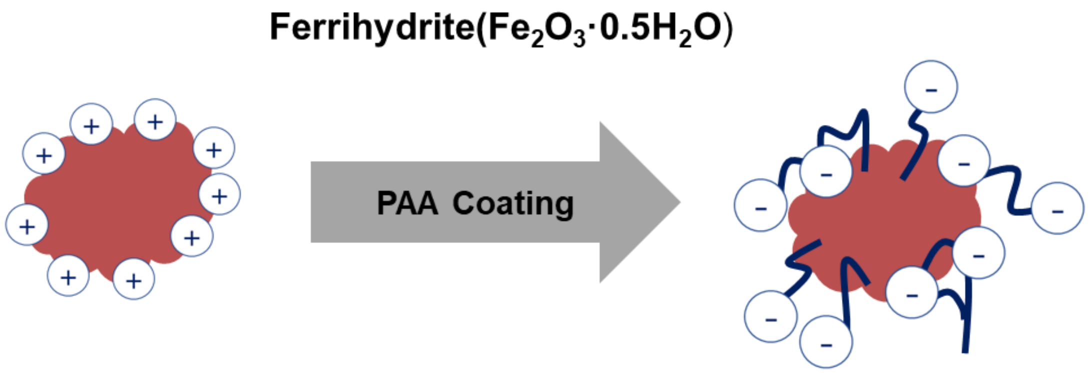
- To operate a PFAS bioremediation scheme utilizing A6, we need to supply an electron donor (NH_4^+) and an electron acceptor Fe(III).
- It will be a challenge to provide and distribute Fe(III) to a soil/sediment medium. Fe(III) solid phases are positively charged, and soil/sediments are negatively charged.
- Hence, we will coat ferrihydrite with polyacrylic acids (PAAs) to alter the surface charge and enhance transport in groundwater and soils.



PAAs are biodegradable and considered safe, used in food packaging and disposable diapers. Can be obtained in many different sizes (molecular weights, MW).

- Is the PAA-coated ferrihydrite bioavailable to A6, and does it affect PFAS defluorination?
- Is there an optimal PAA MW?

Effect of PAA coating on ferrihydrite charge

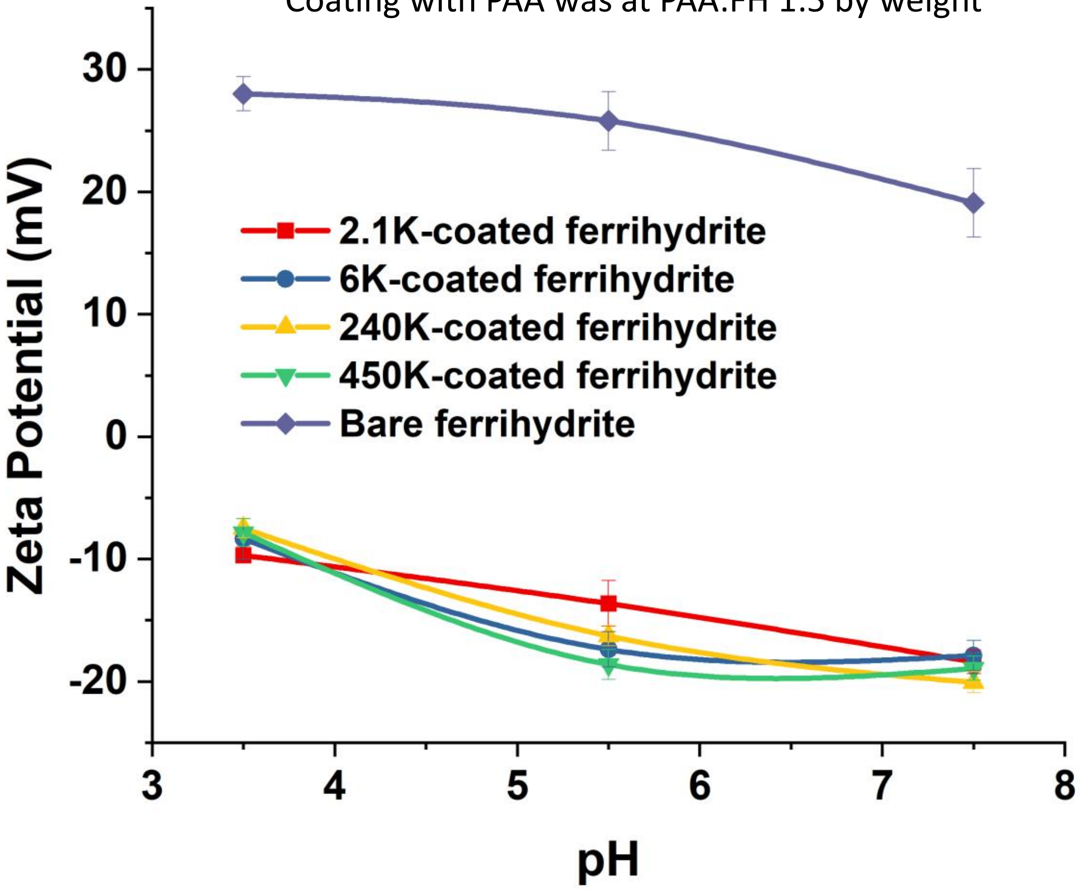


Ferrihydrite($Fe_2O_3 \cdot 0.5H_2O$)

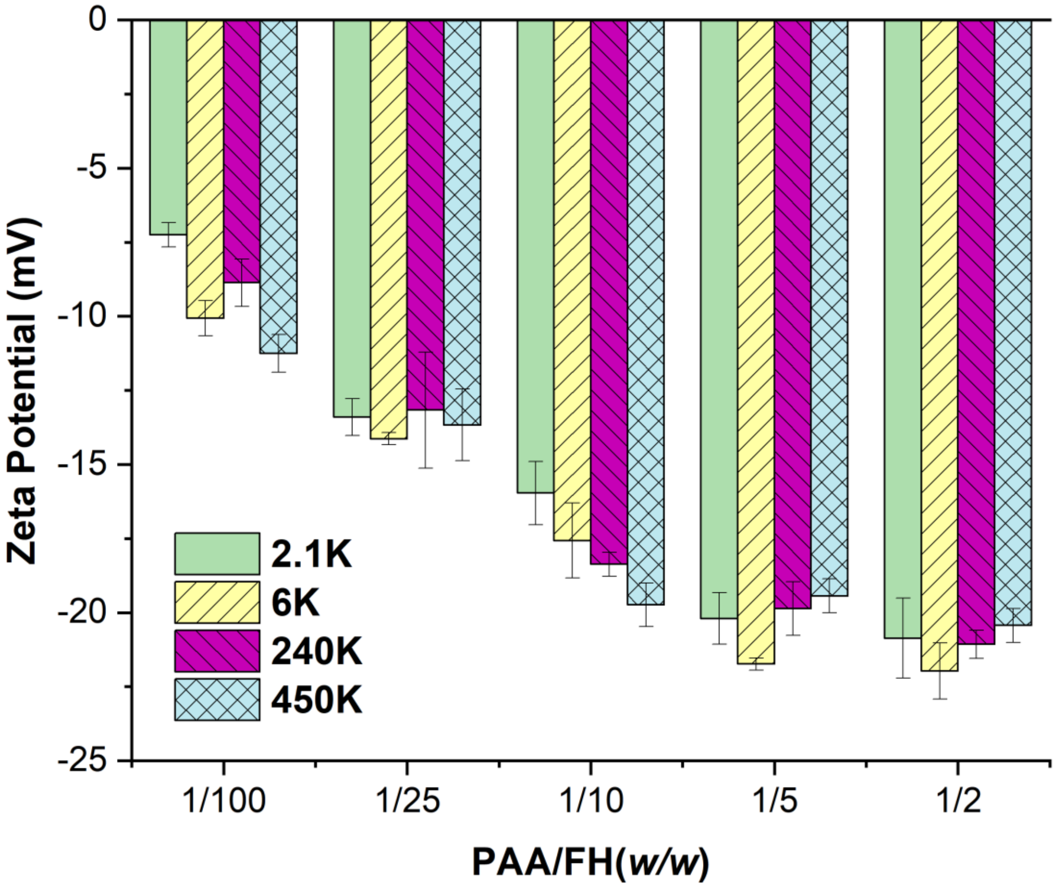
PAA Coating

Zeta potential vs. pH

Coating with PAA was at PAA:FH 1:5 by weight



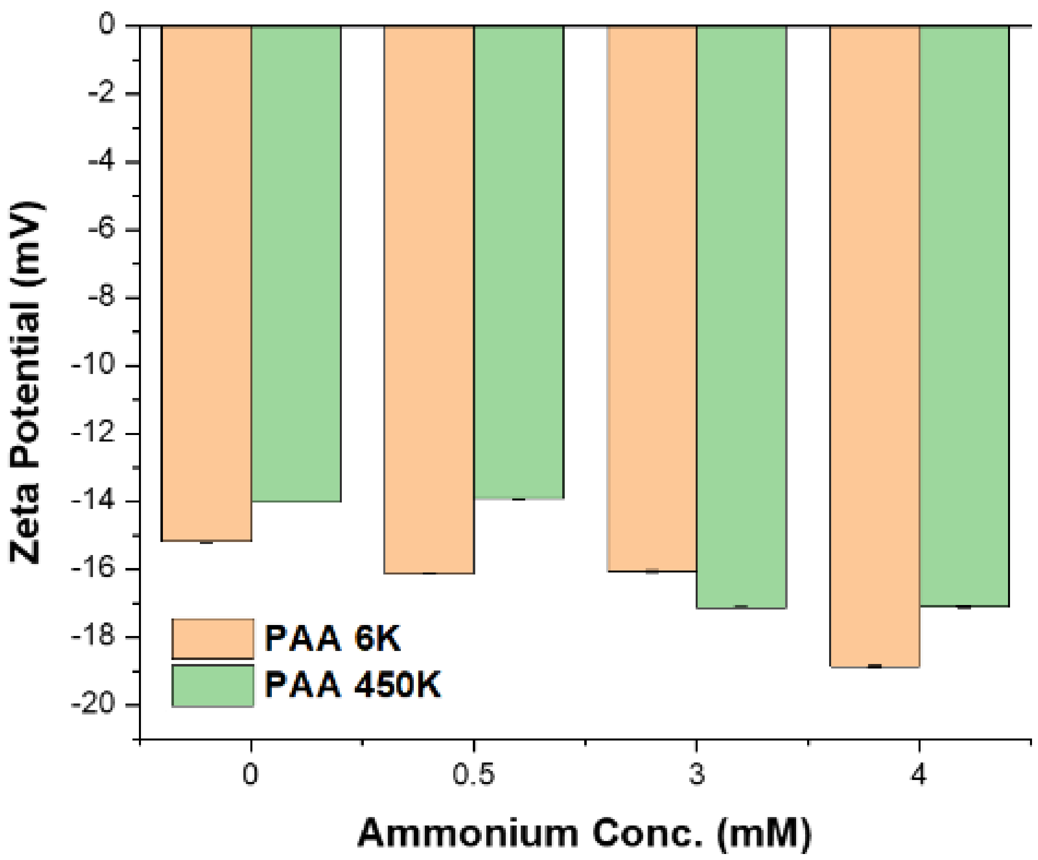
Effect of PAA coated ferrihydrite on zeta potential



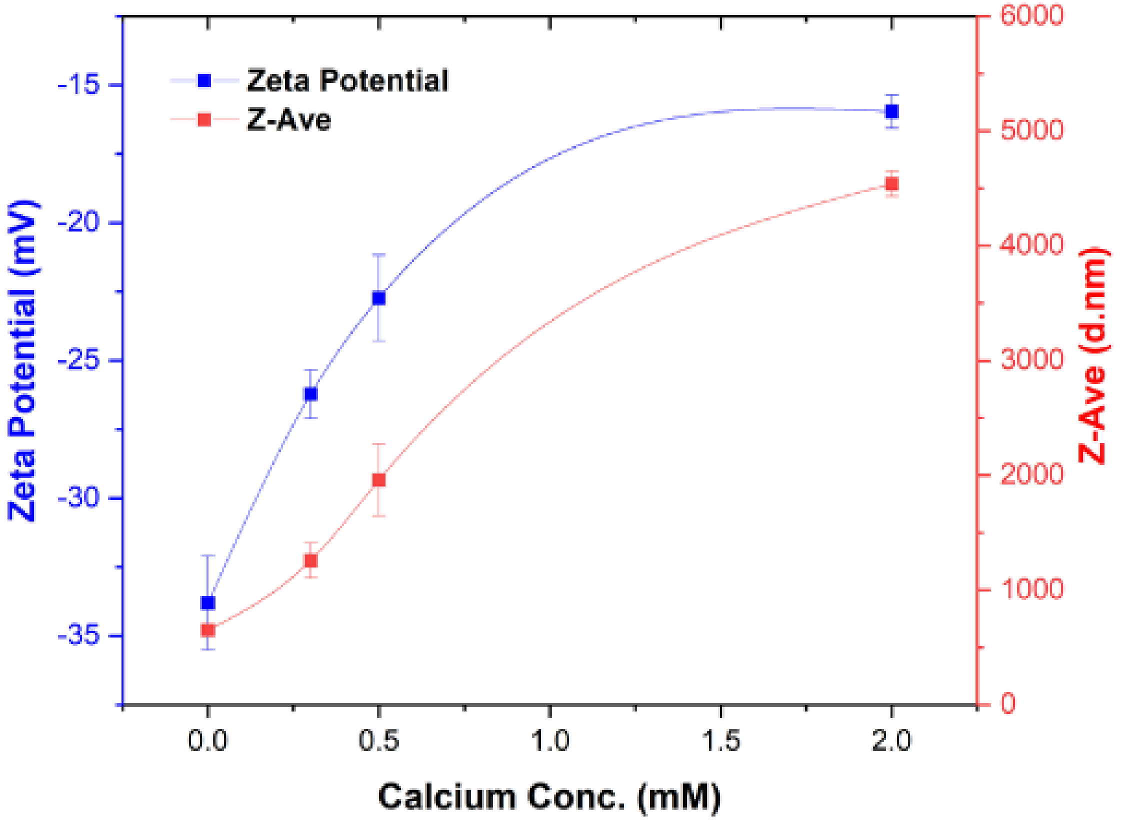
pH = 5.5

We need mM levels of NH_4^+. Does it affect the zeta potential of the PAA coated ferrihydrite? What about Ca^{++}?

(A)

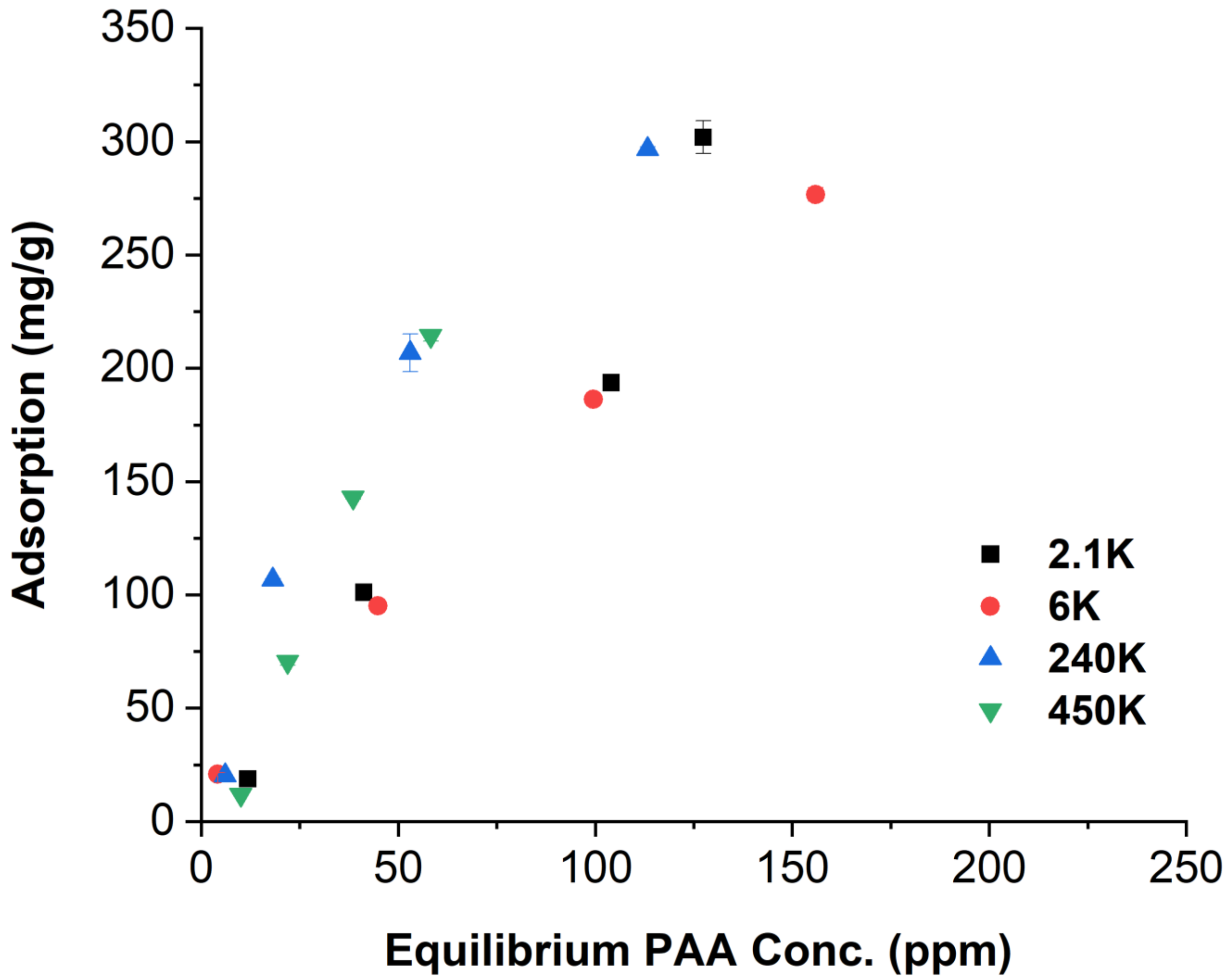


(B)



pH = 5.5

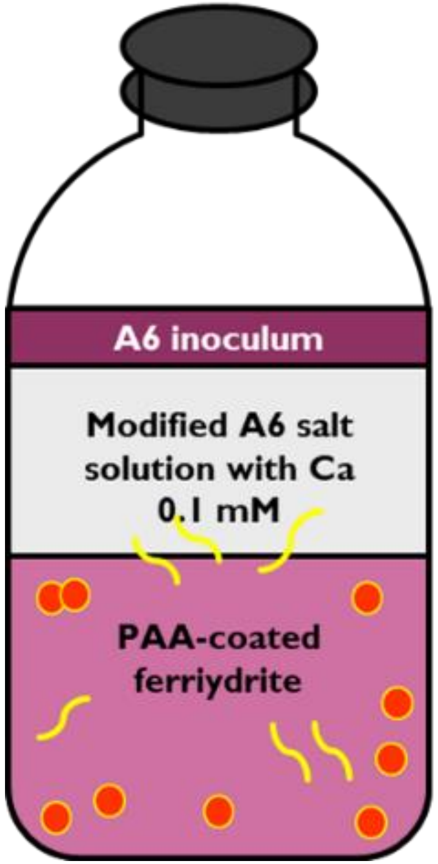
PAA sorption onto ferrihydrite



pH = 5.5

Multiple incubations conducted in 50 ml vials

Headspace CO_2:N_2 20:80 and Feammox medium



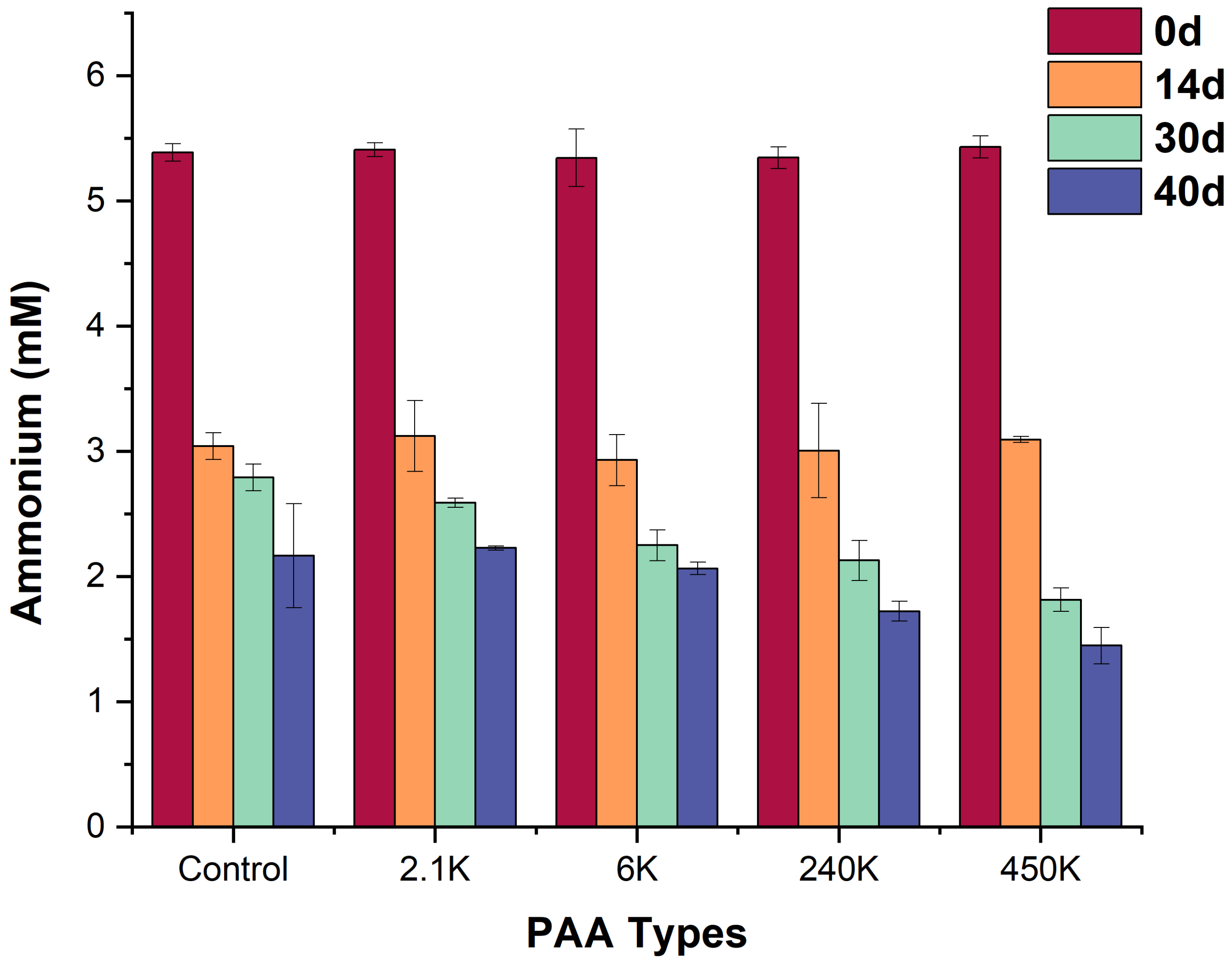
A6 inoculum

Modified A6 salt solution with Ca 0.1 mM

PAA-coated ferriydrite

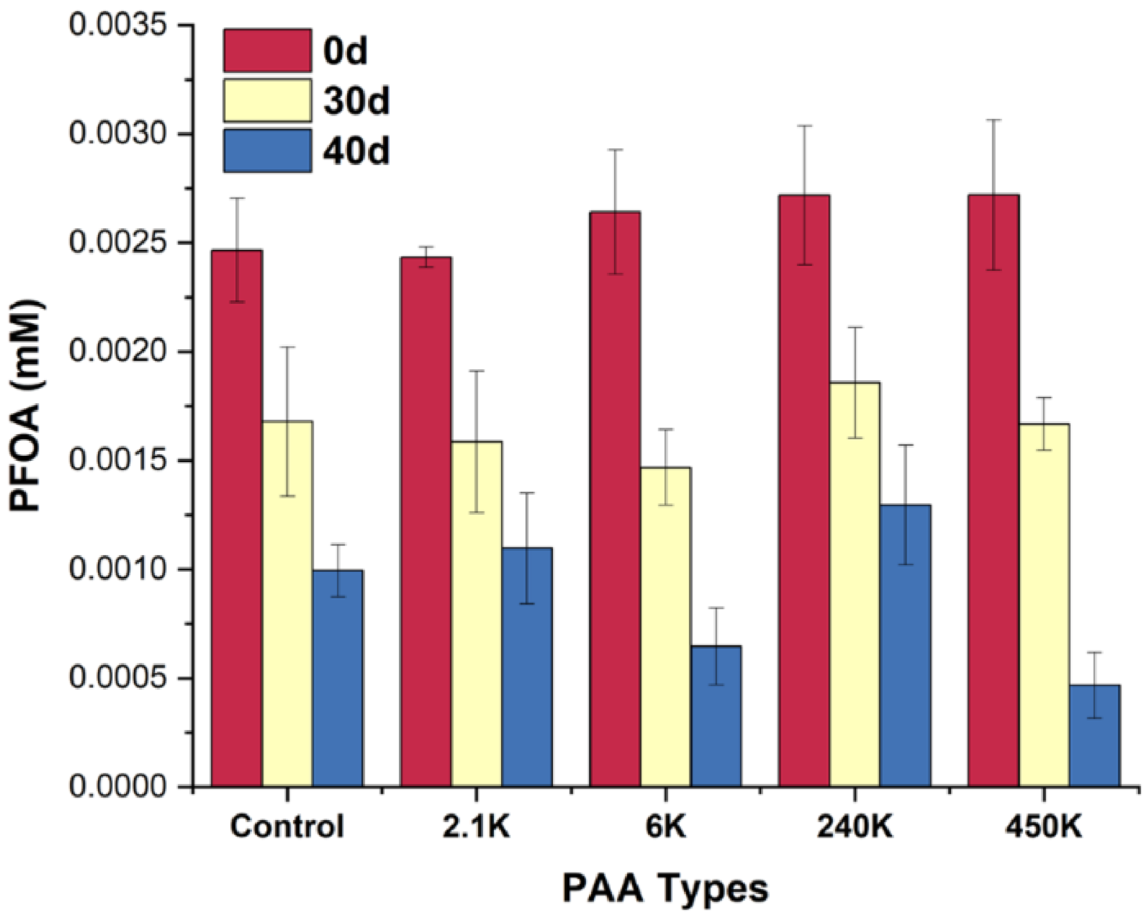
pH = 5.5

Effect of PAA coating on NH_4^+ oxidation by A6



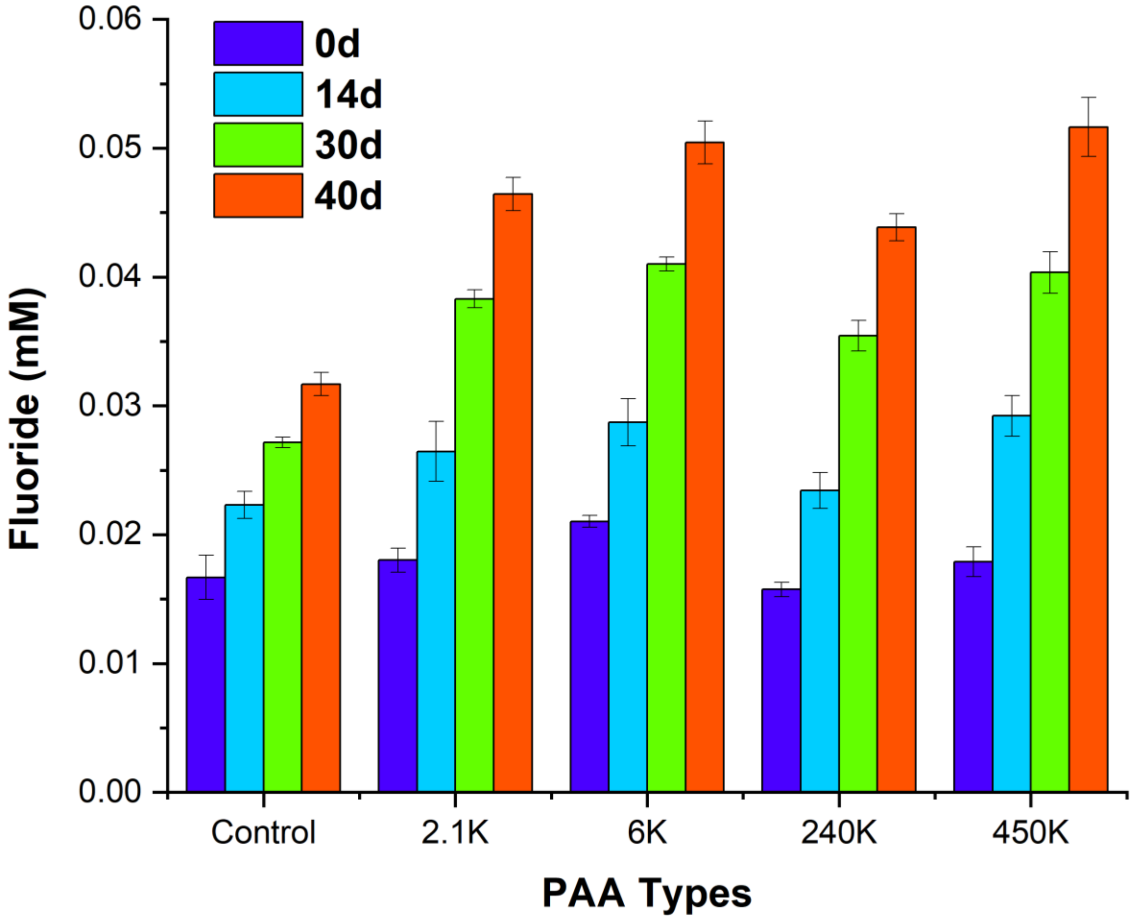
pH = 5.5

PFOA degradation during incubations using the different PAA coatings of ferrihydrite



pH = 5.5

F^- production during the incubations



pH = 5.5

Intermediates

- During the incubations the production of the following shorter carbon chain PFAAs was observed: PFHpA, PFHxA, PFPeA, PFBA.
- There was variability and no clear trend in intermediates for incubations with ferrihydrite coated with different PAAs, but the the sum of their molar concentrations was 4 orders of magnitude lower than that of the initial PFOA concentration (10^{-6} vs. 10^{-2} mM) or F^- produced.
- Separate research has shown that these intermediates can also be defluorinated by A6.

Preliminary F balance (without considering intermediates)

Sample	**0d**			**30d**			**40d**		
	F in PFOA (mM)	**F^- (mM)**	**Total F (mM)**	**F in PFOA (mM)**	**F^- (mM)**	**Total F (mM)**	**F in PFOA (mM)**	**F^- (mM)**	**Total F (mM)**
Control	0.037 (0.004)	0.017 (0.002)	0.054	0.025 (0.005)	0.027 (<0.001)	0.052	0.015 (0.002)	0.032 (0.002)	0.047
2.1K	0.037 (<0.001)	0.018 (0.001)	0.055	0.024 (0.005)	0.038 (<0.001)	0.062	0.016 (0.004)	0.046 (0.004)	0.063
6K	0.040 (0.004)	0.021 (<0.001)	0.061	0.022 (0.003)	0.041 (<0.001)	0.063	0.010 (0.003)	0.050 (0.003)	0.060
240K	0.041 (0.005)	0.016 (<0.001)	0.057	0.028 (0.004)	0.035 (0.001)	0.063	0.019 (0.004)	0.044 (0.004)	0.063
450K	0.041 (0.005)	0.018 (0.001)	0.059	0.025 (0.002)	0.040 (0.002)	0.065	0.007 (0.002)	0.052 (0.002)	0.059

mean value and (SD), n = 3

Conclusions

- PAA-coated ferrihydrite:

  * changes the zeta potential to negative

  * is bioavailable to A6

  * appears to enhance NH_4^+ oxidation and PFOA defluorination
- The higher MW PAA (450K) seems to be more appropriate for the proposed use:

  * sorbs strongest to ferrihydrite

  * for the same mass ratio of PAA: ferrihydrite the zeta potential is lowest

  * appears to yield a higher NH_4^+ oxidation and PFOA degradation

Next steps

- Understand reason for enhanced Feammox activity and PFOA defluorination by PAA-coated ferrihydrite
- For field-scale applications large quantities of goethite might be easier to obtain than ferrihydrite. Can we obtain similar results for PAA-coated goethite?
- Conduct sand-column experiments to test PAA-coated transport/distribution and Feammox activity, including PFOA defluorination.
- Repeat for sediments from a PFAS contaminated site. Develop appropriate transport/biodegradation model formulation.
- Plan a field demonstration experiment (not part of this project).

Acknowledgements

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