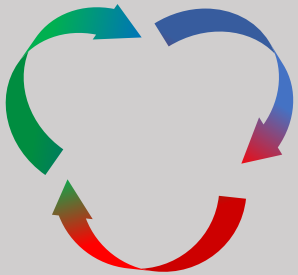
Reusable Magnetite-Activated Carbon for PFAS Removal and Destruction via Microwave Pyrolysis

Research Question

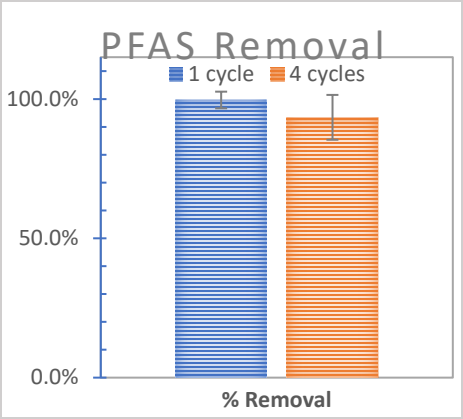
The purpose of this experiment was to determine the regenerative potential of activated carbon with magnetite for energy-efficient removal of PFAS



Procedures

1. Magnetite was synthesized and PFAS dilution was made.
2. Activated carbon was mixed with magnetite (3:1) and added to PFAS solution (1:40).
3. After one hour reaction, samples were filtered to separate the solids from the solution.
4. Filtrates were analyzed by CIC for total organic fluoride concentration (ppb).
5. PFAS loaded solids were dried, then heated to >850 ^{o}C in a microwave kiln for thermal decomposition of PFAS.
6. Repeat steps 1-5 with regenerated activated carbon to reactivate for reuse.

Data Analysis



Nearly 100% removal of PFAS.
No significant change in % removal after 4 cycles.

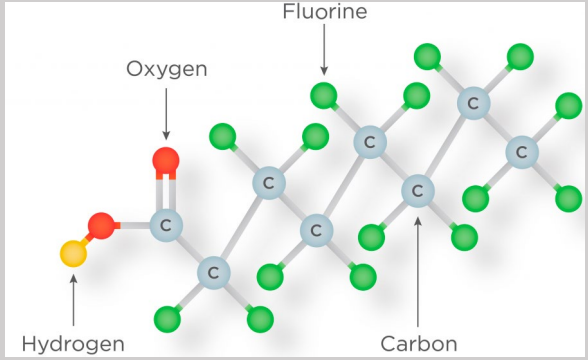
Conclusions

- Microwave-activated magnetite-activated carbon mixture achieved temperatures known to decompose PFAS for regeneration.
- Microwave heating was 10-20 times more energy efficient that conventional heating.
- Water samples sustained 93.4% removal of PFAS after 4 cycles of regeneration.

Per- and Polyfluoroalkyl Substances (PFAS)

What are PFAS?

- A class of over 14,000 chemical compounds (Humphries, 2018)
- Forever chemicals (persistent organic pollutants, resistant to degradation)
- Chain molecules with carbon backbone (C-C) and fluorine appendages
- One of the strongest bonds to exist in organic chemistry
- PFAS chemicals can be used in everyday applications such as waterproof clothing, carpets and furniture, non-stick cookware, fire extinguishing foam, grease-proof food packaging, dental floss, and cosmetics



pfasfacts.com

Concerns of PFAS:

- Endocrine disruptors (interfere with hormones in the body)
- Developmental effects, decreased birth weight, thyroid hormone disruption (Xaio et al., 2020), immunotoxicity, cancer, reproductive effects including infertility (Cohen et al., 2023), high cholesterol, hypertension, type 2 diabetes (Valvi et al., 2017), alterations in liver enzymes (Midya et al., 2022), and lower antibody responses to vaccines in children (Humphries, 2018)
- 98% of the United States population has PFAS chemicals in their blood
- Regulation or very difficult due to thousands of variants of PFAS chemicals
- Extremely persistent in nature for unidentified long periods of time and bioaccumulate throughout the environment

firefighterclosecalls.com

Treatments for PFAS

- Activated carbon has been proven to be a reliable filtering agent for PFAS in water.
- Current methods of PFAS decomposition require extreme temperatures, using large amounts of energy.
- PFAS is known to breakdown under thermal treatments above 650 ^{o}C. In these experiments I targeted >850 ^{o}C heating to be sure we destroy the PFAS.
- With the addition of magnetite as a catalyst for PFAS decomposition, this energy cost can be reduced to a fraction of that of other methods.

https://www.enviro.wiki/index.php?title=PFAS_Ex_Situ_Water_Treatment
Image shows industrial scale PFAS treatment

Research Question, Hypothesis, and Variables

Research Question:
What is the regenerative potential of activated carbon with magnetite for energy-efficient removal of PFAS?

Hypothesis:
Thermal decomposition of PFAS by magnetite assisted pyrolysis of activated carbon is an effective PFAS treatment that can be reused for economical water treatment.

Variables:
Independent- Number of regeneration cycles applied to carbon-magnetite mixture
Dependent- Total PFAS remaining after filtration as recorded via Combustion Ion Chromatography

Materials

Experiment:

- Aqueous PFAS from reagent PFOA and PFOS
- Activated Carbon: To filter PFAS solution
- Magnetite
    - Ferric Chloride Fe(III) 0.2 M solution
    - Ferrous Chloride Fe(II) 0.1 M solution
    - NaOH (Base Solution) to pH 8
- Lab filter: for separating supernatant from solids solutions
- Microwave: for heating activated carbon-magnetite mixture
- Microwave kiln for glass fusing: for heating activated carbon-magnetite mixture in the microwave
- Analytical balance: to measure samples for experimentation and mass changes in substances
- 50 mL plastic test tubes: to measure and hold substances for experiment
- 10 mL plastic test tubes: to measure and hold water samples
- Syringe PFAS rated 0.7 um filter for filtering aqueous samples

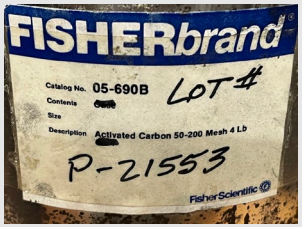
Testing:

- Safety equipment (goggles, gloves, masks, lab coat): to maintain a safe working environment
- Combustion Ion Chromatography Instrument, XRD for mineralogy
- Pipette: to move liquids and separate liquids from mixtures
- Carbon cartridges and holders to run through CIC analysis
- Sample loading instrument for carbon cartridge samples

Procedure

Preparation: Magnetite was made by combining Iron(III) and Iron(II) in a 2:1 molar ratio to make 1L of solution. Sodium hydroxide was added to the solution under constant mixing until the pH reached 8.0. Activated carbon was added to magnetite in a 3:1 mixture. 15 ppb PFAS dilution was made.

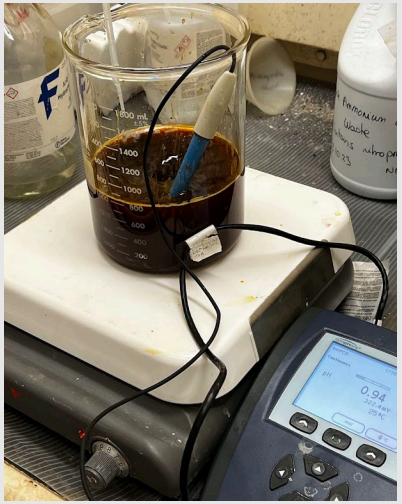
1



Activated carbon used in experiment (left)

Magnetite solution was centrifuged for collection during synthesis (left)

magnetite used in experiment



Magnetite synthesis

Experiment:

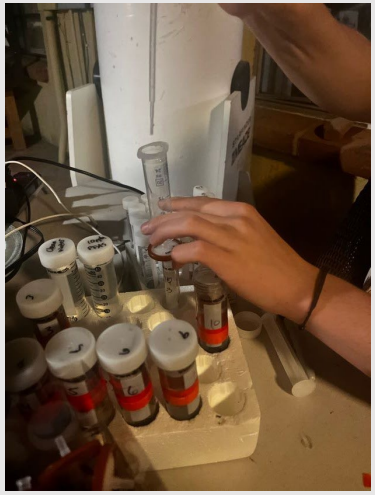
2

One gram of magnetite-activated carbon mixture was added to 10 test tubes, labeled 1 through 10. 40 mL of PFAS solution was added to each test tube and mixed continuously for 1 hour.

Filtration:

3

After mixing for 1 hour, the supernatant was taken off and filtered into separate test tubes. The remainder of the liquid was removed, and the solids were allowed to dry overnight.



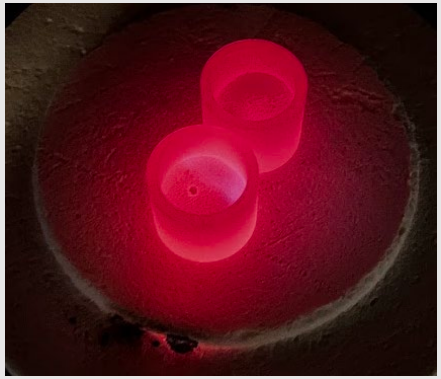
Filtering supernatants

Procedure

Regeneration:

4

The dry solids were removed and put into graphite crucibles before being put into a microwave kiln. Each sample of the solid mixture was microwaved for two cycles of 8 minutes to fully burn off the PFAS.



Activated carbon samples reached temperatures over 900 ^{o}C (left)

Aqueous samples filtered for testing

Graphite crucibles in microwave kiln shortly after heating

Reuse:

5

After regeneration, solids were added back into test tubes along with 40 mL of PFAS solution for an additional cycle of experimentation.

6

Steps 2 through 5 were repeated for 4 cycles, taking out solids from experimentation.

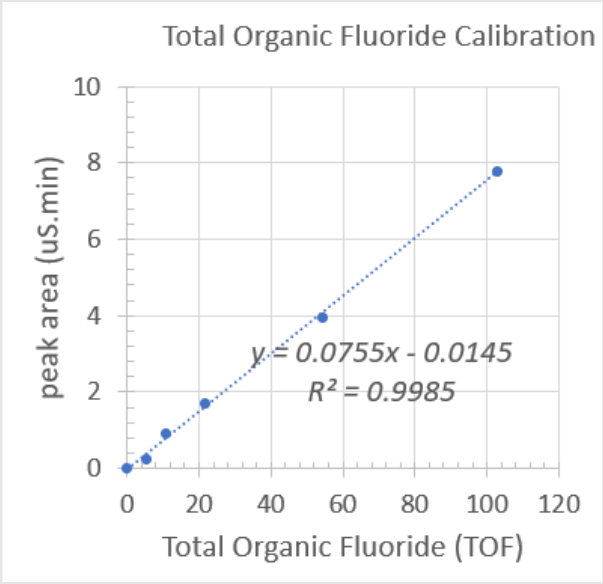
Solids saved for repeated testing; liquids saved for analysis

Procedure

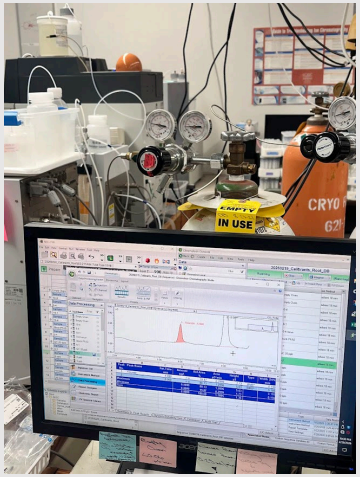
Data Collection:

6

To create a calibration curve, solutions were made of different Fluoride concentrations (50 ppb, 20ppb, 10ppb, 5ppb, and Distilled water).



Loading carbon cartridges with supernatants from PFAS removal experiments



CIC programming

Aqueous samples were analyzed using Combustion Ion Chromatography (CIC). First, two carbon trap cartridges were loaded into each holder. The cartridges were rinsed with sodium nitrate to wash away excess inorganic fluorine. Samples were then loaded onto the trap and rinsed with the $NaNO_3$.

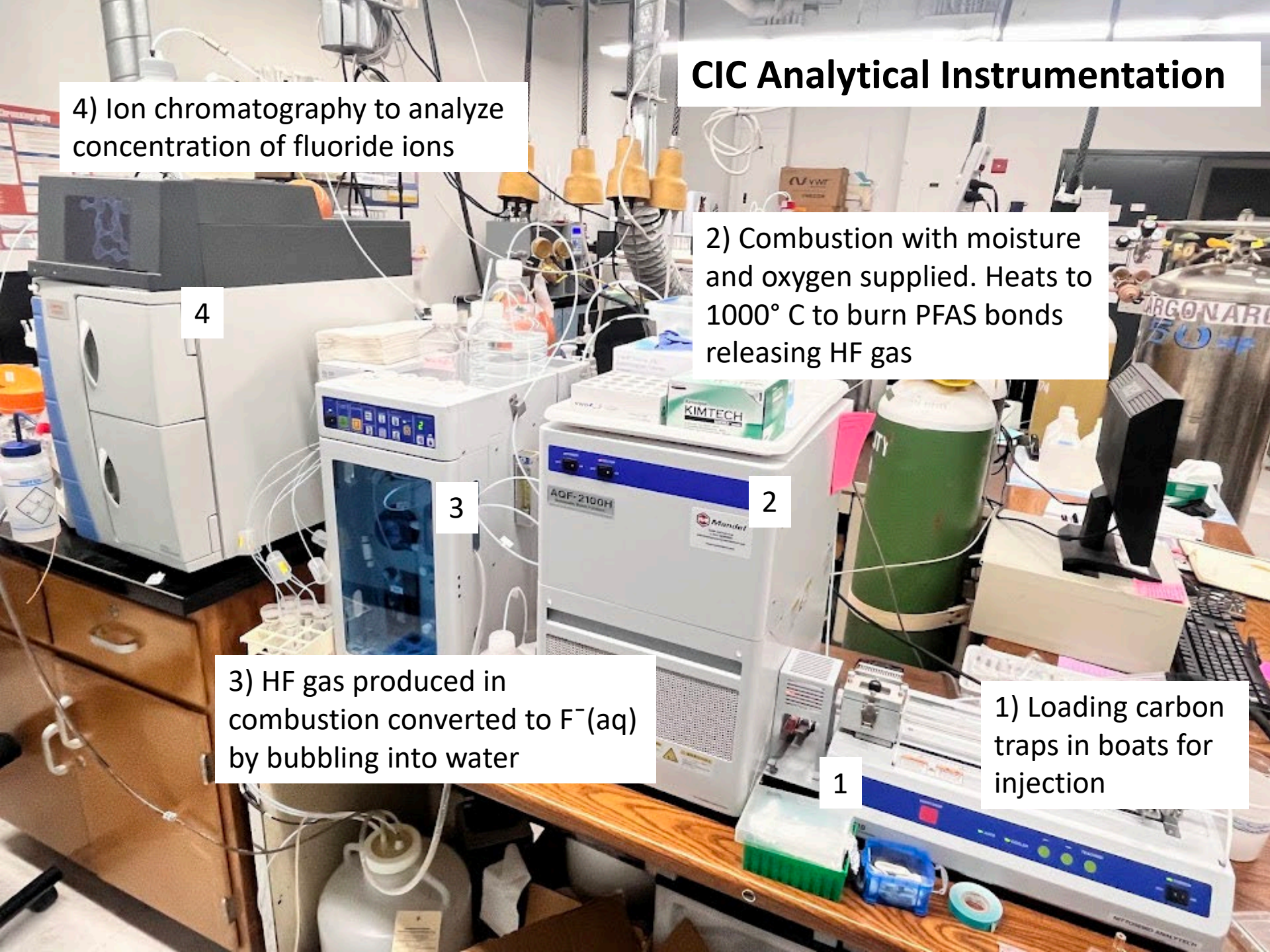
CIC

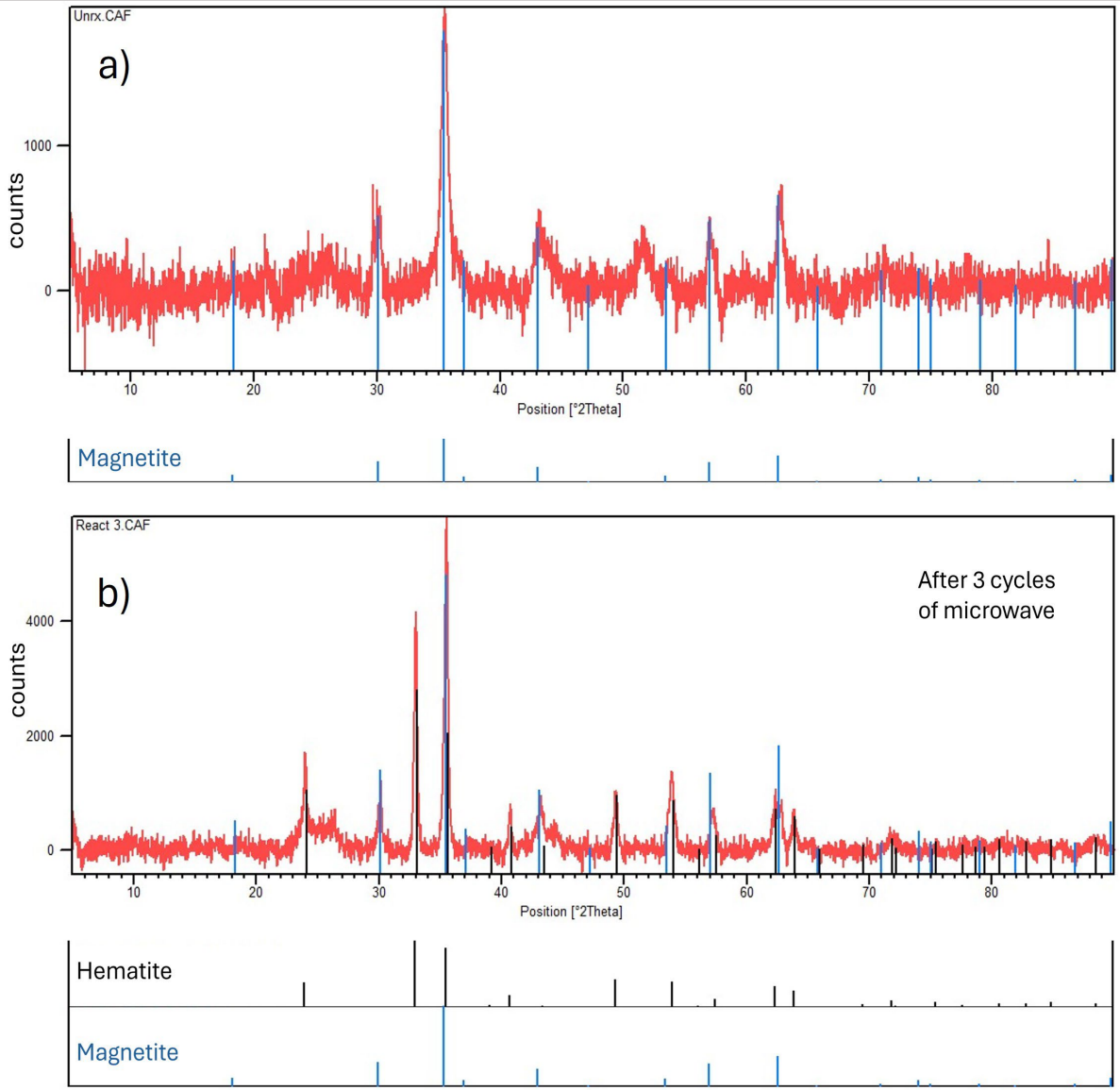
7

The carbon trap with the sample loaded was then placed into ceramic boats to be analyzed in CIC and results were recorded.

Calibrants (MilliQ DI H2O)					
	vial #1	vial #2	vial #3	vial #4	vial #5
Stock	1000 ppb	1000 ppb	1000 ppb	1000 ppb	1000 ppb
Target	100 ppb	50 ppb	20 ppb	10 ppb	5 ppb
Stock:Target (g)	5:50	2.5:50	1:50	0.5:50	0.25:50
Stock (g)	4.957	2.4972	1.0025	0.5046	0.2516
Plus diluent	49.4856	49.5371	50.1058	49.8851	49.814
F by mass	107.85	54.28	21.58	10.89	5.44
Conversion of ppb to uMol					
Grams	2.1570E-08	1.0860E-08	4.3160E-09	2.1780E-09	1.0876E-09
Moles	1.1354E-09	5.7140E-10	2.2720E-10	1.1470E-10	5.7249E-11
umoles	1.1354E-03	5.7140E-04	2.2720E-04	1.1470E-04	5.7249E-05

Standards were made to form a calibration curve for the CIC analysis. Quality control samples were also made to confirm fluoride concentrations were accurate in data collection.


CIC Analytical Instrumentation
4) Ion chromatography to analyze concentration of fluoride ions
2) Combustion with moisture and oxygen supplied. Heats to 1000° C to burn PFAS bonds releasing HF gas
4
3
2
1
3) HF gas produced in combustion converted to F^-(aq) by bubbling into water
1) Loading carbon traps in boats for injection
KIMTECH
AQF-2100H
Mandel



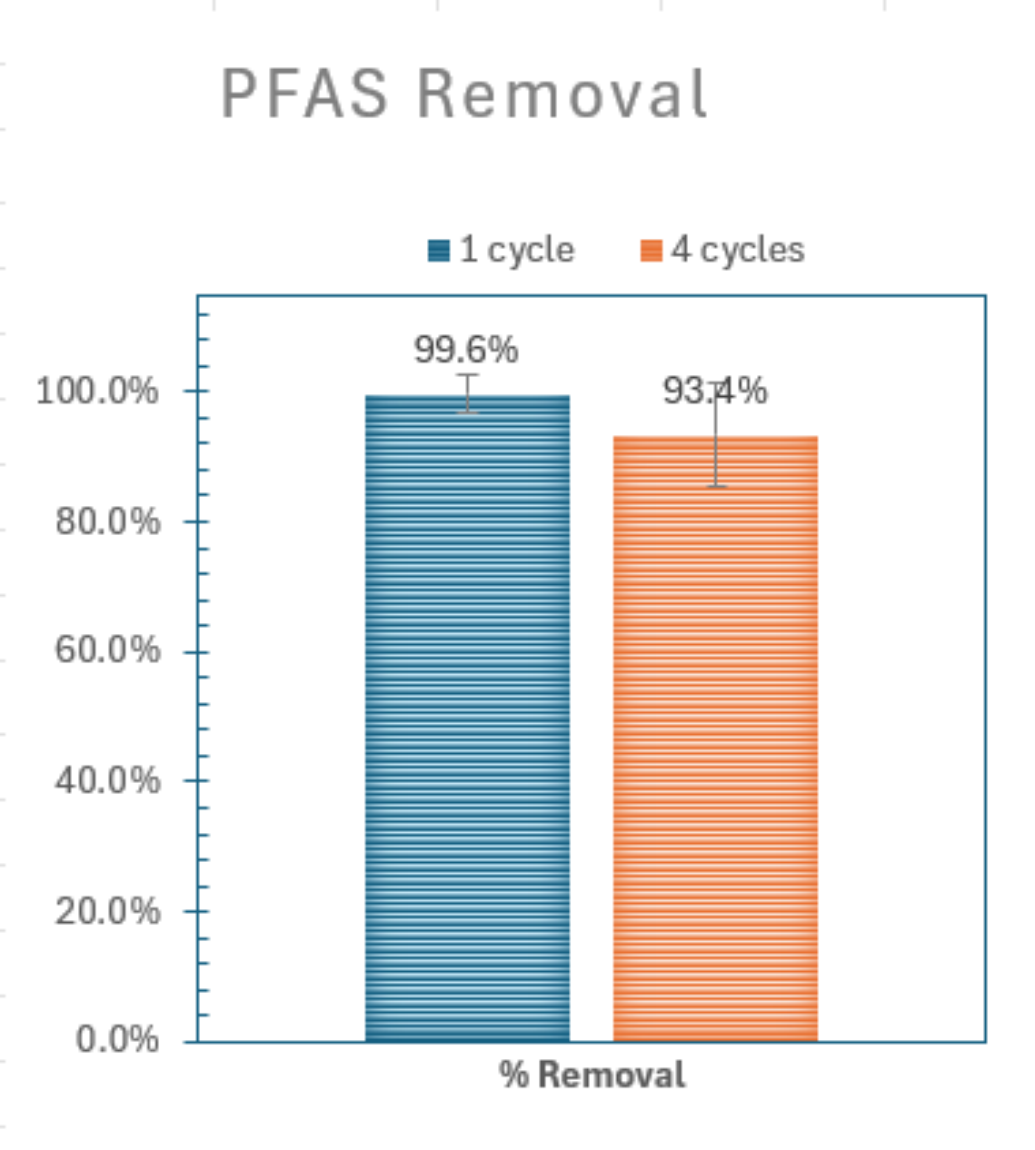
Mineralogy

X-Ray Diffraction (XRD) of a) unreacted and b) reacted granular carbon plus magnetite.

Shows only magnetite as starting material, and a partial transformation to hematite after pyrolysis.

Verifies temperature was > 650 ^{o}C

XRD collected at the University of Arizona Chemistry Department



Results

This graph depicts the percent of PFAS removed from the samples at cycle 1 and cycle 4. The activated carbon remained efficient after several rounds of PFAS removal and pyrolysis, proving that this method is a viable solution for PFAS treatment in water. Comparing 1x to 4x fives a p-value of > 0.05 indicating that the difference between 1 and 4 cycles are not significantly different and are very nearly 100%. This indicates there was little to no degradation of the filtration properties of the activated carbon magnetite mixture

Discussions and Conclusion

This project explored the regenerative properties of activated carbon with magnetite microwave heating, showing successful regeneration for energy efficient removal of PFAS. Previous studies established that activated carbon is an effective means of removal for PFAS chemicals in water. Additionally, it has been established that high temperatures can break down PFAS bonds. This study is the first to experiment with the high microwave activity of magnetite to superheat the activated carbon, regenerating it energy efficiently. It was found that activated carbon retains its efficiency after several rounds of PFAS treatment and microwave superheating. This small-scale proof of concept can be replicated and applied for commercial and municipal uses by military operations or cities.

Household items suspected to contain PFAS chemicals, including floor polish, carpet, personal care products, waterproofing materials, and food preparation.

This method is 10-20 times more energy efficient than current thermal PFAS treatment using conventional furnaces.

Removal, regeneration, and reuse are the key to reducing the issue of PFAS in our communities.

Applications

This data can then be applied to several real-world scenarios. The properties of activated carbon and magnetite and the relationship between them observed in this experiment could this be scaled up for use industrially and militarily. The biggest factor leading to PFAS contamination of our water and environment here in Tucson is military operations. The regeneration of activated carbon can greatly reduce the PFAS levels of our water in an efficient way if it is applied on a large scale. This will limit the adverse health effects caused by PFAS exposure, helping to combat the excessive use of PFAS in the world, and will also significantly reduce costs of PFAS filtering operations.

grist.org/health/the-epas-proposed-pfas-regulations-ignore-a-major-source-of-drinking-water-contamination/

This method of pyrolysis catalyzed by magnetite can be applied to biosolids from water treatment plants as used in agricultural settings, as they contain high levels of PFAS and are used to grow our crops. Adding magnetite-activated activated carbon would allow for the removal and destruction of the PFAS before they are used as fertilizers.

The findings of this study would also be impactful in drinking water treatment plants worldwide, as these processes, if applied on city scales, would make treatment for PFAS easier and more cost efficient than previously possible. Current methods either store PFAS-loaded activated carbon or spend lots of energy to destroy the PFAS. This method solves the issues of cost for water treatment.

Works cited

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