Addressing PFAS Contamination in Blood Bank Supplies with Hydrogel Nanocomposite Sorbents

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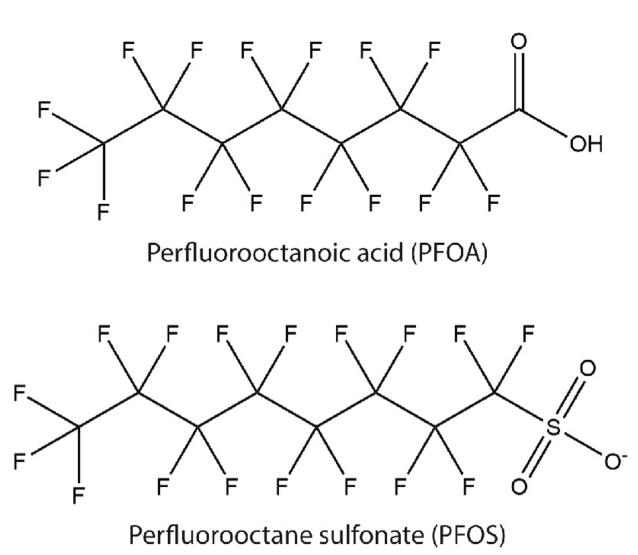
Abstract

Environmental pollutants continue to be a threat to global human health. Persistent contaminants, such as perfluoroalkyl substances (PFAS), have been linked to a multitude of adverse health effects such as cancerous tumors, increased blood cholesterol levels and liver damage. The dominant source of exposure to PFAS is through contaminated drinking water, and accumulation has been found to occur significantly in human blood serum. Thus, high-risk groups who are receiving frequent blood transfusions are exposed to these harmful chemicals in a dual fashion, which could prove detrimental. Traditional sorbents that display an affinity for PFAS include powdered activated carbon and clay. Recently, a protein found in plasma, albumin, has been identified as the major carrier protein for PFAS in human blood [1]. The two most widely detected PFAS in human serum are perfluorooctanesulfonic acid, PFOS, and perfluorooctanoic acid, PFOA. As such, this work aims to develop hydrogel nanocomposites that have the capability to remove PFOA and PFOS from human blood serum. Crosslinked acrylamide polymers were synthesized with varied crosslinking densities of 0.1 mol%, 1 mol%, and 10 mol% to evaluate potential exclusion of serum proteins. In order to incorporate physiochemical properties of sorbents known to bind PFOA and PFOS, varied amounts of dried particulates were integrated into the synthesized hydrogels. Powdered activated carbon, sodium montmorillonite clay, and bovine serum albumin were studied at loadings of 1 wt% and 5 wt% respective to total reactant weight. The synthesized hydrogels were characterized via FTIR and TGA analysis. Competitive binding to evaluate PFOA and PFOS affinity was completed in a binding matrix of pH 7.4, similar to that of blood serum.

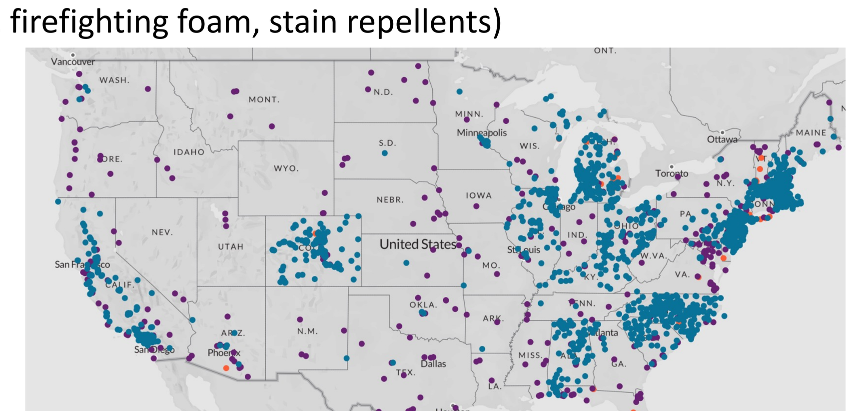
Background

Perfluoroalkyl Substances (PFAS): group of man-made chemicals which have been used in a range of consumer products since the 1940s (Teflon, firefighting foam, stain repellents)



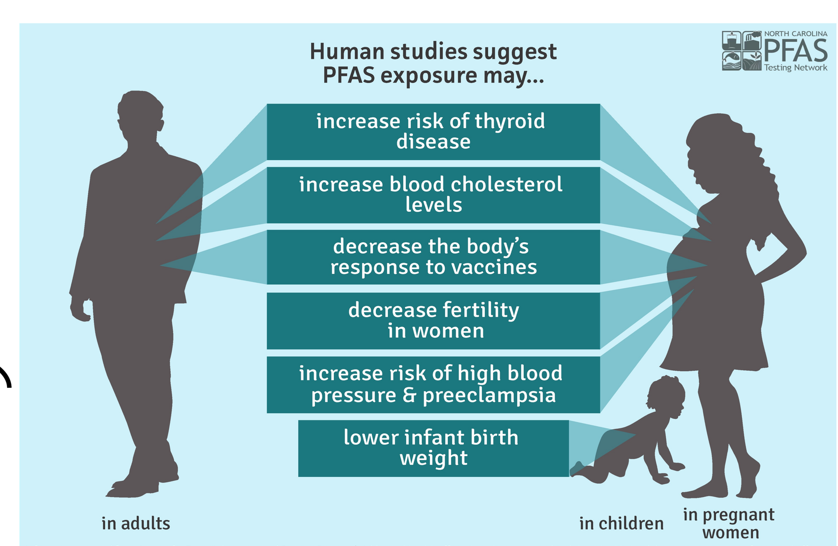
Perfluorooctanoic acid (PFOA)

Perfluorooctane sulfonate (PFOS)



Environmental Working Group's Contamination Map. "PFAS Contamination in the U.S. 10/04/2021"

Average serum concentrations of various PFAS have declined since 2000. However, the detected concentrations (5 ppb PFOS and 1.2 ppb PFOA) are still above safe levels.



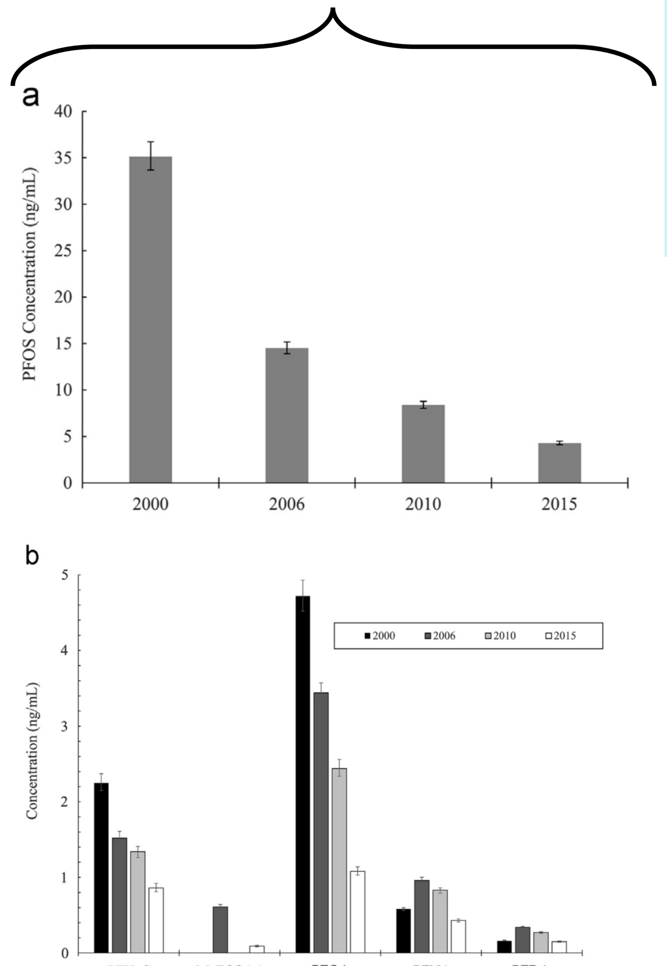


Fig. 1. Age-, sex-, and location-adjusted geometric mean (with 95% confidence intervals) PFOS (Fig. 1a) and PFHxS, MeFOSAA, PFOA, PFNA, and PFDA (Fig. 1b) serum (2000–2001) and plasma (2006, 2010, and 2015) concentrations (ng/mL), American Red Cross adult blood donors, 2000 – 2015. Olsen et al. [2]

PFOS	PFOA
5.4 years	3.8 years

Average half-lives of PFOS and PFOA in circulating human serum [3]

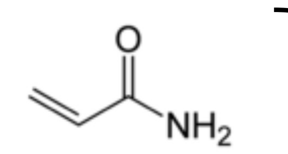
PFAS have no identifiable half-life in the environment. Half-lives within the circulatory system can be attributed to excretion or phlebotomy.

The half-life of PFAS in blood bank supplies is unknown. Thus, blood transfusion recipients are likely receiving contaminated blood, potentially exacerbating preexisting health conditions.

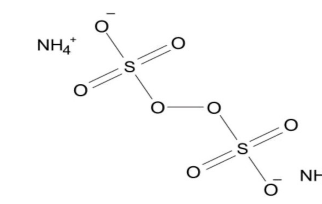
Objectives

1. Synthesize an array of hydrogel nanocomposite with the capability to bind PFAS in contaminated blood supplies
2. Characterize synthesized hydrogels via swelling analysis, FTIR, and TGA
3. Functional assessment, including binding affinity, of synthesized materials and pure albumin, powdered activated carbon and sodium montmorillonite clay

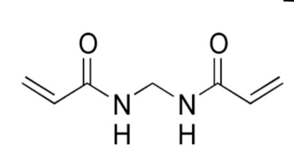
Polymer Reagents



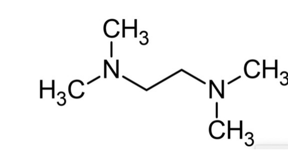
Monomer:
Acrylamide (ACRY)
Compositions:
99.9, 99, 90 mol%



Initiator:
Ammonium persulfate (APS)
Compositions:
0.1 – 1 wt%



Crosslinker:
N,N'-methylenebisacrylamide (N)
Compositions:
0.1, 1, 10 mol%



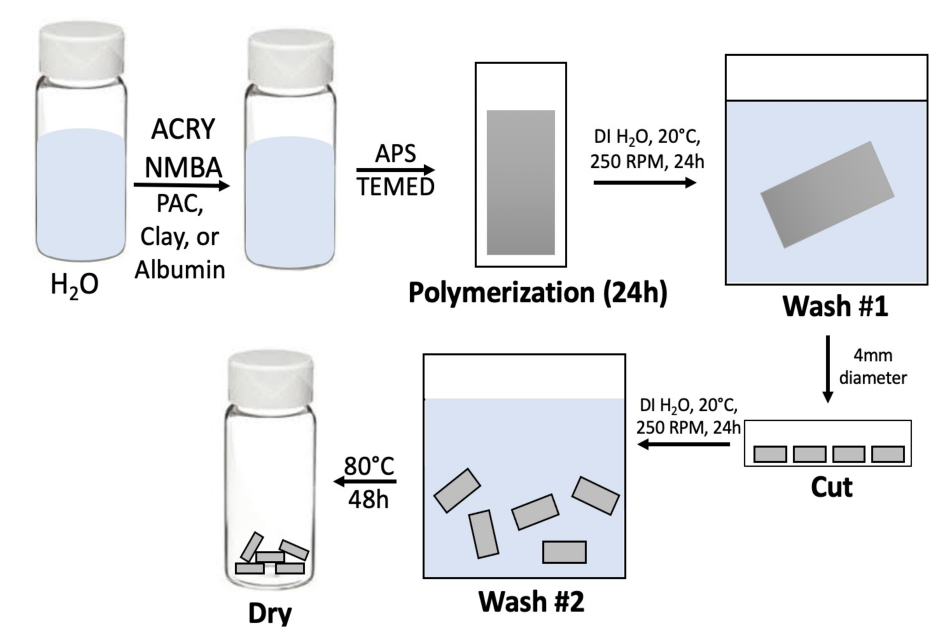
Catalyst:
Tetramethylethylenediamine (TEMED)
Composition:
1/5 APS

Polymer Synthesis

Hydrogel Composites

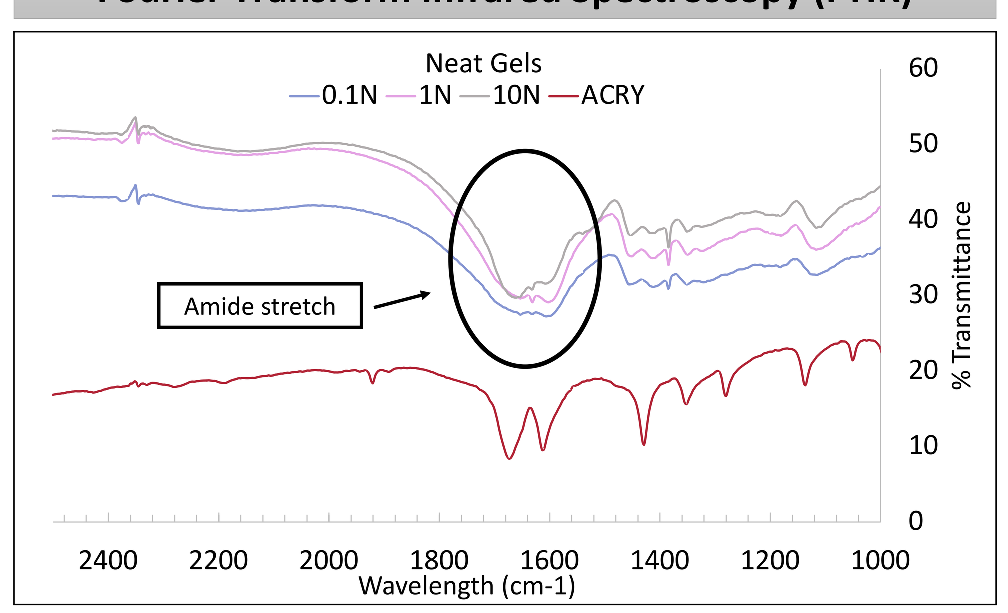
Particulates	Loadings
Bovine serum albumin (Alb) MW: 66.5 kDa	1, 5 wt%
Powdered activated carbon (PAC) MW: 12.01 Da Source: PEAT	
Sodium montmorillonite clay MW: 360.31 Da	

Free Radical Polymerization



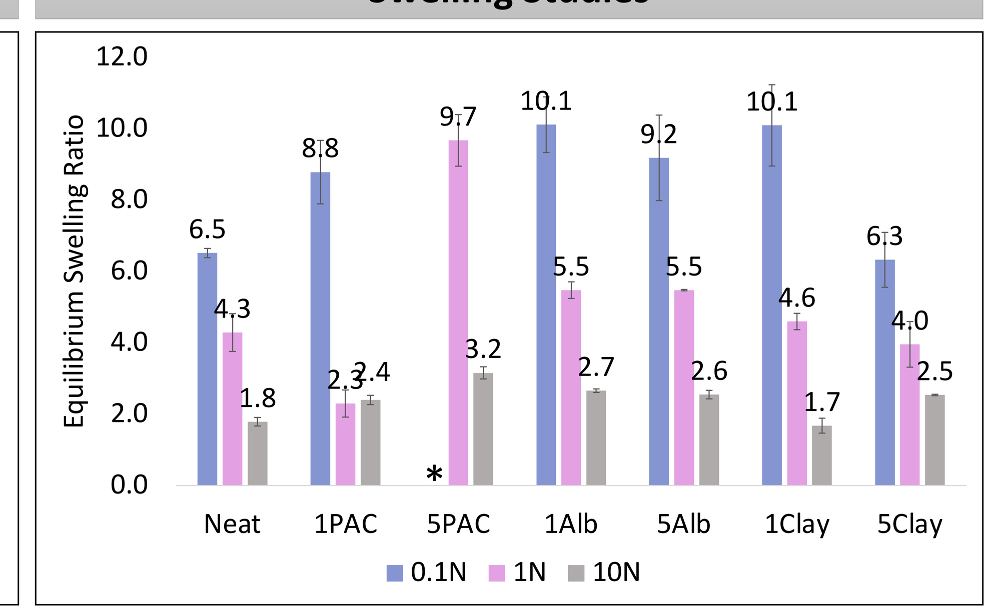
Polymer Characterization

Fourier Transform Infrared Spectroscopy (FTIR)



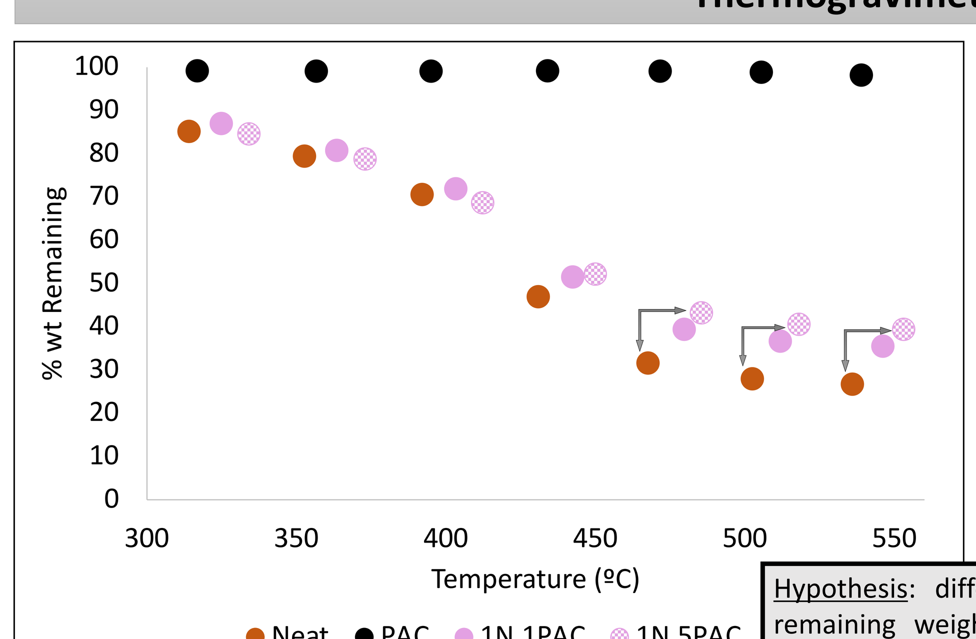
- Peak at 1600 indicative of amide group, formed upon polymerization

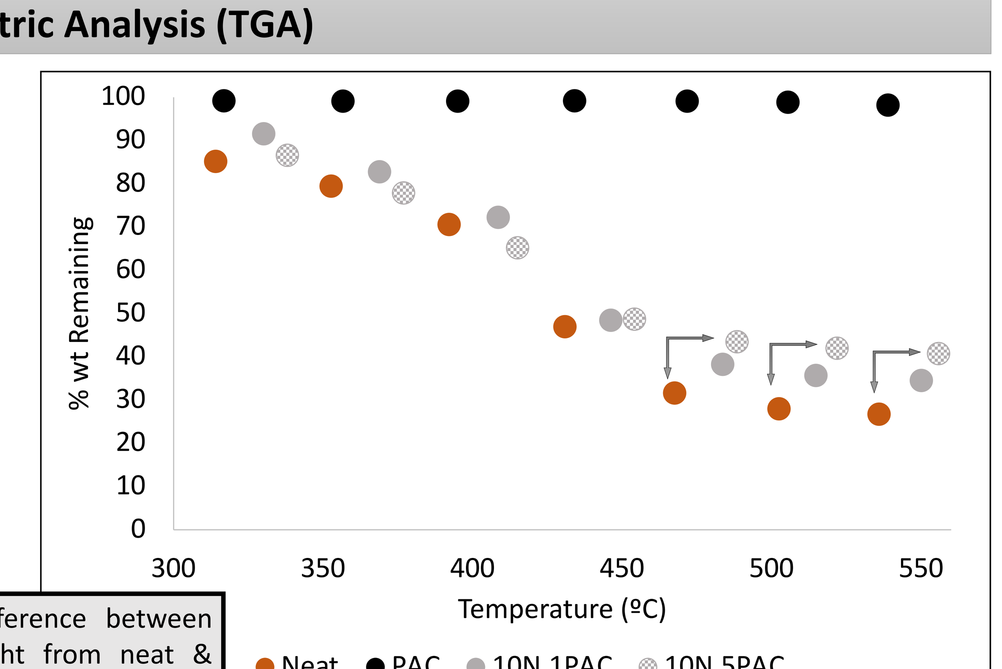
Swelling Studies



- Higher swelling ratio indicative of lower crosslinking density

Thermogravimetric Analysis (TGA)



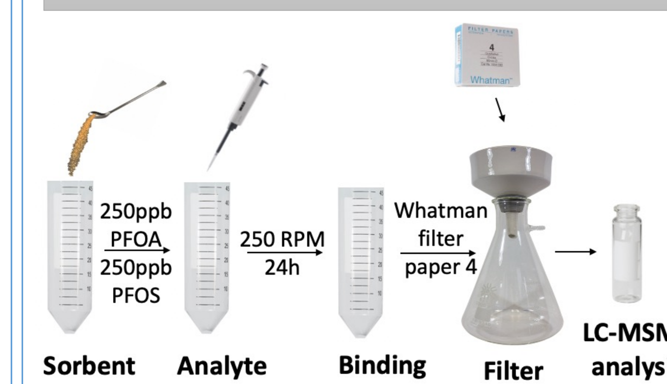


Hypothesis: difference between remaining weight from neat & PAC gels from 450-550 ºC is true incorporation of PAC particulates

*unable to synthesize 5 wt% PAC, 0.1 mol% NMBA

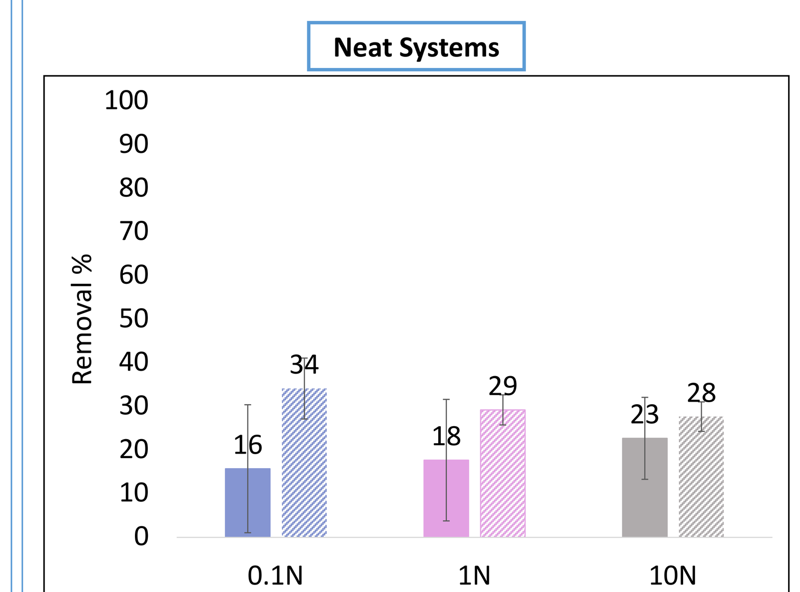
PFAS Binding Studies

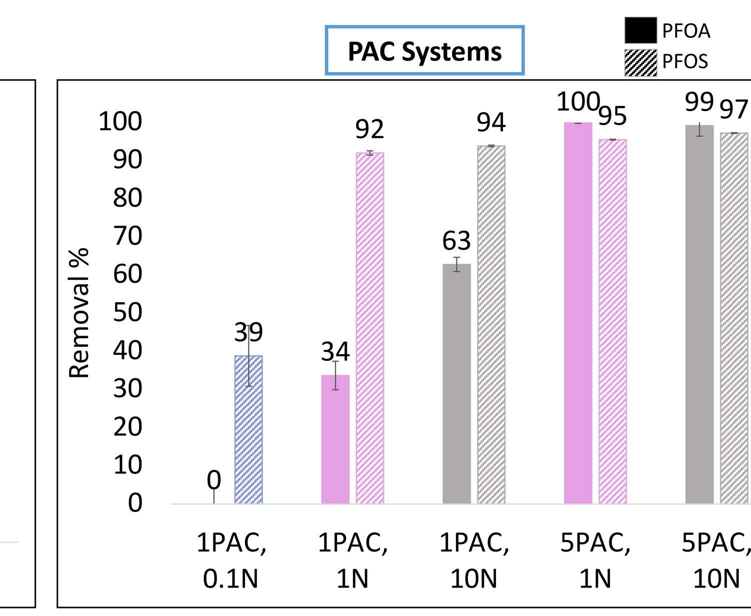
Procedure

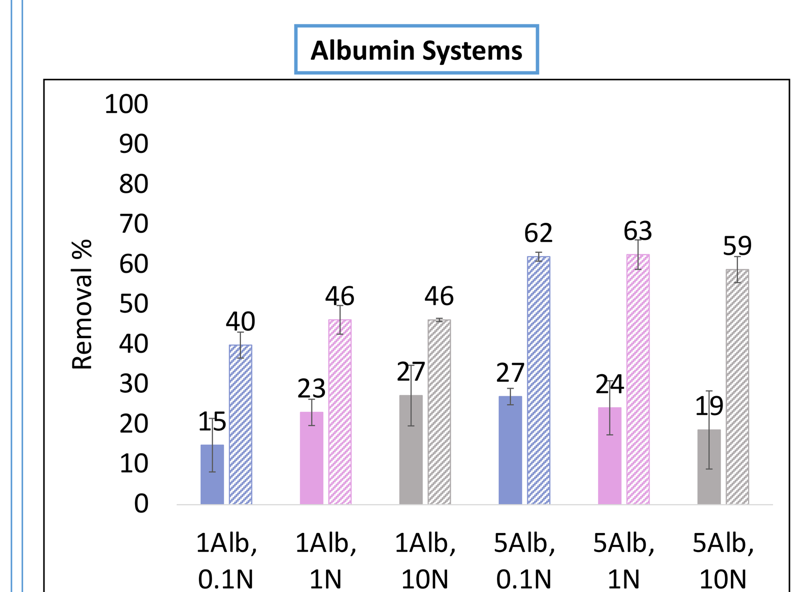


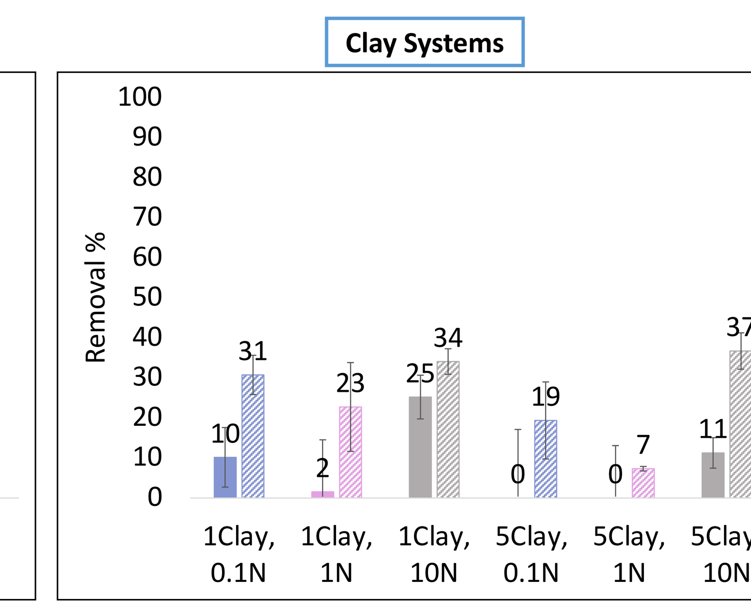
Solvent	Sorbent concentration	Analyte concentration
Water (pH 7.3)	2 mg/mL	250 ppb PFOA & 250 ppb PFOS

Results









- Hydrogels loaded with PAC particulates demonstrate highest removal of both PFOA and PFOS
- Lack of trend across systems implies inconsistent composite incorporation

Outcomes & Future Work

Outcomes

Identified initiator and catalyst ratios for all systems of interest
Successfully synthesized crosslinked polymer systems, as demonstrated by swelling analysis and FTIR
Established PFAS binding experimental procedure

Future Work

1. Continue TGA analysis of synthesized polymers
2. Conduct binding studies with average analyte concentration found in human serum
3. Conduct binding studies in simulated plasma matrix or real human blood serum

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- [1] Forsthuber et al. (2020) Environment International. 137, 105324
- [2] Olsen et al. (2017) Environmental Research. 156, 87-95
- [3] Silver et al. (2021) BMJ Open. 11