

NM WRRI Student Water Research Grant Program Final Report

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Title of Project: Surfactant-Modified Granular Activated Carbon (GAC) for Adsorption of Mixtures of Per- and Polyfluoroalkyl Substances (PFAS) in Groundwater.

1. Description of Research Problem and Research Objectives:

Perfluorinated compounds (PFCs) and their related chemicals are a class of hydrocarbons in which all hydrogen atoms in the structure have been replaced by fluorine atoms and have been developed for many years. Because of their special structure and properties, they are widely used in many fields of industrial production and daily consumption, such as surface treatment agents, lubricants, surfactants, flame retardants, pesticides, and non-stick cookware. Per- and polyfluoroalkyl substances (PFAS) have garnered significant attention in the past decades as a type of emerging contaminant and have been reported in the environmental systems including air, water, soil, plants, and living organisms. Due to their environmental persistence, propensity for bioaccumulation, and widespread presence as contaminants, PFAS is considered to pose substantial threats to both human health and the integrity of ecosystems¹. Moreover, the United States Environmental Protection Agency (US EPA) has also set a health advisory limit of 4 ng/L for Perfluorooctanoic acid (PFOA) and 10 ng/L for Perfluorononanoic acid (PFNA)².

Various treatment technologies have been explored for the treatment of these chemicals. Since in typical environmental aquatic systems, PFAS exists in anionic form and has a long hydrophobic carbon chain, therefore, treatment methods such as adsorption and ion-exchange can be employed to remove PFAS via its electrostatic interaction with cationic functional groups and by hydrophobic attachment of the PFAS' carbon chain with hydrophobic component present in the adsorbent³. The removal of PFAS compounds by adsorption using commercially available adsorbents such as synthetic resins, membrane filtration, biological degradation, and adsorption has been reported³. Among them, the adsorption technique is well recognized as a cost-effective and efficient method for quickly removing PFAS from polluted water sources.

The granular activated carbon (GAC) has been used to capture PFAS in water treatment facilities and residential point-of-use system since GAC's properties are tunable and PFAS-selective functional groups can be incorporated within its framework to facilitate high and targeted PFAS removal⁴. GAC has exhibited effectiveness in absorbing long-chain PFAS, but its slow adsorption kinetics and lower efficiency also hampers the practical application of GAC in real-world drinking water treatment. Consequently, to enhance the adsorption capabilities, the modifications of GAC are necessary⁵. The key point of modification is the utilization of multiple adsorption mechanisms in a single sorbent that can be leveraged to remove a molecule like PFAS via multiple removal pathways. There is a need to develop adsorbents incorporated with diverse physico-chemical properties that can facilitate PFAS removal via a combination of hydrophobic, electrostatic, hydrogen bonding, and ion-exchange interactions. Based on this, the GAC could be used as a base because of its high surface area and framework⁶. Subsequently, chemical additives with desired functional groups can be impregnated within the GAC framework that can boost

electrostatic, hydrogen bonding, or ion-exchange interaction with the targeted PFAS adsorbate. In this study, we synthesized a GAC-based adsorbent through modification of GAC by the cationic quaternary ammonium compound cetyltrimethylammonium chloride (CTAC)⁷.

The goal of this project is to evaluate the retention of multiple PFAS species with the presence of surfactant-modified granular activated carbon (GAC). The two most detected PFAS species, perfluorooctanoic acid PFOA and PFNA, will be selected as representatives and used for adsorption and transport experiments. This project seeks to delve into the potential mechanism underpinning the competitive adsorption between multiple PFAS species during their co-transport, and thus unraveling the nuanced interrelationships governing their retention in the subsurface. Specifically, three objectives are planned to achieve the project goal, including (1) GAC modification, and (2) PFAS competitive adsorption. By amalgamating these multifaceted aspects, this project aspires to not only offer a practical solution for tackling PFAS contamination but also contribute significantly to the expanded understanding of their complex behaviors and potential environmental remediation.

2. Description of the methodology employed:

Material: Cetyltrimethyl ammonium chloride (CTAC, $\geq 95\%$) was purchased from Tokyo Chemical Industry, the Perfluorooctanoic acid and Perfluorononanoic acid were purchased from Sigma-Aldrich. The LC/MS Grade water and methanol was purchased from Fisher Scientific.

GAC Preparation and Characterization: A commercial GAC was obtained from New Mexico Brackish Groundwater National Desalination Research Facility. The unmodified GAC were added to a cationic surfactant solution with CTAC concentration at 10, 25, or 100 mmol/L, and the mixtures were stirred at 800 rpm at 80 °C for 2 h, followed by rinsing with deionized (DI) water three times and drying at 108 °C for 10 h. The morphological and compositional analyses of the unmodified and CTAC-modified GAC (MGAC) have performed with a scanning electron microscope equipped with energy dispersive (SEM-EDS, S-3400N Type II X-ray spectroscopy, Itachi High-Technologies Corp.). The surface area and pore volume of the adsorbents will be determined by a Brunauer–Emmett–Teller Analyzer (BET analyzer, ASAP 2050, Shimadzu).

Batch Adsorption Experiment: Batch adsorption experiments were performed following the methods from previous research. Specifically, 2.5 mg of the adsorbent was added into the HDPE bottles containing 10 mL of PFAS solution ranging from concentration 0.5 to 30 mg/L for 24 h. The initial PFAS concentrations were set as 0.5, 1, 2.5, 5, 10, 20, 25 and 30 ppm for PFOA, PFNA, or their mixture (at 1:1 ratio). Prior to quantification, samples collected in the adsorption experiments were subject to centrifugation for 10 min. PFOA and PFNA in the supernatant samples were quantified by a liquid chromatography–mass spectrometry (LC-MS, 8050 LC-MS, Shimadzu).

3. Results

3.1 Adsorbent's material and performance characterization

Scanning electron microscopy (SEM) was used to investigate the surface morphology of GAC and modified GAC. Fig.1 illustrates that the original GAC had a relatively flat and smooth surface. After the modification, Fig. 2 showed that the CTAC covered GAC to produce a rough surface area⁸. The rough surface could provide more adsorption sites and easier for mass transfer, allowing

adsorbed PFAS molecules to reach available internal pores fast.

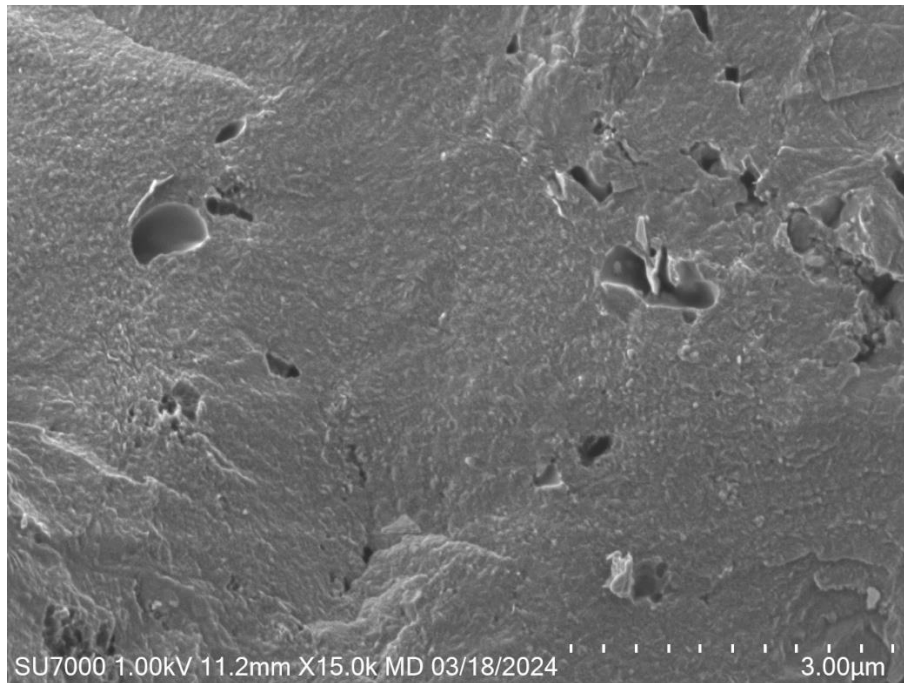


Fig.1 FEG-SEM images of GAC



Fig.2 FEG-SEM images of MGAC

A nitrogen adsorption isotherm test was performed for the analysis of the pore size and surface area of the adsorbents in Fig. 3. The data obtained from the isotherm between the relative pressure

(P/P^0) from 0.01 to 1.0 was plotted by linear isotherm and the BET equation was used for the calculation of surface area. The total surface area of GAC, and MGAC was calculated as $687 \text{ m}^2/\text{g}$ and $518 \text{ m}^2/\text{g}$. The BET surface area of the MGAC experienced a reduction of approximately 24.6 % as a result of the infusion of CTAC particles onto its surface. The pore volume for GAC is $0.183 \text{ cm}^3/\text{g}$ and $0.138 \text{ cm}^3/\text{g}$ for MGAC, which is due to the pore covering by the CTAB molecules on the surface.

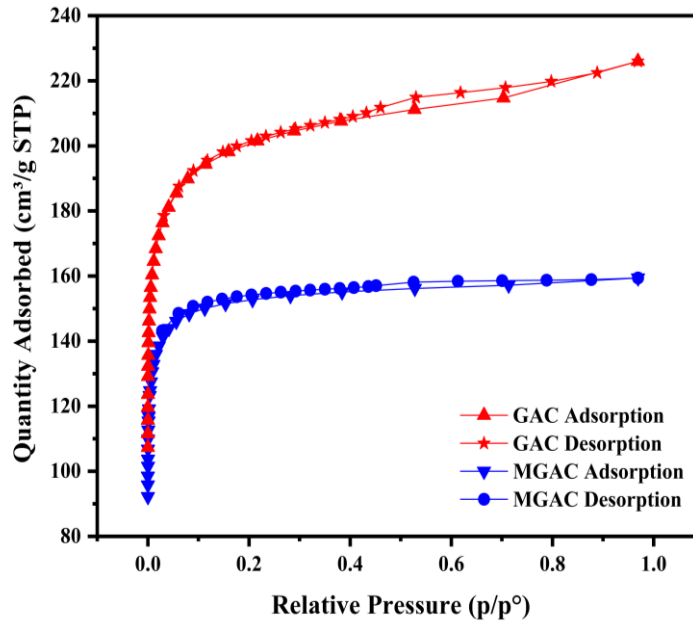


Fig.3 Plot of Nitrogen adsorption isotherm test for the analysis of pore size and surface area of GAC and MGAC

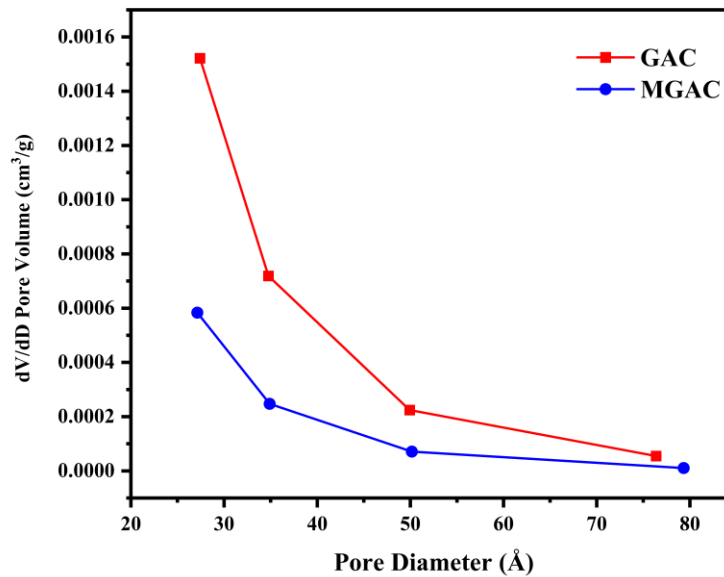


Fig.4 Pore size distribution curves of GAC and MGAC

Table 1 Surface area, Pore Volume and Pore Size of GAC and MGAC

Sample	S_{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
GAC	687.08	0.183	21.53
MGAC	518.47	0.138	19.94

3.2 Batch equilibrium study

The batch PFOA, PFNA, and the mixture of PFOA and PFNA uptake equilibrium isotherms tests were performed for GAC and MGAC, and the obtained data was plotted and curve fitted with a non-linear form of different isotherm models, which are shown in Fig. 5. It was observed that the adsorbed amount of PFOA increased with the increase of equilibrium concentration. With further increase of equilibrium concentration, the adsorbed amount remains almost constant which also indicates possible monolayer formation of adsorbate over the adsorbent surface. Langmuir isotherm model showed the best fitting with the experimental data. The maximum adsorption capacity (Q_{max}) of GAC was 100.11 mg/g and the value of Q_{max} for MGAC was 104.25 mg/g. For the PFOA adsorption in the mixture of PFOA and PFNA, we could also find the adsorbents have reached the maximum capacity, for GAC is 92.64 mg/g, and for MGAC is 93.49 mg/g. For the absorption in the mixture solution, the Q_{max} for GAC and MGAC are all reduced, which indicates that the competitive adsorption could affect the adsorbents' adsorption capacity.

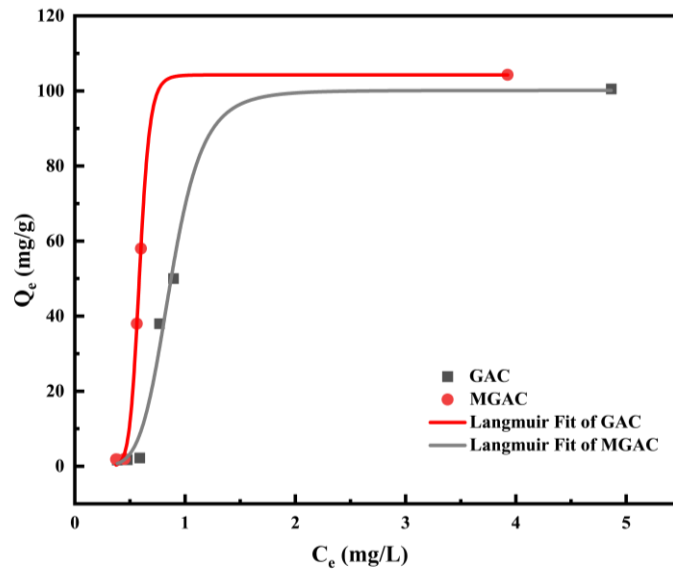


Fig.5 Isotherm model plots of PFOA single solute adsorption with GAC and MGAC

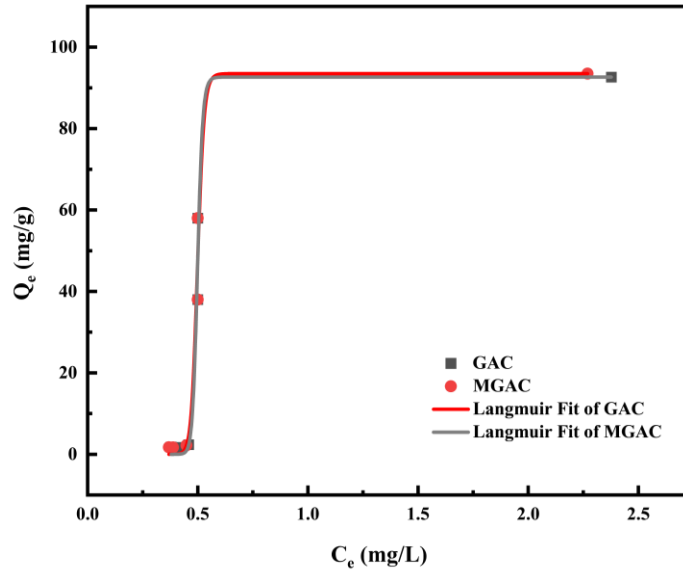


Fig.6 Isotherm model plots of PFOA adsorption in mixture of PFOA and PFNA with GAC and MGAC

For the PFNA adsorption, MGAC also performs better than GAC. The Q_{max} for MGAC was 81.68 mg/g, and for GAC was 67.09 mg/g. From Fig.6 to Fig.10, for the adsorption of PFNA in the mixture of PFOA and PFNA solution, the relationship between Q_e and C_e are linear, which indicates that we haven't reached the maximum capacity. And when competitive adsorption happens, the adsorption capacity for GAC reduced 4.76 % and MGAC reduced 15.25 %.

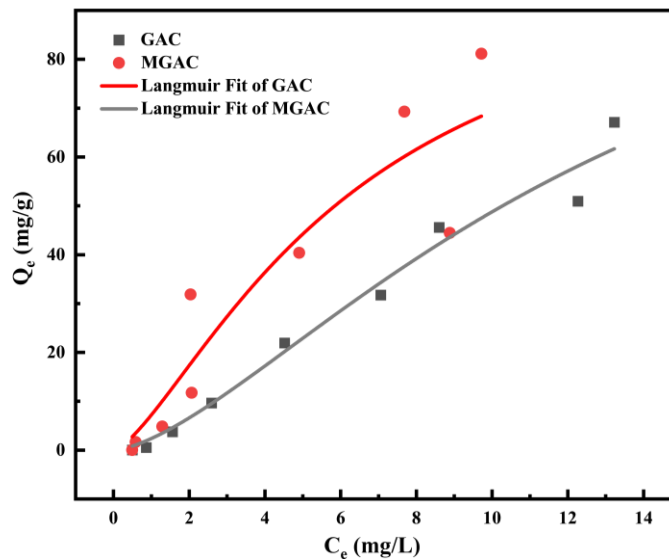


Fig.7 Isotherm Langmuir model plots of PFNA adsorption in mixture of PFOA and PFNA with GAC and MGAC

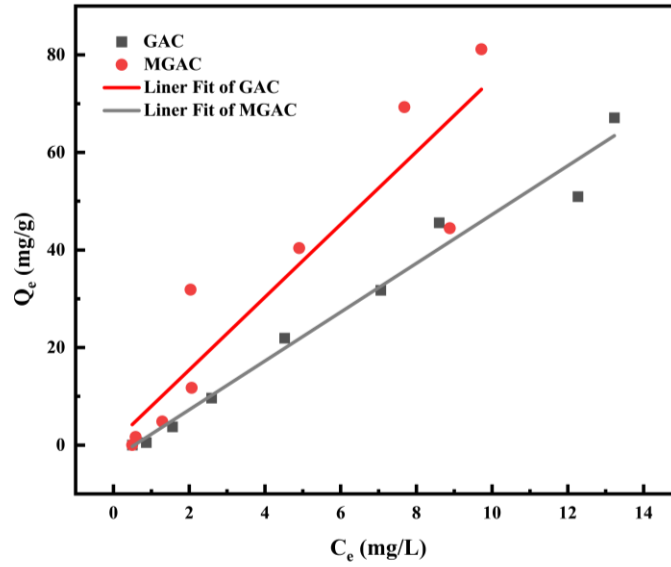


Fig.8 Isotherm Linear model plots of PFNA adsorption in mixture of PFOA and PFNA with GAC and MGAC

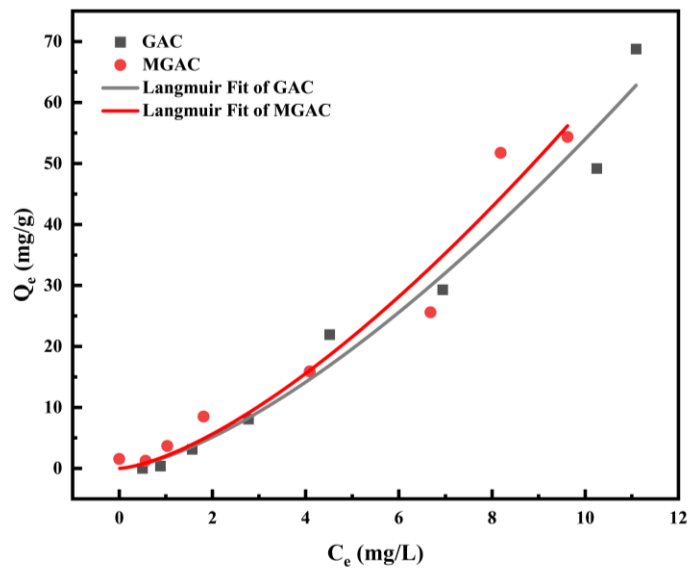


Fig.9 Isotherm Langmuir model plots of PFNA adsorption in mixture of PFOA and PFNA with GAC and MGAC

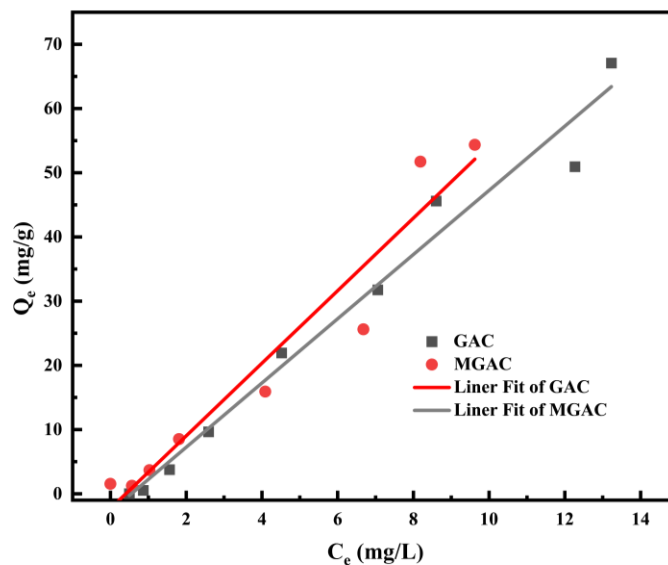


Fig.10 Isotherm Liner model plots of PFNA adsorption in mixture of PFOA and PFNA with GAC and MGAC

Table 2 The maximum adsorption capacity and R-Square of GAC and MGAC

	GAC				MGAC			
	PFOA single	PFNA single	PFOA in mixture	PFNA in mixture	PFOA single	PFNA single	PFOA in mixture	PFNA in mixture
Q_{max} (mg/g)	100.11	67.09	92.64	54.34	104.25	81.68	93.49	49.18
K_L (L/mg)	2.259	0.019	1.05	0.041	2.272	0.074	3.485	0.027
R^2	0.987	0.964	0.951	0.974	0.991	0.956	0.952	0.956

Interestingly, although the surface area of GAC is higher than that of MGAC, MGAC performs better than GAC when absorbing PFAS. This could be because the CTAC via electrostatic interaction increased adsorption efficiency. From Table 2, PFOA adsorption efficacy is only slightly affected by the presence of PFNA. When competition adsorption happens, PFNA is strongly affected by the PFOA, with the Q_{max} reduced by 47.4 %. This indicates that the adsorbent prefers to adsorb PFAS with shorter carbon chain, which is PFOA in this project. The long-chain PFAS, due to their size limit, can only be adsorbed by the outermost sites resulting in a lower adsorption efficiency. Furthermore, a more apparent decrease in PFNA adsorption efficacy has been observed in MGAC, suggesting the interaction introduced by surface modification is more likely affected by the co-occurrence of different PFAS.

The quaternary ammonium group in CTAC is strongly positive in charge, and therefore attracts anionic adsorbate species through electrostatic force resulting in the removal of PFOA and PFNA via electrostatic interaction. Also, the hydrophobic alkyl tail of PFOA and PFNA interacted with the carbonaceous component of the MGAC and adsorbed on it. Hence, the possible mechanism of PFOA and PFNA removal through the MGAC was hydrophobic and electrostatic interactions between the carbon chain of PFOA and PFNA, and carbonaceous matter of the MGAC and carboxylate group in PFOA and PFNA and quaternary ammonium group in MGAC respectively.

4. Conclusion

Our CTAC-modified GAC exhibited slightly enhanced capabilities to adsorb PFAS mixtures compared to the unmodified GAC. The adsorption behavior was significantly dependent on the initial concentration and carbon chain length of PFAS. The physicochemical characterization of the MGAC studied herein facilitated an interpretation of the excellent adsorption performance of MGAC and elucidation of the mechanism by which it adsorbs PFAS. In light of all the findings in this study, an adsorption mechanism associated with electrostatic interactions and hydrophobic interactions was proposed.

Reference:

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