ABSTRACT

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a diverse class of synthetic organofluorine compounds recognized for their remarkable physicochemical stability and resistance to degradation. These characteristics result in environmental persistence and accumulation of PFAS across aquatic, terrestrial, and biotic systems. Conventional water treatment processes are generally ineffective for PFAS removal. Advanced remediation methods such as granular activated carbon and ion exchange resins show some efficacy but are hindered by high operational costs, secondary waste generation, and diminished performance for short-chain PFAS. These limitations create an urgent demand for alternative PFAS remediation strategies that are effective, sustainable, and scalable. This dissertation focuses on the development, characterization, and evaluation of bio-based adsorbents synthesized from waste materials for PFAS removal. The research centers on engineering cationic cellulose nanocrystals (CNCs), CNC-hydrogel (C-Hydrogel), and hydrochar-CNC-hydrogel (HC-Hydrogel) composites, each functionalized to maximize adsorption capacity, kinetics, and selectivity toward multiple PFAS species.

The dissertation is organized into five chapters. The first chapter introduces the scope and urgency of PFAS contamination, outlines current deficiencies in remediation approaches, and posits that rationally designed, waste-derived nanomaterials can provide rapid and efficient PFAS sequestration while supporting circular economy goals. The second chapter reviews the literature on PFAS occurrence, fate, and toxicity, with particular focus on knowledge gaps related to PFAS in waste management infrastructure such as landfill leachate and wastewater. The chapter highlights the potential of cellulose-based adsorbents as future remediation materials.

Chapter three details the extraction of CNCs from household waste with high crystallinity and well-defined morphology. CNCs are functionalized with quaternary ammonium groups to enhance their positive surface charge, thereby increasing their affinity for the anionic functional groups characteristic of PFAS. To address certain limitations associated with CNCs, hydrogel composites containing cationic CNCs and cationic hydrochar were synthesized. Comprehensive material characterization is conducted using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA) to confirm the structure, morphology, crystalline order, and thermal stability of the synthesized materials.

In chapter four, PFAS adsorption by functionalized adsorbents is systematically evaluated, targeting legacy and emerging PFAS such as perfluorobutane sulfonic acid (PFBS), perfluoropentane sulfonic acid (PFPeS), perfluorohexane sulfonic acid (PFHxS), and perfluorooctanoic acid (PFOA). High-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) is used to quantify residual PFAS concentrations in aqueous solutions following adsorption. Experiments assess removal efficiency, equilibrium adsorption capacity, and adsorption kinetics under variable conditions of pH. The adsorption data are modeled using pseudo-first-order and pseudo-second-order kinetic frameworks to extract mechanistic parameters and identify rate-limiting steps. Results indicate that cationic CNCs achieve high adsorption capacities and rapid equilibrium for both long- and short-chain PFAS. The C-Hydrogel format enhances operational feasibility, supporting facile separation and robust regeneration. Mechanistic studies confirm that PFAS removal by C-Hydrogel is governed predominantly by electrostatic attraction. Incorporating cationic hydrochar into the HC-Hydrogel further improves the adsorption performance of C-Hydrogel by introducing additional hydrophobic interactions alongside electrostatic interactions, resulting in two principal mechanisms for PFAS uptake.

The final chapter synthesizes these findings, highlighting the primary advantages of these adsorbents, including rapid and efficient PFAS removal, compatibility with sustainable feedstocks, and practicality for water treatment implementation. Limitations related to scale-up, matrix complexity, and field validation are acknowledged, with recommendations for future research to expand material production, integrate these adsorbents into engineered systems, and broaden contaminant scope. Collectively, this research advances the rational design of waste-derived materials for PFAS remediation, enhances understanding of adsorption mechanisms at the nano-bio interface, and contributes a practical foundation for sustainable water treatment technologies supporting global efforts to address PFAS pollution.

Keywords: *Perfluoroalkyl and polyfluoroalkyl substances, PFAS, Adsorption, Kinetic study*