ABSTRACT

Per- and polyfluoroalkyl substances (PFAS), as a broad class of synthetic chemicals, have been extensively manufactured and used in a wide variety of industrial processes, commercial products, and military applications since the 1940s. Owing to the strong carbon-fluorine covalent bond, PFAS compounds such as PFOS and PFOA display excellent chemical and thermal stability and are persistent to conventional wastewater treatment and biological remediation. Due to their widespread use, as well as their amphiphilic properties and environmental persistence, PFAS are ubiquitous in aquatic and terrestrial ecosystems on a global scale. Accumulating evidence has uncovered links between prolonged exposure to specific PFAS and several adverse health effects. On April 10, 2024, the US Environmental Protection Agency (EPA) issued the final National Primary Drinking Water Regulation for six regulated PFAS chemicals and established enforceable limits in drinking water.

PFAS detection and quantification can help track their occurrence, distribution, and movement in various environmental matrices. Accurate and reliable analytical methods are vital for effective monitoring PFAS level, enforcing regulatory standards and identifying potential contaminated sites and guiding cleanup efforts. The first portion of this study established quantification method for PFAS measurement following revision A of EPA method 1633. The combination of solid-phase extraction and Thermo TSQ Quantis mass spectrometer-based LC-MS/MS analysis achieved linear relationships with correlation coefficient $r > 0.99$ for all 40 PFAS compounds. The reproducibility and sensitivity are satisfactory in the detection of spiked samples with the recovery range of 70-130% and RSDs <20%. This method met regulatory

requirements and can be used for rapid and accurate quantitative analysis of PFAS in the environment.

Understanding of fate and transport processes could aid in the identification of potential PFAS sources and risk assessment of PFAS migration. Among environmental matrices, subsurface systems, like aqueous film-forming foam (AFFF)-based firefighter training and firefighting areas has been found to be a primary environmental reservoir for PFAS. In the second portion of this study, the flow-through column experiments were applied to mimic dynamic adsorption and desorption processes under continuous flow conditions. Several representative PFAS with different carbon-chain lengths and functional groups were tested under various background solution chemistry in saturated porous sand columns. The observed breakthrough curve coupled with mathematical modeling depicted and predicted PFAS transport behaviors in subsurface systems and provided insights into the PFAS adsorption mechanisms including hydrophobic interactions, electrostatic interactions, and hydrogen bonding.

Adsorption is a simple and effective option to address PFAS contamination issues. As three-dimensional crosslinked polymers with porous structure and hydrophilic nature, hydrogels with high efficiency and selectivity have provided alternative solution for PFAS remediation. In the third portion of this study, a series of modified polyacrylamide hydrogels with cationic functional groups were synthesized for removal of selected legacy PFAS. The cationic polyacrylamide hydrogels demonstrated fast removal kinetics and excellent adsorption capacities for both short- and long-chain PFAS. The removal efficiency was evaluated under varying pH range, the coexistence of anions, cations and dissolved organic matters. By applying electrostatic enhanced adsorption, cationic polyacrylamide hydrogel was an attractive adsorbent for PFAS removal from aqueous phase.