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A Mini-Review of The Adsorptive Removal of Poly- And Perfluoroalkyl Substances (PFAS)

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Abstract

In recent years, per- and poly-fluoroalkyl substances (PFAS) have been frequently detected in aquatic environments, posing a serious threat to environmental safety and human health due to their persistence, bioaccumulation, and toxicity. Several technologies are available for PFAS remediation, including adsorption, advanced oxidation, nanofiltration, and microbial degradation. Among these strategies, adsorption is effective, affordable, and easy to access, and therefore has been recommended by the U.S. Environmental Protection Agency. This article reviews the adsorption behaviors between various PFAS and different adsorptive materials, such as activated carbon, resin, minerals, and biosorbents. In addition, this article provides fundamental knowledge of adsorption and an understanding of the difference between adsorptive materials.

Keywords: Adsorption; Active carbon; Resin; Minerals; Biosorbent; Molecularly imprinted polymer

Introduction

Per- or polyfluoroalkyl compounds (PFAS) are compounds produced by replacing all or part of the hydrogen atoms connected to the carbon in the molecules of organic compounds with fluorine atoms [1]. The carbon-fluorine (C-F) bond is the strongest single bond in chemistry and provides PFAS chemicals with high thermal and chemical stability. PFAS contain both hydrophilic functional groups (e.g., sulfonate groups and carboxyl groups) and hydrophobic and oleophobic C-F chains in the structure, and therefore can resist water, oil, and grease [2,3]. Due to their good performance and production suitability, PFAS are widely used in food packaging, textiles, semiconductors metal plating, fire-fighting foam, and other fields [4-6]. In the current decade, traditional PFAS with evidenced toxicity have been phased out due to the raising of public awareness and updated regulations. However, many new PFAS have been produced and widely used as substitutes of banned PFAS, including conventional short-chain PFAS (e.g., Perfluorobutanesulfonic acid, PFBS) and newly identified fluorinated replacements (e.g., Chlorinated polyfluoroalkyl ether sulfonic acids, Cl-PFESAs) [7]. However, several studies have shown that short-chain PFAS compounds are characterized by significant cytotoxicity and potential developmental toxicity, strong environmental persistence, and long-range transport [8-10]. Some of these compounds have similar or even higher bioaccumulation and toxicological effects than traditional PFAS [11-13]. Therefore, emerging PFAS alternatives, including short-chain analogs, precursors, and alternatives, have attracted increasing attention in environmental and ecotoxicological sciences in recent years. Adsorption is a promising technology for removing PFAS from water. Many studies have reported the adsorption and removal of PFAS by various adsorbents, including activated carbon, anion-exchange resins, and biomaterials, and have also investigated the adsorption mechanism of adsorbents on PFAS and its main influencing factors.

Adsorption for PFAS removal

Active Carbon

Activated carbon is one of the most used adsorbents in water treatment, which has been applied to the removal of a variety of pollutants due to its large specific surface area, well-developed pore structure, low cost, and wide range of material sources. It was reported that the structure of PFAS has a strong influence on the adsorption and removal effect, the longer the carbon chain of PFAS, the easier it is to be adsorbed, and the sulfonic acid PFAS is more likely to be adsorbed onto GAC than the carboxylic acid PFAS. This is since long-chain PFAS are more hydrophobic, and the sulfonic acid functional group has a stronger electrostatic attraction than the carboxylic acid functional group.

Resin

Resins, including ion-exchange resins and nonion-exchange resins, have the advantages of good chemical stability, and strong regeneration ability. In terms of adsorption performance and in situ regeneration, anion exchange resins are the most effective adsorbents for PFAS removal [17]. Generally, the anion-exchange resin has permanent positive charge exchange sites on its surface and thus has a high adsorption performance for PFAS [18]. Non-ion exchange resins absorb PFAS mainly through hydrophobic interactions and van der Waals forces. Compared with anion-exchange resins, they are easier to regenerate, but the adsorption performance is much lower than that of anion-exchange resins, so anion-exchange resins Resin is more widely used in practical applications [19].

Minerals

Mineral materials with high surface area, adjustable mesopores, and variable lamellar structure are considered to be suitable materials for the adsorption of PFAS [20]. The mineral materials used for PFAS removal are classified into layered clay minerals (kaolinite, montmorillonite, etc.) and amorphous clay minerals (acicular ferrite, magnetite, hematite, etc.) [21]. pH is a key factor in the removal of PFAS from water. Solution pH can affect the adsorption of PFAS by changing the morphology of PFAS and the surface charge of the mineral material [22].

Biosorbent

Bio-based adsorbent materials prepared from biomass through a series of physical and chemical modifications show great potential for removing pollutants from water due to their higher adsorption properties [23]. Biochar and chitosan are bio-based materials that have been widely used for the removal of PFAS. Biochar and activated carbon have similar adsorption properties for PFAS, and biochar is becoming a sustainable alternative to activated carbon in recent years due to its environmental friendliness [24]. Chitosan contains many amino, acetylamino, primary hydroxyl, and secondary hydroxyl groups, which makes it an excellent chelating site for PFAS, and has great potential in the remediation of PFAS-contaminated water [25].

Molecularly imprinted polymer (MIP)

Wastewater contains many compounds and colloids, and the concentration of these coexisting substances is generally higher than that of PFAS, which makes it easy to compete with PFAS for adsorption, leading to a decrease in the removal rate. Therefore, the selectivity of adsorption is very important for the removal of PFAS in water [26]. Deng et al. prepared MIP adsorbents with high selectivity, which increased the adsorption of PFOS by more than 1-fold compared with non-imprinted polymer (NIP) [27]. This was attributed to the high selectivity of the MIP adsorbent for PFOS, while the NIP adsorbent showed a decrease in adsorption due to competitive adsorption.

Conclusions and future work

This work provides fundamental knowledge of the behavior of adsorption. Adsorption is one of the most efficient and economical technologies for removing PFAS from water. In order to control the pollution of PFAS in water, future research could focus on the following topics:

i. Develop advanced materials with adsorption and synergistic degradation functions to achieve simultaneous enrichment and mineralization of PFAS, extend the service life of adsorbents, and improve PFAS removal efficiency.

ii. Develop an efficient adsorbent regeneration technology to solve the problems of low adsorption efficiency and the generation of secondary pollutants.

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