

Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the Current Literature

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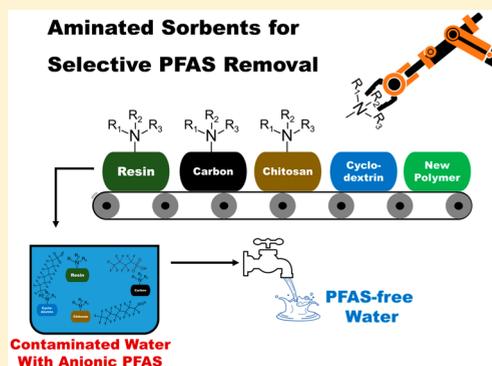
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Supporting Information

ABSTRACT: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of persistent and mobile fluoro-organic chemicals that have been detected in many water supplies, and their recommended safe concentrations in drinking water are as low as 6 ng/L. Current technological advances suggest that amine-containing sorbents can provide alternative solutions to PFAS control in the treatment of municipal water and wastewater at relatively low PFAS concentrations. The objective of this review is to provide critical analysis of the development and application of amine-containing sorbents for PFAS removal. The removal of PFAS by aminated sorbents relies on the combined effects of three main factors: (i) electrostatic interactions with functional groups of the sorbent, (ii) hydrophobic interactions with the sorbent and between PFAS molecules, and (iii) sorbent morphology. The design of next-generation sorbents should take into consideration these three factors and their relative contribution. We also provide an outlook and highlight of the key areas of innovative research needs to develop more efficient sorbents that will enable compliance with the increasingly stringent regulations of PFAS.



1. INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a diverse class of organofluorine compounds that have been used as surfactants in thousands of consumer products and firefighting foams. Because of their widespread use and environmental persistence, PFAS have entered surface waters and groundwaters around the world at concentrations that impact human health and ecosystems.^{1–3} PFAS have physicochemical attributes that include having a fluoroalkyl tail, strong carbon–fluorine bonds, and extremely high thermal and chemical stability.⁴ Although most public and regulatory attentions have so far focused on anionic PFAS with carboxylate or sulfonate polar groups, zwitterionic and cationic polar groups are also found among PFAS.⁵ Their polar head groups make PFAS highly water soluble and nonvolatile, and their carbon–fluorine bonds confer environmental persistence.^{6–10} At least eight states either have regulations in place and/or are pursuing more stringent standards than the combined 70 parts-per-trillion advisory level set by the United States Environmental Protection Agency for perfluorooctane-sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These states include Michigan, Alaska, California, Minnesota, New Hampshire, New Jersey, New York, and Vermont. The United Kingdom and the European Union have also introduced drinking water guidelines at parts-per-billion levels for PFOS/PFOA and an annual average environmental quality standard for ΣPFOS, respectively.¹¹ Currently, activated carbon and ion

exchange (IX) resins are the most used sorbents to remove PFAS from water.^{12–16} Although hydrophobic interactions are the main forces for PFAS adsorption on activated carbons,^{12,16} IX resins, typically polystyrene or polyacrylate beads bearing charged functional groups, remove PFAS using a combination of counterion exchange and hydrophobic interactions.¹⁷ Yet these conventional sorbents have critical deficiencies, such as slow adsorption kinetics and low affinity toward short-chain PFAS.^{1,18} In addition, PFAS concentrations in contaminated waters are usually orders-of-magnitude lower than background constituents, such as natural organic matter (NOM) and other ions, which compete with PFAS for sorption sites and reduce its removal.¹² These shortcomings motivate the development of more effective sorbents that exhibit selective and rapid PFAS removal with high capacity, and facile regeneration.^{19–23}

Among emerging sorbents for PFAS, materials containing amine functional groups have shown superior removal of anionic PFAS (Table S1 in Supporting Information). Some other commercial amine-containing materials (e.g., CARBO-WAX solid-phase extraction cartridges and XAD-7 polymeric resin) have been widely used for sample concentration/extraction. However, these products were not evaluated from

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Table 1. Categories of Reported Amine-Containing Sorbents and Relative Trends in Terms of High (blue ↑) or Low (red ↓) Capability to Tune or Achieve Various Properties

Sorbent Category	Examples	Scalability	Recyclability	Synthetic Tunability	Removal Rates	Removal Capacity	Ref.
1) Low surface area carbohydrate sorbents	- Chitosan MIP - Quaternized cotton - β -CD-polystyrene beads - PEI- <i>f</i> -cellulose	↓	↑	↓	↓	↑	24-28
2) Low surface area non-carbohydrate polymers	- Polyaniline nanotubes - Aminated polyacrylonitrile fibers - Ammoniated hydrogel	↓	↑	↑	↓	↑	29-31
3) High surface area nanostructured polymers	- MIL-101(Cr) MOFs - X%-[NH ₂]-COFs	↓	↑	↑	↑	↓	32, 33
4) Nanostructured inorganic materials	- Magnetic carbon nitride - Hexagonal mesoporous silica - Fe ₃ O ₄ /SiO ₂ magnetic nanoparticles - Titanate nanotubes	↓	↑	↓	↑	↓	34-37
5) Commercial ion exchange resins (proprietary monomers & porosity)	- IRA400 - IRA910 - Purolite A600 - DowMarathonA and AmbI-RA400	↑	↓	↑	↓	↑	17, 38-40

the water treatment perspective and thus were not included in this review. The roles of the amine groups, hydrophobic segments, and porosity of these sorbents on PFAS removal efficiency, kinetics, and capacity have been demonstrated, but the interplay between these three key parameters is often unclear. The objective of this Review is to analyze the development and water treatment application of different amine-functionalized sorbents for anionic PFAS removal. We also highlight key research needs to develop more efficient sorbents for meeting increasingly stringent PFAS regulations.

2. AMINATED SORBENTS: CATEGORIES AND FUNCTIONAL GROUPS

As summarized in Table S1, the amine-containing sorbents that have been studied for PFAS removal feature a variety of nitrogen substituents. Some materials have an inherent amine loading, such as chitosan and polyaniline. No extra synthetic effort is needed for the introduction of the amine groups, which is highly desirable for simplicity and cost yet limits the tunability of these polymers. Designed polymers, such as linear and cross-linked polymers, as well as porous crystalline frameworks known as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), have tunable amine identity, chemical versatility, and good control of charge, hydrophobicity, and functionality. However, this tunability comes at the expense of additional postsynthetic transformations and/or monomer synthesis. These factors may ultimately influence their commercial viability or limit the use of more expensive sorbents to lower volume use cases. Based on the constituent monomers and porosity, these sorbents can be classified into five categories. Table 1 shows the relative capability and tunability of sorbents of each category in regard to their scalability, recyclability, synthetic tunability, and PFAS removal rates and capacities. The high (blue ↑) or low (red ↓) capability terminology is relative among the five listed categories, and it represents general trends, although there might be a few exceptions that show different trends. The detailed descriptions of the comparison criteria, which were

used to assign symbols (blue ↑) or (red ↓), are discussed in the Supporting Information. It should be highlighted that removal kinetics can be influenced by the particle size and experimental design and thus the comparison in Table 1 is based on the reported experimental results with taking into consideration the water matrix (i.e., deionized water or natural water samples). Additionally, only a few studies on aminated sorbents have been benchmarked directly against activated carbons, as conventional PFAS adsorbents.^{16,17,22,27,35,40,46} The current observations have indicated that aminated sorbents were superior in the adsorption capacity, kinetics, synthetic tunability, and recyclability. However, activated carbons were excluded from the comparison herein to maintain the focus of the Review on aminated sorbents.

The performance of aminated sorbents is also greatly influenced by the type of amine functionalities. While most IX sorbents (category 5) carry charged quaternary ammonium groups, as reported by the manufacturers, many other sorbents of categories 1–4 feature primary, secondary, or tertiary amine groups. Sorbents with these three groups may also be easier to regenerate as compared to quaternary amine-based sorbents because they can be easily deprotonated to the corresponding neutral species at elevated pH. The distribution of amine functionalities according to the number of studies in the literature is shown in Figure S1. The influence of amine functionalities on the performance of aminated sorbents is discussed in detail in Section 4.

3. FACTORS AFFECTING PFAS REMOVAL BY AMINATED SORBENTS

3.1. PFAS initial concentration.

PFAS are found in contaminated water sources at concentrations ranging from low ng/L to hundreds of $\mu\text{g/L}$.^{1,41} Since the sorption rate and capacity are dependent on the initial concentration of the analyte, all sorbents should be evaluated under representative PFAS levels commonly detected in natural waters. It should be also highlighted that the selection of PFAS initial concentration is dependent on the experimental mode, whether it is

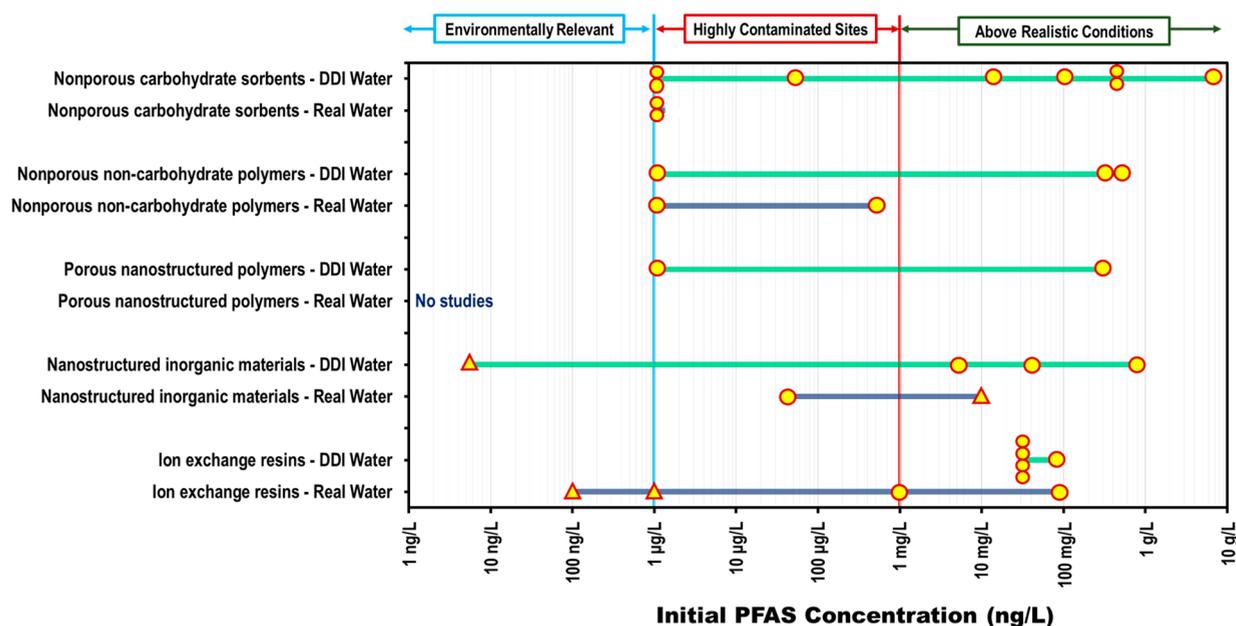


Figure 1. Overview of the range of tested initial PFAS concentrations in both DDI water and real water samples. Yellow circles indicate the initial concentration for studies in batch mode. Yellow squares indicates the initial concentration for studies in column mode.

batch or column mode. Only seven studies have used water samples containing 1000 ng/L or less of various PFAS, in the presence and the absence of NOM, to evaluate the removal efficiency of aminated sorbents (e.g., poly(ethylenimine)-functionalized cellulose [PEI-*f*-cellulose] and amine-functionalized COF).^{23,33} Yet, most of the literature studies on PFAS removal were conducted in batch mode under very high initial concentrations (Figure 1). Batch mode studies enable quick evaluation of new sorbents and provide important information such as sorbent capacity and sorption kinetics. However, it is difficult to use batch mode results to extrapolate the likely performance of sorbents under column mode with low initial PFAS concentrations. Therefore, the effective capacity of any new adsorbent should be ultimately benchmarked by the PFAS uptake at environmental concentrations of PFAS using column mode. The limited number of studies in column mode at low PFAS levels is mainly attributed to the required sensitive and high-end analytical techniques, such as liquid chromatography–mass spectrometry with in-line concentration/extraction units, which are expensive, require significant expertise, and are not available to all researchers.⁴² However, given the current standards or advisory levels for PFAS (e.g., 8 and 14 ng/L for PFOA in MI and CA, respectively), the next-generation sorbents are advised to be tested under representative conditions using analytical techniques with a low limit of quantification (i.e., < 1 ng/L).

3.2. PFAS Headgroup and Chain Length. The sorption capacities of perfluorinated sulfonates (PFSA) onto other adsorbents, such as ACs, resins, silica, zeolites, sediments, and sludges, were also observed to be higher than that of perfluorinated carboxylates (PFCA) with the same carbon numbers. The PFAS with longer C–F chain lengths have lower water solubility and higher hydrophobicity, and thus, their adsorption capacities are higher when the hydrophobic interaction is involved in the adsorption.¹ As a result, aminated sorbents show a lower affinity toward PFOA as compared with PFOS (Table S1). Only a limited number of studies in the literature have examined short-chain vs long-chain PFAS

removal by aminated sorbents. These studies indicated that aminated sorbents remove short-chain PFAS less efficiently than long-chain PFAS. For instance, aminated sorbents such as PEI-*f*-cellulose²³ and amine-functionalized COF³³ exhibited lower sorption efficiency (i.e., 11% for PFPeA (C5), 39% for PFHxA (C7), and 88% for PFOA (C8)),²⁴ earlier breakthrough volumes (e.g., PFBA (C3) at 18,000 BV, PFHxA (C5) at 30,000 BV, and PFOA (C7) at 60,000 BV),¹⁷ and desorption in batch mode reactors for short-chain PFAS as compared with long-chain PFAS.³³ In addition, short-chain PFAS displacement by long-chain PFAS was observed in pilot-scale experiments using ion exchange resins.⁴³ Apparently, long-chain PFAS outcompete short-chain analogs when both are present in solution, due to the higher hydrophobicity of long-chain PFAS.^{44,45}

3.3. Coexistence of Background Contaminants. The presence of organic micropollutants (MPs) and inorganic anions (e.g., Cl^- , NO_3^- , SO_4^{2-}) may significantly affect PFAS affinity on aminated sorbents. For instance, the coexistence of anionic MPs such as dodecyl benzenesulfonate and pentachlorophenolate decreased the uptake of PFOS by chitosan molecularly imprinted polymers from ~48% to ~42% and ~33%, respectively.²⁵ The removal of PFAS by a quaternary amine-functionalized hydrogel was decreased with increasing the concentrations of background anions (i.e., SO_4^{2-} and Cl^-).³¹ Some studies indicate that these anions may screen the adsorption sites by forming electric double layers.^{26,39,26,39} These observations suggest that solutions of these anions (i.e., Cl^- or SO_4^{2-}) may be promising to regenerate aminated sorbents.

4. PFAS ADSORPTION MECHANISM AND KINETICS ON AMINATED SORBENTS

The hydrophilic character of PFAS makes their removal quite challenging, especially on hydrophobic sorbents, due to the competition with other background water constituents.⁴⁶ The characteristics and mechanism of PFAS on aminated sorbents rely on the combined effects of three main factors: (i)

electrostatic interactions with charged groups on the sorbent, (ii) hydrophobic interactions between the sorbent and PFAS molecules, and (iii) morphology (i.e., shape and size of sorbent particles) and porosity of the sorbent. Thus, the design of an efficient sorbent should take into consideration the interplay among the three parameters and their relative contribution to PFAS removal. Since the selectivity has not been determined rigorously for many adsorbents (i.e., removal of PFAS versus other pollutants/solutes), the interplay among the three parameters is not fully understood yet. We illustrate below systems that give some insight into how the three parameters affect the sorbent affinity for PFAS.

4.1. Role of Electrostatic Interactions. Electrostatic interactions between the carboxylate or sulfonate headgroup of the anionic PFAS and the cationic amines of the sorbent are thought to play predominant roles in controlling the affinity and efficiency. Evidence for the role of the amine groups for anionic PFAS sorption was obtained using infrared (IR) spectroscopy. IR analysis of cross-linked chitosan sorbent before and after PFOS adsorption, for instance, indicated that the N–H stretch peaks at 3429 cm^{-1} shifted to 3470 cm^{-1} , and the N–H bending band at 1649 cm^{-1} shifted to 1635 cm^{-1} , suggesting that amine groups in the sorbent were interacting directly with the adsorbed PFOS.²⁶ The strong dependence of PFAS sorption on solution pH also suggests that amine groups in the sorbent bind PFAS via electrostatic interaction. The substitution pattern of the amine, ranging from primary amines to quaternary ammonium salts, dictates the pH-dependence of sorption. In almost all literature reporting sorbents bearing protonatable amines, PFAS sorption capacity is significantly increased when the solution pH decreases.^{12,25,28–30,32,36,37,47} Aminated polyacrylonitrile fibers (APANFs), for example, made by surface modification of polyacrylonitrile fibers with diethylene triamine, exhibited 15.0 mmol/g adsorption capacity for PFOS at pH 3, whereas the capacity of APANFs dropped to below 5 mmol/g when the solution pH was increased to 10.³⁰ In contrast, sorbents bearing quaternary ammonium salts show PFAS adsorption performance that is independent of solution pH, as they do not rely on protonation to take on positive charges.^{17,32,40,46}

Most sorbents with low charge density, such as ACs and nonionic resins, have much lower adsorption affinity toward anionic PFAS as compared with aminated sorbents and IX resins.¹² The importance of the amine for electrostatic binding of anionic PFAS has been highlighted in several studies. A recent study reported carbohydrate sorbents based on β -cyclodextrin tetrafluoroterephthalonitrile (TFN-CDP) polymers, which rapidly remove a wide range of organic MPs from water. The as-synthesized TFN-CDP polymers incorporate anionic phenolates during their formation and therefore show the highest affinity for cationic micropollutants and low affinity for anionic PFAS.^{48–51} However, the conversion of the nitrile groups in TFN-CDP to primary amines reversed its surface charge and PFAS affinity, and as a result, the cationic amine-TFN-CDP removed 10 anionic PFAS, including short-chain derivatives, at environmentally relevant concentrations.⁵¹

PFAS adsorption studies on quaternary amine-functionalized ion exchange resins also illustrate the value of amine groups for PFAS sorption. Ray et al.,⁵² for instance, compared PFOA and PFOS adsorption on negatively charged montmorillonite clay with that of positively charged montmorillonite clay, which is functionalized with quaternary amine poly(diallyldimethylammonium) chloride (PDADMAC) polymer

or pyridine-containing poly(4-vinylpyridine-*co*-styrene) (PVPcoS) polymer. The two cationic amine montmorillonite clays exhibited orders of magnitude higher capacity to remove PFOA and PFOS as compared with negatively charged unmodified montmorillonite clay.

Crystalline-designed sorbents have also shown promise for PFAS removal. Liu et al.³² reported a series of quaternary and tertiary amine-functionalized MIL-101(Cr) mesoporous MOFs and studied their PFOA adsorption as compared with nonaminated MIL-101(Cr) MOF. The aminated MOF exhibited superior PFOA removal capacity over nonaminated MIL-101(Cr) MOF. Punyapalukul et al. also investigated PFOA and PFOS adsorption on four surface-functionalized hexagonal mesoporous silica (HMS) sorbents bearing amine (A-HMS), mercapto (M-HMS), titanium (Ti-HMS) or *n*-octyl (OD-HMS) groups. Among the different HMSs examined, only amine-functionalized A-HMS had a positive surface charge, and therefore, it showed superior PFOA and PFOS adsorption capacity over all other functionalized HMSs and pristine HMS.³⁵

4.2. Role of Hydrophobic interactions. Almost exclusively, aminated sorbents have higher efficiency toward sulfonated PFAS as compared with similar chain length carboxylic acid PFAS, which is closely related to the higher hydrophobicity of sulfonated PFAS as compared with carboxylic PFAS.^{24,25,28,29,33,34,36,52} Similarly, the sorption capacity increases as the perfluorocarbon chain length increases, and therefore, the hydrophobicity of PFAS increases.^{17,33,36,39,53} Competitive kinetic sorption of mixtures of different chain length PFAS, for instance, demonstrate that not only long-chain (C_7 – C_{14}) PFAS have higher adsorption capacity at equilibrium than short-chain (C_4 – C_6) PFAS, but also desorption of short-chain PFAS can occur after their initial adsorption, indicating that long-chain PFAS can displace shorter chain adsorbed PFAS over time.^{39,54} This suggests that the more hydrophobic long-chain PFAS have stronger adsorption and retention than less hydrophobic short-chain PFAS since long-chain PFAS can adsorb by both electrostatic and hydrophobic interactions, whereas short-chain PFAS adsorb through mainly electrostatic interactions.^{39,54} This explanation is usually adopted when the sorption process fits the Langmuir model of adsorption (monolayer adsorption).^{25,34,54} Another explanation for the observed efficiency of aminated sorbents toward longer chain and more hydrophobic PFAS relies on the increased potential to form multilayer adsorption as the hydrophobicity of PFAS increases. It is well known that PFAS critical micelle concentration decreases as the hydrophobicity of the PFAS increases. For instance, the critical micelle concentration values of PFOS and PFOA are 4573 and $45,696\text{ mg/L}$, respectively, which is consistent with the higher hydrophobicity of PFOS.^{17,55} Furthermore, it was demonstrated that PFOS can form hemimicelles on sorbent surfaces at solution concentration that is much lower than critical micelle concentration (0.01 – 0.001 of critical micelle concentration).⁵⁶ Therefore, it is also possible that the efficiency and higher adsorption capacity of longer chain and more hydrophobic PFAS is due to their higher tendency to form multilayer aggregation or hemimicelle on the sorbent, whereas short-chain PFAS cannot.^{25,52} This explanation is mainly invoked when the sorbent pore size is large enough to accommodate multilayer or hemimicelle adsorption and when PFAS sorption fits the Freundlich model.⁴⁶ Regardless, it is evident that hydrophobic interactions

between PFAS and the sorbent as well as between PFAS molecules play important roles in PFAS sorption capacity.

4.3. Interplay between Electrostatic and Hydrophobic Segments. The cooperation between electrostatic and hydrophobic segments in the sorbent maximizes the adsorption capacity of anionic PFAS and potential selectivity by aminated sorbents. For instance, Zhang et al.³⁶ reported on F_3O_4/SiO_2 magnetic nanoparticles, which were surface-functionalized with octadecyltriethoxysilane (hydrophobic C_{18} group) and aminopropyltrimethoxysilane (electrostatic NH_2 group) groups via sol–gel approach. The optimum $C_{18}:NH_2$ proportion of 2:3 has led to the maximum PFAS sorption capacity and lowest dependency on chain length, whereas higher or lower proportions of these two groups reduced the PFAS sorption capacity. The effect of air bubbles that are entrapped in the sorbent matrix on the sorption capacity of APANFs sorbent is another example. The presence of air bubbles almost doubled PFOS sorption on APANFs as compared with degassed PFOS solution. The increase in PFOS sorption by air bubbles was reasoned to the accumulation of several PFOS molecules at the solution/air bubble interface and then the adsorption of PFOS/air bubble assembly on the APANFs.³⁰ In another example, Ji et al.³³ reported amine-functionalized mesoporous covalent organic frameworks (COF) bearing varying densities of primary amine groups. These COFs were prepared by polymerizing 1,3,5-tris(4-aminophenyl)benzene with various molar ratios of terephthalaldehyde and a dialdehyde-bearing azide (N_3) group to yield azide-functionalized COFs, which were subsequently reduced to produce amine-functionalized COFs. The amine-functionalized COFs exhibited rapid removal of GenX, whereas azide-functionalized and nonaminated COFs showed very poor removal of GenX (i.e., hexafluoropropylene oxide; PFOA replacement).³³ The best performing COFs had only 20% amine loading, (20% of the comonomers bearing amine groups), and the sorption capacity of GenX was inversely correlated with higher or lower NH_2 loading. This indicates an optimal balance of electrostatic and hydrophobic segments to bind GenX head groups via electrostatic interactions and to accommodate its hydrophobic tail in the hydrophobic pores of the COF.³³ The synthetic tunability and design control of ordered nanostructured materials including COFs and MOFs enable the control of the ratios and spatial arrangement of the electrostatic and hydrophobic segments, which can help to better understand the influence of the interplay between the two segments on PFAS adsorption.

4.4. Role of Sorbent Particle Morphology and Porosity. Particle morphology and porosity of aminated sorbents play a key role in sorption kinetics, and they determine the sorbate diffusion rate and access to sorption sites. It is evident that sorbents having a BET surface area <50 m^2/g , such as carbohydrate and ion exchange sorbents, exhibit very slow sorption kinetics, reaching equilibrium after several hours of contact time.^{25,30,39,40,46,54} Adsorption kinetics on these sorbents fit a pseudo-second-order kinetic model displaying rapid initial adsorption followed by slow adsorption until they reach equilibrium.^{25,40,46,54} The intraparticle diffusion was found to be the rate-limiting step, especially for long-chain and large size PFAS.^{46,54} Reducing sorbent particle size increases the sorption kinetics, although the sorption capacity is unaffected.^{24,26}

High surface area mesoporous sorbents (i.e., SSA > 50 m^2/g and pore size between 2–50 nm), on the other hand, showed

much faster sorption kinetics, and they usually reach equilibrium in less than 60 min, implying that the adsorption sites are easily accessible by the sorbate. Examples of these porous aminated sorbents include nanostructured sorbents such as MOF-based MIL-101(Cr),³² COF-based $X\%[NH_2]$ -COFs,³³ and hexagonal mesoporous silica.³⁵ $X\%[NH_2]$ -COFs, for instance, have BET surface areas above 1000 m^2/g and an average pore width around 2.6 nm, and therefore, it displays very rapid PFAS adsorption kinetics, reaching equilibrium in just a few minutes of contact time.³³ Although intraparticle diffusion remains the rate-limiting step in these sorbents, their porosity and high surface area enable much faster intraparticle diffusion as compared with nonporous sorbents.

The pore size of nanostructured sorbents can also have an apparent effect on PFAS sorption capacity, especially if the amines were placed in nanopores that are not accessible by PFAS. Aminated MOF MIL-101(Cr)- NH_2 , for instance, exhibits a PFOA adsorption capacity of 0.70 $mmol\ g^{-1}$, lower than that of the nonaminated MOF MIL-101(Cr). This reduction was due to the steric hindrance caused by the aromatic amine in the narrower nanopore of MIL-101(Cr)- NH_2 , which obstructs the micelles or hemimicelle of PFOA from entering the nanopores.³² Overall, engineered mesoporous materials may provide a better approach to develop the next generation PFAS sorbents since they combine fast sorption kinetics, tunable pore size, high sorption capacity, and regeneration capability.

5. CHALLENGES IN THE APPLICATION OF CURRENT AMINATED SORBENTS

5.1. Application Mode. Aminated sorbents in the literature were evaluated by batch and column application modes. Batch tests are commonly the preferred method for laboratory studies, and they are essential from the evaluation perspective, especially to rapidly assess the sorbent adsorption kinetics and capacity. However, batch mode would be limited in real-life applications to industrial wastewater treatment since the separation and recovery of the sorbent are very difficult on large scale. Therefore, from practical and economical perspectives, adsorption in column mode, where the solid-to-total volume of water is much higher in comparison with batch mode and the sorbent can be recovered, regenerated, and reused, can indicate sorbent performance in real-life applications. As illustrated Figure S2B, only three aminated sorbents were tested in column mode, whereas all other sorbents were tested in batch mode. This is because column application mode can be difficult to use when the sorbent has a small particle size (i.e., nm– μm size range), and column experiments take a much longer time than batch experiments (Table S1). Therefore, innovative agglomeration methods that produce granular forms of the aminated sorbents while maintaining their superior PFAS removal efficiency are needed to demonstrate the scalability and usability of the sorbents in practical applications.

5.2. Regeneration of Aminated Sorbents. Establishing the regeneration capability of aminated sorbents is critical not only to reduce the environmental impact of used sorbents but also to improve their economic competitiveness with conventional activated carbons and ion exchange resins. It should be noted that the total elimination of PFAS will require efficient destruction methods for treating the regenerant solutions. Table S1 shows the reported aminated sorbents and their regeneration potential. The desorption methods to regenerate

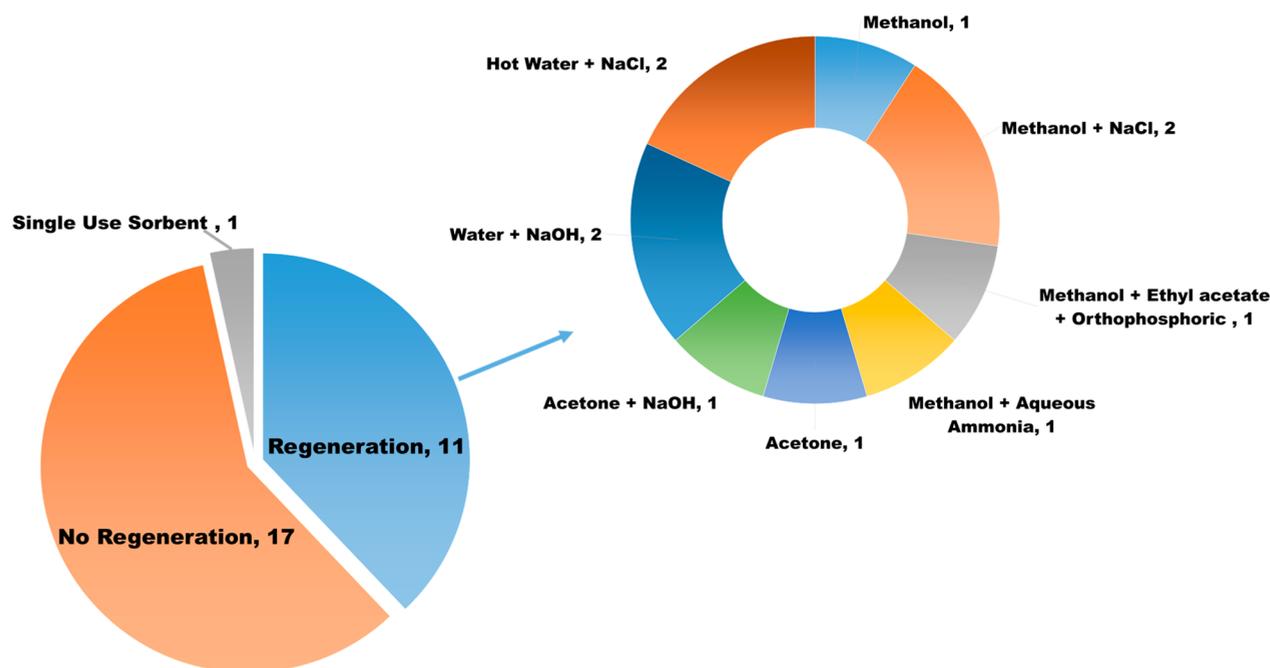


Figure 2. Overview of regeneration of aminated sorbents for PFAS removal. The number beside each category indicates the number of studies in this category.

spent aminated sorbents depend heavily on their structure and amine functionality (Figure 2). These regeneration methods include washing with (1) methanol, (2) a mixture of methanol and NaCl, (3) a mixture of methanol, ethyl acetate, and orthophosphoric, (4) a mixture of methanol and aqueous ammonia, (5) acetone, (6) a mixture of acetone and NaOH, (7) a NaOH solution, and (8) a hot NaCl solution. Most literature studies presented only one method of regeneration, and thus, it is not clear whether the selected regeneration methods were the best options. One study by Kawano et al.²⁸ compared different regeneration solutions (i.e., methanol, acetone, and NaOH solution) and indicated that acetone was the most efficient regeneration solvent. The reason why acetone was the most efficient solvent was not discussed by the authors, but we believe that the most efficient regeneration method of a given sorbent will greatly depend on the sorbent characteristics (e.g., porosity, functional groups, hydrophobicity). The efficiency of the desorption process depends on the distribution coefficient of PFAS between the sorbent and the solvent, which can heavily depend on the composition of the electrostatic and hydrophobic segments in the sorbent. For instance, IX resins and MOFs featured relatively highly electrostatic segments (i.e., quaternary amines), and therefore, the most efficient desorption solvents included highly polar NaCl solutions in ethanol or water.^{32,38} Meanwhile, acetone was an efficient desorption solvent for sorbents with relatively more hydrophobic segments, such as surface-tethered polystyrene particles, for which the desorption solvent should have a polarity which counterplay the interaction between the sorbent and PFAS.²⁸

6. THE WAY FORWARD

PFAS adsorption kinetics and mechanism depend heavily on sorbent morphology, as well as PFAS electrostatic and hydrophobic interactions with the sorbent. Next-generation sorbent materials which are more efficient for anionic PFAS

removal should contain electrostatic functionalities along with considerable hydrophobic segments to enable efficient and high capacity PFAS removal and porous and high surface area structures to enable rapid kinetics. One promising direction, in our perspective, is the development of novel porous sorbents in which we can control the composition, ratios, and spatial arrangements of the hydrophobic and electrostatic segments, such as porous cross-linked polymers and nanostructured crystalline polymers. For instance, porous cross-linked polymers can be made by polymerization of two rigid monomers (usually aromatic groups), one featuring an amine or amine-generating group and the other hydrophobic, and the ratio of the two monomers dictates the interplay between the hydrophobic and electrostatic segments and the affinity for PFAS. Bottom-up nanostructured crystalline polymers including COFs and MOFs, on the other hand, may offer the possibility to engineer the electrostatic and hydrophobic segments and enable the control of the spatial arrangement of these segments and pore size and morphology for optimal control of the sorption properties. The experimental data can be also combined with computer-aided molecular design frameworks for the development of sorbents with adsorbents with good chemical stability, high selectivity and capacity, and good reusability. The current proof-of-concept studies on aminated sorbents, especially the recent emerging sorbents, are not enough and need to be more comprehensive for industrial production. It will be necessary to scale-up the production of the most promising materials, for which materials and manufacturing costs will heavily influence what markets, if any, these novel sorbents will impact. Indeed, further investigations with respect to large-scale production of aminated sorbents and the development of efficient engineered processes for their use and reuse under environmentally relevant conditions is desired. Although the removal efficiency of cationic and zwitterionic PFAS by aminated sorbents is still unknown, pretreatment (e.g., oxidation by chlorine or

ozone)⁵⁷ might be beneficial to transform them to anionic PFAS before adsorbing them on aminated sorbents.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.9b00659>.

Comparison Criteria for Table 1. Summary table of all studies on aminated sorbents for PFAS removal. Two figures on the distributions among studies based on the amine functional groups, application mode of sorbents, and the water matrix. (PDF)

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Notes

The authors declare the following competing financial interest(s): Alaaeddin Alsaiee is employed by DuPont in its Electronics & Imaging business unit. DuPont also has a Water Solutions business unit in its Safety & Construction business, which offers products for ion exchange and other water purification materials.

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