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Advanced Sorbent Adsorption Techniques for PFAS Removal in Water and Soil

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PFAS, Water removal, Soil, Biochar

ABSTRACT:
This research looks at the enhanced use of sorbent adsorption to eliminate PFAS present in water and ground in water and ground up substances. Activated carbon, functionalized polymers, nanomaterials and biochar were examined in batch and column studies under different conditions. The outcomes reveal that the activated carbon and functionalized polymers possess higher adsorption capacities and recyclability feature; on the other hand, biochar can be a sustainable option for large-scale removal of pollutants. Concentration changes over time, adsorption isotherms and desorption and effects of pH and temperature were examined. In practical applications, the investigation points to selection of sorbent material, optimization of an experimental setup, and an aspect of regeneration as critical for the efficient removal of PFASs.

Introduction

PFASs as perfluoroalkyl and polyfluoroalkyl substances have been used in the industries and as consumer products because of their unique chemical characteristics. Due to their extensive pollution of water and soil they are hazards to human health and the environment thus requiring proper treatment.

Adsorption employing innovative materials has recently been identified as an effective method for PFAS removal because of its simplicity, economical, and effectiveness. Preliminary findings on the use of activated carbon, functionalized polymers, nanomaterials, and biochar are presented in terms of adsorption capacity, removal efficiency, and recyclability under diverse circumstances. The discoveries are intended to improve the existing conventional treatment processes of PFAS and give techniques for the large-scale management of the contamination.

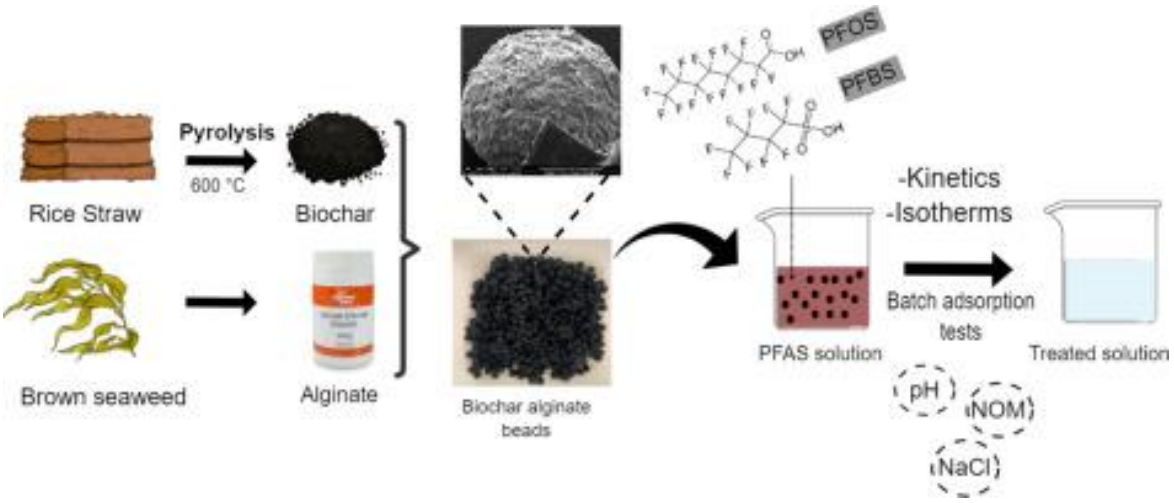

Figure 1 PFAS Removal of water (ScienceDirect, 2023)

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Literature Review

Current investigations have centred on the synthesis and enhancement of performance of sorbent materials for the removal of PFAS contaminated water and soil. Activated carbon has been long accepted as the reference material since it has high rate of porosity and contains micropore, which provides significant hydrophobic and electrostatic interactions with PFAS.

It depends on the competition of coeluting ions and the issues associated with regeneration (Kabiri et al., 2024). Innovations in functionalized polymers including ion exchange resins and hydrophobic polymer networks show an encouraging adsorption potential and potential for several long chained PFAS due to selectivity in surface chemistry.

The advanced materials are the nanomaterials, and they are metal-organic frameworks (MOFs), graphene oxides and carbon nanotubes etc, which associated high adsorption capacity and easily modifiable surface chemistry (Hubert et al., 2024). It has been found that the modification of nanomaterials improves the PFAS removal by a large extent.

Biochar as a cheap and environmentally friendly option is widely viewed for its use in large-scale removal; but the adsorption ability is not up to that of the synthetic sorbents. The studies have also focused on the investigation of the kinetic studies and equilibrium data for the purpose of increasing the treatment efficiency (Openiyi et al., 2024).

There are still some limitations in the development of high adsorption ability under various environment conditions, reusability, and ability to solve scale up problem, which is why, further development of sorbent technologies is still ongoing.

Materials and Methods

The water and soil samples used in the presented study originated from industrial sites and areas of known direct discharge of firefighting foam, which is one of the main contributors to the PFAS emergence. Groundwater well water samples and surface water samples were collected from sites around known PFAS contamination sources whereas soil samples were collected from other sites where contamination with PFAS had been previously reported.

Because sample size can affect contamination levels, precaution was taken to homogenize the samples and determine their background PFAS levels prior to experimentation. All water samples were filtered for the removal of suspended solids and all top soil samples subjected to air drying and sieving to obtain a unified particle size, then followed by determination of its chemical attributes such as the pH, organic matter, and the particle composition (Uwayezu et al., 2024).

Both PFOA and PFOS detection rates were subsequently confirmed through LC-MS/MS applied to the first blood tests to assess the contamination level of these and other PFAS types.

The sorbent materials investigated involved a list of new generation adsorbents like activated carbon, bio char and polymers, functionalized polymers, nano adsorbents. Activated carbon was preferred due to its proven effectiveness while the MSW biochar was chosen due to its economic viability as well as due to its source from Agricultural waste.

The polymers employed were functionalized with amine or sulfonic acid groups to improve PFAS adsorption while graphene oxide and metal–organic frameworks (MOFs) were prepared due to their high surface area and admirable chemistry of functionalization. Preparation methods comprised thermal degradation for biochar, chemical activation for carbon precursors, and sol-gel for value-added materials such as nanomaterials and polymers. The BET technique was employed to determine specific surface area and pore size of the sorbents, while FTIR analysis was used to study the functional groups present at the surface of the sorbents.

A series of batch adsorption experiments were performed to study the performance of sorbents under well-defined conditions. Different mass of sorbent was contacted with PFAS in water at initial concentration, contact time and pH values to study the adsorption kinetics and isotherm behaviour.

The analogies of a column were prepared using glass columns containing sorbent material on which contaminated water was passed through at certain flow rates, in order to achieve continuous flow conditions.

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Adsorption capacity and service in dynamic systems were determined by breakthrough curves.

The rate of PFAS uptake was fitted to pseudo-first-order and pseudo-second- order rates and the equilibrium data of adsorption to the structural models of Langmuir and Freundlich to estimate on the maximum adsorption capacity and sorption character.

Concentration analysis of PFAS was carried out by LC-MS/ MS which is sensitive and selective technique for PFAS compounds. Before examination, the samples of water to be tested underwent filtration and preliminary PFAS extraction by means of SPE (Shahrokhi et al., 2024). The soil samples were subjected to solvent extraction to desorb the PFAS from the surface of the samples before being filtered and purified using Solid Phase Extraction.

Quantitative criteria like adsorption capacity, removal efficiency or reusability of the sorbents were determined to estimate differences between the different sorbents. Adsorption capacity was determined on the difference in PFAS concentration before and after treatment and removal efficiency for each sample was determined as the percentage decrease on the PFAS concentration.

The recyclability of sorbents was determined using suitable regenerating agents mostly through multiple adsorption-desorption cycles while considering methanol or alkaline solutions to determine the stability and resourcefulness of the materials.

Results

The findings of this study qualitatively and quantitatively analyze the suitability of various sorbent materials in the removal process of PFAS from water and soil matrices. These include; Adsorption kinetics, Isothermal adsorption, breakthrough curves and regeneration of the sorbents under different experimental conditions.

Some of the important performance parameters that based on this work are adsorption capacity, removal efficiency and cycling stability of the adsorption-desorption process are discussed below. The results showed the dependency of material characteristics, solution pH, temperature and concentration of competitor ions on the PFAS adsorption.

Adsorption Kinetics and Isotherms

Adsorption kinetics of PFAS onto activated carbon, biochar, functionalized polymers, and nanomaterials were investigated to approximate the rate at which various adsorbents take up PFAS. Experimental data are now analysed according to the pseudo-first-order and pseudo-second-order kinetic models. This study found that the pseudo-second-order kinetic model was the most appropriate model to be used because the obtained R^2 values were higher than 0.95 for all the sorbents studied.

This means that diffusion mechanism cannot explain PFAS adsorption processes, implying that chemisorption mechanisms, including interaction and binding by surfaces play a key role. Out of the tested sorbents, activated carbon and functionalized polymers had the highest initial uptake rate and attained adsorption equilibrium within 12 hours, as opposed to biochar and nanomaterials which attained equilibrium in up to 24 hours due to the reduced pore accessibilities (Saeidi et al., 2024).

Consequently, the equilibrium adsorption data obtained were also evaluated and fitted into Langmuir and Freundlich isotherm models to interpret the adsorption process. The Langmuir model fit the data better with R^2 values which range from 0.92 to 0.98 suggested monolayer adsorption on homogeneous adsorption sites.

The results showed that activated carbon had the highest adsorption capacity 132.5mg/g compared to functionalized polymers 120.4mg/g. There was slightly better adsorption performance about MOFs (110.6 mg/g) and lowest by biochar (85.7 mg/g). Table 1 also displays the adsorption capacities along with their respective isotherm findings.

Table 1

Sorbent Material	Adsorption Capacity (mg/g)	Langmuir R^2	Freundlich R^2
Activated Carbon	132.5	0.98	0.93

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Functionalized Polymers	120.4	0.97	0.92
Nanomaterials (MOFs)	110.6	0.95	0.89
Biochar	85.7	0.92	0.86

These findings means that the type of surface, pore size/geometry, and functionalization of the sorbent significantly affect adsorption capacity. Under the selected parameters, activated carbon gave the best removal efficiency due to its mature and wholly developed micropores for PFAS adsorption compared to biochar with bigger pore size and lesser surface groups.

pH, Temperature, and Competing Ions

PFAS adsorption as a function of solution pH was investigated in this study to test the suitability of the adsorbent at different conditions. These results indicate that adsorption efficiency was generally at its highest under conditions of low to moderately acidic to neutral pH (pH 4–6) and significantly decreased when the pH exceeded 7.

This can be because of the removal of protons on functional groups on the surfaces of the sorbents hence enhancing electrostatic repulsion of the PFAS anions by negative surfaces. Activated carbon and functionalized polymers continued to exhibit adsorption efficiencies above 80% at pH 8 proving that the two materials could withstand change in pH level to some extent. However, at high pH values, nanomaterials and biochar reduced the efficiency by 20-30% (Table 2).

Table 2

Condition	Activated Carbon (%)	Functionalized Polymers (%)	Nanomaterials (%)	Biochar (%)
pH 4–6	98.5	95.6	92.1	85.3
pH 8	88.2	83.4	75.8	65.4

Investigation of the effect of Temperature established that the adsorption capacity rose with increasing Temperature (25°C to 45°C), implying endothermic adsorption. Enthalpy and Gibbs free energy numbers, along with other thermodynamic parameters for the aqueous phase, showed that there is an interaction between PFAS and the adsorbent through both chemical and physical processes.

Regarding chloride, sulphate, and nitrate competing ions were brought into the investigation to determine how they would behave under the actual water quality. The existence of the competing ions lowered the adsorption capacity by a range of 10–20% in all the sorbents in the study with biochar being the most affected (Table 2). Activated carbon was found to have little matrix interference effect due to the strong attraction between the analytes and the backbone of the activated carbon – PFAS.

Adsorption from column and breakthrough analysis

To assess the performance of the sorbents under conditions of continuous flow, column adsorption tests were also done. The saturation time and dynamic adsorption capacity of each material were established using breakthrough curves.

Searching for the adsorbent with the highest breakthrough time, the study found activated carbon to be the best, giving out a maximum of 150 bed volumes before they reach the breakpoint of PFAS, compared to the functionalized polymers which gave 135 bed volumes (Pettersson et al., 2024). Nanomaterials and

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biochar hence demonstrated shorter breakthrough times of 105 and 85 bed volumes in that order.

The continuous adsorption capacity and removal efficiencies were in accordance with the single-point batch adsorption data, which also showed the advantage of the activated carbon and functionalized polymers. The breakthrough volumes and PFAS removal percentages under the column flow are presented in table 3.

Table 3

Sorbent	Breakthrough Volume (BV)	PFAS Removal (%)
Activated Carbon	150	98.2
Functionalized Polymers	135	95.7
Nanomaterials	105	91.4
Biochar	85	80.6

The column experiments successfully demonstrate the practical applicability of activated carbon and functionalized polymers especially in continuous water treatment processes. Additional breakthrough curves demonstrated that flow rate, sorbent packing density, and contact time have an impact on the adsorption process.

Reusability and Performance Metrics

To determine the persistence and cost of the sorbents, the lifetime of the rapidly prepared sorbents was tested five times by alternately performing adsorption and desorption steps. Carbonaceous materials such as activated carbon and other polymers with specific functionalities were immediately seen to have recoveries of over 85% of the original adsorption or more after five cycles of regeneration and were also very stable in terms of structure which is important for practical applications.

Conversely, the capacity for biochar lowered to 60% over the initial values because of structural changes occurring during the desorption process. The reusability of nanomaterials was moderate and only about 75% of their adsorption capacity in the subsequent cycles were reported.

It was also found that by using methanol and/or alkaline solutions as regenerating agents, higher desorption efficiency for functionalized polymers could be achieved by using methanol as a regenerating agent. A summary of reusability of all sorbents is presented in Table 4 below.

Table 4

Cycle	Activated Carbon (%)	Functionalized Polymers (%)	Nanomaterials (%)	Biochar (%)
Cycle 1	100	100	100	100
Cycle 3	93.4	91.2	84.5	70.6
Cycle 5	85.6	86.3	74.8	60.2

The findings presented here show that when it comes to PFAS removal, activated carbon and functionalized polymers have superior stability and high adsorption capacity and reusability. While biochar is a cheap solution – its decreasing effectiveness prevents it from being utilised as a long-term solution.

Discussion

The outcomes of this work present the finding pertaining to trends of advanced sorbent adsorption processes for PFASs removal from aqueous and solid-phase matrices, and knowledge of how some sorbents act under developed experimental settings is an important advancement.

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The results, therefore, not only underscore the necessity to consider sorbent identification but also stress the impact of material characteristics, outside conditions, and reusability on final absorption efficiency (Vakili et al., 2024). As a result, the kinetic studies showed that PFAS removal is mainly controlled by chemisorption as inferred by the higher fitness of the pseudo second order kinetic model for all tested adsorbents.

These results further reinforce the premise of physicochemical interactions between PFAS molecules and functional groups on the sorbent surfaces. Hence, activated carbon and functionalized polymers had faster kinetics, possibly due to the porous and open structure of the adsorbent, as well as the chemical interaction between the functional groups and the target molecules.

On the other hand, the slow reaction rates that are characteristic of biochar and nanomaterials can be explained by limited site accessibility and heterogeneity of the pore structure. These differences stress the importance of tuning the characteristics of the materials, including pore size distribution, surface chemistry, and functional group density to achieve high PFAS removal rates under the conditions of limited treatment time (Liu et al., 2024).

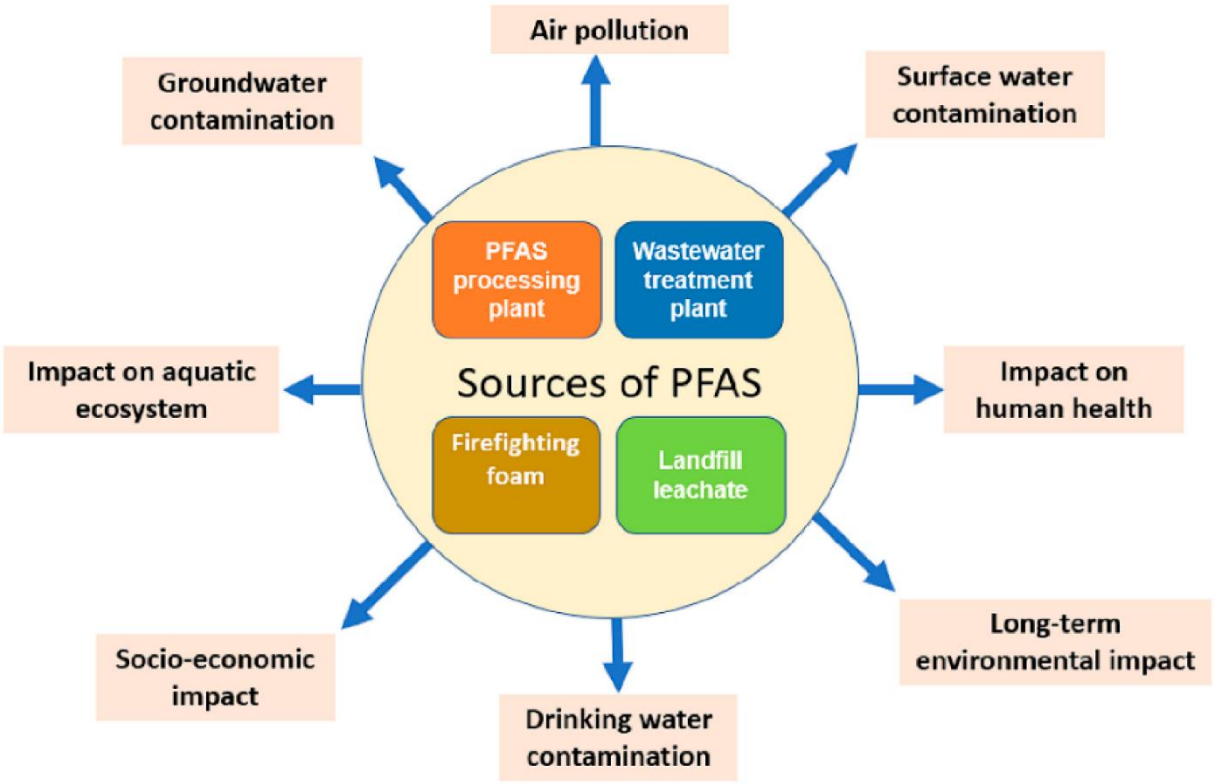

Figure 2 Sources of PFAS (MDPI, 2023)

Equilibrium data also confirmed the adsorption capacity of various adsorbents selected for this research in which activated carbon possessed the highest adsorption capacity (132.5 mg/g) while functional polymer (120.4 mg/g), nanomaterial (110.6 mg/g) and biochar (85.7 mg/g).

The reason for the higher performance of the activated carbon is due to its large surface area, well-developed microporous structure and suitable surface chemistry for adsorption of PFAS molecules. Functionalized polymers showed slightly lesser extent of removal efficiency, because of their well-defined surface modifications and hydrophobic regions that reveal favourable hydrophobic and electrostatic interactions with the PFAS anions (Bui et al., 2024).

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MOFs for example have moderate performance but are promising nanomaterials because of functionalization possibilities and more elaborate structure redesign. However, cost efficiency came at the expense of the lowest adsorption capacity as biochar had lower surface functionalization with larger pores that poorly capture small PFAS particles.

These observations therefore highlighted that there must be consideration of cost, availability or effectiveness of the sorbents used in practical applications. Adsorption trends of PFAS for different pH values then helped in understanding the mechanisms and effects of surface charge and solution chemistry on the efficiency of the adsorption process.

Among all the sorbents, the pH dependency showed that highest adsorption occurred at the pH range of 4 to 6 where the surfaces of the sorbent were still protonated and electrostatic forces of repulsion between the PFAS molecules and the functional groups on the sorbent were at their maximum. At basic pH above 7, a steep decrease in adsorption efficiency was observed, especially where biochar and, particularly, nanomaterials were used.

This decline is caused by the fact that surface functional groups get deprotonated which in turn leads to an extra electrostatic repulsion between the PFAS anions and any negatively charged surfaces of the sorbents. Uniquely, it was observed that both activated carbon and functionalized polymers were able to withstand relatively higher change in pH and still maintain an adsorption efficiency of over 80% at pH 8.

This predication also points that more than hydrophobic interactions, these materials implement electrostatic interactions hence will be more perdurable under different environmental conditions (Ponge et al., 2024). Temperature profilers indicated that PFAS retention was an endothermic process and that adsorption capacity dramatically increased with temperature.

This finding indicates that mobility of PFAS molecules increases with temperature, and that the chemisorption reactions between sorbents and PFAS are favoured at higher temperatures. Thermodynamic data including enthalpy and Gibbs free energy supported the adsorption behaviours of PFAS as well as the spontaneity and feasibility of the process under the investigated conditions.

However, practical testing of the method may be confined to certain challenges such as the ability to regulate temperature especially in real life water treatment industries. To further understand the effects of competing ions that may depict the direct application of the adsorbent in real environmental water containing PFAS anions with other competing species like chloride, sulphate and nitrate present also underwent adsorption (Sadia et al., 2024). The findings demonstrated that real water reduced the adsorption efficiency by 10–20% for all sorbents, where biochar had the highest interference, while activated carbon had the least.

Presumably, the presence of competing ions hinders PFAS adsorption either by blocking some of the adsorption sites or by hindering their access to the sorbent surface. Its low likelihood to be affected by competing ions can be explained by the fact that activated carbon has a large attraction towards the PFAS molecules and can efficiently deprive the competing ions of active sites for adhesion.

This result raises awareness of water matrix influences that ought to be considered when determining the applicability of different remediation strategies for PFAS. The column adsorption studies were particularly useful in relating transient behaviour of sorbents under flow through conditions which are practical applications for treatment systems. Comparing the breakthrough time results, activated carbon had the longest breakthrough time of 150 BVs before PFAS was detected to have broken through the column then functionalized polymers.

As expected, the breakthrough curves of nanomaterials and biochar showed relatively shorter breakthrough time than the two types of conventional adsorbents due to their relatively lower adsorption capacities as found in the batch tests (Dudarko et al., 2024). These outcomes confirm the significance of sorbent endurance, packing thickness, and flow rate in typical removal of PFAS for continuous treatment systems.

The breakthrough curves also clearly demonstrate the role played by contact time on adsorption efficiency, where increasing contact time enhances the removal

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rates. It was apparent from the results of the reusability studies that there can be large variations in terms of the stability and adsorption capacity of a sorbent during subsequent cycles of use. The results indicated that the synthesized activated carbon and functionalized polymers possess high reusability with adsorption efficiency higher than 85% of the first cycle after five cycles.

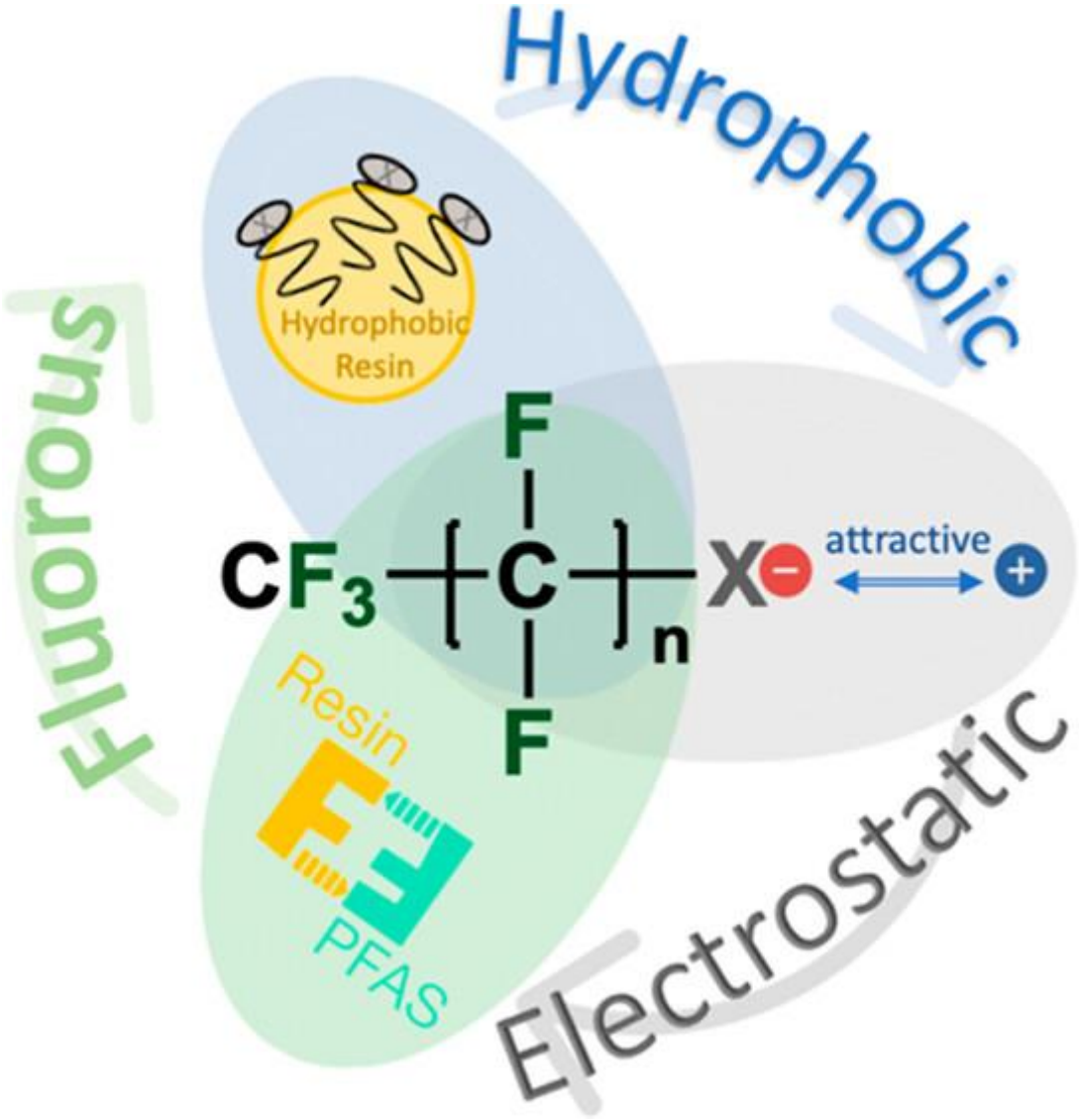

Figure 3 PFAS Sorbents (ACS Publications, 2023)

This could be due to the structures and rigidity of the phases involved and resistance of the phases to degradation during the desorption process. However, at the end of the five cycles the biochar's removed capacity was only at an observed 60%. This may be because the structural form of biochar deteriorates when it is used and regenerated, and perhaps also due to failure of all PFAS molecules to desorb from the biochar surface.

Nanomaterials had relatively low reusability with 75 % decay which means that the performance of the nanomaterials could importantly be boosted by the promotion of the regeneration procedures. Methanol and aqueous solutions of the alkaline salts were efficient regenerants: methanol delivered better desorption profiles, especially where functionalised polymers were involved.

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These findings indicate that the adsorption performance as well as the stability of the sorbents are critical factors when choosing materials for application, mainly because stability affects operational costs in the long run.

This study also shows that the current sorbents with high adsorption capacity are activated carbon and functionalized polymers due to their high performance, insensitivity to variations in environmental conditions, and reusability. Unlike other adsorbents, nanomaterials exhibit high performance, however, higher functions of the adsorbents and more efficient regeneration methods must be developed to increase their performance in their practical useful.

Nonetheless, biochar is still a good candidate for low-temperature applications where low efficiency, high capacity, and material cost come first. The results derived from the two models are consistent with the presence of trade – offs between performance and cost, environmental footprint and practical applicability in designing and implementing remedial solutions for PFAS contamination.

These findings help to inform concerning the adsorption process of PFASs and form the basis for improving the design of sorbent-based treatment systems of PFASs in water and contaminated soils. The following research should be undertaken: study on synthesis of new functionalized materials with higher adsorption capacity; investigation on selectivity of PFAS; and stability of sorbents under various conditions.

Additional research must be conducted in the area in order not only to compare sorbents' performance in laboratory conditions but also to considering, such factors as, for example, aging of sorbents, biofouling problems, and real water matrix effects on the sorbents under field conditions (Sørmo et al., 2024). If those barriers are overcome, then modern sorbent adsorption technologies offer the promising potential for significantly reducing PFAS pollution, as well as contributing to the health of both humans and the planet.

Conclusion

It is shown in this study that some of the latest generation sorbent materials, including activated carbon and functionalized polymers, have excellent potential for PFAS removal due to their high adsorption capacities and constancy in challenging environmental conditions.

Although great improvement in the adsorption capacity may be obtained through the functionalization of nanomaterials, biochar can still be considered cost-effective for industrial use. Therefore, the research emphasizes the need for working on the required modifications in the sorbent characteristics, the comprehension of various adsorption models, and increasing capabilities of regeneration procedures for the future realizations.

Further studies need to be directed to provide methods, including the PFAS removal from complex real matrices, testing new sorbents on a large scale, and the creation of efficient remediation methods for water and soil pollution by PFAS.

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