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Review

Removal of Per- and Polyfluoroalkyl Substances by Adsorption on Innovative Adsorbent Materials

Maria Cristina Collivignarelli [1,2], Stefano Bellazzi [3,*], Francesca Maria Caccamo [3], Silvia Calatroni [3], Chiara Milanese [4], Marco Baldi [5], Alessandro Abbà [6], Sabrina Sorlini [6] and Giorgio Bertanza [6]

[1] Department of Civil Engineering and Architecture & C.S.G.I., University of Pavia, Via Ferrata 3, 27100 Pavia, Italy; mcristina.collivignarelli@unipv.it
[2] Interdepartmental Centre for Water Research, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy
[3] Department of Civil Engineering and Architecture, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy; francescamaria.caccamo01@universitadipavia.it (F.M.C.); silvia.calatroni01@universitadipavia.it (S.C.)
[4] Pavia Hydrogen Lab, Department of Chemistry & C.S.G.I., University of Pavia, Viale Taramelli 16, 27100 Pavia, Italy; chiara.milanese@unipv.it
[5] Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy; marco.baldi@unipv.it
[6] Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, Via Branze 43, 25123 Brescia, Italy; alessandro.abba@unibs.it (A.A.); sabrina.sorlini@unibs.it (S.S.); giorgio.bertanza@unibs.it (G.B.)
* Correspondence: stefano.bellazzi01@universitadipavia.it; Tel.: +39-0382-985311

Abstract: Per- and polyfluoroalkyl substances (PFAS) constitute a group of organofluorine chemical synthetic compounds widely used in industries and manufacturing due to their hydrophobic properties. However, PFAS have been found to cause negative human health outcomes. Therefore, a strong interest in the possible removal of these compounds from wastewater (WW) has been shown. This work aims to present a systematic analysis of the scientific literature related to the innovative and alternative adsorbent materials that can be used for treating PFAS-contaminated WW. Moreover, the adsorption processes are considered, focusing the attention on virgin adsorbent materials and biochar as adsorbents. Virgin adsorbent materials comprise conventional adsorbent materials, functional clays, metal–organic frameworks, and functionalized organic polymers. Biochar includes materials obtained from agricultural or food residues and from sewage sludge. The review shows that conventional treatment units using virgin adsorbent materials are characterized by high adsorption capacity, but also high costs. In addition, the refunctionalization of adsorbent materials is difficult to obtain. On the contrary, biochar, which is a residual product of other production processes, appears to be a cost-effective solution.

Keywords: PFAS; wastewater; adsorbent materials; biochar

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of organofluorine chemicals of strong scientific interest. Their thermal resistance, in addition to their hydrophobic and lipid properties, have been the reason for their extensive use over the past decades. Perfluoroalkyl products are found in household products such as paper and nonstick cookware and in textile company products such as T-shirts and carpets [1,2]. The better-known typologies of PFAS use are textile impregnation, fire foam, and electroplating, but many categories not described in the scientific literature should not be overlooked, including PFAS in ammunition, climbing ropes, guitar strings, synthetic grass, and soil remediation [3].

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) contain a long hydrophobic chain (eight carbon atoms) completely saturated with fluorine atoms (i.e., perfluoroalkyl chains) and a hydrophilic polar functional group [4]. These compounds can decrease surface tension: this property has contributed to their previous use in surfactant applications. Their water solubility is largely influenced by their shape, being the anion species significantly more water soluble than the neutral species. Poly- and perfluoroalkyl compounds are therefore of great interest in water treatment because they are particularly present in the processing waters of textile industries and in landfill leachates [5].

Very few experimental information is available about the physicochemical properties of PFAS. Microbial processes and the presence of cocontaminants can influence their fate and transport. Landfill leachate contains PFAS concentrations higher than most of the other environmental media, with the exception of fire training and affected production sites [6]. The production and use of PFOS was restricted by the Stockholm Convention on Persistent Organic Pollutants in 2009 [7], and the industry started to stop the production of long-chain PFAS (seven or more perfluorinated carbon atoms), which are generally considered to be more toxic than the shorter-chain forms and bioaccumulative. Indeed, control at the source may be the most effective measure to address specific harmful substances, as pointed out by [8]. Despite the possible phaseout of selected PFAS, landfills will continue to serve as a long-term point repository, highlighting the need for further investigation [9]. In Australia and New Zealand, for human health surveys, soil PFOS levels have been suggested to be no higher than 0.009, 2, and 20 mg/kg for land use in residential areas with a garden, residential areas with minimal access to land, and industrial areas, respectively [10].

The effects on human health of PFAS exposure have been extensively studied. As reported by the National Institute of Environmental Health Sciences of NIH [11], concerns about PFAS are related to their widespread occurrence, numerous exposures, growing number, and in particular, bioaccumulation. A group from the Australian National University [12] demonstrated in a systematic literature review sufficient evidence of an association of PFOA and PFOS exposure with hypercholesterolemia and hyperuricemia. Associations also were found between PFAS and decreased glomerular filtration rate (GFR), increased chronic kidney disease, kidney cancer and testicular cancer, and reduced vaccine antibody response to diphtheria and rubella. However, as most of the health outcomes are concerned, the amount of data and the number of studies suggest the need for further investigations. The accumulation of perfluoroalkyl substances is influenced by the concentration, the length of the chain, the typology of the functional group, the plant species, and the variety and type of soil with which they are placed in contact. The adsorption of PFAS by plants involves a bioaccumulation of the shorter-chain compounds in the leaves and fruits [13], causing limits in their use for human purposes. Toxicity and adsorptive capacity differ between flora and fauna: PFOS have been observed to accumulate in higher concentrations than PFOA in aquatic organisms, while the opposite occurs for plants [14]. However, also on this subject, information is currently too limited to draw firm conclusions. PFAS derivatives have been widely used in various industries due to their water and oil repellent properties. However, these derivatives have raised concerns regarding their impact on the environment and human health. Here are some of the main effects associated with PFAS derivatives: environmental persistence, bioaccumulation, toxicity, endocrine disruption, impact on wildlife, and concerns for drinking water [15]. Perfluoroalkyl acids have been extensively detected in both wastewater treatment plant (WWTP) tributaries (up to 1000 ng/L) and effluents (from 15 to 1500 ng/L) [16]. PFAS concentrations were compiled for WWTP in the United States: PFOA increased by an average of 6.0 ± 1.6 ng/L from WWTP influents to effluents, while PFOS did not change significantly. The occurrence of individual PFAS can vary over time; perfluoropentanoic acid was weakly correlated with seasonal temperature values at a site in Virginia [17]. In one study applied to Australian wastewater, as in WWTPs worldwide, perfluorocarboxylic acid amounts were generally higher in the effluent than the influent. The solids partitioning within the WWTPs increased with increasing fluoroalkyl chain length from 0.05 to 1.22 log units [18]. Compared with the concentrations of PFOS and PFOA in the influents in Chinese wastewaters, high concentrations were observed in the effluents of the WWTPs applying the anaerobic–anoxic–oxic treatment. The levels of PFOS and PFOA in the effluents were approximately 27 and 2 times higher than those found in the seawater receiving the effluents [19]. In 2010, effluents from 90 European WWTPs were analyzed for 156 polar organic chemical contaminants. Target microcontaminants included perfluoroalkyl substances (PFAS). The results show the presence of 125 substances (80% of the target compounds) in European wastewater effluents, in concentrations ranging from few nanograms to milligrams per liter [20]. Most WWTPs have shown low removal efficiency for PFAS, and many studies have reported increased levels of PFAS after WW treatment. The measurement uncertainty is caused by a difficulty in analyzing the aqueous matrix with significant turbidity. More accurate results were obtained in the case of clarified effluent with an increase in measured concentrations [21]. These data suggest that PFAS that are difficult to detect may even be present; such difficulty can decrease in case of a clarified effluent.

To date, several treatment technologies have been used to reduce or destroy PFAS in the environment [22]. In this work, the removal of PFAS with adsorption on innovative and/or alternative adsorbent materials has been studied. Recent research papers have been analyzed to show and compare performance depending on the type of per- and poly-fluoroalkyl pollutant, type of adsorbent, and operational conditions. The authors believe that this review will be helpful for the scientific community given the tips for future research according to current main literature gas, and for water utilities to enhance the knowledge about PFAS in WWTP and possible remediation using adsorption on innovative and/or alternative materials.

2. Methods: Analysis of Literature

Peer-reviewed literature has been considered and selected according to preferred reporting items for systematic reviews and meta-analysis (PRISMA) guidelines, as widely accepted by the scientific community [23].

To consider only peer-reviewed documents, the Scopus® database was used to search relevant literature on this topic. Data extraction from the database was made using the following query: TITLE-ABS-KEY (perfluoroalkyl) OR TITLE-ABS-KEY (pfas) OR TITLE-ABS-KEY (pfoa) OR TITLE-ABS-KEY (pfos) AND TITLE-ABS-KEY (removal OR degradation) AND TITLE-ABS-KEY (wastewater).

Period limits were imposed from 2015 to today, because this work has focused on the most recent results obtained using innovative/alternative materials. Only research articles and book chapters that present innovative and original results were inserted in the study. The documents were also screened individually to exclude papers that do not (i) treat specifically the subject in the scope of the research and (ii) report the results on treatments that can be implemented in existing plants. If full text was not available for screening the record, it was excluded.

To keep the adsorption treatments applicable in WWTPs, the selected materials were

- Virgin adsorbent materials
    - Granular activated carbons (GAC) and powdered activated carbons (PAC);
    - Functional clay;
    - Metal–organic adsorbents;
    - Functionalized organic polymers
- Biochar
    - Biochar from agricultural or food residues;
    - Biochar from sewage sludge of WWTPs.

In Figure 1, the results of the literature search and the number of studies included according to PRISMA guidelines [23] are presented. As clearly reported, the original search found 206 papers corresponding to the search conditions presented above. The first screening excluded papers related to reviews, papers not written in English, and articles related to water purification. Papers were further limited to treatments already applied to existing plants and hence not presenting relevant implementation problems, in terms of either complexity or cost. Of the final 55 papers, only 53 were fully available.

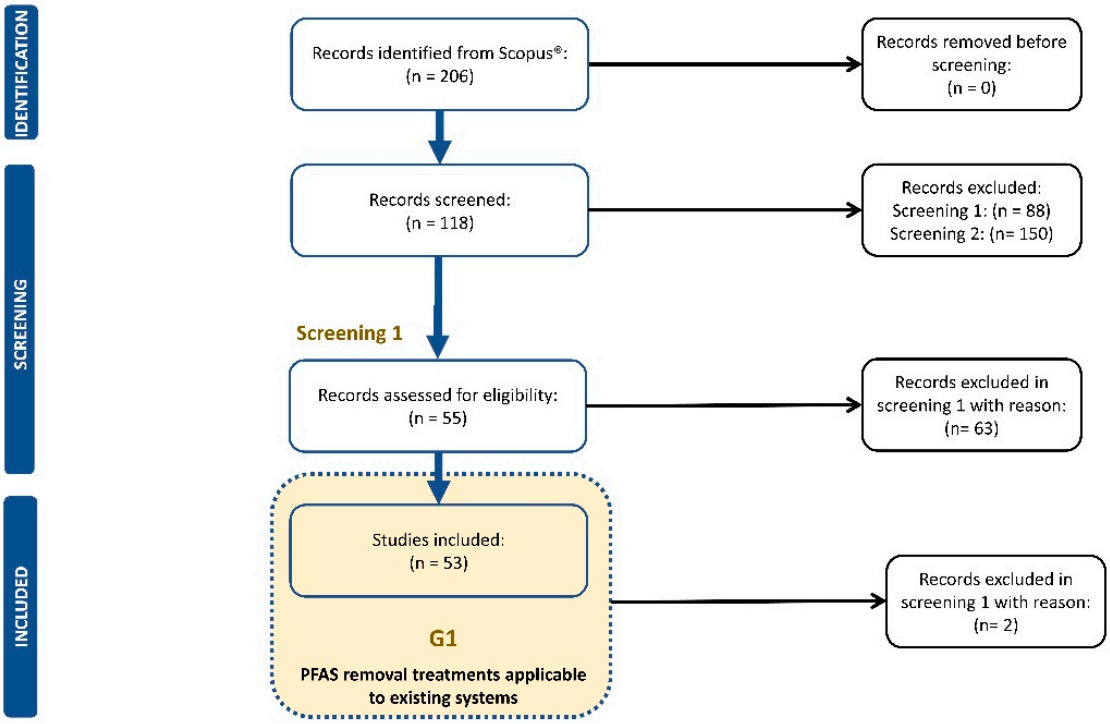

Figure 1. Flow diagram of the identification of studies for inclusion in the present systematic review and meta-analyses.

Mechanism of PFAS Removal

The adsorption of different PFAS has been studied on several materials with different chemical natures, such as activated carbon, functionalized clays, metal–organic frameworks (MOFs), functionalized organic polymers, and biomass-based materials (BIOCHAR). The number of scientific articles on this topic has increased significantly in recent years, with activated carbon being the most studied adsorbent. To develop efficient adsorbent materials, it is necessary to understand the interaction mechanisms that occur among PFAS molecules and the adsorbent surface. The adsorption of PFAS involves different mechanisms, such as electrostatic interaction, hydrogen bonding, ligand exchange, and hydrophobic interactions. This section details and illustrates the different interaction mechanisms that involve the adsorption of PFAS.

Electrostatic interactions are one of the most common mechanisms responsible for PFAS adsorption by various materials. The amphiphilic nature of PFAS provides them with a hydrophobic part composed of C–F chains and a hydrophilic functional head. The functional head of PFAs is commonly negatively charged due to its low acid dissociation constant values (pK_a) [24]. Consequently, PFAS can interact by electrostatic interactions with positively charged groups on the adsorbent surface (Figure 2a). Additionally, divalent cations commonly found in natural waters (Ca^{2+}, Mg^{2+} and Mn^{2+}) can induce a cation bridge effect between the negatively charged head of the PFAS and the negatively charged adsorbent [25]. Reports in the literature suggest that ion exchange resins can efficiently remove short-chain PFAS mainly via a electrostatic mechanism [26,27], meanwhile, long-chain PFAS can be more efficiently removed by hydrophobic interactions [28].

Hydrophobic interactions are an important mechanism responsible for the adsorption of PFAS, especially on carbon-based materials [29,30]. This process can occur either between the hydrophobic tail of PFAS and the hydrophobic surface of the adsorbents or by a self-aggregation step, which allows PFAS to form bilayer structures, micelles, or hemimicelles (Figure 2c) [31]. The driving force behind the hydrophobic effect is entropy; when PFAS molecules are dispersed in water, they are solvated by a high number of water molecules. These ordered water molecules have a lower entropy content compared with the free water molecules from the bulk solution. However, the coalescence of several hydrophobic PFAS molecules will cause a decrease in the amount of water molecules needed to surround them. This process increases the entropy of water, thus favoring the formation of clusters of PFAS molecules over the surface of a hydrophobic adsorbent or by the formation of micelles or hemimicelles. Reports in the literature found that the hydrophobic interaction effects are stronger as the PFAS chain length increases [32]. Additionally, strong hydrophobic interactions between PFAS molecules allow the formation of hemimicelles or micelles within the pores of the adsorbent at a concentration much lower than the critical micelle concentration, CMC [33,34]: the formation of these structures might enhance the adsorption capacity of a material. In contrast, short-chain PFAS have a higher CMC than long-chain PFAS; consequently, they are less prone to form micelles or hemimicelles [35]. As a conclusion, hydrophobic interactions are the key aspect for the high affinity of PFAS towards any hydrophobic medium from carbon-based adsorbents and natural sediments to fatty tissues. This aspect turns PFAS into recalcitrant pollutants in the environment and makes the regeneration of adsorbent materials a challenging issue.

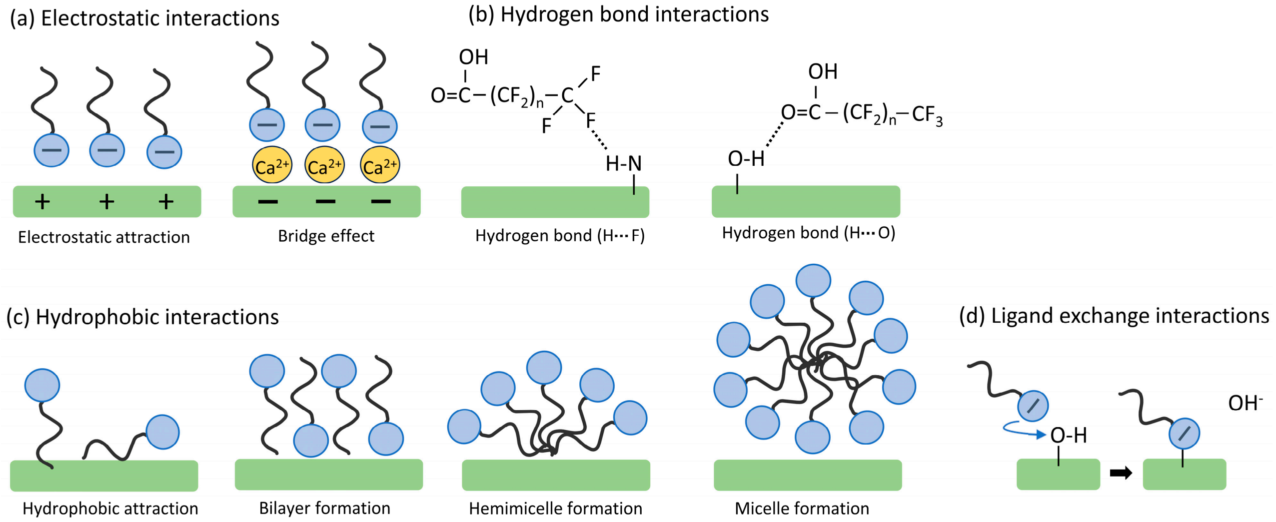

Figure 2. Different adsorption mechanisms for the removal of PFAS in aqueous solutions: (**a**) electrostatic interactions, (**b**) hydrogen bond interactions, (**c**) hydrophobic interactions, and (**d**) ligand exchange interactions.

Hydrogen bonding is another adsorption mechanism that takes place between the oxygen atoms in the PFAS structure and the carboxylic, hydroxyl, or amine groups that might be present on the surface of the adsorbent (Figure 2b) [36]. It has been suggested that the hydrophobic tails composed of C–F bonds can interact with -OH groups from the surface of the adsorbents via hydrogen bonding [37]. Furthermore, it has been reported that hydrogen bonds contributed to the adsorption of PFOAs by interactions between -COOH groups and the amino group present in a mesoporous resin [38]. Hydrogen bonding might be important at high pH values or in negatively charged adsorbents, where the electrostatic interactions are weak. However, hydrogen bonding between PFAS and adsorbents can easily compete by the interaction of PFAS with water molecules. Consequently, hydrogen bonding might not be considered to be a pivotal adsorption strategy for the removal of PFAS.

Ligand exchange is an adsorption mechanism that takes place on the surface of minerals, such as silica, aluminum oxyhydroxide, or iron oxides that contain abundant hydroxyl groups (Figure 2d). The negatively charged PFAS can replace hydroxyl groups via a ligand exchange mechanism, as follows [39,40]:

$$Al - OH + PFA^{-} \rightarrow Al - PFA + OH^{-}$$

$$Fe - OH_2^+ + PFA^- \rightarrow Fe - PFA + H_2O$$

The former equations indicate that the adsorption performance on mineral compounds strongly depends on the density of hydroxyl groups, which is given by the pH of the solution. Moreover, this adsorption mechanism provides insights on the use of inexpensive minerals as adsorption medium.

3. Properties of the Different Adsorbent Materials for PFAS Removal

3.1. Virgin Adsorbent Materials

The newly synthesized materials belonging to the adsorbent material family are by far the most promising alternative for the treatment of liquid waste contaminated by perfluoroalkyl substance, allowing their efficient removal. The analysis of the literature allows for grouping the approaches related to this strategy into four main categories: (i) conventional adsorbent materials, such as granular adsorbent materials (GAC) and powder adsorbent materials (PAC); (ii) functional clays; (iii) metal–organic frameworks (MOF); and (iv) functionalized organic polymers. Subsequently summarized in Table 1.

3.1.1. Conventional Adsorbent Materials: Activated Carbons, GAC, and PAC

Kaiser et al. [41] tested PAC and GAC combined with an ozone treatment for the removal of 31 synthetic PFAS species with a starting concentration of 60 ng/L. The batch experiments involved the use of 2 mg of AC (activated carbons) for 300 mL of effluent to be treated. For both treatments, the obtained yields were not satisfactory. The PFAS removal efficiency for the PAC alone was equal to 21.7%, and for the PAC + OZONE treatment, it was 18.9%; the treatment with GAC alone instead led to an increase in the concentration of PFAS, probably related to the measurement uncertainty. Wang et al. [42] tested two types of reactivated carbons (R-GACs) with an adsorption capacity of 0.35 nmol/g and a BET of 1705 m^2/g: the activation of carbon with KOH led to an increase in pore size; instead, the use of NaOH was excellent for regenerating spent coal. The increase in hydrophilicity increased the depurative yields, and the interparticle diffusion was the main limiting step of the adsorption process, limiting its rate. Sun et al. [43] tested PAC adsorbent materials functionalized with sulfate radicals and found that under acidic conditions, PFOA was transformed into shorter-chain perfluorinated compounds. The removal of PFAS occurred by covalent bond for a percentage between 10% and 40%. Schuricht et al. [44] analyzed the adsorption yields of the perfluoroalkyl substances on polymeric adsorbents, adsorbent materials, and ion exchange resins by means of batch and column tests. From this study, it appears that the selectivity of PFOS adsorption increases when the character of the functional groups becomes more hydrophobic and that a fundamental role is given by the presence of cationic functional groups. The performances were found to be maximum for the polymeric adsorbents, just followed by the adsorbent material ones.

3.1.2. Functional Clays

Functionalized clay can retain particles in the liquid phase, thanks to the combination of two different phenomena, namely, imbibition and capillarity, the first being of physico-chemical nature, while the second of physical nature. In both cases, the retention capacity is due to electrostatic forces that are established between the molecules of pollutants in the dissolved phase and the solid matrix. Thanks to their high adsorbent capacity, functionalized clays represent an alternative for the removal of perfluoroalkyl substances from an aqueous matrix. Dong et al. [45] tested the removal of PFOA and PFOS through an ionic-liquid-modified natural clay. The experiments were carried out in batches with a clay dosage of 0.25 g/L. The removal yields were lower than 10% for the unmodified clay, while they were higher than 70% for the material modified with ionic liquid. The longer-chain perfluoroalkyl pollutants were removed with yields up to 99%; moreover, the presence of natural organic matter (NOM) greatly lowered the clay transfer performance. Khodabakhshloo et al. [46] tested chemically activated clays in refinery waters: the tests were carried out in batches with the use of 0.02 g of adsorbent per 40 mL of wastewater to be treated. The maximum adsorption capacity was 163 mgPFOS/g, and it was noted that the presence of the copper ion Cu^{2+} can create bridges for the adsorption of PFOS. Ray et al. [47] tested polymer clay functionalized with a specific surface area (Brunauer–Emmett–Teller (BET)) of 2.5 m^2/g to treat urban rainwater. The experiments were carried out in triplicate in a column with a clay dosage of 0.5 g/L. The abatement yields on PFOA and PFOS were around 95%. The electrostatic attraction of the acid head groups is the main cause of adsorption; it was also noted that the increase in hydrophobicity of the clay leads to an increase in its adsorption performance.

3.1.3. Metal–Organic and Metal—Inorganic Adsorbents

Metal–organic frameworks (MOFs), also called metal–organic structures, are defined by the IUPAC as coordination polymers. They consist of a three-dimensional crystalline lattice formed in turn by two fundamental units: organic linkers and metal ions or clusters. Inorganic clusters and organic groups bond to form an open structure that has cavities. The three-dimensional structure of MOFs does not deteriorate easily with the capture process, allowing for extended use over a high number of cycles. The lattice structure is composed by metal ions, oxygen (polar sites), and organic linkers (nonpolar sites, which represent the major fraction of the internal surface) generally connected with weak van der Waals bonds. Inorganic minerals such as hydroxides, zeolites, and boron nitrides have also been successfully employed. Ahmed et al. [48] tested the adsorption of PFOA via bilayered hydroxides of magnesium (Mg) and aluminum (Al). The material showed a specific surface area (BET method) between 29.1 and 37 m^2/g. The tests were carried out in batches with an adsorbent dosage of 20 mg/L; the adsorption capacity was between 244 mgPFOA/g using manganese and 667 mgPFOA/g using aluminum, while the removal yields were equal to 98.9%. Tang et al. [49] used adsorbent materials (AC) coated with zinc oxide. These experiments were conducted in batches with a CA dosage of 0.8 g/L. The wastewater to be treated, sewage ingoing to a WWTP, was added to synthetic solutions of perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorobutanoic acid (PFBA), and perfluorobutanesulfonic acid (PFBS). The adsorption capacity was of 996 mg/g. Teng et al. also evaluated the competitive adsorption of this material, which was found to prefer COD to perfluoroalkyl structures, putting the selectivity of the latter in order according to the length of the molecule: PFOA > PFOS > PFNA > PFBS > PFBA. It was noted that the processing yields of the material increased with exposure to the sun. Sini et al. [50] tested a zirconium-based MOF activated with HCl for PFOA and PFOS abatement. The adsorption capacity of the tested materials ranged from 160 to 743 mg/g. The main adsorption mechanism was the hydrophobic interactions between the pollutant and the cavities in the MOF structures. Meng et al. [51] used magnetic adsorbent materials composed of PAC + Fe_3O_4 in proportions of 3:1, obtaining good adsorption rates and an efficiency of 1.63 nmol/g for PFOS and 0.21 nmol/g for PFBS, respectively. The tested perfluoroalkyl solutions were synthetic with an initial concentration of 0.3 nmol/L. The experiments were carried out in batches using 5 mg of magnetic adsorbent in 35 mL of solution. The noticeable difference in the use of this material was the possibility of being separated by a magnet at very low management costs and then regenerated. Clarck et al. [52] tested the adsorption of PFOS and PFBS via structurally defective MOFs activated with HCl with a specific surface area of 1423 m^2/g and an adsorption capacity between 1.24 and 6.23 nmol/g. Badruddoza et al. [53] tested a multifunctional magnetic MOF sorbent for the adsorption of PFOS and PFOA. The adsorption capacity was 13.2 mg/g for PFOS and 2.5 mg/g for PFOA. According to this study, the mechanism underlying the removal yields was the hydrophobic interactions between the perfluoroalkyl molecules and the MOF active sites and electrostatic attraction. Du et al. [54] tested a magnetic fluorinated adsorbent that fits both synthetic substrates and real wastes with an initial PFAS concentration of 22.5 mg/L. The maximum removal yield was 3759.4 mg/(g·h), finding an adsorption hierarchy in line with that already shown, namely, PFAS > PFOS

> PFOA > PFBS > PFBA. Qian et al. [55] tested a model of coabsorption of PFOS and phosphates by using a basic aluminum oxide boehmite. The specific surface of the material was 299.2 m^2/g, and the pore size was 37 µm. The experiments were carried out in batches at a volume of 30 mL with an adsorbent dosage of 2 g/L initial concentrations of PFOS and PO_4^{3-} of 300 µg/L and 50 mg/L, respectively, making them vary with incremental steps over time. Adsorption was facilitated by an acid environment, and the amount absorbed decreased with increasing temperature, in fact demarcating that adsorption is an exothermic reaction. Feng et al. [56] tested boron nitride as an adsorbent for PFOS and PFDA with an initial concentration of 50 mg/L. The experiments were conducted in batches in 10 mL centrifuge tubes with yields of 0.72 mg/m^2 for PFOS and 0.45 mg/m^2 for PFDA; also, for this material, the mechanism underlying the process of adsorption was the electrostatic attractions. Licato et al. [57] tested a composite material of zeolite and sodium silicate for the adsorption of molecules of perfluoroalkyl nature from three matrices, one of which was synthetic and two real from WWTP. The experiments were conducted in batches in triplicate to confirm the obtained results. The concentration of PFAS in the samples ranged from 92 to130 µg/L with a removal yield equal to 72% and an adsorption capacity between 13.6 and 18.3 mg/g. Chang et al. [58] tested a new organic metal structure, MOF808, for the adsorption of PFOS. The experiments were carried out in batches in duplicate from synthetic solution with an initial concentration of PFOS equal to =50–500 mg/L. The optimal obtained pH was between 2 and 7, while the adsorption capacity varied between 833 and 939 mg/g. The specific surface of MOF808 was very high (1610 m^2/g) with an electrostatic attraction adsorption mechanism.

3.1.4. Functionalized Organic Polymers

An organic polymer, in general, has covalent bonds, which allow the formation of unique structures, such as long carbon chains that, linked to a reticular structure, allow the creation of materials with a high specific surface. Liu et al. [59] tested a new synthetic adsorbent material consisting of an organic polymer functionalized with fluorine and amine. The composite has a very high surface area equal to 479 m^2/g. The tests were carried out in batches with pH conditions equal to 3: with an initial concentration of PFOA equal to 1 mg/L, the adsorption capacity was 107 mg/g. Ateia et al. [60] have synthesized a new synthetic adsorbent consisting of a polyacrylamide hydrogel capable of removing 16 types of PFAS with a concentration lower than 1000 ng/g. The experiments were carried out in batches with an adsorbent concentration equal to 70 mg/L. They also observed a removal of sulphonated PFAS better than those of carboxyl nature. Lei et al. [61] tested the adsorption of PFOA on graphene oxide modified with polyethyleneimine; the adsorption was guaranteed by the presence of the amino groups. The surface area of this activated material was 263.77 m^2/g, and the adsorption capacity was 368.2 mg/g. The experiments were conducted in batches with a PFOA concentration of 50 mg/L. The adsorption that occurred through electrostatic attraction was inhibited by the presence of humic acid (HA), background salts, and soluble ions. Kong et al. [62] studied the removal of PFOS from an aqueous matrix, thanks to the use of a covalent organic polymer modified with tetraethylenepentamine; also, in this case, the presence of amino groups guaranteed excellent purification yields equal to 99%, thanks to a surface area of 180 m^2/g and an adsorption rate of 6.45 nmol/(g·h).

It should be kept in mind that the maximum concentration allowed for industrial discharge today is as follows:

- Perfluorooctane sulfonic acid (PFOS) 0.03 µg/L;
- Perfluorooctanoic acid (PFOA) 0.5 µg/L;
- Perfluorobutanoic acid (PFBA) 0.5 µg/L;
- Perfluorobutanesulfonic acid (PFBS) 0.5 µg/L;
- Sum of other PFAS 0.5 µg/L.

Techniques that lead, after treatment, to concentrations higher than those indicated above are to be considered inadequate also for wastewater.

Table 1. Adsorbent materials: GAC, PAC, functional clays, metal–organic adsorbents, and functionalized organic polymers.

Macrocategory	Type of Adsorbent Materials	Type of Treated Water	Operating Condition	Adsorption Capacity	Publication
Adsorbent materials, GAC, and PACS	GAC and PAC + ozone	Synthetic solution	Batch, 22 families of PFAS tested, initial concentration of 840 ng /L, pH 3–12	\	[41]
	R-GAC	Wastewater	Column tests–Semi Batch, PFOS, PFOA, PFBS, PFBA tested, initial concentration of 0.032 mmol/L, pH 2–8	0.35 nmol/g	[42]
	PAC	Synthetic solution	Batch, PFOA tested, initial conditions: 0.5 µM PFOA, pH 1.0–13.0	\	[43]
	PAC + and ion exchange resins + polymeric adsorbents	Synthetic solution	Column tests–Semi Batch, PFOS tested, concentration varying at 1–1000 mg/L	\	[44]
Functional clays	Ionic-liquid-modified natural clay	Synthetic solution	Batch, PFOA and PFOS tested, initial concentration of PFOA or PFOS was 1 mg/L, pH 5	\	[45]
	Activated clays	Refinery waters	Batch, PFOS tested, initial concentration in the range 5–300 mg/L, pH 7.8	163 mg/g	[46]
	Polymer clay functionalized	Urban rainwater	Column tests–Semi Batch, PFOA and PFOS tested, pH 7.5	\	[47]
Metal–organic and inorganic adsorbents	Bilayer hydroxides of magnesium (Mg) and aluminum (Al)	Synthetic solution	Batch, PFOA tested, initial concentration of PFOA was 20 mg/L, pH 2–12	244 mg/g manganese–667 mg/g aluminum	[48]
	Adsorbent materials coated with zinc oxide	Wastewater	Batch, PFOA PFOS PFBA PFBS tested, concentration of PFOA PFOS PFBA PFBS from 20 to 175 mg/L, pH 6.8	996 mg/g	[49]
	Organic zirconium—metal structures	Synthetic solution	Batch, PFOA and PFOS tested, initial concentration of PFOA or PFOS was 100–1000 mg/L, pH 4	743–160 mg/g	[50]
	PAC + Fe_3O_4	Synthetic solution	Batch, PFOS PFOA PFHxS PFBS tested, initial concentration of PFOS PFOA PFHxS PFBS was 0.21–1.63 nmol/g, pH 3–10	1.63 nmol/g for PFOS and 0.21 nmol/g for PFBS	[51]
	Organic metal structures	Synthetic solution	Batch, PFOS and PFBS tested, initial concentration of 500 mg/L, pH 3–5	1.24 and 6.23 nmol/g	[52]
	Organic metal structures	Synthetic solution	Batch, PFOS PFOA tested, initial concentration of 40–1000 mg/L, pH 5.5	13.2 mg/g for PFOS and 2.5 mg/g for PFOA	[53]
	Magnetic fluorinated adsorbent	Wastewater + synthetic solution	Batch, PFOS PFOA PFBA PFBS tested, initial concentration of 25 mg/L, pH 6	\	[54]
	Basic aluminum oxide boehmite	Synthetic solution	Batch, PFOA tested, initial concentration 300 of mg/L, pH 3–10	\	[55]
	Boron nitride	Synthetic solution	Batch, PFOS and PFDA tested, initial concentration of 50 mg/L, pH 6	\	[56]
	Zeolite and sodium silicate	Wastewater + synthetic solution	Batch, 12 families of PFAS tested, initial concentrations of PFAS 92–130 ng/L	13.6 and 18.3 mg/g	[57]
	Organic metal structure	Synthetic solution	Batch, PFOS tested, initial concentration 50–500 mg/L, pH 2–7	833–939 mg/g	[58]
Functionalized organic polymers	Organic polymer functionalized with fluorine and amine	Synthetic solution	Batch, PFOA tested, initial concentration of 1 mg/L PFOA, pH 3	107 mg/g	[59]
	Polyacrylamide hydrogel	Wastewater	Batch, 16 families of PFAS tested, initial concentration of 1 mg/L, pH 6.5–7	\	[60]
	Graphene oxide modified with polyethyleneimine	Synthetic solution	Batch, PFOA tested, initial concentration of 10–100 mg/L, pH 3–12	368.2 mg/g	[61]
	Covalent organic polymer modified with tetraethylenepentamine	Synthetic solution	Batch, PFOS tested, initial concentration 1.15 mmol/L, pH 3–10	6.45 nmol/g	[62]

3.2. Adsorbent Materials from Pyrolysis of Biomass: Biochar

From an environmental perspective, as well as in the light of the circular economy, the elective choice to treat PFAS is to resort to biochar adsorbent materials. In the current literature, we can distinguish two main approaches: (i) biochar from agricultural or food residues and (ii) biochar from sludge treatment. In accordance with the definition of the European Biochar Certificate, a biochar must be considered a heterogeneous material rich in aromatic and mineral systems. It is obtained by pyrolysis of sustainably produced biomass under controlled conditions and with clean technology; it has properties thanks to which it can be used for all purposes that do not require rapid mineralization into carbon dioxide, and it retains its characteristics, which also make it an effective soil conditioner. Subsequently summarized in Table 2.

3.2.1. Biochar from Agricultural or Food Residues

Biochar from agricultural waste or food processing residues is by far the most used material today. The large carbon content contained within the organic material allows the formation of carbon-based reticular structures, which in turn allow for obtaining a material characterized by a good number of cavities and, therefore, a high specific surface. Wu et al. [63] tested the removal of a long-chain perfluoroalkyl molecule PFOA by adsorbent materials from recovered raw materials (leaves, wooden material, biosolids) added with $FeCl_3$ to help the formation of carbon nanotubes, leading to an increase in the specific surface of about 8 times compared with traditional adsorbent materials. The tests were carried out in batches with an initial concentration between 10 and 2000 µgPFOA/L; the pH was kept around 5 and the adsorption temperature between 30 and 50 °C. The adsorption capacity of the tested material varied between 39.5 and 469.5 µmol/g, depending on the initial concentration of the pollutant to be removed. Steigerwald et al. [64] prepared biochar from spent coffee peat activated with different alkali agents at different temperatures for PFOS removal. The samples were pyrolyzed at temperatures of 400, 600, and 800 °C and subsequently activated with KOH and NaOH, followed by a neutralization phase with HCl. The maximum adsorption capacity equal to 43.4 mg/g was obtained with the biochar obtained with pyrolysis at 400 °C and with activation by KOH. The treatment yields on the perfluoroalkyl molecule reached a value of 99.6% against an initial concentration of PFOS varying between 2 and 8000 µg/L. In this case, it has been observed that, in the case of competitive adsorption, the biochar prefers the removal of the organic substance, leading to a reduction in the removal yields of PFAS substances. Zhou et al. [65] evaluated the removal of perfluoroalkyl molecules by adsorption from biochar obtained starting from coconut shells pyrolyzed at a temperature of 950 °C and activated with two alkaline agents, namely, NaOH and KOH. The obtained material showed an adsorption capacity on PFOA of 1269 µg/g and yields after a contact time of 30 min of 90% for the long-chain molecules and 60% for the short-chain molecules compared with an initial concentration in the wastewater to be treated of 50 µg/L. The performance after the coal regeneration phase was also evaluated; in this case, the PFOA abatement yields (long-chain molecule) were 65%. Zhang et al. [66] tested the removal of two perfluoroalkyl molecules (PFOA and PFOS) by adsorption from biochar produced from wood processing waste. The experiments were conducted in batches with the use of 7.5 mg of biochar in 150 mL of synthetic solution to be treated. Additionally, in this case, it was noted that the adsorption of PFAS increased with a decrease in pH and that the removal by adsorption of the perfluoroalkyl substances undergoes the competitive effect of the organic substance. It must be noted that this effect is less perceived in the case of treatment of PFOA and PFOS, representing two long-chain molecules. The adsorption capacities obtained were 123.5 µmolPFOS/g and 86.2 µmolPFOA/g for PFOA and PFOS, respectively. Liu et al. [67] tested four adsorption process strategies based on silica sand, zerovalent iron, biochar, and a mixture of biochar and zerovalent iron. Biochar alone was the best for PFAS removal. The experiments were conducted in batches on real wastewater from WWTP with an initial PFOA concentration of 50 µg/L. Inyang et al. [30] investigated the removal of short-chain perfluoroalkyl molecules, such as PFAA, PFBA, PFPnA (perfluoropentanoate), PFHxA (perfluorohexanoic acid), and long chains such as PFOA and PFOS. Removal was tested using biochar obtained by pyrolysis from hardwood and pine wood. Experiments were carried out both in batches and in pilot scale as a tertiary refinement treatment for a period of 18 months. The abatement yields amounted to approximately 70% in both tested conditions. Du et al. [68] tested the removal of the perfluoroalkyl molecule (PFOS) from wastewater derived from the chrome plating industry. The biochar was obtained from pyrolyzed coconut processing waste at a temperature between 800 and 1000 °C and activated with an alkaline agent (KOH). Experiments were conducted in batches using 200 mL of substrate to be treated with an initial concentration of PFOS of 44.1 µg/L and 10 mg of biochar. The treatment yields were equal to 93.3% with an adsorption capacity of 267.2 µg/g.

3.2.2. Biochar from Biosolids of WWTP

Biosolids are generally used to define "sewage sludge". The term "sludge" refers to a liquid that does not undergo further treatments, while the term "biosolids" indicates a residue that has undergone refinement, such as aerobic or anaerobic digestion, alkaline stabilization, thermal drying, oxidation/acid disinfection, and composting [69]. Biochar from biosolids represents an interesting alternative to biochar made from agricultural waste as it appears to be a waste material with no other destination than its use as a soil improver in agriculture. Furthermore, the high content of heavy metals in addition to the presence of molecules of organic nature (high carbon content) inside the sludge coming out from a WWTP could lead to the formation of numerous biochar sites during the biochar formation phase. Mohamed et al. [70] tested the application of recovered adsorbent materials obtained from the pyrolysis of sewage sludge. The tests were conducted in batches with an initial PFAS concentration of 50 µg/L. The biochar was tested with both a powder configuration, like PAC, and a granular configuration (like GAC). The smaller granulometry configuration allowed for obtaining better yields, which amounted to around 91% at a time of about 15 min with better performance compared with molecules with longer chains. It was also observed that the adsorption of PFAS increased with the increase in temperature between 5 and 35 °C. The advantage of this application was the very low cost of adsorbent materials made from biosolids, estimated to be around EUR 1.2/kg. Zhang et al. [71] tested the removal of two perfluoroalkyl molecules (PFOA and PFOS) by aluminum-based wastewater treatment residues. The experiments were conducted in batches with a pH equal to 3, an initial concentration of PFOA/PFOS of 1 mg/L, and a volume to be treated of 600 mL in contact with 6 g of adsorbent material. The adsorption capacity was 0.232 µgPFOA/g and 0.316 µgPFOS/g with an adsorption time of about 2 h. Thanks to leaching tests, a possible release of PFOA/PFOS from the adsorbent material was also evaluated, finding that the adsorption was effectively irreversible. Hassan et al. [72] tested the monolayer and multilayer adsorption process from biochar produced by pyrolysis at 600 °C for 2 h of woodworking waste and woodworking waste mixed with red mud at refinery output. Despite the strong difference in surface area between the two materials, the first has 395 m^2/g, while the mixed biochar has an area of 120.7 m^2/g, and the adsorption was higher for the second material probably due to a greater chemoabsorption, thanks to the presence of Fe_3O_4. The primary mechanism of adsorption was hydrophobic interaction, while the aromatic structure was noted to enhance adsorption by nonionic interaction. It was also noted that metal-based functional groups improve adsorption capacity through ion exchange and electrostatic interactions.

Table 2. Biochar adsorbent materials: agricultural or food residues and residues of sludge treatment.

Macrocategory	Type of Adsorbent Materials	Type of Treated Water	Operating Condition	Adsorption Capacity	Publication
Biochar from agricultural or food residues	Raw materials (leaves, wooden material, biosolids) added with $FeCl_3$	Synthetic solution	Batch, PFOA tested, initial concentration 2 mg/L, pH 3–7	39.5 and 469.5 μmol/g	[63]
	Spent coffee peat	Synthetic solution	Batch, PFOS tested, initial concentration of 240 mg/L, pH 7	43.4 mg/g	[64]
	Coconut shells	Wastewater	Batch, PFOA tested, initial concentration 100 mg/L, pH 3.8	1269 μg/g	[65]
	Wood	Synthetic solution	Batch, PFOA PFOS PFBA PFBS tested, initial concentration of 1 mg/L, pH 3–9	123.5 μmolPFOS/g and 86.2 μmolPFOA/g	[66]
	Biochar and a mixture of biochar	Wastewater	Batch, PFOA and PFOS tested, initial concentration of 50–100 mg/L, pH 7–9	\	[67]
	Hardwood and pine wood	Wastewater	Batch and in pilot scale, PFOA PFOS PFAA PFPnA PHxA PFBA PFHxA, initial concentration of 0.01–10,000 μg/L, pH 6.8–7.2	\	[30]
	Coconut	Wastewater	Batch, PFOS tested, initial concentration of 44.1 mg/L, pH 8.6	267.2 mg/g	[68]
Biochar from sludge depuration	Sewage sludge	Synthetic solution	Batch, families of 9 PFAS, initial concentration of 50 μg/L	\	[70]
	Wastewater treatment residues	Synthetic solution	Batch, PFOA PFOS tested, initial concentration of 1.0 mg/L, pH 3	0.232 mgPFOA/g–0.316 mgPFOS/g	[71]
	Woodworking waste and woodworking waste mixed with red mud at refinery output	Synthetic solution	Batch, PFOS tested, initial concentration of 4.57–45.7 mg/L, pH 3.1	\	[72]

4. Discussion

In this work, we have reviewed many studies concerning alternatives for the treatment of liquid matrices contaminated by perfluoroalkyl substances. Figure 3 shows the temporal and spatial distribution of the papers that have been reviewed. After a careful analysis, it has been noticed that no alternatives were proposed to the transfer of the pollutant from a liquid matrix to a solid matrix through a chemicophysical adsorption process. Therefore, there is concentrated attention to research works that propose the removal of these persistent pollutants, thanks to the use of virgin adsorbent materials, functionalized inorganic materials, and synthetic engineered materials. Such materials should have both a high specific surface area and, considering biochar-based composites obtained using waste products, a high carbon content. Among the newly synthesized carbon-based materials, the application of MOFs particularly stands out. The use of a material that combines the organic substance, characterized by a high carbon content, and the presence of metals leads to the formation of many active sites [73], which by electrostatic attraction can retain the perfluoroalkyl molecules, above all with longer chains. Furthermore, the presence of a metal component allows for great application advantages: in fact, the coal can be separated, thanks to a magnetic force, and then be regenerated [74]. The active surface of regenerated adsorbent materials is always smaller than the surface of virgin adsorbent materials [75]. Adding this aspect to the fact that the perfluoroalkyl molecules with shorter chains are able to resist the thermal treatments of carbon regeneration and are very often found in the fumes [76], the use of adsorbent materials made from recycled material, biochar, is highly advisable. Among the biochar, the performance of adsorbent materials, the ones obtained by agricultural material waste, was evaluated. This type of biochar, starting from materials with a high cellulose content [77], has a great advantage to possess a high specific surface area. In the engineered materials obtained by the purification of wastewater, on the other hand, the carbon content is slightly lower as it is a residual product of the oxidation/reduction treatment of the organic substance. However, the high metal content makes this mixture very interesting, since the mixture of metals and organic matter in the pyrolysis phase leads to the formation of numerous active sites. The possibility of using residues from wastewater treatment (mainly biosolids), enhanced thanks to thermal activation, combustion, or pyrolysis, fits perfectly into the concept of circular economy, which provides for the use of resources within the production cycle that originated them [24]. The biochar produced from biological sludge can be used as a polishing stage to increase the overall performance and to obtain the removal of emerging pollutants resistant to conventional treatments, such as perfluoroalkyl substances. A new possibility is the synthesis of adsorbent materials. Green, renewable, and sustainable materials are newly synthesized biopolymers to remove per- and polyfluoroalkyl substances (PFAS) from water [78]. The possible reuse of PFAS after their transfer from the liquid phase to the solid phase remains one of the still-unresolved questions in the panorama of scientific research.

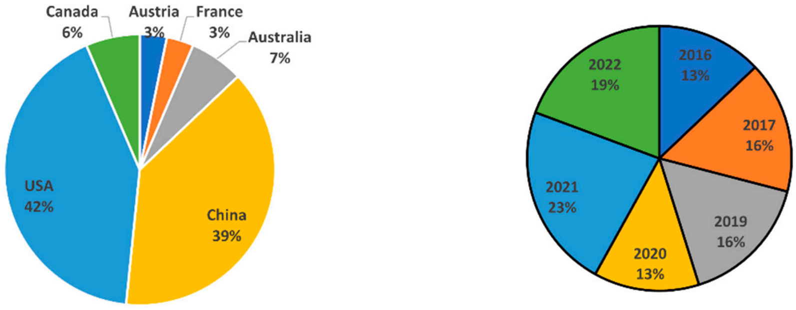

Figure 3. Spatial (**left**) and temporal (**right**) distributions of the reviewed paper.

5. Conclusions

In this review, we have systematically analyzed the treatment of PFAS in wastewater given the high contents found in landfill leachates, which suggest their presence for the next few years [78].

The comparison between the two groups of materials showed that conventional treatments based on virgin adsorbent materials have a higher adsorption capacity, but also much higher implementation costs than the biochar-based solutions. Moreover, since the reactivation of carbon after PFAS adsorption is hardly achievable, the use of biochar, which is a residual product of other industrial processes, appears to be a cost-effective and promising solution.

In conclusion, since the C–F bond is difficult to biodegrade, the treatment really applicable to already-existing wastewater treatment plants for high-performance PFAS-contaminated water is the removal of the molecules with adsorbent materials. All in all, this is a transfer from a liquid to a solid matrix, achieved by flocculation and coagulation, thus obtaining a more concentrated form. The solid matrix is easier to manage and store but does not carry out a real degradation of the micropollutants especially in relation to the short-chain molecules of the perfluoroalkyl substances. Therefore, as a recommendation, at least in the long run, the main strategy should be to reduce or eliminate the PFAS from the production line of the different industrial processes. Even this recommendation is certainly not a novelty; it is still actual and needs to be transferred from theory to practice in real-scale plants.

6. Future Directions

In future research, it is advisable to devote efforts towards the reuse of sewage sludge and biochar adsorbent materials for PFAS removal. The analysis of the literature suggests that this strategy may lead to decreasing the costs of sewage sludge disposal and, at the same time, developing a PFAS cleaning treatment that allows for reusing wastewater in agriculture. This strategy fits with the circular economy approach and may combine cost reduction and environment protection.

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