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Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration

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Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration

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Journal

| 1 | Removal of poly- and perfluoroalkyl substances |
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| 2 | (PFAS) from water by adsorption: role of PFAS chain |
| 3 | length, effect of organic matter and challenges in |
| 4 | adsorbent regeneration |
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14 Abstract

Poly- and perfluoroalkyl substances (PFAS) are a wide group of environmentally 15 16 persistent organic compounds of industrial origin, which are of great concern due to their harmful impact on human health and ecosystems. Amongst long-chain PFAS, 17 perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most 18 detected in the aquatic environment, even though their use has been limited by recent 19 regulations. Recently, more attention has been posed on the short-chain compounds, 20 due to their use as an alternative to long-chain ones, and to their high mobility in the 21 water bodies. Therefore, short-chain PFAS have been increasingly detected in the 22 environmental compartments. The main process investigated and implemented for 23 PFAS removal is adsorption. However, to date, most adsorption studies have focused 24 on synthetic water. 25

The main objective of this article is to provide a critical review of the recent peer-26 reviewed studies on the removal of long- and short- chain PFAS by adsorption. Specific 27 objectives are to review 1) the performance of different adsorbents for both long- and 28 short-chain PFAS, 2) the effect of organic matter, and 3) the adsorbent regeneration 29 techniques. Strong anion-exchange resins seem to better remove both long- and short-30 chain PFAS. However, the adsorption capacity of short-chain PFAS is lower than that 31 observed for long-chain PFAS. Therefore, short-chain PFAS removal is more 32 33 challenging. Furthermore, the effect of organic matter on PFAS adsorption in water or wastewater under real environmental conditions is overlooked. In most studies high 34 PFAS levels have been often investigated without organic matter presence. The rapid 35

- 36 breakthrough of PFAS is also a limiting factor and the regeneration of PFAS exhausted
- adsorbents is very challenging and needs more research. 37
- Keywords: 38
- Adsorption; anion-exchange; Long- and short- chain PFAS; organic matter; 39
- regeneration; adsorption mechanism. 40

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76 List of abbreviations

| Main PFAS and alternative compounds | | |
|-------------------------------------|--|--|
| F-53B | Potassium salt of 6:2 chlorinated polyfluorinated ether sulfonate | |
| FOSA | Perfluorooctane sulfonamide | |
| PFAS | Poly- and perfluoroalkyl substances | |
| PFCAs | Perfluoroalkyl carboxylic acids | |
| PFSAs | Perfluoroalkane sulfonates | |
| PFBA | Perfluorobutanoic acid | |
| PFBS | Perfluorobutane sulfonic acid | |
| PFDA | Perfluorodecanoic acid | |
| PFDoDA | Perfluorododecanoic acid | |
| PFDS | Perfluorodecane sulfonic acid | |
| PFHpA | Perfluoroheptanoic acid | |
| PFHpS | Perfluoroheptane sulfonic acid | |
| PFHxA | Perfluorohexanoic acid | |
| PFHxS | Perfluorohexane sulfonic acid | |
| PFNA | Perfluorononanoic acid | |
| PFNS | Perfluorononane sulfonic acid | |
| PFOA | Perfluorooctanoic acid | |
| PFOS | Perfluorooctane sulfonic acid | |
| PFPeA | Perfluoropentanoic acid | |
| PFPeS | Perfluoropentane sulfonic acid | |
| PFTrDA | Perfluorotridecanoic acid | |
| PFUnDA | Perfluoroundecanoic acid | |

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Adsorbent materials

| 2-MNPs@FG | Magnetic-nanoparticles attached into fluorographene (mass ratio of MNPs and FG is 3:5) |
|--|--|
| AC | Activated carbon |
| ACF | Activated carbon fiber |
| ARH | Aminated rice husk |
| BdAC | Bamboo-derived AC |
| CTF | Covalent triazine-based framework |
| DFB-CDP | Cross-linked polymer network where β -Cyclodentrix substitutes decafluorobiphenyl (DFB) |
| Fe ₃ O ₄ NP | Magnetite nanoparticles |
| Fe ₃ O ₄ @SiO ₂ - NH ₂ &F ₁₃ | Silica membrane functionalized with amino group and octyl-perfluorinated chain on the $\rm Fe_3O_4$ NP surface |
| GAC | Granular activated carbon |
| h-BNs | Porous hexagonal boron nitride nanosheets |
| HDPE | High-density polyethylene |

| HMS | Hexagonal mesoporous silica |
|-----------|--|
| HWC | Hardwood biochar |
| MIMs | Macromolecular imprinted materials |
| MIP-CMs | Molecularly imprinted carbon microspheres |
| MWNT | Multi-walled carbon nanotubes |
| NIP-CMs | Non-imprinted carbon microspheres |
| OD-HMS | N-octyldichlorosilane grafted hexagonal mesoporous silica |
| PAC | Powdered activated carbon |
| PACFs | Polyacrylonitrile fiber (PANF)-derived activated carbon fibers |
| PAF-45 | Porous aromatic framework constructed from benzene rings |
| PCMAs | Permanently confined micelle arrays |
| PEI-f-CMC | Poly(ethylenimine)-functionalized cellulose microcrystals |
| PS | Polystyrene |
| PS-COOH | Poly-styrene carboxylic acid |
| PWC | Pinewood biochar |
| R-CAC | Reactivated coconut shell-based AC |
| SWNT | Single walled carbon nanotubes |
| | |
| 0.1 | |
| Other | |
| AE | Anion-exchange |
| AFFF | Aqueous fil-forming foam |
| AOPs | Advanced oxidation processes |

| Other | |
|-------|--|
| AE | Anion-exchange |
| AFFF | Aqueous fil-forming foam |
| AOPs | Advanced oxidation processes |
| ATRP | Atom transfer radical polymerization |
| BET | Brunauer, Emmett and Teller |
| BSA | Bovine serum albumin |
| DBP | Disinfection by-products |
| DI | Deionized water |
| DMC | Methacryloyloxyethyl trimethyl ammonium chloride |
| DOC | Dissolved organic carbon |
| DOM | Dissolved organic matter |
| DW | Drinking water |
| DWTPs | Drinking water treatment plants |
| EBCT | Empty bed contact time |
| EfOM | Effluent organic matter |
| EWTP | Electroplating WWTP |
| FA | Fulvic acids |
| GW | Groundwater |
| HA | Humic acids |
| LW | Lake water |
| MB | Methylbenzene |
| | |

| MPLs | Microplastics |
|---------------------|---|
| ОМ | Organic matter |
| NDMA | N-Nitrosodimethylamine |
| NOM | Natural organic matter |
| NPs | Nanoparticles |
| PFSOF WWW | Perfluorooctanesulfonyl fluoride washing wastewater |
| RSSCT | Rapid small-scale column tests |
| RW | River water |
| SBET | BET surface area |
| SDS | Sodium dodecyl sulphate |
| SeaW | Seawater |
| SUVA ₂₅₄ | Specific ultra-violet absorbance at 254 nm |
| SW | Surface water |
| TCE | Tri-chloroethylene |
| ТЕМ | Transmission electron microscopy |
| TMFA | 2-(trifluoromethyl)acrylic acid |
| тос | Total organic carbon |
| WW | Wastewater |
| WWTPs | Wastewater treatment plants |
| | |
| | |

1. Introduction

82

1.1. PFAS classification

Poly- and perfluoroalkyl substances (PFAS) are a large group of anthropogenic aliphatic 83 compounds that are of increasing concern worldwide due to their impact on 84 environment and human health. For many decades, they have been used in an array of 85 formulations as surfactants intermediates (i.e., firefighting foams, hydraulic fluids for 86 aircrafts), waterproofing treatment for textiles (i.e., apparel, carpet) and household 87 products (i.e., paper and non-stick cookware coating) (Buck et al., 2011; Rahman et al., 88 2014; Xiao, 2017). PFAS contamination is the result of consumer-product degradation, 89 firefighting activities and discharges of fluorochemical manufacturing facilities (Hu et al., 90 2016). 91

PFAS are made up of a chain of varying carbon length, on which at least one 92 (polyfluoroalkyl acids) or all (perfluoroalkyl acids) of the hydrogen atoms bound to 93 carbon-chain in the nonfluorinated substances have been replaced by fluorine atoms 94 (Buck et al., 2011). Their chemical structure also includes a charged functional group 95 commonly carboxylic or sulfonic acids attached at one end. Polyfluoroalkyl acids have 96 also been indicated as "precursors" of perfluoroalkyl ones, hence the non-fluorinated 97 bond provides a biotic or abiotic degradation pathway (ITRC, 2017). Depending on their 98 terminal functional group, PFAS can be distinguished in perfluoroalkyl carboxylic acids 99 (PFCAs) and in perfluoroalkyl sulfonic acids (PFSAs) (Buck et al., 2011). However, an 100 abridged way to distinguish among PFAS subclasses is that referred to carbon-chain 101 102 length. According to the Organization for Economic Co-operation and Development (OECD), the term "long-chain compound" indicates PFCAs with eight or more carbons, 103 and PFSAs with six or more carbons. Whereas, "short-chain" is related to PFCAs with 104

105 seven or fewer carbons and PFSAs with five or fewer carbons (OECD/UNEP Global 106 PFC Group, 2013). It should be noted that PFCAs and PFSAs classification, based on 107 chain length, is different in terms of number of carbon atoms. However, PFAS 108 bioaccumulation and biomagnification into biota increase with the increasing of carbon-109 chain length, PFSAs are more bioaccumulate than PFCAs with the same chain length 110 (Ahrens, 2011).

111

1.2. PFAS properties

The knowledge of PFAS physical and chemical properties is paramount to understand 112 their fate and transport in the environment. The C-F bound is the strongest covalent 113 bond in organic chemistry and it leads to PFAS thermal stability (ITRC, 2017). In 114 addition, PFAS exhibit mutually hydrophobic and lipophobic properties, which are 115 primarily attributed to the low polarizability of fluorine atoms. Moreover, the terminal 116 functional group attached to fluoroalkyl chain provides PFAS chemical stability. With the 117 increasing replacement of hydrogen by fluorine as well as the increasing carbon-chain 118 length, PFAS become more chemically inert. On the contrary, their water solubility 119 increases with the decreasing carbon-chain length (Kucharzyk et al., 2017). PFCAs and 120 PFSAs are characterized by a low vapour pressure, which makes air stripping an 121 122 unsuitable technique for PFAS removal (Rahman et al., 2014). With the increasing C-F chain length, PFAS become more lipophilic as demonstrated by octanol/water partition 123 coefficients (Kow). At environmentally relevant pH, PFAS exhibit anionic species 124 according to their low values of acid dissociation constant (pK_a). Other properties, such 125 as resistance to thermal, biological and chemical degradation and redox stability, impart 126 unique features to PFAS, making them suitable for several industrial applications. 127 Information regarding chemical formulas and Chemical Abstracts Service (CAS) of 128

selected per-fluoroalkyl substances along with their physical and chemical propertiesare reported in Table 1.

131

1.3. Occurrence of PFAS in water

In the aquatic environment, PFAS have been detected at low concentrations ranging 132 from pg L⁻¹ to µg L⁻¹ (Kaboré et al., 2018; Rahman et al., 2014) and long-chain 133 compounds, such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid 134 (PFOA), are the most commonly measured PFAS around the world (ITRC, 2017). 135 Widespread occurrence of PFAS in urban water cycle including wastewater (WW), river 136 water (RW), lake water (LW), drinking water (DW), stormwater, and groundwater (GW) 137 has been demonstrated by several studies (Appleman et al., 2014; Arvaniti and 138 Stasinakis, 2015; Ateia et al., 2019; Hölzer et al., 2009; Munoz et al., 2017; Rahman et 139 140 al., 2014). The amount of PFAS not removed in wastewater treatment plants (WWTPs) and, consequently, released into the receiving environment is a concern for the possible 141 presence of these compounds in water used for potable supply production. 142

A recent research suggests that the possible impacts of PFAS on GW is linked to the use of treated WW for irrigation (Szabo et al., 2018). The occurrence and distribution of PFAS remain not completely identified, due to the limited data about the removal efficiency of conventional water treatment plants and about the transformation of PFAS precursor compounds (Appleman et al., 2014; Arvaniti and Stasinakis, 2015).

Although the use of PFOS and PFOA has been reduced due to their health impact, the total amount of PFAS introduced into the environment has not been reduced because the long-chain compounds have been replaced by short and ultra-short PFAS (Ateia et al., 2019). The latter are potentially less bioaccumulated and bioconcentrated through

- trophic levels as compared to long-chain but they are still environmentally persistent
 (Brendel et al., 2018; OECD/UNEP Global PFC Group, 2013).
- 154

1.4. PFAS toxicity

PFAS are absorbed in human body after oral ingestion, they are not metabolized and 155 they are detected in human tissue and blood serum at typical concentrations of ng mL⁻¹. 156 Long-chain PFAS are taken up and stored preferentially in the liver. Half-life values of 157 PFOS and PFOA in humans range from 2.3 to 5.4 years (Hölzer et al., 2009; Stubleski 158 et al., 2017). Epidemiological studies have shown that the occurrence of PFOA and 159 PFOS in humans is probably linked to a high incidence of thyroid disease, high 160 cholesterol, ulcerative colitis, kidney cancer, testicular cancer, and pregnancy-induced 161 hypertension (Crawford et al., 2017; Domingo and Nadal, 2017). More details 162 concerning PFAS toxicological properties are reported in literature (Dewitt, 2015). 163

Based on WHO's recommendation and on the precautionary principle, the proposal for 164 a recast of the Drinking Water Directive (98/83/CE, Directive on the quality of water 165 intended for human consumption) published on 1st February 2018, has included the 166 group of poly- and perfluoroalkyl substances in the list of regulated chemicals. The 167 proposal recommends the values of 0.5 μ g L⁻¹ for the total amount of PFAS and 0.1 μ g 168 L⁻¹ for each single compound. In 2017, the Veneto Region (Italy) set drinking water 169 guality standards for PFAS (Veneto Legislation 1590/201), with a limit value of 90 ng L⁻¹ 170 for PFOA and PFOS (with PFOS < 30 ng L^{-1}), and a limit value of 300 ng L^{-1} for the 171 other PFAS (sum of PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFHxS, PFNA, PFDeA, 172 PFUnA, PFDoA). Such regulation came after a large contamination of surface water 173 and GW due to industrial WW discharges, with the subsequent bioaccumulation of 174

175 PFAS in the serum of the exposed population. As a result, PFAS are emerging 176 contaminants already regulated in Italy.

177

1.5. PFAS removal

Conventional treatment processes are ineffective for PFAS degradation due to the high 178 straight of the covalent C-F bond of their chain, their low concentration in water and 179 their high hydrophilicity (Rahman et al., 2014; Ross et al., 2018). Biological treatment 180 both aerobic and anaerobic are only able to break the C-C bond, and they lead to the 181 formation of short-chain PFAS. When advanced treatment technologies are not 182 implemented, biological WWTPs affect the receiving water bodies and the concentration 183 of PFAS detected in finished water is often higher than in the untreated water (Arvaniti 184 and Stasinakis, 2015; Kaboré et al., 2018). This fact gives evidence to recalcitrant 185 behaviour of PFAS to biological treatment and, consequently, their formation via 186 biodegradation of precursor compounds (Rahman et al., 2014). According to data 187 obtained from monitoring studies, PFAS with long carbon-chain, such as PFOS, tend to 188 accumulate in sludge, whereas perfluorobutane sulfonic acid (PFBS) has been mainly 189 detected in the effluents of WWTPs and in drinking water treatment plants (DWTPs) 190 (Arvaniti and Stasinakis, 2015; Rahman et al., 2014). 191

Under typical water treatment plant conditions, disinfection by free chlorine or UV irradiation are ineffective (Appleman et al., 2014; Rahman et al., 2014). PFAS are also much more resistant than other micro-contaminants to the oxidation by ozone and hydroxyl radicals due to the strong C-F bond and the electron withdrawing of their functional groups (Nzeribe et al., 2019; Trojanowicz et al., 2018). Furthermore, advanced oxidation processes (AOPs) often result in a partial degradation of PFAS,

with formation of PFAS with shorter perfluorinated alkyl chain (Nzeribe et al., 2019;
Trojanowicz et al., 2018).

Adsorption, anion-exchange (AE), high pressure nanofiltration and reverse osmosis membrane processes are effective for substantial PFAS removal (Appleman et al., 202 2013; Du et al., 2014; Kucharzyk et al., 2017).

Main issues inherent with PFAS removal through these mentioned techniques are the influence of water matrix (i.e., competing anions, organic matter), frequent regeneration (due to fast breakthrough), and disposal of concentrate with high PFAS concentration (Appleman et al., 2013; Rahman et al., 2014; Zaggia et al., 2016).

Adsorption is actually an established technology for PFAS removal, both as single process of point-of-use applications and as step of water treatment plants (Arvaniti and Stasinakis, 2015; Eschauzier et al., 2012; Quiñones and Snyder, 2009). Moreover, it shows a more economical performance compared to high pressure membrane processes (Rizzo et al., 2019; Roccaro et al., 2013).

As previously mentioned, PFAS exist as anions at ambient pH values and this makes strong base AE resins suitable for their removal. However, AE treatment efficiency depends on the resin properties, including porosity, functional group and polymer matrix (Deng et al., 2010).

To date, adsorption studies have addressed single long-chain PFAS (i.e., PFOA and PFOS), even though long- and short-chain co-removal requires further investigation (Ateia et al., 2019; Maimaiti et al., 2018; McCleaf et al., 2017). Moreover, many compounds, commonly present in water bodies, could affect adsorption efficiency and

additional studies should regard their potential competition (Ateia et al., 2019; Du et al.,
2015, 2014; Yu et al., 2012).

222

2. PFAS adsorption and scope of the review

223 **2.1. PFAS adsorption mechanism**

Electrostatic and hydrophobic interactions are considered the predominant forces that govern adsorption of PFAS on several adsorbent materials. Other less important mechanisms of PFAS adsorption are hydrogen bonding and covalent bonding. PFAS molecular structure, adsorbent chemistry and physical properties (i.e., surface functional groups, polarity, and porosity), as well as liquid phase composition should be considered as the main factors affecting PFAS adsorption efficiency (Du et al., 2014).

Electrostatic interactions occur between anionic PFAS and adsorbent material positively 230 charged. Consequently, any changes in ionic strength (i.e., co-existing inorganic anions 231 and changing solution pH) could affect adsorption efficiency, due to electrostatic 232 repulsions (Du et al., 2014). Change in solution pH has an effect on the charge 233 characteristics of PFAS molecules and surface properties of adsorbents (Liu et al., 234 2018; Yu et al., 2008). As reported in several studies, an increase in pH solution led to a 235 decrease in adsorption capacity of most adsorbents (Deng et al., 2010; Gao et al., 236 2017; Qian et al., 2017). Nevertheless, an increase of ionic strength ascribed to the 237 presence of monovalent and divalent cations (i.e., Na⁺, K⁺, Ca²⁺, Mg²⁺) might enhance 238 the PFAS removal due to the compression of the electrical double layer (Du et al., 2014; 239 Xiao et al., 2011). The salting-out effect should be also mentioned as reported in 240 previous studies (Carter and Farrell, 2010; Chen et al., 2016). This effect occurs at high 241 salt concentrations and it involves a decline of PFAS solubility and, consequently, their 242 adsorption on adsorbent surface could be encouraged (Du et al., 2014). It is clear that 243

the presence of inorganic anions (i.e., Cl⁻ and SO⁴⁻) involves a competition with PFAS for adsorption sites (Deng et al., 2010; Gao et al., 2017). However, the worsening of PFAS removal occurred when solution pH was higher than point of zero charge of the adsorbents, due to the establishment of electrostatic repulsions (Chen et al., 2017; Zhou et al., 2009).

Electrostatic repulsions between anions PFAS and negatively charged surfaces can be overcome through hydrophobic interactions of fluorinated chain (Zaggia et al., 2016). Moreover, removal efficiency of individual PFAS into adsorbent materials depends on the compound functional groups and C-F chain length. In detail, PFSAs are removed better than PFCAs, and long-chain compounds with the same functional group are more efficiently removed than short-chain ones (Appleman et al., 2014; Du et al., 2014; McCleaf et al., 2017; Xiao et al., 2011; Zaggia et al., 2016).

256 Hydrophobic effect has been found to increase with the increasing C-F chain length (Du et al., 2014; McCleaf et al., 2017; Rahman et al., 2014). This was also demonstrated in 257 a prior work that investigated the competitive adsorption among PFAS with different 258 chain length on kaolinite (Xiao et al., 2011). The authors argued that, due to a stronger 259 hydrophobic interaction with the tested adsorbent, the longer-chained PFAS 260 outcompeted the shorter during adsorption. Based on PFAS functional group, the 261 presence of one more C-F bond in PFSAs compared to corresponding PFCAs results in 262 stronger hydrophobic properties and increasing adsorption of PFSAs (Chen et al., 2016; 263 Zaggia et al., 2016). Moreover, strong hydrophobic interactions favour the formation of 264 molecular aggregates during PFOA and PFOS removal, while highly hydrophilic 265 compounds, such as PFBA and PFBS, are removed as single molecules on adsorbent 266

active sites (Du et al., 2014). Exceeding the critical micelle concentration (c.m.c) may 267 lead to the formation of multilayer structures (i.e., micelles and hemi-micelles) on 268 adsorbent surfaces that may play an important role in PFAS adsorption (Appleman et 269 al., 2014; Deng et al., 2013; Du et al., 2014). However, at the PFAS environmental level 270 the formation of micelles is unlikely and only aggregates have been observed (Zaggia et 271 al., 2016). McCleaf et al. (2017) reported that PFAS adsorption process may include 272 two distinct phases. Initially removal occurs through PFAS adsorption on open sites of 273 adsorbents, gradually pore sites become clogged and removal becomes a function of 274 molecular aggregation of PFAS (McCleaf et al., 2017). 275

Since electrostatic negativity is originated from PFAS functional head and hydrophobic 276 interaction is linked to C-F chain, the electrostatic interactions seem to be dominant for 277 short-chain PFAS, while longer PFAS are adsorbed through hydrophobic interactions, 278 279 which favour the formation of molecular aggregate on the active surface (Deng et al., 2012; Du et al., 2014; Zaggia et al., 2016). 280

2.2. 281

Scope of the review

An important limitation of prior research on PFAS adsorption is that the evaluation of 282 adsorption efficiency has been explored at high PFAS concentrations, which are not 283 representative of the environmental concentration level. Furthermore, very high doses 284 of adsorbents have been used which do not reflect the actual water treatment plant 285 adsorption processes (Rahman et al., 2014). 286

Another relevant limitation of prior researches is that the experiments have often been 287 carried out by using deionized water (DI) spiked with selected PFAS, and the effect of 288 organic matter (OM) was not accounted for (Du et al., 2014). Recent studies have 289 shown that OM may not affect PFAS removal (Sgroi et al., 2018a) or may positively 290

influence the PFAS adsorption (McCleaf et al., 2017). However, natural organic matter (NOM) and effluent organic matter (EfOM) often play a competitive role in the adsorption process (Appleman et al., 2013; Kothawala et al., 2017). Therefore, a critical review of the published data is needed to better understand the OM effect on long- and short-chain PFAS removal.

Furthermore, the regeneration of adsorbents exhausted by PFAS is not fully addressed (Woodard et al., 2017). Since PFAS breakthrough is fast, adsorbent regeneration is a very important and challenging task.

Previous published review papers deals with PFAS classification and origins (Buck et 299 al., 2011; Xiao, 2017), their occurrence and fate in aquatic environments (Ahrens, 2011; 300 Arvaniti and Stasinakis, 2015; Rahman et al., 2014) and the treatment technologies for 301 long-chain PFAS removal (Appleman et al., 2014; Kucharzyk et al., 2017). A critical 302 303 review concerning PFAS adsorption previously published is mainly concerned with PFOS and PFOA (Du et al., 2014) and it does not include recent scientific findings on 304 OM effect as well as the performance and the regeneration of novel adsorbents. 305 Recently, the removal of short-chain PFAS by different processes, including different 306 adsorbents, has been critically reviewed by Ateia et al. (2019). However, such prior 307 review papers concerning PFAS adsorption were not focused on the role of PFAS chain 308 length, OM effect and adsorbents regeneration. 309

Therefore, the objective of this paper is to critically discuss data concerning PFAS adsorption with particular focus on: 1) recent published data about adsorption capacity of different materials for both long- and short-chain PFAS; 2) effect of OM on the PFAS adsorption; 3) role of adsorbent regeneration.

314 3. Adsorption of long chain PFAS

3.1. PFOA and PFOS

A number of studies have been carried out worldwide in order to investigate long-chain PFAS removal by adsorption on different materials. PFOA and PFOS are commonly regarded as the most representative PFAS, due to their persistence in the environment and occurrence in industrial applications. A prior review paper indicated that long-chain PFAS (i.e., PFOA and PFOS) have been mainly removed through hydrophobic interactions and adsorbents with amine groups generally have high adsorption capacity (Du et al., 2014).

The adsorption of long-chain PFAS on different adsorbents (commercially available or synthetized) obtained from batch adsorption tests is discussed in the following sections. Table 2 reports the adsorption capacity obtained from published data fitting the Langmuir model along with adsorbent material type and dosage, long-chain PFAS initial concentrations and experimental setups.

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3.2. Activated carbon and biochar

Among commercial adsorbents, activated carbon (AC) has been widely investigated for PFOS and PFOA removal (Liang et al., 2011; Ochoa-Herrera and Sierra-Alvarez, 2008; Rattanaoudom et al., 2012). In detail, powdered activated carbon (PAC) had higher adsorption capacity than granular activated carbon (GAC) for both PFOA and PFOS (Chen et al., 2017; Yu et al., 2009).

Results about adsorption of PFOA on bamboo-derived activated carbon (BdAC) have shown that a long time (about 34 h) was required to reach adsorption equilibrium (Du et al., 2015). The comparison between BdAC and microporous AC revealed that the adsorption capacity of BdAC was higher than that of microporous AC (Du et al., 2015;

Wang et al., 2016). This evidence corroborates that microporous adsorbents are not suitable for removing large molecules (i.e., long-chain PFSAs and PFCAs) and it is in agreement with results from fixed-bed column tests, as detailed below (Appleman et al., 2013; Du et al., 2014; McCleaf et al., 2017; Rattanaoudom et al., 2012; Zaggia et al., 2016).

Chlorinated polyfluorinated ether sulfonate (F-53B) is a PFOS alternative compound. 343 Both F-53B and PFOS compounds have been detected at high concentrations in an 344 actual chrome plating WW (Du et al., 2016a). Electroplating wastewater treatment plant 345 (EWTP), employing reduction reaction (adding Na₂S₂O₅), precipitation (adding 346 $Ca(OH)_2$), and flocculation-sedimentation (adding anionic polyacrylamide, PAM), was 347 unable to effectively remove PFOS and F-53B. Hence, batch adsorption experiments 348 were performed and a commercial coconut shell based GAC (R-CAC), after an 349 activation process at low KOH/C ratio, was selected as adsorbent material for PFOS 350 and F-53B removal (Du et al., 2016a). F-53B is more hydrophobic than PFOS, due to 351 an ether unit in the molecular structure, and this led to a much higher adsorption 352 capacity of F-53B (two-fold higher than PFOS) onto R-CAC (Table 2). Single walled 353 carbon nanotubes (SWNT) are hollow cylindrical tubes, made of graphene layers and a 354 lattice of C atoms, and they have been investigated for PFOS and PFOA removal 355 (Wang et al., 2016). The comparison of microporous AC efficiency with SWNT, in 356 removing PFOA at the same concentration, revealed that microporous AC has a higher 357 adsorption capacity than SWNT. This difference may be linked to the higher surface 358 area of microporous AC than that of SWNT (Table 2). Moreover, adsorption capacities 359 of SWNT and AC for PFOS were 6 and 2 times higher, respectively, than that of PFOA, 360

probably due to the one more C-F unit of the PFOS molecule (Wang et al., 2016). In addition, SWNT exhibited higher adsorption capacity than multi walled carbon nanotubes (MWNT), consistent with their higher Brunauer, Emmett and Teller (BET) surface area (Chen et al., 2011; Li et al., 2011).

PFAS adsorption on biochar has also been investigated because of its costeffectiveness and affinity with organic compounds (Guo et al., 2017; Inyang and Dickenson, 2017; X. Xiao et al., 2017).

Pinewood (PWC) and hardwood (HWC) biochars have been tested for PFOA removal and the adsorption capacity of the biochar was lower than that of AC (Table 2). Guo et al. (2017) have demonstrated that the adsorption capacity of corn-straw-derived biochar for PFOS removal increased with the increase of pyrolytic temperature, which is related to BET surface area of biochar (Table 2).

373 Reported data from fixed-bed column tests showed the ability of GAC to remove traces of PFAS (as both complex mixture or single solute) from water intended for human 374 consumption (Appleman et al., 2014; Chularueangaksorn et al., 2014; McCleaf et al., 375 2017; Pramanik et al., 2017, 2015; Sgroi et al., 2018a; Zaggia et al., 2016). GAC 376 (Filtrasorb 400, Calgon) column tested for PFOA removal has shown that the bed 377 volumes were about 55,000 at 90% breakthrough point (Chularueangaksorn et al., 378 2014). The same GAC (Filtrasorb 400, Calgon) has been tested for long-chain PFCAs 379 (i.e., PFOA, PFNA, PFDA, PFUnA, PFDoDA, PFTeDA) and PFSAs (i.e., PFHxS and 380 PFOS) removal, and the observed removal efficiencies were in the range 65-80% 381 (McCleaf et al., 2017). Information about the influence of GAC pore distribution on 382 adsorption capacity of PFOS and PFOA were reported by Zaggia et al. (2016). Results 383

from continuous adsorption experiments have demonstrated the great efficiency of 384 bituminous AC, characterized by meso- and macropores, for PFOA and PFOS removal, 385 whose maximum adsorption capacity was 39.6 and 4.1 µg g⁻¹, respectively (Zaggia et 386 al., 2016). In fact, meso- and macro-porous adsorbent materials are more easily 387 accessed by long-chain PFAS resulting in higher adsorption capacity (Kothawala et al., 388 2017; McCleaf et al., 2017; Zaggia et al., 2016). A high dosage of GAC (Filtrasorb 400, 389 Calgon) was tested in a pre-equilibrium batch study for the removal of a complex 390 mixture of long-chain PFSAs (PFHxS and PFOS) and PFCAs (PFOA, PFNA, PFDA, 391 PFUnDA, PFDoDA) from LW (Kothawala et al., 2017). Regardless of OM concentration, 392 long-chain PFAS removal was in the range of 50-90% (Kothawala et al., 2017). 393 However, these results were obtained from a pre-equilibrium study (contact time was 15 394 min) with a GAC dose (10 g L^{-1}) that is not typically employed at water treatment plants. 395

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3.3. Molecularly imprinted polymers

Several experimental works have explored the PFAS adsorption onto synthetically 397 modified polymers, which are adsorbents conveniently synthetized to have high affinity 398 and selectivity towards the target contaminants (Guo et al., 2018; Karoyo and Wilson, 399 2016; L. Xiao et al., 2017). The macromolecular imprinted materials (MIMs), containing 400 401 β -Cyclodextrin (β -CD) within a urethane framework, provide two types of binding sites. One binding site is a β -CD inclusion site, the second is a non-inclusion (interstitial) site 402 of the cross-linker domains, where aggregates, micelles and other inclusion complexes 403 could be formed (Karoyo and Wilson, 2016). Formation of bilayer and multilayer 404 structures is the dominant adsorption process for both PFOA and PFOS in these 405 materials, as observed in several studies (Du et al., 2014; Gao et al., 2017; Karoyo and 406 Wilson, 2016). The modification of CD-based polymer adsorbents composition may 407

allow an increasing of PFOA removal (L. Xiao et al., 2017). Nevertheless, the removal 408 efficiency of cross-linked polymer network, where β-CD substitutes decafluorobiphenyl 409 (DFB-CDP), was comparable with that of biochar tested by Inyang and Dickenson 410 (2017). Adsorption efficiency of non-imprinted carbon microspheres (NIP-CMs) for 411 PFOS removal has been compared with a surface imprinted polymer (MIP-CMs) in 412 which double functional monomers of methacryloyloxyethyl trimethyl ammonium 413 chloride (DMC) and 2-(trifluoromethyl)acrylic acid (TFMA) have been synthetized on 414 carbon microspheres (Guo et al., 2018). The adsorption capacity was higher for MIP-415 CMs than NIP-CMs (Table 2), due to the effect of molecularly imprinting technique in 416 417 enhancing PFOS removal. The molecular imprinting technique has also been employed in order to prepare a novel adsorbent using chitosan crosslinked for PFOS removal and 418 its adsorption capacity was higher than that observed for non-imprinted ones (Yu et al., 419 420 2008).

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3.4. Anion-exchange resin

Several studies have indicated the suitability of the AE process for PFAS removal. 422 Otherwise, PFAS removal efficiency varied greatly among AE resins, due to their 423 properties, such as polymer matrix, functional group and porosity (Zaggia et al., 2016). 424 425 It was demonstrated that large pores of macroporous resin allow a faster diffusion of PFOS than the gel one (Deng et al., 2010). This evidence is confirmed by comparing 426 the adsorption capacity of IRA910 (polystyrene-DVB, macroporous-type) and IRA400 427 (styrene-DVB, gel-type) for PFOS removal (Maimaiti et al., 2018; Wang et al., 2016; Yu 428 et al., 2009). Moreover, polymer matrixes led to different intraparticle diffusion and a 429 polyacrylic resin has shown higher efficiency for PFOS removal than polystyrene one 430 (Deng et al., 2010). IRA910 exhibited a good selectivity also for PFHxS as 431

demonstrated by Maimaiti et al. (2018). When IRA67 (polyacrylic-DVB, gel-type) has
been employed, its adsorption capacity was higher than styrene type resins (Table 2).
Gao et al. (2017) demonstrated the great applicability of polyacrylic resin for F-53B
removal, since the adsorption capacity of IRA67 (about 2400 mg g⁻¹) was higher than
that of R-CAC in batch experiments (Table 2).

As regards long-chain PFCAs, PFOA removal has been investigated on different kinds 437 of strong AE resins (Du et al., 2015; Maimaiti et al., 2018; Wang et al., 2016; Yu et al., 438 2009). Based on Table 2, the highest adsorption capacity was obtained when IRA910 439 (polystyrene-DVB, macroporous-type resin) was employed (Maimaiti et al., 2018). The 440 441 adsorption capacity of IRA67 was higher than that of BdAC, both adsorbents tested at the same PFOA initial concentration (Table 2). The efficiency of IRA67 may be ascribed 442 to the amine groups on the resin surface, which involve the PFOA adsorption via AE 443 444 mechanisms. Besides, the open pore structure of IRA67 also allowed a better diffusion of PFOA molecules. Moreover, as demonstrated by Zaggia et al. (2016), the selectivity 445 of larger and more hydrophobic anions (i.e., PFOS and PFOA) increased with the 446 increasing of alkyl chain length of the functional group of AE resins. Differences in terms 447 of equilibrium exchange capacity of different type of resins are linked with the strength 448 of hydrophobic interactions between resin functional groups and PFAS molecules. 449 Considering hydrophobicity of resin, highly hydrophobic resins (such as A532E) favour 450 PFOA and PFOS passage from hydrated state to adsorbed state as confirmed by the 451 highest adsorption capacity values obtained on both batch and continuous-flow pilot 452 scale experiments (Zaggia et al., 2016). The comparison between the performance of 453

AE resin and GAC for long-chain PFAS removal has also been carried out by employing
the fixed-bed column tests.

Particularly, as demonstrated by Chularueangaksorn et al. (2014), PFA300 (AE resin, 456 polystyrene crosslinked DVB) could treat a higher amount of water than GAC (Filtrasorb 457 400, Calgon) before the saturation (at a 90% breakthrough point, bed volumes were 458 119,880 and 55,080, respectively). A532E (polystyrene-DVB gel-type, bifunctional 459 quaternary amine) exhibited the highest adsorption capacity for both PFOS and PFOA 460 among several adsorbent materials tested (i.e., coconut based GAC, bituminous coal 461 based GAC, mildly hydrophobic and non-hydrophobic resins) during continuous 462 experiments (Zaggia et al., 2016). Removal efficiencies of AE resin (A600, polystyrene-463 DVB gel-type) for long-chain PFCAs (PFOA, PFNA, PFDA, PFUnA, PFDoDA, PFTeDA) 464 and PFSAs (PFHxS and PFOS) were in the range 33-94% after 50,704 bed volumes 465 466 (BVs), whereas removal efficiencies of GAC (Filtrasorb 400, Calgon) column were in the range 28-94% after 49,523 BVs (McCleaf et al., 2017). 467

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3.5. Synthetized materials

With the purpose of identifying the best suitable adsorbent for PFAS removal, it is 469 currently practice to synthesize new materials with properties and structures easy to 470 471 control and modify. To date, new adsorbents with higher selectivity and specificity designed towards PFAS removal are also becoming commercially available for water 472 treatment applications. For instance, a porous aromatic framework constructed from 473 benzene rings (PAF-45) was employed for PFOS removal (Luo et al., 2016). Despite 474 the remarkable adsorption capacity (Table 2), PAF-45 feasibility was influenced by pH 475 solution and ionic strength since the adsorption capacity was higher at acidic pH values 476 (i.e., pH ~ 3). Moreover, the adsorption isotherm experiments have been carried out at 477

478 PFOS concentrations in the range of 50-200 mg L^{-1} (Luo et al., 2016), which are much 479 higher than the PFAS concentrations typically detected in the water environment 480 (Rahman et al., 2014).

Covalent triazine-based framework (CTF) has been investigated for removing different 481 long-chain compounds (PFOA, PFHxS and PFOS), due to its large surface area and 482 rigid pore structure (Wang et al., 2016). Among the three long-chain PFAS tested, 483 Wang et al. (2016) have demonstrated that the adsorption capacity of CTF was highest 484 for PFOS (Table 2). The electrostatic interaction between PFAS anion head and triazine 485 groups of CTF (positively charged) represents the main driving force for PFAS 486 adsorption on CTF. Based on electrostatic interactions, which are the main adsorption 487 mechanism of short-chain PFAS, CTF exhibited a good adsorption capacity for PFBS 488 and PFBA removal, as it will be discussed below. 489

Boron nitride, characterized by lightness structure and thermal stability, has been 490 synthesized as porous hexagonal boron nitride nanosheets (h-BNs) for PFOS and 491 PFDA removal (Feng et al., 2016). The efficiency of this adsorbent material has been 492 demonstrated to be linked with chain length and functional group of PFAS, since PFDA 493 was more favourable adsorbed than PFOS (adsorption capacity of 0.16 mg m^{-2} and 494 0.04 mg m⁻², respectively). Among novel adsorbent materials investigated, magnetic-495 nanoparticles attached into fluorographene (2-MNPs@FG, mass ratio of MNPs and FG 496 is 3:5) exhibited the highest adsorption capacity for PFOS instead of PFOA (Table 2). 497 However, adsorbent dosage was not coherent with that really employed in full-scale 498 treatment plants (Wang et al., 2018). 499

500 Quaternized cotton and aminated rice husk (ARH) both prepared with atom transfer 501 radical polymerization (ATRP) technique were tested for PFOS and PFOA removal 502 (Deng et al., 2013, 2012). Results have demonstrated that quaternized cotton had 503 higher adsorption capacity than ARH for both PFOS and PFOA (Table 2).

Polyacrylonitrile fiber (PANF)-derived activated carbon fibers (PACFs) showed a remarkable adsorption capacity for PFOS and PFOA (Chen et al., 2017). The adsorption affinity could be ascribed to its high specific surface area and micro- and mesoporous structure which allowed the establishment of multilayer adsorption (formation of hemi-micelles and micelles). The latter was also the main adsorption mechanism on crosslinked chitosan beads employed for PFOS removal, as demonstrated by Zhang et al. (2011).

511 Poly(ethylenimine)-functionalized cellulose microcrystals (PEI-f-CMC) have been tested 512 for removing long-chain PFAS at environmentally relevant concentration level (Ateia et 513 al., 2018). Long-chain PFAS removal percentage was in the range of 80-98%. Despite 514 its low surface area, PEI-f-CMC exhibited a good adsorption affinity both in DI and in the 515 presence of co-existing OM, as discussed in section 5.

The main drawback of those synthetized materials is the application at full-scale treatment plants because their production is not industrialized and, probably, they are not commercially available, unlike AC and AE resins. Economic assessment for new synthetized materials is needed.

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3.6. Nanoparticles materials

The adsorption of PFAS into nanoparticles (NPs) has recently been investigated due to their co-existing in aquatic environments (i.e., marine debris plastic) or their high surface area and reactivity (i.e., iron oxides). As demonstrated by Lu et al. (2016), nano-oxides

such as titania (TiO₂), iron oxides (Fe₂O₃), alumina (Al₂O₃) and silica (SiO₂) have the 524 ability to sorb PFOS. Among the different nano-oxides tested, Al₂O₃ showed the highest 525 PFOS adsorption capacity (1.1 μ g m⁻²), whereas SiO₂ exhibited the lower adsorption 526 capacity (0.1 µg m⁻²). This difference in terms of PFOS removal should be ascribed to 527 the different hydroxyl groups and surface area. Furthermore, the main adsorption 528 mechanism of PFOS on nano-oxides was not only electrostatic interaction, but also the 529 formation of hydrogen bounds between the PFOS sulfonic terminal group and nano-530 oxides surface (Lu et al., 2016). 531

Magnetite nanoparticles (Fe₃O₄ NP) were used as the substrate of a novel magnetic 532 nanocomposite (Fe₃O₄@SiO₂- NH₂&F₁₃), in which silica membrane functionalized with 533 amino group and octyl-perfluorinated chain was synthesized on the Fe₃O₄ NP surface 534 (Zhou et al., 2016). Based on kinetic data, the predominant adsorption mechanism 535 536 between the magnetic adsorbent and PFAS tested was chemisorption, which includes both electrostatic and F-F interaction (Zhou et al., 2016). In detail, the selective F-F 537 interaction between octyl-perfluorinated chain on the magnetic composite surface and 538 perfluoroalkyl dipole shell in PFAS molecule was enhanced by electrostatic attraction of 539 -NH₂ and the anionic -COOH or -SO₃H of PFCAs and PFSAs molecules, respectively. 540 Due to size exclusion effect, PFCAs were better adsorbed than PFSAs on Fe₃O₄@SiO₂-541 NH₂&F₁₃. Considering perfluoroalkyl chain length, PFUnDA exhibited the highest 542 adsorption capacity onto Fe₃O₄@SiO₂- NH₂&F₁₃, due to the formation of aggregate 543 structure between long-chain PFAS which could stick together and, consequently, the 544 amount of PFAS adsorbed increased (Zhou et al., 2016). 545

A recent experimental work investigated the capability of microplastics (MPLs) to sorb a 546 complex mixture of PFAS from RW (Ebro river) and seawater (SeaW), simulating 547 realistic environmental conditions (Llorca et al., 2018). High-density polyethylene 548 (HDPE), polystyrene (PS) and poly-styrene carboxylic acid (PS-COOH) were selected 549 due to their wide occurrence as marine debris plastic. Results of batch adsorption 550 experiments showed low removal percentages (< 27%) of long-chain PFAS in RW after 551 7 days (with few exceptions of PFTrA and PFTeA whose percentages were between 552 65% and 70%). Moreover, MPLs efficiency in SeaW was affected by water chemistry 553 such as salinity and OM concentration. This point will be deeply explained later (see 554 section 5). Overall, carboxylated compounds with more than 11 C atoms were the most 555 removed (Llorca et al., 2018). In detail, HDPE exhibited the worst adsorption capacity 556 due to its granular shape, which limited the intraparticle diffusion (Llorca et al., 2018). In 557 RW, PFOA, PFNA, PFHxS and PFOS did not present any adsorption on both HDPE 558 and PS-COOH throughout the experiment period. On the contrary, affinity between 559 carboxylated compounds with less than 10 C atoms and HDPE was higher in SeaW. 560 Adsorption rates of PFCAs on PS-COOH in RW increased with the increasing of chain 561 length. Comparing PFCAs to PFSAs, with the same chain length, the carboxylated 562 compounds were less removed (Llorca et al., 2018). Whereas, in SeaW, the presence 563 of carboxylic group in the PS-COOH surface implicated an increase of adsorption rates 564 of carboxylated compounds. Adsorption kinetics were influenced by adsorbents size, 565 therefore PS exhibited faster kinetic than HDPE, since it had the smallest particles 566 (Llorca et al., 2018). 567

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4. Adsorption of short chain PFAS

4.1. Challenges in short chain PFAS adsorption

Short-chain PFAS and their precursors are as persistent as those long-chained. 570 571 Therefore, although they show less bioaccumulation potential, their environmental occurrence is of concern (Ateia et al., 2019; Brendel et al., 2018; Zhao et al., 2016). 572 While long-chain PFAS are binding with particles present in solution, those short-chain 573 are mainly in the dissolved phase resulting in long-range transport in aquatic 574 environments (Ahrens, 2011). Therefore, short-chain PFAS have higher mobility in 575 water bodies than long-chain compounds. Specifically, short-chain compounds could 576 significantly affect drinking water supplies, increasing the human exposure to PFAS 577 compounds. Considering the properties of short-chain PFAS (Table 1), it is expected 578 that the large-scale remediation treatments, currently suitable for long-chain PFAS, are 579 ineffective for short-chain PFAS (Ateia et al., 2019; Brendel et al., 2018). This evidence 580 is consistent with data from full-scale drinking water treatment plants (Arvaniti and 581 Stasinakis, 2015; Rahman et al., 2014). Moreover, it is widely reported that carbon-582 chain length influences adsorption capacities of PFAS onto various materials, since 583 adsorption rate seems to increase with the increase of molecular size (Appleman et al., 584 2014). 585

586 Data collected from full-scale treatment plants (drinking and wastewater facilities) 587 suggested that the removal of short-chain compounds is still a challenge task, due to 588 their early and faster breakthrough (Arvaniti and Stasinakis, 2015; McCleaf et al., 2017; 589 Zaggia et al., 2016). To date, a restricted number of published data have addressed 590 short-chain PFAS adsorption by using different materials, because most of the 591 experimental works have focused on the removal of long-chain PFAS (i.e., PFOA and

592 PFOS). Adsorption capacities obtained by fitting the Langmuir model along with type 593 and dosage of adsorbent materials, initial concentration of short-chain PFAS and 594 experimental setup are reported in Table 3. Comparisons between several adsorbent 595 materials tested for short-chain PFAS are reviewed based on both batch experiment 596 studies (Table 3) and fixed-bed column tests.

The adsorption capacity of materials tested for PFBA removal observed during batch tests (Table 3) follows the order: microporous AC < CTF < IRA910 (strong AE resin). However, results obtained by continuous experiments have demonstrated that the adsorption capacity of meso-porous GAC (meso-porous bituminous coal-derived AC) was higher than A532E (strong AE resin) (4.3 and 3.3 μ g g⁻¹, respectively) (Zaggia et al., 2016). In the following sections the removal of short chain PFAS by adsorption is discussed based on the type of adsorbent.

4.2. Activated carbon, biochar and other adsorbents

The performance of BdAC and coal-based AC (microporous type), used for removing 605 PFHxA, has been compared. The adsorption capacity of BdAC was 13 times lower than 606 microporous AC probably due to its low BET surface area and the presence of OM in 607 the solution tested (Du et al., 2015; Wang et al., 2016). The adsorption capacities of 608 609 HWC and PWC biochars for PFBA and PFOA removal were investigated by Inyang and Dickenson (2017). Results from adsorption kinetic tests showed that the amount of 610 PFBA adsorbed on both HWC and PWC was 3-4 times lower than that of PFOA. This 611 evidence suggests the incapability of biochar for short-chain PFAS removal and it may 612 prove the competition between long- and short-chain PFAS for the adsorption sites 613 and/or competition with OM (Inyang and Dickenson, 2017). 614

Short-chain PFAS adsorption on GAC and PAC has also been investigated by using batch test (Hansen et al., 2010). Tests have been carried out at real concentrations of short-chain PFAS (range about 73 – 320 ng L⁻¹) and using an adsorbent dose comparable to that used in real water treatment plants (range about 25 – 125 mg L⁻¹). Results have demonstrated that PAC has higher adsorption capacity than GAC (more than twice), due to the shorter internal diffusion distances and its higher BET surface area (Hansen et al., 2010).

MWCNTs functionalized in different ways (MWCNTs-PRI, MWCNTs-COOH, MWCNTs-622 OH) were tested for PFBS removal (Deng et al., 2015a). Removal percentage of PFBS 623 on MWCNTs was about 30% in DI water, whereas when humic acids (HA) and phenol 624 co-existed in the solution, this percentage was lower than 20% (Deng et al., 2015a). 625 Moreover, due to the weak hydrophobicity of PFBS, its percentage removal was lower 626 627 than that of long-chain compounds (Deng et al., 2015a). Results of adsorption isotherm of PFOS and PFBS on boehmite showed that PFOS was better removed than PFBS, 628 since the effect of surface aggregation enhanced long-chain PFAS removal (Wang et 629 al., 2015). 630

Among fixed-bed column experiments carried out in order to assert the short-chain PFAS removal, McCleaf et al. (2017) reported faster breakthrough and lower removal percentage of short-chain PFCAs on GAC column (F400, Calgon) than long-chain ones. The removal efficiencies of the short-chain PFCAs tested (i.e., PFBA, PFPeA, PFHxA and PFHpA) were lower than 19% on GAC column after 49,523 BVs. Whereas, the removal efficiency of PFBS (short-chained PFSAs tested) was ~10%. Those results suggest that short-chain PFAS removal depends mainly on the availability of active

sites, since they do not bind with other particles and, consequently, the formation of 638 aggregates does not occur (McCleaf et al., 2017; Zaggia et al., 2016). Moreover, 639 desorption of short-chain PFAS has been also hypothesized, due to the competition of 640 long-chain PFAS and/or OM. Similar fast breakthrough of short-chain PFAS has also 641 been observed in rapid small-scale column tests (RSSCT) carried out on different types 642 of GAC columns (Appleman et al., 2013). Among the three activated carbons tested, 643 F300 (microporous bituminous coal-derived) exhibited the lowest efficiency for the 644 short-chain PFCAs tested (i.e., PFBA, PFPeA and PFHxA), due to its pores distribution 645 (mainly microporous type) and BET surface area. Others GAC tested, coconut based 646 GAC (AquaCarb 1240) and bituminous coal based ones (F600), performed better for 647 the removal of selected short-chain PFAS (Appleman et al., 2013). 648

PFBA uptake on different types of biochar was influenced by BET surface area. Indeed, the highest percentage removal has been found on the hardwood sawdust pellets gasified at 900 °C (HWC), which had the highest BET surface area among the different biochars tested (Inyang and Dickenson, 2017). However, results obtained from batch adsorption kinetic tests have demonstrated that GAC removed PFBA better than HWC (Inyang and Dickenson, 2017).

Short-chain PFAS adsorption on microplastics (HDPE, PS and PS-COOH) has recently
been investigated in simulated realistic environmental conditions (Llorca et al., 2018).
Due to the increase in ionic strength, short-chain carboxylates compounds have been
better removed by PS-COOH in SeaW than in RW. Whereas, short chain PFAS were
almost not adsorbed onto PS and HDPE (Llorca et al., 2018).

Removal of PFBS (short-chain PFSAs) has been investigated at batch mode by means 660 of AC (i.e., microporous AC and Calgon F400) and CTF (Ochoa-Herrera and Sierra-661 Alvarez, 2008; Wang et al., 2016). The difference of adsorption capacity between CTF 662 and AC may be related to their different structure and, consequently, adsorption 663 mechanisms established, since the electrostatic interactions between PFAS anion head 664 and triazine groups of CTF involved short-chain PFAS adsorption on CTF (Wang et al., 665 2016). However, CTF exhibited a lower affinity with PFBA than ARH (Table 3). 666 Adsorption capacity of ARH was 4 times higher than CTF (Deng et al., 2013; Wang et 667 al., 2016). 668

A novel adsorbent poly(ethylenimine)-functionalized cellulose microcrystal (PEI-f-CMC) has been synthetized and its efficiency for short-chain removal has been evaluated at environmental relevant concentration levels (Ateia et al., 2018). Results have demonstrated that short-chain with sulfonate terminal group were removed better than short-chain PFCAs, in agreement with previous experimental studies (McCleaf et al., 2017; Rahman et al., 2014).

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4.3. Anion-exchange

The removal efficiency of three PFCAs owning different chain lengths, including PFHxA 676 (with 6 C atoms), PFHpA (with 7 C atoms) and PFOA (with 8 C atoms) from industrial 677 WW (perfluorooctanesulfonyl fluoride washing wastewater, PFSOF WWW) by AE resin 678 has been evaluated during batch experiments conducted by Du et al. (2015). Results 679 demonstrated that adsorption sites on IRA67 were occupied by PFOA molecules prior 680 to the others PFCAs and, therefore, the adsorption rates of short-chain were lower. 681 Consequently, short-chain PFCAs reached the equilibrium very fast (Du et al., 2015). 682 Moreover, comparing the efficiency of two different anion-exchange resins (i.e., IRA910 683
and IRA67) for removing the same compound (PFHxA), IRA910 (polystyrene-DVB macroporous-type) exhibited higher adsorption capacity than IRA67 (polyacrylic-DVB gel-type) (Du et al., 2015; Maimaiti et al., 2018). This difference in adsorption capacity for PFHxA may be linked to the resin properties, such as polymer matrix and porosity, and/or to the effect of OM present in the solution. In fact, IRA910 was tested in DI water, whereas IRA67 was employed for PFHxA removal from PFSOF WWW (Du et al., 2015; Maimaiti et al., 2018).

Moreover, when tested for the same actual WW, IRA67 had higher affinity with PFHpA 691 than BdAC, as demonstrated by the adsorption capacity, which was 3 times higher than 692 that of BdAC (Du et al., 2015). Furthermore, amine groups on adsorbent surface 693 improved the short-chain PFAS removal, due to the establishment of electrostatic 694 interactions, which are the main driving force during short-chain adsorption (Deng et al., 695 2013; Du et al., 2014; Zhang et al., 2011). Results provided by fixed-bed column tests 696 demonstrated that the adsorption capacity of A532E (strong AE resin) was almost equal 697 to that of GAC (meso-porous bituminous-coal derived AC), when tested for PFBS 698 removal (4.7 μ g g⁻¹ and 4.1 μ g g⁻¹, respectively) (Zaggia et al., 2016). 699

Results from fixed-bed column experiments carried out by McCleaf et al. (2017) have shown fast breakthrough and low removal percentage for short-chain PFCAs on AE resin (A600, polystyrene-DVB gel-type). The removal efficiencies of short-chained PFCAs tested were ~11% on A600 column after 50,704 BVs. The same anionexchange resin better removed PFBS (short-chain PFSAs tested) than other short-chain compounds, and the removal efficiency of PFBS was ~55% (McCleaf et al., 2017).

706 Results from a pre-equilibrium study carried out by Kothawala et al. (2017) demonstrated that fresh adsorbent materials (i.e., AE resin, Purolite A600, and GAC, 707 Filtrasorb 400) could remove short-chain PFAS from water solutions. Nevertheless, 708 709 anion-exchange showed the highest percent of removal. In detail, removal percentages of short-chain PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFBS) were about 90% and 50% 710 on A600 and Filtrasorb 400, respectively. However, those results have been obtained 711 712 from a pre-equilibrium study (contact time was equal to 15 min) with a high dosage of adsorbent materials (Kothawala et al., 2017). 713

Analysis of transmission electron microscopy (TEM) carried out on AE resins allowed a deep understanding of the predominant adsorption mechanism involved during shortchain PFAS removal (Zaggia et al., 2016). Indeed, TEM images showed that the weak hydrophobic interactions between PFBA (or PFBS) and resin surface did not allow the formation of aggregates and, consequently, AE of single molecules was the main mechanism for short-chain removal.

Overall, AE resins exhibit a remarkable adsorption capacity for both long- and shortchain PFAS. Nevertheless, the possible release of disinfection by-products (DBP) such as N-Nitrosodimethylamine (NDMA) may represent the main drawback for their full-

scale application (Sgroi et al., 2018b). Particularly, the amount of NDMA and their precursors released upon usage depends on the resin functional group (such as amine groups) and operational conditions (such as regeneration activities and flow interruptions).

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4.4. Comparison between long- and short-chain PFAS adsorption

In order to provide a deeper analysis on the long- and short-chain PFAS removal by 729 adsorption, data from Table 2 and Table 3 have been elaborated to build a box-and-730 whiskers plot (Figure 1) that allows the comparison between the removals of long- and 731 short-chain PFAS by different adsorbents (classified as activated carbon, resin, and 732 synthetized materials). Figure 1 shows that the adsorption capacity of a wide range of 733 adsorbents is lower for short-chain PFAS compared to that observed for long-chain 734 PFAS. This result emphasizes that the removal of short-chain PFAS by adsorption is 735 very challenging and it will need more research in the future. A comparison in 736 adsorption capacity of the different adsorbents employed have shown that resins are 737 more effective than activated carbons for both long- and short-chain PFAS removal. 738 Activated carbon exhibited the lowest adsorption capacity. A significant variation in 739 adsorption capacity of synthetized materials used for long-chain removal was observed. 740 Such variation ranged from the lowest to the highest adsorption capacity observed for 741 long-chain PFAS removal. However, the latter best results were often obtained at acid 742 pH. For instance, the best adsorption capacity (5847 mg g⁻¹) was found by using the 743 PAF-45 adsorbent at pH 3. Therefore, the real operating conditions may affect the 744 removal efficiency. For instance, the effect OM may significantly influence the 745 performance of adsorbents, as discussed in the next section. 746

5. Effect of organic matter (OM) on PFAS adsorption

5.1. PFAS adsorption in presence of OM

OM is ubiquitous in the aquatic environment and it can be distinguished between NOM,
regarded as OM naturally present in surface water, and EfOM, the OM released from
WWTPs (Shon et al., 2006).

OM could affect adsorption efficiency of adsorbent materials due to binding and 752 adsorption interactions with PFAS, including long- and short-chain compounds. As 753 illustrated by Du et al. (2014b), NOM could interact with PFAS via electrostatic and/or 754 hydrophobic interactions. Firstly, OM is mostly constituted of anionic species and, after 755 adsorbing on materials, it can lead to repulsive electrostatic interactions. Meanwhile, 756 NOM can also lead to PFAS adsorption via hydrophobic interaction between 757 perfluoroalkyl tail and NOM adsorbed on the adsorbent surfaces. To date, it is not well 758 understood how these effects co-exist and which is predominant. 759

Most of undertaken experimental works investigated adsorption properties of PFAS on 760 different adsorbent materials in DI (Deng et al., 2012; Guo et al., 2018; Maimaiti et al., 761 2018; Yu et al., 2009). Many researches have selected fulvic and humic acids (FA and 762 HA) as the model DOM in order to evaluate the impact of DOM on PFAS adsorption 763 (Deng et al., 2015a; Du et al., 2016b; Maimaiti et al., 2018; Pramanik et al., 2015; F. 764 Wang et al., 2015; L. Xiao et al., 2017). Actually, NOM consists of a wide range of 765 organic compounds, such as hydrophilic acids, proteins, carboxylic and amino acids in 766 addition to the already mentioned HA and FA. When using a synthetic solution of OM 767 during experimental studies, some interactions between PFAS and water matrix have 768 not been described in detail. Table 4 reports the main experimental works published 769 related to the adsorption of PFAS (both long- and short-chain compounds) on different 770

adsorbent materials in the presence of OM. However, some of those studies lacked adetailed discussion on the effect of OM on PFAS adsorption.

Most of these experimental studies (Appleman et al., 2013; Du et al., 2016b, 2016a; Y. 773 Wang et al., 2015; L. Xiao et al., 2017) have investigated the effect of OM on PFAS 774 adsorption through comparison between synthetic OM solution and OM free solution 775 (Table 4). Only few experimental works compared the effect of different DOM sources 776 777 on PFAS adsorption and tested water had different dissolved organic carbon (DOC) concentrations (Ateia et al., 2018; Inyang and Dickenson, 2017; Kothawala et al., 2017; 778 Sgroi et al., 2018a; Wang et al., 2018) . Furthermore, the simultaneous effect of ionic 779 strength and OM on the PFAS adsorption is very complex. For instance, it was 780 demonstrated that the presence of monovalent and divalent cations increases PFAS 781 adsorption on different materials, i.e. sediments (Higgins and Luthy, 2006), activated 782 carbon (Du et al., 2015), synthesized material (PAF-45) (Luo et al. 2016), resin (Du et 783 al., 2015) and kaolite (Xiao et al., 2011). Particularly, the adsorption of short-chain 784 PFAS (i.e., PFHxA and PFBA) on kaolinite was more thermodynamically favorable at a 785 higher Na⁺ concentration due to the compression of the electrical double layer and 786 ensuing reduced electrostatic repulsion between PFAS and kaolite surface (Xiao et al., 787 2011). In addition, divalent cations (such as Ca²⁺ and Mg²⁺) could also improve PFAS 788 removal by divalent cation-bridging effect (Du et al., 2015, 2014). On the contrary, the 789 presence of inorganic anion negatively affects the adsorption of PFAS due to the 790 competition for adsorption sites (Deng et al., 2010). Whereas, it was observed that the 791 presence of ionic OM (i.e., HA, SDS, FA) compete with both long- (F. Wang et al., 2015; 792 Zhao et al., 2011) and short-chain PFAS (Maimaiti et al., 2018; Zhao et al., 2011). 793

Specifically, such effect seems more relevant for short-chain PFAS due to the 794 competition for active sites (Maimaiti et al., 2018; McCleaf et al., 2017; Zhao et al., 795 2011). On the other hand, hydrophobic DOM was found to improve the PFAS retention 796 in GAC adsorption, while hydrophilic DOM seems do not affect significantly PFAS 797 adsorption in both GAC and AE adsorption experiments (Kothawala et al., 2017). The 798 positive impact of DOM on the adsorption of long-chain PFAS has been ascribed to the 799 800 formation of PFAS aggregate or DOM-PFAS complexes (Kothawala et al., 2017; McCleaf et al., 2017) but such bonds have been rarely demonstrated. Consequently, 801 the impact of DOM and ionic strength on the PFAS adsorption need more investigation. 802 A systematic review concerning the effect of OM on PFAS adsorption for different 803 classes of adsorbents is reported in the following sections. 804

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5.2. Activated carbon

Among adsorbent materials, AC has proven to be effective for PFAS removal and its 806 efficiency in presence of OM has been investigated both in batch and column 807 experiments (Table 4). Contrasting trends have been observed in experimental studies 808 because of the influence of co-existing OM. Indeed, the performance of PFAS 809 adsorption onto AC was found negatively impacted, enhanced or not influenced by the 810 811 presence of OM. The main interactions that could be established between OM molecules and PFAS (both long- and short-chain) during adsorption on GAC column are 812 illustrated in Figure 2. In detail, hydrophobic interactions mainly concern long-chained 813 C-F molecules, while short-chain PFAS interact with OM molecules through pore 814 blockage and electrostatic repulsions. 815

In many cases, activated carbon performance was negatively influenced by co-existing OM and its efficiency decreased with the increase of DOC concentrations (Du et al.,

2016a, 2015; Hansen et al., 2010; Kothawala et al., 2017; Pramanik et al., 2017, 2015; 818 Y. Wang et al., 2015; Yu et al., 2012; Zhao et al., 2011). On the contrary, adsorption 819 capacity on GAC did not significantly decrease in the presence of GW NOM probably 820 due to the high concentration of PFAS tested (50 mg L⁻¹) and to the effect of ionic 821 strength (Zhao et al., 2011). Results from the previously mentioned study demonstrated 822 that PFBA removal was affected by OM since the results from adsorption equilibrium 823 suggested a reduction of 40% (Zhao et al., 2011). Results from adsorption kinetic 824 experiments provided by Yu et al. (2012) suggested that adsorption equilibrium for 825 PFOA and PFOS on PAC was reached at 4 h and 24 h in the absence and in the 826 presence of EfOM, respectively (Yu et al., 2012). The competition between PFAS and 827 DOM for AC adsorption sites has also been investigated in RSSCTs (Appleman et al., 828 2013; McCleaf et al., 2017; Pramanik et al., 2017, 2015; Sgroi et al., 2018a). Results 829 obtained from the latter mentioned experimental works are in disagreement about the 830 effect of OM. This discrepancy may be related to the different experimental setups, such 831 as PFAS initial concentration, source and concentration of DOM, empty bed contact 832 time (EBCT), and to the kind of AC tested. As suggested by Pramanik et al (2015), 833 when DOC concentration increased from 5 to 25 mg L^{-1} the removal efficiency of PFOA 834 and PFOS on PAC decreased by 50% and 35%, respectively. On the contrary, the 835 performance of bituminous coal-based GAC was less influenced by variation of DOC 836 concentration (Pramanik et al., 2015). Similar results have asserted that proteins 837 resulted in a low retention of PFOA and PFOS through hydrophobic and electrostatic 838 interactions (Pramanik et al., 2017). Moreover, breakthrough > 20% has been reached 839 at 125,000 BVs during DOM-free experiments, and at ~ 11,000 BVs when DOC 840

concentration was equal to 1.7 mg L⁻¹. This observation highlights that faster 841 breakthrough of PFAS takes place during RSSCT experiments in presence of DOM 842 (Appleman et al., 2013). Nevertheless, Sgroi et al. (2018a) found that breakthrough 843 curves of some long-chain PFAS (i.e., PFOS, PFOA and PFDA) were similar in column 844 beds packed tests by using Norit Darco 12x40. In those experiments, waters with 845 different DOM concentrations and compositions fed the packed columns (Table 4). The 846 observed behaviour for the investigated long-chain compounds may be ascribed to the 847 hydrophobic interactions occurring between long-chain PFAS and GAC. Indeed, 848 hydrophobic interactions are the main adsorption mechanisms for long-chain PFAS, and 849 the hydrophobic interactions may be only slightly influenced by OM presence. 850

Results of pre-equilibrium study by Kothawala et al. (2017) are in contrast with other 851 findings (Du et al., 2016a; Wang et al., 2016; Yu et al., 2012; Zhao et al., 2011), since 852 the increase in DOC concentration seems to enhance long-chain PFAS removal due to 853 the formation of DOM-PFAS complex and, consequently, their co-adsorption. In detail, 854 removal efficiency of PFAS with a fluorocarbon-chain length of 8 C atoms increased by 855 50% when DOC concentration of a hydrophobic DOM passed from 0 to 8 mg L⁻¹ using 856 GAC (Kothawala et al., 2017). It should be highlighted that these results were obtained 857 in pre-equilibrium conditions (contact time about 15 min), at PFAS initial concentration 858 of about 2.5 μ g L⁻¹ and at batch dose of GAC of about 10 g L⁻¹, which is much higher 859 than doses typically used in full-scale treatment plants (Ziska et al., 2016). Performance 860 of BdAC for PFCAs removal from PFSOF WWW has been investigated in the presence 861 of high total organic carbon (TOC) concentration. Co-existing OM competed with 862 PFCAs for adsorption sites on the BdAC (Du et al., 2015). The same achievement was 863

obtained using R-CAC for PFOS and its alternative compound, F-53B, removal from 864 electrochemical WWTP effluent (Du et al., 2016a). The high concentration of TOC (78.3 865 mg L⁻¹) was linked to the high amount of hydrocarbon surfactants which were 866 unfavourable for the adsorption of PFOS and F-53B on R-CAC, since adsorption sites 867 were manly occupied by co-existing organic compounds (Table 4). Depending on OM 868 concentration and source, dose and kind of AC employed (powdered or granular, and 869 870 its porosity), and PFAS tested (long- or short-chain), the effect of OM is different, due to adsorption mechanisms established. The presence of OM can lead to the enhancement 871 of PFAS adsorption through the formation of agglomerations between long-chain PFAS 872 and OM. Otherwise, OM can negatively influence the adsorption efficiency, due to the 873 reducing of accessible binding sites and pore spaces (i.e., pore blockage) (Figure 2). 874

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5.3. Anion-exchange resin

Main interactions occurring between OM and PFAS molecules during AE process are reported in Figure 3. As previously asserted about the influence of OM on AC performance, the effect of co-existing OM on AE resins for PFAS removal depends on several factors, including OM composition and concentration, kind of resin and PFAS concentration tested.

To date, the competition between OM and PFAS on AE resins is not fully understood. This evidence is confirmed by several experimental studies carried out both on batch and column setups (Du et al., 2015; Kothawala et al., 2017; Maimaiti et al., 2018; McCleaf et al., 2017; Wang et al., 2016; Zaggia et al., 2016). Organic compounds, such as HA, tri-chloroethylene (TCE), methylbenzene (MB) and sodium dodecyl sulphate (SDS), have been selected to evaluate their effect on PFHxS removal on AE resin (i.e., IRA910, a macroporous polystyrene resin with a dimethyl ethanol ammonium functional

group) during batch experiments (Maimaiti et al., 2018). Results suggested that PFHxS 888 retention on IRA910 was not affected by non-ionic co-existing organic compounds (i.e., 889 MB and TCE), regardless of their concentration in the solution. Whereas, IRA910 890 efficiency decreased with the increasing of HA and SDS concentrations, due to the 891 competition for adsorption sites. A slight effect on PFAS retention has been highlighted 892 under pre-equilibrium condition since AE resin (A600, polystyrene-DVB gel-type with 893 quaternary ammonium functional group) performance was independent from DOM 894 concentration and source (Kothawala et al., 2017). In detail, PFAS removal has been 895 reduced by 10% at the highest DOM concentration tested. This result is consistent with 896 data reported by previous experimental works which have demonstrated that OM 897 weakly interferes with PFAS removal during AE process (Du et al., 2015; Wang et al., 898 2016). Resins gel-type polymer matrixes, such as IRA400 and IRA67, showed a 899 900 remarkable affinity with PFAS (both long- and short-chain), which was independent of OM present. In an opposed way, the performance of macroporous resins (i.e., IRA910) 901 could be affected by background DOM levels. 902

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5.4. Other adsorbents (biochar, multi-walled carbon nanotubes, mineral materials, nanoparticles)

Effect of co-existing HA on boehmite surface was investigated during PFOS and PFBS batch adsorption experiments (F. Wang et al., 2015). Due to the electrostatic interactions between PFAS and boehmite, strong competition between PFOS (or PFBS) and HA occurred. Electrostatic repulsions increased with the increasing of HA accumulation on boehmite surface (F. Wang et al., 2015). The competition between PFAS and synthetic OM (HA, phenol, 1-naphthol and benzoic acids) has also been investigated on MWCNTs (Deng et al., 2015a). The pronounced influence on PFOS removal was provided by HA, whereas phenol had a lesser influence. Moreover, PFBS
removal was the worst in the presence of HA or phenol (Deng et al., 2015a).

As demonstrated by Inyang and Dickenson (2017), HWC and PWC biochar 914 performances were affected by OM, since adsorption capacities decreased with the 915 increase of DOC concentration. In particular, OM molecules could lead to pore blockage 916 and may occupy high-energy pore sites. The adsorption capacities were about 41.3 and 917 27.7 mg g⁻¹ when LW (DOC = 2 mg L⁻¹) and tertiary treated WW effluent (DOC = 4.9 mg 918 919 L¹) were tested, respectively (Inyang and Dickenson, 2017). Results from pilot-scale tests have demonstrated that the breakthrough of some PFAS (i.e., PFPeA, PFHxA, 920 PFOA and PFOS) was faster on biochar HWC filter than on GAC column, since OM 921 adsorbed on biochar surface caused changes on biochar surface charge. 922 Consequently, the electrostatic repulsions between PFAS and biochar surface 923 increased. Adsorption kinetic tests were performed for both PFBA and PFOS, and the 924 observed slow kinetics could have been caused by pre-loaded OM on biochar (Inyang 925 and Dickenson, 2017). 926

The efficiency of novel magnetic adsorbent,2-MNPs@FG, has been investigated for 927 PFOA and PFOS removal from different water matrixes (Wang et al., 2018). Its 928 performance was independent of OM content also at the highest DOC concentration 929 tested (1.7 mg L⁻¹). Indeed, the removal efficiencies were always found around 99% for 930 both PFOA and PFOS in all performed experiments. However, it should be noted that 931 those efficiencies have probably been obtained because of a high dosage of adsorbent 932 employed (400 mg L⁻¹). The competition between NOM (both SeaW and RW) and PFAS 933 (both long- and short-chain compounds) has also been investigated during PFAS 934

adsorption onto HDPE, PS and PS-COOH particles (Llorca et al., 2018). Results asserted that aromatic rings of PS contrasted NOM competition and, consequently, they favoured PFAS adsorption. By contrast, NOM influenced PFAS adsorption on HDPE and its effect was higher in SeaW than in RW (Llorca et al., 2018). Sun et al. (2018) investigated the effect of co-existing organic compounds on GAC biofilter. They reported that more active sites were available for PFAS adsorption in the pre-ozonated regenerated GAC biofilter, due to the oxidation of competitive DOM (Sun et al., 2018).

Recently, the performance of new synthetized adsorbent (PEI-f-CMC) for PFAS removal 942 (both long- and short-chain) was evaluated using three different NOM solutions (Ateia et 943 al., 2018). Firstly, experiments were carried out in LW (Hartwell Lake, South Carolina) 944 and PFAS removal efficiency has been compared with that resulted from DOC free 945 solution. PFOA and PFOS removal efficiency was almost equal in both LW and DI. 946 PFAS with longer chain than PFOA and PFOS ($C_{12} - C_{13}$ PFCAs, $C_9 - C_{10}$ PFSAs) 947 were removed better from LW than from DI using PEI-f-CMC. This result can be 948 explained by the co-removal of long-chain PFAS aggregated with OM (Du et al., 2014; 949 McCleaf et al., 2017). By contrast, short-chain PFAS removal was higher in DI than in 950 LW. Indeed, OM competed with short-chain PFAS during adsorption process (Ateia et 951 al., 2018). Overall, lower removal efficiency has been obtained for short-chain PFAS 952 compared with that observed for long-chain ones (removal <20% and >70%, 953 respectively). The effect of different types of NOM (with different hydrophobicity) was 954 also investigated in order to assert the performance of PEI-f-CMC for PFAS removal. 955 The two NOM solutions tested had the same DOC concentration (2 mg L^{-1}) but a 956 different value of specific ultra-violet absorbance at 254 nm (SUVA₂₅₄). Results have 957

demonstrated that short-chain removal was lower than 30% from both NOM solutions and the competition between short-chain PFAS and hydrophilic NOM (SUVA₂₅₄ = 1.7 L $mg^{-1} m^{-1}$) was higher than that with hydrophobic NOM (SUVA₂₅₄ = 4.9 L mg^{-1} m^{-1}). The hydrophobicity of NOM does not seem to influence the adsorption of long-chain PFAS on PEI-f-CMC and their removal efficiency was higher than 70% for both NOM solutions.

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6. Regeneration of adsorbents

Despite the widespread use of adsorption and anion-exchange processes for PFAS removal, the main drawback of their application at full-scale is the regeneration of spent materials when their adsorption capacity has been exhausted. Regeneration must allow the removal of adsorbed PFAS in order to restore the adsorption capacity of spent materials by means of technologies, which have economic viability and environmental security.

For instance, chemical regeneration of saturated adsorbents is usually performed in situ at full scale treatment processes. However, it is not always feasible because of the related costs or environmental issues, as discussed in the next section. On the other hand, the thermal regeneration is often performed off-site at the adsorbent manufacturing establishment. Therefore, a direct comparison between the abovementioned techniques is not easy. Overall, in-situ regeneration should be pursued to avoid the transportation, treatment and/or disposal of exhausted materials.

To date, regeneration and reuse of materials saturated with PFAS is challenging, asdiscussed in the following sections.

980 6.1. Chemical regeneration

PFAS anionic head could be desorbed using a solution of sodium salts (such as sodium chloride, NaCl, and sodium hydroxide, NaOH), whereas a solution of organic alcohol is required to desorb the hydrophobic C-F chain (Wang et al., 2014; Woodard et al., 2017). Figure 4 depicts a schematic view of PFAS-saturated adsorbent which is regenerated using a chemical solution made of sodium salts and organic alcohol. In Figure 3 the desorption mechanisms related to the use of sodium ions and organic solvents are illustrated as well.

Table 5 reports a compilation of data on chemical regeneration of PFAS-exhausted 988 adsorbents with particular attention to chemical solution employed and regeneration 989 percentage achieved. Due to the lower solubility of PFAS on ionic strength media, 990 conventional solutions of sodium salts were ineffective in regenerating adsorbents 991 exhausted by both long- and short-chain PFAS (Conte et al., 2015; Deng et al., 2015b). 992 Regeneration percentages were lower than 10% when regeneration agents, including 993 994 NaCl and NaOH, were adopted for desorbing PFBS and PFOS from acrylic resins (Carter and Farrell, 2010; Deng et al., 2010). The deprotonation of amine groups on 995 acrylic gel-type resins allowed the desorption of PFOS at a low concentration of NaOH 996 solutions, although a regeneration percentage of about 90% was achieved when a 997 solution of sodium hydroxide and methanol was tested (Table 5). 998

Mixture of sodium salts and organic solvents (such as CH_3OH , C_2H_5OH and C_3H_6O) have been widely used in order to involve the desorption of PFAS (Deng et al., 2015b; Yu et al., 2008; Zaggia et al., 2016). Moreover, the efficiency of regenerating solution depends on resin properties and, in particular, on the interactions established between PFAS and resin functional groups (Deng et al., 2010). In fact, data from regeneration

1004 experiments carried out using different mixtures of inorganic salts with or without organic alcohol demonstrated that the amount of PFAS desorbed from three different 1005 types of strong AE resins depends on resin hydrophobicity and, consequently, on the 1006 interactions between PFAS and the alkyl chains of the functional exchange group 1007 (Zaggia et al., 2016). Solution of ammonium salts (such as NH₄OH and NH₄CI) showed 1008 a good efficiency for the desorption of PFBA, PFBS, PFOA and PFOS from AE resins 1009 1010 with trimethyl quaternary amine functional group (i.e., Purolite A600E and A520E). 1011 Whereas, the same regenerating solution was totally ineffective in reactivating highly hydrophobic resin (i.e., Purolite A532E), since the solvatation of fluorine chain was 1012 1013 needed in order to remove PFAS molecules from the active sites of the resin (Table 5). In that case, the organic solvent could slacken the hydrophobic interactions between 1014 PFAS and resin, then the inorganic anions of ammonium salts (OH⁻ or Cl⁻) could replace 1015 1016 PFAS (Figure 4), achieving the recovery of the exchange capacity of the resin.

The effect of different temperatures of DI water as regenerating solution on PFOS 1017 desorption from BdAC was also investigated (Deng et al., 2015b). Results from 1018 regeneration experiments demonstrated that a higher temperature of DI water (about 80 1019 °C) enhanced the PFOS desorption and the regeneration percentage was about 53% 1020 (Table 5). Furthermore, PFOS desorption from PACFs was about 5% when DI water 1021 was employed as regenerating solution (Chen et al., 2017). By contrast, the 1022 regeneration percentage increased with the increase of ethanol concentration in the 1023 1024 regeneration solution (Chen et al., 2017; Punyapalakul et al., 2013; Wang et al., 2014). Nevertheless, regenerating solution made of organic solvent is not suitable for the 1025 treatment of drinking water on full-scale applications, and consequently on-site 1026

regeneration is not feasible. It is noteworthy that the effect of OM co-adsorbed on 1027 materials may affect regeneration efficiency. After five successive adsorption-1028 regeneration cycles, the efficiency of BdAC for PFCAs removal (PFHxA, PFHpA and 1029 PFOA) decreased, while AE resin (IRA67) performance was relatively stable (Du et al., 1030 2015). Co-adsorbed organic pollutants on surface or pores of AC could interfere with 1031 the regeneration process. It was the case of the R-CAC, which was regenerated 1032 1033 through different regenerating solutions (made of 70% ethanol, 90% methanol or 90% 1034 acetone). After the regeneration, R-CAC was reused for PFOS and F-53B removal from industrial wastewater (Du et al., 2016a). Due to the presence of non-desorbed OM, the 1035 1036 adsorption efficiency of regenerated R-CAC decreased after each regeneration cycle. For this reason, persulfate oxidation was tested as alternative regeneration process to 1037 the conventional elution with organic solvents. Regeneration results demonstrated that 1038 1039 sulphate free radicals were able to diffuse into pores of activated carbon and they allowed the degradation of both PFAS and other organic compounds. However, 1040 sulphate free radicals could cause the release of fluorine and short-chained PFAS due 1041 to break-down of long-chained PFAS (Du et al., 2016a). Consequently, further 1042 investigations should be addressed in order to better understand the effect of sulphate 1043 and other free radicals on degradation of PFOS. 1044

1045 Overall, the need of organic solvents for the chemical regeneration of PFAS saturated 1046 adsorbents is a relevant limitation of this technique.

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6.2. Thermal regeneration

Thermal regeneration in N_2 gas stream of GAC saturated with long-chain PFAS (PFOS, PFHxS and PFOA) has been investigated in order to evaluate the release of volatile organic fluorine (VOF) or other compounds such as short-chain compounds (Watanabe 1051 et al., 2016). Thermal regeneration may be optimized when GAC is maintained at 700 °C and later off-gases will be kept at 1000 °C. Nevertheless, the high temperature 1052 needed for thermally regenerating AC may cause the decreasing of their adsorption 1053 properties and a change in AC morphology (Watanabe et al., 2018). These described 1054 aspect of thermal regeneration of activated carbon deserve a deep investigation. 1055 Calcination at 600 °C in air for 20 min has been investigated for the reusability of h-BNs 1056 saturated with PFDA and PFOS (Feng et al., 2016). A temperature of 600 °C was 1057 1058 selected in order to reach the complete decomposition of the investigated PFAS compounds, since PFOS and PFDA are decomposed at about 480 °C and 200 °C, 1059 1060 respectively, as inferred from differential scanning calorimetry curves (Feng et al., 2016). Moreover, calcium hydroxide $(Ca(OH)_2)$ was employed as additive to avoid the 1061 formation of short-chain fluorinated gases during calcination process. Results about 1062 1063 regeneration experiments of h-BNs via calcining demonstrated that adsorption capacity was maintained approximately constant during different adsorption-regeneration cycles 1064 (the amount of PFOS or PFDA on the surface of h-BNs at equilibrium ranged about 0.35 1065 -0.45 mg m⁻²) (Feng et al., 2016). 1066

1067 Recently, microwave (MW) irradiation became an alternative process to conventional 1068 thermal regeneration due to its advantages, such as rapidity and selectivity heating 1069 (Falciglia et al., 2018). This technique includes the conversion of MW electric field 1070 energy adsorbed by the solid medium (i.e., activated carbon) into heat at the molecular 1071 level (Falciglia et al., 2017). The dielectric properties of activated carbon combined with 1072 PFAS properties (such as their volatility) could allow the regeneration of PFAS-

- 1073 exhausted AC by means of the interactions between delocalized π -electrons of AC and
- 1074 the MWs. MW regeneration of PFAS-exhausted AC deserve further investigation.

Poly- and perfluoroalkyl substances (PFAS) are a large group of manmade chemicals characterized by high stability and persistence on environmental compartments. Among interim response measures, adsorption technologies (i.e., by activated carbon or anionexchange resin) are currently employed for treatment of PFAS-impacted water.

7. Conclusions and future research recommended

1081 The present critical review of data on PFAS adsorption suggests that:

7.1. Conclusions

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 To date, most of the experimental works published have been carried out under unrealistic operating conditions, such as high dosage of adsorbent materials, long EBCT, acid pH, and high concentrations of PFAS spiked in DI water. Such conditions are not representative of either full-scale treatment plants or actual environmental contaminations.

Long-chain PFAS adsorption can involve the formation of aggregates on surface
 materials that may improve the adsorption efficiency by hydrophobic interactions.
 Furthermore, when different long-chain PFAS co-exist in solution, the longest
 PFAS outcompete the shorter due to a stronger hydrophobic interaction between
 the longest PFAS and the adsorbent surface.

Meso- and macro-porous adsorbents (both AC and resin) showed high
 adsorption capacity because long-chain PFAS can easily access.

Anion-exchange resins are more effective than activated carbon for both long and short-chain PFAS removal.

Regardless of the adsorbent used, the adsorption capacity of short-chain PFAS
 is lower than that observed for long-chain PFAS. Therefore, short-chain PFAS
 removal is more challenging.

- Adsorption of short-chain PFAS seems related to the availability of active pore
 sites because the formation of micelles (multi-layer adsorption) does not occur.
- Studies focused on the effect of OM during adsorption process report contrasting
 results. Overall, co-existing OM negatively affects short-chain PFAS adsorption
 due to active site competition, whereas the effect of OM seems less relevant
 during long-chain PFAS adsorption.
- Due to pore blockage and electrostatic repulsions, negative effect of OM on other
 adsorbent materials (such as biochar, mineral materials and magnetic nanoparticles) is also reported.
- Effect of co-existing OM should be taken into account during both adsorption and
 regeneration processes.
- Chemical regeneration of PFAS saturated adsorbents requires the use of organic
 solvents, which are harmful. Nevertheless, thermal regeneration at high
 temperature of exhausted activated carbon causes the decline of adsorption
 capacity and may release dangerous short-chain fluorinated gases. Overall, the
 in-situ implementation of either chemical or thermal regeneration is not feasible.
- 1115

7.2. Research needs

The following specific research needs can be drawn based on the observed gaps inPFAS removal by adsorption:

- The investigation of PFAS removal by adsorption (especially short-chain PFAS)
 under typical water treatment conditions (i.e., adsorbent dose or EBCT, pH,
 PFAS concentrations) is strongly advised.
- An advanced characterization of OM before and after the adsorption processes is also advised. In particular, fractionation of OM measuring hydrophobic,

transphilic and hydrophilic fractions as well as acid, neutral and base fractions is
relevant to better understand the adsorption mechanism and the effect of OM.
Size exclusion chromatography (SEC) is also suggested to ascertain the effect
of molecular weight of OM.

- Characterization of adsorbent morphology by means of transmission electron
 microscopy, scanning electron microscopy and Fourier transform infrared
 spectroscopy before and after PFAS uptake is also useful.
- The simultaneous effect of ionic strength and OM should be considered during PFAS adsorption and further investigations are required in order to better understand the contribution of ionic OM and inorganic ions (i.e., monovalent and divalent cations) on PFAS removal. Further experimental works should be performed at different OM fractions but at the same ionic strength in order minimize the possible effect of inorganic ions.
- Economic assessment of PFAS removal techniques should also address the
 adsorbent disposal/regeneration. For instance, the management of the eluate
 produced by chemical regeneration of the resins should be considered.
- Other unconventional techniques, such as microwave irradiation, may help to overcome issues concerning the regeneration of PFAS-saturated adsorbents.
- A novel treatment train, which allows the combination of separation and destructive technologies is expected for the sustainable removal of PFAS.

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Journal Pression

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- 1485 **Figure 1** Box-and-whiskers plot concerning the adsorption capacity of long- and short-chain
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- 1492 Figure 4 Chemical regeneration of PFAS-exhausted adsorbents using a solution of sodium salt
- 1493 and organic alcohol.

Table 1 Physic-chemical properties of selected PFAS.

| Compound name | _ | _ | MW | | Solubility in | | | Boiling point | Melting | Density | |
|---|---------|--|----------------------|---------------------|--|--|----------------------------|-----------------------------------|----------------------|---|--|
| (CAS No.) | Acronym | Formula | g mol ⁻¹ | Log K _{ow} | water (mg L ⁻¹) | Vapor pressure | рКа | (°C) | point (°C) | (g cm ⁻³) | |
| Perfluoroalkyl carboxylic acids (PFCAs) | | | | | | | | | | | |
| Short-chain (C ₄ -C ₇) | | | | | | | | | | | |
| Perfluorobutanoic acid (375-22-4) | PFBA | C ₃ F ₇ COOH | 214.039 ^a | 2.31 ^b | 2.14 · 10⁵ (at 25 °C) [°] | 6.38 mm Hg (25° C) [°] | 1.07 ^b | 121° | -17.5 [°] | 1.651° | |
| Perfluoropentanoic acid (2706-90-3) | PFPeA | C ₄ F ₉ COOH | 264.047 ^a | 3.01 ^b | n.a. | n.a. | 0.34 ^b | n.a. | n.a. | n.a. | |
| Perfluorohexanoic acid (307-24-4) | PFHxA | C ₅ F ₁₁ COOH | 314.054 ^ª | 3.48 ^d | 15700 (at 25 °C) ^d | 198 mm Hg (at 25 °C) ^d | -0.16 ^d | 157 ^d | n.a. | | |
| Perfluoroheptanoic acid (375-85-9) | PFHpA | C ₆ F ₁₃ COOH | 364.062 ^ª | 4.15 ^d | 3.65 (at 25 °C) ^d | 0.133 mm Hg (at 25 °C) ^d | -2.29 ^d | 175 ^d | 30 ^d | 1.792 (at 20 °C) ^d | |
| | | | | Long-c | hain (C ₈ -C ₁₄) | | | | | | |
| Perfluorooctanoic acid (335-67-1) | PFOA | C ₇ F ₁₅ COOH | 414.07 ^ª | 4.81 ^d | 2290 (at 24 °C) | 3.16 · 10 ⁻² mm Hg (at 25 °C) ^d | -0.5 – 4.2 ^d | 192 ^d | 54.3 ^d | 3300 g mL ⁻¹ (at 24 °C) ^d | |
| Perfluorononanoic acid (375-95-1) | PFNA | C ₈ F ₁₇ COOH | 464.078 ^a | 5.48 ^d | n.a. | 8.3 · 10 ⁻² mm Hg (at 25 °C) ^d | -0.21 ^d | n.a. | n.a. | n.a. | |
| Perfluorodecanoic acid (335-76-2) | PFDA | C ₉ F ₁₉ COOH | 514.086 ^a | 6.51 ^b | n.a. | n.a. | -5.2 ^b | 217 (at 740 mmHg) ^a | 77 – 78 ^ª | 1.707 (at 68 °F)ª | |
| Perfluoroundecanoic acid (2058-94-8) | PFUnDA | C ₁₀ F ₂₁ COOH | 564.093ª | 7. 21 [⊳] | n.a. | n.a. | -5.2 ^b | n.a. | n.a. | n.a. | |
| Perfluorododecanoic acid (307-55-1) | PFDoDA | C ₁₁ F ₂₃ COOH | 614.101ª | 7.92 ^b | n.a. | n.a. | -5.2 ^b | n.a. | n.a. | n.a. | |
| Perfluorotridecanoic acid (72629-94-8) | PFTrDA | C ₁₂ F ₂₅ COOH | 664.109ª | 8.62 ^b | n.a. | n.a. | -5.2 ^b | n.a. | n.a. | n.a. | |
| Perfluorotetradecanoic acid (376-06-7) | PFTeDA | C ₁₃ F ₂₇ COOH | 717.117ª | 9.32 ^b | n.a. | n.a. | -5.2 ^b | n.a. | n.a. | n.a. | |
| | | | Perf | luoroalkyl s | ulfonic acids (PF | SAs) | | | | | |
| | I | 1 | | Short-o | chain (C₄-C₅) | -2 | | I | | -1 | |
| Perfluorobutane sulfonic acid (375-73-5) | PFBS | C₄F₃SO₃H | 300.095ª | 1.82 ^d | 344 (at 25°C) ^d | 2.68 · 10 ⁻² mm Hg (at 25 °C) ^d | -3.31 ^d | 210 – 212 ^d | n.a. | 1.811 g mL ⁻¹ (at 25 °C) ^d | |
| Perfluoropentane sulfonic acid (2706-91-4) | PFPeS | $C_5F_{11}SO_3H$ | 350.102ª | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| Long-chain (C ₆ -C ₁₄) | | | | | | | | | | | |
| Perfluorohexane sulfonic acid (355-46-4) | PFHxS | $C_6F_{13}SO_3H$ | 400.11ª | 3.16 ^d | 6.2 (at 25°C) ^d | 4.6 · 10⁻³ mm Hg (at 25°C) ^d | 0.14 ^d | 238 - 239 ^d | n.a. | 1.841 g L ^{-1 d} | |
| Perfluoroheptane sulfonic acid (375-92-8) | PFHpS | C ₇ F ₁₅ SO ₃ H | 450.118 ^a | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| Perfluorooctane sulfonic acid (1763-23-1) | PFOS | C ₈ F ₁₇ SO ₃ H | 500.126 ^ª | 4.49 ^d | 3.2 · 10 ⁻³ (at 25°C) ^d | 2 · 10 ^{·3} mm Hg (at 25°C) ^d | < 1.0 ^d | 249 ^d | n.a. | n.a. | |
| Perfluorononane sulfonic acid (474511-07-4) | PFNS | $C_9F_{19}SO_3H$ | 549.126 ^ª | 6.13 [♭] | n.a. | n.a. | -3.24 ^b | n.a. | n.a. | n.a. | |

| Compound name (CAS No.) | Acronym | Formula | MW g mol⁻¹ | Log K _{ow} | Solubility in water (mg L⁻¹) | Vapor pressure | pKa | Boiling point (°C) | Melting point (°C) | Density (g cm ⁻³) | |
|--|---------|---|----------------------|---------------------|--|--------------------------------------|--------------------|-----------------------|--------------------------|----------------------------------|--|
| Perfluoroalkyl sulfonic acids (PFSAs) | | | | | | | | | | | |
| Long-chain (C_6 - C_{14}) | | | | | | | | | | | |
| Perfluorodecane sulfonic acid (335-77-3) | PFDS | C ₁₀ F ₂₁ SO ₃ H | 600.141 ^b | 6.83 ^b | n.a. | n.a. | -3.24 ^b | n.a. | n.a. | n.a. | |
| Perfluoroundecane sulfonic acid (749786-16-1) | PFUnDS | $C_{11}F_{23}SO_3H$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| Perfluorododecane sulfonic acid (79780-39-5) | PFDoDS | $C_{12}F_{25}SO_3H$ | 700.157 ^a | 8.23 ^b | n.a. | n.a. | -3.24 ^b | n.a. | n.a. | n.a. | |
| Perfluorotridecane sulfonic acid (n.a.) | PFTrDS | $C_{13}F_{27}SO_3H$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| Perfluorotetradecane sulfonic acid (n.a.) | PFTeDS | $C_{14}F_{29}SO_3H$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | |
| | | | Perflu | oroalkane s | ulfonamides (FAS) | As) | | | | | |
| Perfluorooctane sulfonamide (754-91-6) | FOSA | $C_8H_2F_{17}NO_2S$ | 499.142 ^a | 5.8 ^d | 8.04 ·10 ⁻³ (at 25°C) ^d | 0.31 mm Hg (at 25°C) ^d | 3.37 ^b | n.a. | n.a. | n.a. | |
| Potassium salt of 6:2 chlorinated polyfluorinated ether sulfonate (73606-19-6) | F-53B | 6:2 CI-PFAES | 570.67 ^f | 4.84 ^e | n.a. | n.a. | < 1 ^e | n.a. | n.a. | n.a. | |
| n.a. not available, [®] PubChem (URL: https://pubchem.ncbi.nlm.nih.gov); [©] Chemicalize (URL: https://chemicalize.com/#/); [©] Lide (2007); ^d Hazardous Substances Data Bank (HSDB) (URL:https://toxnet.nlm.nih.gov); [®] predicted by software SPARC (Xiao, 2017); ¹ (Gao et al., 2017). | | | | | | | | | | | |
| | | | | | | | | | | | |

Table 1 Physic-chemical properties of selected PFAS (continued).

Table 2 Batch adsorption experiments of long-chain PFAS fitted by Langmuir model.

| Adsorbate | | Adsorbent | | | | | |
|-----------|-----------------------------------|--|---|-------------------------------------|---|---|---|
| Compound | [PFAS]₀ | Type and properties | Batch dose (mg L ⁻¹ , except stated otherwise) | Water matrix | Experimental setup | Adsorption capacity (mg-PFAS/g- <mark>ad</mark> sorbent) | References |
| | | | | | | | |
| | 15 – 150 mg L ⁻¹ | GAC Calgon F400 | 1000 | DI | T = 30 °C, pH 7.2, | 112.1 | (Ochoa-Herrera and Sierra- Alvarez, 2008) |
| | 1 – 1000 mg L ⁻¹ | PAC | 1000 | DI | T = 25 °C, 140 rpm, 48 h | 426.49 (1.03 mmol g ⁻¹) | (Rattanaoudom et al., 2012) |
| | 120 mg L ⁻¹ | BdAC $S_{BET} = 2450 \text{ m}^2 \text{ g}^{\cdot 1}$ Effective size = 0.6–0.85 mm | 200 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4.0 | 372.6 (0.9 mmol g ⁻¹) | (Du et al., 2015) |
| | | Biochar HWC Socr = $453 \text{ m}^2 \text{ a}^{-1}$ | ratio of | LW (DOC=2 mg L ⁻¹) | | 41.2 | |
| | 0.01 – 100.000 µg l ⁻¹ | pore volume= $0.11 \text{ cm}^3 \text{ g}^{-1}$ | mg mL ⁻¹ | WW (DOC=4.9 mg L ⁻¹) | T= 22 °C, 30 d, pH 7.2 | 31.7 | (Inyang and Dickenson, 2017) |
| | 0.01 – 100,000 µg L | Biochar PWC Sper = $413 \text{ m}^2/\text{q}$ | ratio of biochar:PEOA 1:3 | LW (DOC=2 mg L ⁻¹) | | 41.3 | |
| PFOA | | pore volume= 0.10 cm ³ /g | mg mL ⁻¹ | WW (DOC=4.9 mg L ⁻¹) | | 27.7 | |
| | 3.8 – 259 mg L ⁻¹ | SWNT Single walled carbon nanotubes $S_{BET} = 468 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.52 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, | 78.67 ± 8.28 (190 ± 20 mmol kg ⁻¹) | (Wang et al., 2016) |
| | | AC Calgon, microporous $S_{BET} = 825 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.54 cm ³ g ⁻¹ | | | μπισ | 194.6 ± 4.14 (470 ± 10 mmol kg ⁻¹) | |
| | 20 – 250 mg L ⁻¹ | PAC $S_{BET} = 812 \text{ m}^2 \text{ g}^{-1}$ micropore area = 466 m ² g ⁻¹ | 100 | DI | T = 25 °C, 150 rpm, 168 h (12 h for PAC) | 277.42 (0.67 mmol g ⁻¹) | (Yu et al., 2009) |
| | | GAC S _{BET} = 712 m ² g ⁻¹ micropore area = 313 m ² g ⁻¹ | | | | 161.48 (0.39 mmol g ⁻¹) | |
| | 0.05 - 10 mg L ⁻¹ | MWNT $S_{BET} = 519.7 \text{ m}^2 \text{g}^{-1}$ | 50 | DI | T = 25 °C, pH 6.5 | 2.69 ± 0.29 (0.0065 ± 0.0007 mmol g ⁻¹) | (Li et al., 2011) |
| | 20 – 300 mg L ⁻¹ | PAC $S_{BET} = 1227.19 \text{ m}^2 \text{g}^{-1}$ GAC $S_{PET} = 815.34 \text{ m}^2 \text{g}^{-1}$ | 100 | DI | T= 25 °C, 180 rpm, pH 5 | 202.9 (0.49 mmol g ⁻¹) 178.05 (0.43 mmol g ⁻¹) | (Chen et al., 2017) |
| | | GAC Calgon F400 | | | | 236.4 | (Ochoa-Herrera |
| | 15 – 150 mg L ⁻¹ | GAC Calgon F300 | 1000 | DI | T = 30 °C, pH 7.2 | 196.2 | and Sierra- Alvarez, 2008) |
| | - | GAC Calgon URV-MOD1 | | | | 211.6 | |
| PFOS | $1 - 1000 \text{ mg L}^{-1}$ | PAC | 1000 | DI | T = 25 °C, 140 rpm, 48 h | 440.11 (0.88 mmol g ⁻¹) | (Rattanaoudom et al., 2012) |
| | 44.1 μg L ⁻¹ | R-CAC S _{BET} = 1125 m ² g ⁻¹ pore volume = 0.90 cm ³ g ⁻¹ | 50 - 250 | Effluent EWTP | T= 25 °C, 170 rpm, 48 h | 0.345 mg g⁻¹ (345 µg g⁻¹) | (Du et al., 2016a) |

| Adsorbate | | Adsorbent | | | | | | | | |
|------------------|---|--|---|---|--------------------------------------|---|------------------------|--|--|--|
| Compound | [PFAS]₀ | Type and properties | Batch dose (mg L ⁻¹ , except stated otherwise) | Water matrix | Experimental setup | Adsorption capacity (mg-PFAS/g- <mark>ad</mark> sorbent) | References | | | |
| Activated carbon | | | | | | | | | | |
| | 20 – 250 mg l ⁻¹ | PAC $S_{BET} = 812 \text{ m}^2 \text{ g}^{-1}$ micropore area = 466 m ² g ⁻¹ | - 100 | DI | T = 25 °C, 150 rpm, 168 | 520.13 (1.04 mmol g ⁻¹) | | | | |
| | | GAC $S_{BET} = 712 \text{ m}^2 \text{ g}^{-1}$ micropore area = 313 m ² g ⁻¹ | | | n (12 n for PAC) | 185.04 (0.37 mmol g ⁻¹) | (Yu et al., 2009) | | | |
| | 20 – 300 mg L ⁻¹ | $\frac{FAC}{S_{BET} = 1227.19 \text{ m}^2 \text{ g}^{-1}}$ GAC $S_{BET} = 815.34 \text{ m}^2 \text{ g}^{-1}$ | - 100 | DI | T= 25 °C, 180 rpm, pH 5 | 535.13 (1.07 mmol g ⁻¹) 390.1 (0.78 mmol g ⁻¹) | (Chen et al., 2017) | | | |
| | 0.5 – 10 mg L ⁻¹ | Corn-derived-biochar (T=250 °C) $S_{BET} = 2.5 \text{ m}^2 \text{ g}^1$ total pore volume = 0.013 cm ³ g ¹ | 200 | DI + 0.01 mol L ⁻¹ of CaCl ₂ + 200 mg L ⁻¹ of NaN ₃ | T= 25 ± 1 °C, 150 rpm, 48 h, pH 7 | 135.53 | - (Guo et al., 2017) | | | |
| PFOS | | $S_{BET} = 3.75 \text{ m}^2 \text{ g}^{-1}$ total pore volume = 0.017 cm ³ g ⁻¹ | | | | 146.52 | | | | |
| | | Corn-derived-biochar (T=550 °C) $S_{BET} = 41.10 \text{ m}^2 \text{ g}^{-1}$ total pore volume = 0.043 cm ³ g ⁻¹ | | | | 166.42 | | | | |
| | | Corn-derived-biochar (T=700 °C) $S_{BET} = 297.58 \text{ m}^2/\text{g}$ total pore volume = 0.199 cm ³ /g | 2 | | | 169.90 | | | | |
| | $59.9 - 415 \text{ mg L}^{-1}$ | SWNT S _{BET} = 468 m ² g ⁻¹ pore volume = 0.52 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 560.14 ± 40.01 (1120 ± 80 mmol kg ⁻¹) | (Wang et al., 2016) | | | |
| | 1 – 500 mg L ⁻¹ | SWNT S _{BET} = 547.2 m ² g ⁻¹ | 200 - 1200 | DI | T= 25 °C, 150 rpm, 2 h, pH 7 | 712 | (Chen et al., 2011) | | | |
| | | MWN110 $S_{BET} = 324.9 \text{ m}^2 \text{ g}^{-1}$ | | | | 656 | | | | |
| | | $S_{BET} = 97.2 \text{ m}^2 \text{ g}^{-1}$ | | | | 514 | | | | |
| | 59.9 – 415 mg L ⁻¹ | microporous $B_{BET} = 825 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.54 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 480.12 ± 10 (960 ± 20 mmol kg ⁻¹) | (Wang et al., 2016) | | | |
| | 0.05 - 10 mg L ⁻¹ | MWNT $S_{BET} = 519.7 \text{ m}^2 \text{g}^{-1}$ | 50 | DI | T = 25 °C, pH 6.5 | 5.00 ± 0.5 (0.010 ± 0.001 mmol g ⁻¹) | (Li et al., 2011) | | | |
| | 30 – 200 mg L ⁻¹ (30 – 200 ppm) | PAC $S_{BET} = 1521.85 \text{ m}^2 \text{g}^{-1}$ 40% Ni-PAC $S_{BET} = 947.98 \text{ m}^2 \text{g}^{-1}$ | - 133.3 | DI | T= 25 °C, 170 rpm | 360.1 (0.72 mmol g ⁻¹) 355.1 (0.71 mmol g ⁻¹) | (Liang et al., 2011) | | | |
| F-53B | 102.9 µg L ⁻¹ | R-CAC $S_{BET} = 1750 \text{ m}^2 \text{ g}^{-1}$ pore volume = 1.36 cm ³ g ⁻¹ | 50 - 250 | Effluent EWTP | T= 25 °C, 170 rpm, 48 h | 1.059 (1059.4 μg g ⁻¹) | (Du et al., 2016a) | | | |

Table 2 Batch adsorption experiments of long-chain PFAS fitted by Langmuir model (continued).

Table 2 Batch adsorption experiments of long-chain PFAS fitted by Langmuir model (continued).

| Adsorbate | | Adsorbent | | | | | | | | | |
|--------------------------------|------------------------------|---|-------------------------------------|-------------------------------------|--------------------------------|--|----------------------------|--|--|--|--|
| Compound | [PFAS]₀ | Type and properties | Batch dose (mg L ⁻¹) | matrix | Experimental setup | (mg-PFAS/g- <mark>adsorbent</mark>) | References | | | | |
| Molecularly imprinted polymers | | | | | | | | | | | |
| PFOA | 1-12 mg L ⁻¹ | DFB-CDP S _{BET} < 10 m ² g ⁻¹ | 100 | DI | T= 23 °C, 400 rpm, 2 h | 34 | (L. Xiao et al., 2017) | | | | |
| | 20 – 550 ma L ⁻¹ | Chitosan-based MIP | 100 | DI | T = 25 °C, 36 h, pH 5 | 1455.52 (2910.3 μmol g ⁻¹) | (Yuetal 2008) | | | | |
| PFOS | | Chitosan-based NIP | | | | 1203.51 (2406.4 μmol g ⁻¹) | (1 0 01 0, 2000) | | | | |
| | 10 - 80 ma l ⁻¹ | MIP-CMS | 250 | DI | T= 25 °C, 150 rpm, 2 h, pH 3 | 75.99 | (Guo et al., 2018) | | | | |
| | | NIP-CMS | 250 | | · | 43.94 | (800 81 01., 2010) | | | | |
| | | | Anio | n-exchange res | sin | T | | | | | |
| F-53B | 25-400 mg L ⁻¹ | Polyacrylic-DVB gel-type Polyamine Exchange capacity = 1.6 meq mL^{-1} Effective size = $0.3-1.2 \text{ mm}$ | 50 | Actual WW (chrome plating WW) | T=25 °C, 150 rpm, 48 h, pH 3 | 2396.84 (4.2 mmol g ⁻¹) | (Gao et al., 2017) | | | | |
| PFOA | 120 mg L ⁻¹ | IRA67Polyacrylic-DVB gel-typePolyamineExchange capacity = 1.6 meq mL^{-1} Effective size = $0.3 - 1.2 \text{ mm}$ | 100 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4.0 | 1167.67 (2.82 mmol g ⁻¹) | (Du et al., 2015) | | | | |
| | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous- type Dimethyl ethanol ammonium Exchange capacity = 1.0 meq mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 1436.82 (3.47 mmol g ⁻¹) | (Maimaiti et al., 2018) | | | | |
| | $20 - 250 \text{ mg L}^{-1}$ | IRA400 Styrene-DVB gel-type | 100 | DI | T = 25 °C, 150 rpm, 168 h | 1209.08 (2.92 mmol g ⁻¹) | (Yu et al., 2009) | | | | |
| | 3.8 – 259 mg L ⁻¹ | Quaternary ammonium Exchange capacity = 1.4 meq mL ⁻¹ | 375 | DI | Room temperature, 3 d, pH 6 | 331.25 ± 8.28 (800 ± 20 mmol kg ⁻¹) | (Wang et al., 2016) | | | | |
| PFHxS | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous- type Dimethyl ethanol ammonium Exchange capacity = 1.0 meq mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 1364.37 3.41 mmol g ⁻¹ | (Maimaiti et al., 2018) | | | | |
| PFOS | 25-400 mg L ⁻¹ | IRA67 Polyacrylic-DVB gel-type Polyamine | 0.05 | Actual WW (chrome plating WW) | T=25 °C, 150 rpm, 48 h, pH 3 | 2750.71 (5.5 mmol g^{-1}) | (Gao et al., 2017) | | | | |
| | 400 mg L ⁻¹ | Exchange capacity = 1.6 meq mL^{-1} Particle size = $16 - 50 \text{ mesh}$ | 35 - 500 | DI | | 2000.52 - 2500.65 (4 - 5 mmol g ⁻¹) | (Deng et al., 2010) | | | | |

| Adsorbate | | Adsorbent | | Matan | | | | | | | |
|----------------------|----------------------------------|---|-------------------------------------|-----------------|---|--|-------------------------------|--|--|--|--|
| Compound | [PFAS]₀ | Type and properties | Batch dose (mg L ⁻¹) | matrix | Experimental setup | (mg-PFAS/g- <mark>adsorbent</mark>) | References | | | | |
| Anion-exchange resin | | | | | | | | | | | |
| PFOS | 400 mg L ⁻¹ | IRA958Polyacrylic macroporous-typeQuaternary ammoniumExchange capacity = 3.7 meq g^{-1} Effective size = $0.3 - 1.2 \text{ mm}$ | 35 - 500 | DI | T=25 °C, 150 rpm, 48 h, pH 3 | 2000.52 - 2500.65 (4 - 5 mmol g ⁻¹) | (Deng et al., 2010) | | | | |
| | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous- type Dimethyl ethanol ammonium Exchange capacity = 1.0 meq mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 1395.36 2.79 mmol g ⁻¹ | (Maimaiti et al., 2018) | | | | |
| | $20 - 250 \text{ mg L}^{-1}$ | IRA400 Styrene-DVB gel-type | 100 | DI | T = 25 °C, 150 rpm, 168 h | 210.05 (0.42 mmol g ⁻¹) | (Yu et al., 2009) | | | | |
| | 59.9 – 415 mg L ⁻¹ | Quaternary ammonium Exchange capacity = 1.4 meq mL ⁻¹ | 375 | DI | Room temperature, 3 d, pH 6 | 165.04 ± 20 (330 ± 40 mmol kg ⁻¹) | (Wang et al., 2016) | | | | |
| | | | Ot | ther materials | | | | | | | |
| | 15 – 150 mg L ⁻¹ | 13X zeolite | 1000 | | T = 30 °C, pH 7.2 | 12.0 | (Ochoa-Herrera | | | | |
| | | NaY80 zeolite | | DI | | 114.7 | and Sierra- Alvarez, 2008) | | | | |
| PFOS | 1 – 500 mg L ⁻¹ | Chars from maize straw pyrolysis $S_{BET} = 11.6 \text{ m}^2 \text{ g}^{-1}$ | 200 - 1200 | DI | T= 25 °C, 150 rpm, 384 h, pH 7 | 164 | (Chen et al., 2011) | | | | |
| | | Chars from willow sawdust pyrolysis S _{BET} = 7.21 m ² g ⁻¹ | | | | 91.6 | | | | | |
| | | MA S _{BET} = 38.3 m ² g ⁻¹ | P | | | 811 | | | | | |
| | | | Synth | nesized materia | lls | | | | | | |
| PFDA | 0.4 – 50 mg L ⁻¹ | h-BNs $S_{BET} = 125.5 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.915 cm ³ g ⁻¹ | 200 | DI | T= 23 ± 2 °C, 150 rpm, 5 mM ammonium acetate | 0.16 mg m ⁻² | (Feng et al., 2016) | | | | |
| PFHxS | 19.2 – 180 mg L ⁻¹ | CTF $S_{BET} = 1270 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.63 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 224.06 ± 28 (560 ± 70 mmol kg ⁻¹) | (Wang et al., 2016) | | | | |
| PEOS | 46.51 – 372.1 mg L ⁻¹ | Crosslinked chitosan beads $S_{BET} = 14.1 \text{ m}^2 \text{ g}^{-1}$ Particle diameter = 4 – 5 mm | 60.8 | DI | T= 25 °C, 150 rpm, 150 h, pH 3 | 2605.67 (5.21 mmol g ⁻¹) | (Zhang et al., 2011) | | | | |
| PFOS | $50 - 200 \text{ mg L}^{-1}$ | PAF-45 S _{BET} = 875.38 m ² g ⁻¹ pore volume = 0.40 mL g ⁻¹ | 12.5 | DI | T= 25 °C, 180 rpm, 48 h, pH 3 | 5847.39 | (Luo et al., 2016) | | | | |

Table 2 Batch adsorption experiments of long-chain PFAS fitted by Langmuir model (continued).
| | Adsorbate | Adsorbent | | | | Advertisen consolity | | | |
|--|---|--|-------------------------------------|-------------------|---|--|------------------------|--|--|
| Compound | [PFAS] ₀ | Type and properties | Batch dose (mg L ⁻¹) | Water matrix | Experimental setup | (mg-PFAS/g- <mark>adsorbent</mark>) | References | | |
| | | | Syn | thesized material | S | | | | |
| | 0.1 – 250 mg L ⁻¹ | ARH | 100 | DI | T= 25 °C, 150 rpm, 24 h, pH 5 | 1325.34 (2.65 mmol g ⁻¹) | (Deng et al., 2013) | | |
| | 0.4 – 50 mg L ⁻¹ | h-BNs $S_{BET} = 125.5 \text{ m}^2 \text{g}^{-1}$ pore volume = 0.915 cm ³ g ⁻¹ | 200 | DI | T= 25 °C, 180 rpm, 5 mM ammonium acetate | 0.04 mg m ⁻² | (Feng et al., 2016) | | |
| PFOS | 59.9 – 415 mg L ⁻¹ | CTF $S_{BET} = 1270 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.63 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 665.17 ± 40.01 (1330 ± 80 mmol kg ⁻¹) | (Wang et al., 2016) | | |
| | 95.02 – 460.12 mg L ⁻¹ | Quaternized cotton | 100 | DI | T= 25 °C, 150 rpm, 24 h, pH 5 | 1650.43 (3.3 mmol g ⁻¹) | (Deng et al., 2012) | | |
| | $0.5 - 40 \text{ mg L}^{-1}$ | 2-MNPs@FG S _{BET} = 169.85 - 225.42 m ² g ⁻¹ | 250 | DI | 220 rpm, 30 min | 17.2 | (Wang et al., 2018) | | |
| | $20 - 300 \text{ mg L}^{-1}$ | PACFs S _{BET} = 1782 m ² g ⁻¹ | 100 | DI | T= 25 °C, 180 rpm, pH 5 | 760.2 (1.52 mmol g ⁻¹) | (Chen et al., 2017) | | |
| | $3.8 - 259 \text{ mg L}^{-1}$ | CTF $S_{BET} = 1270 \text{ m}^2 \text{ g}^{-1}$ pore volume= 0.63 cm ³ g ⁻¹ | 250 | Ы | Room temperature, 3 d, pH 6 | 269.14 (650 ± 30 mmol kg ⁻¹) | (Wang et al., 2016) | | |
| | 78.67 – 381 mg L ⁻¹ | Quaternized cotton | 100 | DI | T= 25 °C, 150 rpm, 24 h, pH 5 | 1283.61 (3.1 mmol g ⁻¹) | (Deng et al., 2012) | | |
| PFOA | 0.1 – 207.03 mg L ⁻¹ | ARH | 100 | DI | T= 25 °C, 150 rpm, 24 h, pH 5 | 1031.03 (2.49 mmol g ⁻¹) | (Deng et al., 2013) | | |
| | 0.5 – 40 mg L ⁻¹ | 2-MNPs@FG S _{BET} = 169.85 - 225.42 m ² g ⁻¹ | 250 | DI | 220 rpm, 30 min | 50.4 | (Wang et al., 2018) | | |
| | $20 - 300 \text{ mg L}^{-1}$ | PACFs $S_{BET} = 1782 \text{ m}^2 \text{ g}^{-1}$ | 100 | DI | T= 25 °C, 180 rpm, pH 5 | 302.27 (0.73 mmol g ⁻¹) | (Chen et al., 2017) | | |
| | $2 - 50 \ \mu g \ L^{-1} \qquad \left \begin{array}{c} \textbf{PEI-f-CMC} \\ S_{BET} = 7.8 \ m^2 \ g^{-1} \end{array} \right \qquad 10 \qquad DI \qquad T = 25 \pm 1 \ ^\circ \text{C}, \ 150 \ \text{rpm}, \ 24 \ \text{h} \qquad 2.32 \qquad (Ateia \ et \ al., \ 2018) \\ 2018 \end{array}$ | | | | | | | | |
| S _{BET} : BET sur activated carb shell-based G substitutes de CTF: Covalen MNPs@FG: M CMC: Poly(et) | S _{BET} : BET surface area; DI: Deionized water; PESOF WWW: Perfluorooctanesulfonyl fluoride washing wastewater; LW: Lake water; EWTP: Electroplating wastewater treatment plant; GAC: Granular activated carbon; PAC: Powdered activated carbon BdAC: Bamboo-derived activated carbon; 40% Ni-PAC: Ni-compounded PAC with Ni loading an amount of ~40 wt%; R-CAC: reactivated coconut shell-based GAC; HWC: Harwood; PWC: Pinewood; SWNT: Single-walled carbon nanotubes; MWNT: Multi-walled carbon nanotubes; DFB-CDP: cross-linked polymer network where β-CD substitutes decafluorobiphenyl (DFB); MIP-CMS: molecularly imprinted carbon microsphere; NIP-CMS: non-imprinted carbon microsphere; MA: Ash from burning maize straw on stainless steel plate; CTF: Covalent triazine-based framework; h-BNs: porous hexagonal boron nitride nanosheets; PAF-45: porous aromatic framework constructed from benzene rings; ARH: Aminated rice husk; 2-MNPs@FG: Magnetic nano-particles attached into fluorographene (mass ratio of MNPs and FG is 3:5); WW: wastewater; PACFs: Polyacrylonitrile fiber (PANF)-derived activated carbon fibers; PEI-f-CMC: Poly(ethylenimine)-functionalized cellulose microcrystals | | | | | | | | |

Table 2 Batch adsorption experiments of long-chain PFAS fitted by Langmuir model (continued).

Table 3 Batch adsorption experiments of short-chain PFAS fitted by Langmuir model.

| Ads | sorbate | Adsorbent | | Water | | A da a mati a m | |
|----------|------------------------------|---|-------------------------------------|-----------------------------|--------------------------------|--|--|
| Compound | [PFAS] ₀ | Type and properties | Batch dose (mg L ⁻¹) | matrix | Experimental setup | (mg-PFAS/g- <mark>adsorbent</mark>) | References |
| | | · | Act | ivated carbon | | • | |
| PFBA | 6.5 – 204 mg L ⁻¹ | AC Calgon microporous $S_{BET} = 825 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.54 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 51.36 ± 4.28 (240 ± 20 mmol kg ⁻¹) | (Wang et al., 2016) |
| | 31.4 mg L ⁻¹ | $\begin{array}{c} \textbf{BdAC} \\ \textbf{S}_{\text{BET}} = 2450 \text{ m}^2 \text{ g}^{-1} \\ \textbf{Effective size} = 0.6 0.85 \text{ mm} \end{array}$ | 200 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4 | 18.84 (0.06 mmol g ⁻¹) | (Du et al., 2015) |
| PFHxA | 7.2 – 217 mg L ⁻¹ | AC Calgon microporous $S_{BET} = 825 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.54 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 235.54 ± 72.23 (750 ± 230 mmol kg ⁻¹) | (Wang et al., 2016) |
| PFHpA | 40.04 mg L ⁻¹ | $\begin{array}{l} \textbf{BdAC} \\ \textbf{S}_{\text{BET}} = 2450 \text{ m}^2 \text{ g}^{-1} \\ \textbf{Effective size} = 0.6 0.85 \text{ mm} \end{array}$ | 200 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4 | 65.53 (0.18 mmol g ⁻¹) | (Du et al., 2015) |
| DEDE | 6 – 247 mg L ⁻¹ | AC Calgon microporous $S_{BET} = 825 \text{ m}^2 \text{ g}^{-1}$ pore volume = 0.54 cm ³ g ⁻¹ | 250 | DI | Room temperature, 3 d, pH 6 | 51.01 ± 3 (170 ± 10 mmol kg ⁻¹) | (Wang et al., 2016) |
| FFB3 | 15 – 150 mg L ⁻¹ | GAC Calgon F400 | 1000 | DI | T = 30 °C, pH 7.2 | 98.7 | (Ochoa- Herrera and Sierra-Alvarez, 2008) |
| | | - | Anior | exchange res | sin | | |
| PFBA | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous-type Dimethyl ethanol ammonium Exchange capacity = 1.0 meg mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 635.69 (2.97 mmol g ⁻¹) | (Maimaiti et al., 2018) |
| | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous-type Dimethyl ethanol ammonium Exchange capacity = 1.0 meg mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 1089.76 (3.47 mmol g ⁻¹) | (Maimaiti et al., 2018) |
| PFHxA | 31.4 mg L ⁻¹ | IRA67 Polyacrylic-DVB gel-type Polyamine Exchange capacity = 1.6 meq mL ⁻¹ Effective size = 0.3–1.2 mm | 100 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4 | 37.68 (0.12 mmol g ⁻¹) | (Du et al., 2015) |
| РҒНрА | 40.04 mg L ⁻¹ | IRA67 Polyacrylic-DVB gel-type Polyamine Exchange capacity = 1.6 meq mL ⁻¹ Effective size = 0.3–1.2 mm | 100 | Actual WW (PFOSF WWW) | T=25 °C, 170 rpm, 48 h, pH 4 | 192.95 (0.53 mmol g ⁻¹) | (Du et al., 2015) |
| PFBS | 50 – 400 mg L ⁻¹ | IRA910 Polystyrene-DVB macroporous-type Dimethyl ethanol ammonium Exchange capacity = 1.0 meq mL ⁻¹ | 100 | DI | T= 25 °C, 160 rpm, 240 h, pH 6 | 1023.32 (3.41 mmol g ⁻¹) | (Maimaiti et al., 2018) |

| A | dsorbate | Adsorbent | | Watar | | Advantion conscitu | |
|--|---|---|-------------------------------------|---------------|------------------------------------|---|------------------------|
| Compound | [PFAS]₀ | Type and properties | Batch dose (mg L ⁻¹) | matrix | Experimental setup | (mg-PFAS/g- <mark>adsorbent</mark>) | References |
| | | • | Synth | esized materi | als | • | |
| DERA | $0.1 - 107.02 \text{ mg L}^{-1}$ | ARH | 100 | DI | T= 25 °C, 150 rpm, 24 h, pH 5 | 363.86 (1.70 mmol g ⁻¹) | (Deng et al., 2013) |
| FIDA | $6.5 - 204 \text{ mg L}^{-1}$ | CTE | | | X | 92.03 ± 4.28 (430 ± 20 mmol kg ⁻¹) | |
| PFHxA | $7.2 - 217 \text{ mg L}^{-1}$ | $S_{BET} = 1270 \text{ m}^2 \text{ g}^{-1}$ | 250 | DI | Room temperature, 3 d, pH 6 | 376.86 ± 94.21 (1200 ± 300 mmol kg ⁻¹) | (Wang et al., 2016) |
| PFBS | PFBS $6 - 247 \text{ mg L}^{-1}$ pore volume = 0.63 cm ³ g ⁺ | | | | | 141.04 ± 12 (470 ± 40 mmol kg ⁻¹) | |
| AC: activated carbon; S _{BET} : BET surface area; DI: deionized water; PI | | | OSF WWW: perf | luorooctanesu | Ifonyl fluoride washing wastewater | ; GAC: granular activated carbon; | BdAC: bamboo- |
| | | | | | | | |

Table 3 Batch adsorption experiments of short-chain PFAS fitted by Langmuir model (continued).

| Adsor | oate | Adsorbe | ent | Organic matter | | | | |
|---|---|--|--------------------------|--|---|--|--|----------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| PFOS PFOA | 200 µg L ⁻¹ Spiking (Single solute) | PAC | 10 mg L ⁻¹ | EfOM (WWTP effluent) | DOC =7.3 mg L ⁻¹ | Batch • PFOA or PFOS + EfOM • PFOA or PFOS + PAC loaded of EfOM | PFOA (or PFOS) needs much contact time to reach the equilibrium in the presence of EfOM, in particular onto EfOM-preloaded PAC; EfOM (especially low-molecular-weight compounds) impacts negatively adsorption rate and capacity. | (Yu et al., 2012) |
| PFBA PFPeA PFHxA PFOA PFNA PFDA PFBS PFHxS PFOS | 1 μg L ⁻¹ of each PFAS Spiking (Mix) | GAC (F300, F600, 1240C) | 0.38 min | DOM (SW) Clear Creek (Golden, CO) | DOC = 1.7 mg L ⁻¹ | Column RSSCT experiment | The presence of DOM leads to faster breakthrough of PFAS, in particular shortest chain compounds. Breakthrough of >20% for all PFAS tested has been reached at 11,000 BVs and 125,000 BVs, respectively in the presence and absence of DOM. F300 is less effective with PFBA and PFPeA. | (Appleman et al., 2013) |
| PFOS PFOA PFBS PFHxS | 250.06 µg L ⁻¹ 207.03 µg L ⁻¹ 150.04 µg L ⁻¹ 200.05 µg L ⁻¹ Spiking (Single solute) | MWCNTs (MWCNTs-Pri MWCNTs-COOH MWCNTs-OH) | 20 mg L ⁻¹ | Synthetic OM (HA, 1- naphthol, phenol, benzoic acid) (Sinopharm Chemical Regent) in DI | Range of tested concentration of HA, 1-naphtol, phenol and benzoic acid 0 - 2.5 mg L ⁻¹ | Batch • PFOS + HA (or 1- naphthol, phenol, benzoic acid) • PFBS (or PFHxS, PFOA) + HA or Phenol | Competition between PFAS and organic compounds on the adsorption sites of the MWCNTs; Effect of co-existing organic compounds on PFOS removal: HA > 1-naphtol > benzoic acid > phenol; % removal in the presence of HA or phenol: PFOS > PFOA > PFHxS > PFBS. | (Deng et al., 2015a) |
| PFOS F-53B | 44.1 μg L ⁻¹ 102.9 μg L ⁻¹ Real (Mix) | R-CAC | 100 mg L ⁻¹ | EfOM (EWTP effluent) | TOC = 78.3 mg L ⁻¹ | Batch adsorption experiments of actual WW and synthetic PFAS solution (OM free) | EWTP effluent contains high amount of hydrocarbon surfactants (high concentration of TOC) which are in competition with PFOS and F-53B for active sites on R-CAC; F-53B is better adsorbed on R-CAC than PFOS due to its more hydrophobic chain and its higher concentration in the actual wastewater. | (Du et al., 2016a) |
| PFOS PFOA | 280 ng L ⁻¹ 550 ng L ⁻¹ (read from graph) | PAC (BET 880 m ² g ⁻¹) GAC (BET 800 m ² g ⁻¹) | 10 min | Synthetic HA and FA (Sigma- Aldrich) in DW | Range of tested concentration of HA and FA $5 - 25 \text{ mg L}^{-1}$ | Column | PAC and GAC efficiencies decrease with the increasing of DOC concentration. | (Pramanik et al., 2015) |

| Adsorbate | | Adsorbe | ent | 0 | Drganic matter | | | |
|--|---|--|--------------------------|---|---|---|--|-----------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| C ₄ – C ₁₂ , C ₁₄ PFCAS (PFBA,PFPeA , PFHxA, PFHpA, PFOA, PFNA, | 0.1 μg L ⁻¹ Spiking (Mix) | GAC (F400) | 6.1 min | DOM (DW) | DOC = 1.8 mg L ⁻¹ | Column RSSCT experiment | DOC removal is not linked to PFAS removal from AE or GAC column. DOC loading seems to favour the agglomeration of PFAS on the adsorbent surface. | |
| PFDA, PFUnDA, PFDoDA, PFTeDA) C ₄ , C ₆ , C ₈ PFSAs (PFBS, PFHxS, PFOS) FOSA | | AE resin (A-600, Polystyrene- DVB gel-type Quaternary ammonium) | 4.9 min | | ore-pro |)` | | (McCleaf et al., 2017) |
| PFBS PFHxS PFOS PFHxA | 0.073 ± 0.01 µg L ⁻¹ 0.47 ± 0.08 µg L ⁻¹ 1.4 ± 0.2 µg L ⁻¹ 0.28 ± 0.04 µg L ⁻¹ | GAC (coal-based, Silcarbon) | 125 mg L ⁻¹ | DOM (GW) (well at 9.5 m depth, downstream a | $DOC = 5.27 \pm 0.12 \text{ ng } \text{L}^{-1}$ | Batch adsorption isotherm for each | Effect of OM has not been highlighted. | |
| PFHPA PFOA PFNA PFDA | 0.32 ± 0.04 μg L 1.4 ± 0.13 μg L ⁻¹ 0.067 ± 0.005 μg L ⁻¹ 0.04 ± 0.02 μg L ⁻¹ Real (Mix) | PAC (anthracite coal, Silcarbon TH90 extra) | 25 mg L ⁻¹ | water-resistant clothing manufacture) | | adsorbent have been measured for the undiluted PFAS contaminated GW | | (Hansen et al., 2010) |
| C₄ – C₁₂ PFCAs (PFBA, PFPeA, PFHxA, PFHpA, | 2.5 µg L ¹ of each PFAS Spiking (Mix) | AE resin (A600, Polystyrene- DVB gel-type Quaternary ammonium) | 10 g L ⁻¹ 🧹 | DOM (LW) •Görväln (autochtonous DOM, hydrophobic) • Bolmen | •DOC = 8.3 mg L ⁻¹ •DOC = 10 mg L ⁻¹ | Batch Pre- equilibration condition (contact time about 15 min) | Effect of DOM is weak during PFAS removal by AE, in fact at the highest DOM concentration PFAS percentual removal has been reduced by 10% in comparison with DOC free solution; | |
| PFOA, PFNA, PFDA, PFDnDA, PFDoDA) C4, C6, C8 PFSAS (PFBS, PFHxS, PFOS) FOSA | | GAC (Filtrasorb 400, Calgon) | | (terrestrial, algal and bacterial- derived DOM, hydrophilic) | | 4 discrete DOM levels (8, 4, 2, 0 mg DOC L ⁻¹) for the two lake waters + PFAS mix | GAC performance is affected by DOC source and concentration. Most hydrophobic long chain PFAS are better removed at highest DOC concentration, in detail the increase of hydrophobic DOM (Görväln) concentration enhances progressively PFAS removal. Whereas, only the absence or presence of hydrophilic DOM (Bolmen) seems to influence PFAS adsorption. | (Kothawala et al., 2017) |

| Adso | rbate | Adsorbent | | Organic matter | | | | |
|------------------------|--|---|--------------------------|---|--|---|--|----------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| PFOS PFOA PFDA | 0.153 µg L ⁻¹ 0.138 µg L ⁻¹ 0.282 µg L ⁻¹ Spiking (Mix) 0.153 µg L ⁻¹ 0.269 µg L ⁻¹ 0.238 µg L ⁻¹ Spiking (Mix) 0.556 µg L ⁻¹ | GAC (Norit Darco 12x40) | 5.2 min | Synthetic NOM (Suwanne river, International Humic Substances Society) in DI NOM (SW) | $DOC = 4.3 \text{ mg L}^{-1}$ $DOC = 5.4 \text{ mg L}^{-1}$ $DOC = 7 \text{ mg L}^{-1}$ | Column RSSCT experiment | Similar breakthrough curves of PFAS tested have been obtained despite different DOM composition and concentration. DOM seems not influenced the amount of long-chained PFAS adsorbed since hydrophobic interaction represents the main adsorption mechanism. | (Sgroi et al., 2018a) |
| | 0.174 µg L ⁻¹ Real (Mix) | | | (WWTP effluent secondary) | | | | |
| PFHxS | 200 mg L ⁻¹ Spiking | AE resin (IRA910, Polystyrene-DVB macroporous-type Dimethyl ethanol ammonium) | 0.1 g L ⁻¹ | Synthetic TCE, MB, SDS (Sinopharm Chemical Reagent) in DI Synthetic HA (Sinopharm Chemical Reagent) in DI | Range of tested concentration of TCE, MB, SDS $0 - 5 \text{ mmol L}^{-1}$ Range of tested concentration of HA $0 - 200 \text{ mg L}^{-1}$ | Batch adsorption experiments are carried out by dissolving PFHxS with different organic compounds at varying concentration | Non-ionic co-existing organic compounds (i.e. MB and TCE) do not impacted PFHxS removal, regardless their concentration. Due to the affinity of AE with anionic species, IRA910 performance decreases with the increase of HA and SDS concentrations. In detail, HA and SDS occupies adsorption sites on IRA910 and the latest could form aggregates in competition with PFHxS. | (Maimaiti et al., 2018) |
| PFOA | 100 mg L ⁻¹ | ACF | 800 mg L ⁻¹ | Synthetic FA (Sinopharm Chemical Regent) in DI | Range of tested concentration of FA 0 – 500 mg L ⁻¹ | Batch adsorption experiments at varying FA concentrations are compared with blank experiments (FA free solution) | FA concentration of 100 mg L ⁻¹ causes a decrease of PFOA adsorbed (about 75.4% lower than that of FA free solution). | (Y. Wang et al., 2015) |
| PFHxA PFHpA PFOA | 31.4 mg L ⁻¹ 40.04 mg L ⁻¹ 120.08 mg L ⁻¹ Real (Mix) | AE resin (IRA67, Polyacrylic-DVB gel- type Polyamine) | 0.2 g L ⁻¹ | DOM (PFOSF WWW) | TOC = 63.2 mg L ⁻¹ | Batch adsorption experiments of simulated (DI+PFAS) and actual WW | Co-existing organic matter in actual WW has no effect on PFCAs adsorption on IRA67, whereas their presence influences negatively BdAC efficiency. | (Du et al., 2015) |

| | Adsorbate | Adsor | bent | Organic matter | | | | |
|------------------------------|--|---|------------------------|--|--|---|--|----------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| PFOA | 1 μg L ⁻¹ Spiking | DFB-CDP | 10 mg L ⁻¹ | Synthetić HA (n.a.) in DI | 20 mg L ⁻¹ | Batch kinetic experiments are performed by adding HA to the adsorbent suspension together with PFOA solution. Comparison between PFOA removal by DFB- CDP in the presence or absence of HA | DFB-CDP adsorption efficiency is unaffected by HA. | (L. Xiao et al., 2017) |
| PFOS PFBS | 50 – 1000 μg L ⁻¹ Spiking (Single compound) | Boehmite | 5 g L ⁻¹ | Synthetic HA in DI Fluka Co. (Buchs, Switzerland) | Range of tested concentration of HA 2 – 50 mg L ⁻¹ | Batch adsorption experiments performed for 72 h for achieving the equilibrium | With the increasing of HA adsorbed, boehmite surface becomes negative and electrostatic repulsions cause the reduction in PFOS and PFBS sorption. | (F. Wang et al., 2015) |
| PFOA PFOS | 340 ng L ⁻¹ 520 ng L ⁻¹ Real (Mix) | GAC (BET = 800 m ² g ⁻¹) | 20 min | Commercial organics: BSA, sodium alginate and HA (Sigma- Aldrich) in LW | DOC= $7.88 \pm 0.07 \text{ mg L}^{-1}$ Protein = $11.54 \pm 0.22 \text{ mg L}^{-1}$ Carbohydrate = 8.92 ± 0.28 mg L ⁻¹ | Column | Removal efficiency is the highest at the lower DOC concentration, due to the competition for adsorption sites. Protein has the greater influence on PFOA and PFOS adsorption behaviour by means of hydrophobic and electrostatic interactions. | (Pramanik et al., 2017) |
| PFOA PFOS | 103.5 – 4140.7 µg L ⁻¹ 125 – 5001.2 µgI L ⁻¹ Spiking (Single compound) | F-MT | 10 mg L ⁻¹ | Synthetic HA (n.a.) in DI | Tested concentration of HA 1 and 10 mg L ⁻¹ | Batch comparison of PFOA and PFOS adsorbed amounts in absence or in presence of HA | Due to nanoscale interlayers and high hydrophobicity of F-MT, HA macromolecular with hydrophilic groups could not be adsorbed. Consequently, co-existing HA weakly interferes with PFOS and PFOA adsorption (little decrease of PFOS and PFOA adsorption appeared in the presence of 10 mg L ¹ HA). | (Du et al., 2016b) |
| PFOS PFOA PFBA PFBS | 50 mg L ⁻¹ Spiking (Mix) | GAC (Filtrasorb 600, Calgon) | 400 mg L ⁻¹ | DOM (Landfill GW) | Range of tested concentration of TOC 5-20 mg L ⁻¹ | Batch adsorption isotherm experiments are conducted on both DI and landfill GW | Organic compounds in groundwater can competitive with PFAS for GAC adsorption sites as it is demonstrated by the great equilibrium and fast kinetic adsorption in DI instead of in the landfill groundwater. | (Zhao et al., 2011) |

| Ac | Isorbate | Adsorbe | Adsorbent Organic matter | | | | | |
|---|---|--|--|--|--|---|---|--------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| C4 - C14, C16, C18 PFCAS (PFBA, PFPeA PFHpA, PFOA, PFNA, PFOA, PFNA, PFDoDA, PFDoDA, PFTrDA PFTrDA PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTeDA, PFTAS (PFBS, PFHxS PFOS, PFDS) FOSA | 10 μg L ⁻¹ of each PFAS (ΣPFAS=180 μg L ⁻¹) Spiking (Mix) | HDPE PS PS-COOH | 5 mg L ⁻¹ 2 mg L ⁻¹ 2 mg L ⁻¹ | NOM SeaW (Alfacs Bay) RW (Ebro River) | TOC = 7.735 mg L ⁻¹ TOC = 4.386 mg L ⁻¹ | Batch Contact time 0, 4, 7, 50 days | PFAS adsorption on HDPE is influenced by the presence of NOM and this effect is more evidence in seawater where NOM concentration is higher than in river water. Percentages of adsorption on HDPE are below 30% and carboxylic acids are adsorbed better than PFSAs (PFOS and PFDS no adsorption). Higher adsorption velocity despite HDPE. Aromatic rings of PS monomer favour PFAS adsorption on PS and they go against organic matter competition. PFAS adsorption on PS-COOH is similar to that on PS, but adsorption rate is lower. C₁₁ and C₁₈ are the most adsorbed compounds. Effect of NOM not assessed. | (Llorca et al., 2018) |
| | 180 μg L ⁻¹ of each compound Spiking (Mix) | MNPs@FG (1-MNPs@FG, 2-MNPs@FG, 3-MNPs@FG) | 400 mg L ⁻¹ | Synthetic NOM (Internationa I Humic Substance Society) in DI | DOC = 2 mg L ⁻¹ | Batch adsorption experiments in orbital shaker at room temperature | The performance of MNPs@FG tested is slightly influenced by the presence of synthetic NOM. | |
| PFOA PFOS | 5 μg L ⁻¹ of each compound Spiking (Mix) | MNPs@FG (2-MNPs@FG) | 400 mg L ⁻¹ | NOM (LW, RW, DW) | DOC = 1.7 mg L ⁻¹ DOC = 0.6 mg L ⁻¹ DOC < 0.1 mg L ⁻¹ | Batch, investigation of PFOA and PFOS removal from environmental water | After 11 minutes, 2-MNPs@FG exhibits high removal efficiencies (about 99.2 %) for both PFOA and PFOS in all water matrixes tested. The residual concentration of PFOA and PFOS are 11 and 28 ng L ⁻¹ , 16 and 22 ng L ⁻¹ , 31 and 18 ng L ⁻¹ , in lake, river and drinking waters, respectively. Residual combined concentration of PFOA and PFOS (49 ng L ⁻¹) in DW is lower than health advisory level of 70 ng L ⁻¹ (US EPA, 2016) | (Wang et al., 2018) |

| Ac | Isorbate | Adsorb | ent | 0 | rganic matter | | | |
|---|--|--|--|--|--|--|---|---------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| C₄ - C8 PFCAs (PFBA, PFPeA PFHxA, PFHpA, PFOA) C₄ - C8 PFBS, PFHxS, PFHxS, PFHpS, PFOS) | 3.7 ± 0.9 μ g L ⁻¹ 5.2 ± 0.4 μ g L ⁻¹ 7.6 ± 0.5 μ g L ⁻¹ 1.5 ± 0.1 μ g L ⁻¹ 10.7 ± 0.9 μ g L ⁻¹ 1.8 ± 0.0 μ g L ⁻¹ 21.0 ± 0.3 μ g L ⁻¹ 1.7 ± 0.1 μ g L ⁻¹ 33.1 ± 0.6 μ g L ⁻¹ Real (Mix) | GAC (Filtrasorb 300, Calgon) Biochar (Mountain Crest Gardens, MCG, pine needle- derived biochar) | 100 mg L ⁻¹ | DOM (AFFF- impacted GW) | DOC = 46.0 ± 0.9 mg L ⁻¹ | Batch adsorption experiments with unfiltered AFFF- impacted GW for 5 days (no equilibrium reached) | Effect of OM has not been highlighted. | (X. Xiao et al., 2017) |
| PFOA PFOS | 82.8 mg L ⁻¹ 129.12 mg L ⁻¹ Spiking (Single compound) | CTF AE resin (IRA- 400, Amberlite Sinopharm Chemical Regent Co., China) Microporous AC (Calgon Carbon Co., USA) SWNT (Nanotech Port Co., China) | 250 mg L ⁻¹ 375 mg L ⁻¹ 250 mg L ⁻¹ | Synthetic HA (soil- extracted) in DI | Range of tested concentration of HA 10 – 40 mg L ⁻¹ | Batch single-point adsorption data (equilibrium pH equal to 6) of each chemical testing the different adsorbent materials | HA do not strongly interfere with CTF adsorption since HA molecules are unable to enter in the internal pores of CTF due to size-exclusion mechanism. HA present slightly increases PFOA and PFOS adsorbed rates, maybe due to a weak expansion of the polymer matrix and consequently an increase of PFOA and PFOS access to more adsorption sites. Direct competition for adsorption sites on AC and SWNT between dissolved HA and PFOA or PFOS. At the highest concentration of HA (40 mg L ⁻¹), the reduction of PFOA and PFOS adsorption rates are 31-48 % and 95% for both AC and SWNT, respectively. | (Wang et al., 2016) |

| | Adsorbate | Adsorbe | nt 🛛 | Organic matter | | Experimental | | |
|--|---|--|---|--|--|---|---|------------------------------------|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | setup | Remarks | References |
| C4 - C14 PFCAS (PFBA, PFPeA PFHpA, PFHpA, PFOA, PFDA, PFDA, PFDDA, PFDDA, PFDDA, PFDDA, PFDDA, PFDDA, PFDDA, PFD | 212 ng L ⁻¹ 133 ng L ⁻¹ 109 ng L ⁻¹ 24 ng L ⁻¹ 430 ng L ⁻¹ <1 ng L ⁻¹ | AE resin (A600E Polystyrene- DVB gel-type Trimethyl quaternary amine A520E Polystyrene- DVB macroporous- type Trimethyl quaternary amine A532E Polystyrene- DVB gel-type Bifunctional quaternary amine) | 10.1 min | DOM (GW) | n.a. | Column Pilot-scale | Effect of OM has not been assessed. | (Zaggia et al., 2016) |
| PFOS) | 27 ng L ⁻¹ Real (Mix) | GAC C (mesh: 8x30, iodine number 900 mg g ⁻¹) J (mesh: 12x40, iodine number 1100 mg g ⁻¹) S (mesh: 12x40, iodine number 1000 mg g ⁻¹) | 10 – 11 min | 2 | | Column Full-scale | | |
| PFBA PFOA | 1 μg L ⁻¹ Spiking (Single compound) | Biochar (HWC, PWC) | 50 mg in 150 mL 333 mg L ⁻¹ 1:3 mg mL ⁻¹ (biochar:PFAA volume ratio) | EfOM (Tertiary treated WW effluent) | $DOC = 4.9 \text{ mg L}^{-1}$ | Batch adsorption kinetic tests, samples are continuously mixed over 30 days on an orbital shaker | Slow kinetics for PFBA and PFOA adsorption may be attributed to pre- loaded EfOM on the biochar surface. At the equilibrium, the amount of PFOA adsorbed is 3-4 times higher than the amount of PFBA sorbed on both HWC and PWC. | |
| PFOA | 0.01 – 100000 μg L ⁻¹ Spiking | Biochar (HWC, PWC) | 1:3 mg mL ⁻¹ (biochar:PFAA volume ratio) | EfOM (Tertiary treated WW effluent) NOM (LW, Lake Mead in Southern Nevada) | DOC = 4.9 mg L ⁻¹ DOC = 2.0 mg L ⁻¹ | Batch adsorption isotherm tests using two test waters for evaluating the impact of source water on the adsorption of PFOA on different type of biochar | Effect of OM on PFOA adsorption is more intense in WW in which the higher DOC concentration has been measured. OM molecules occupy high-energy pore sites and consequently they lead to pore blockage during PFOA adsorption. OM adsorbed leads also to a change in surface charge with the increasing of repulsion forces between anionic PFOA molecules and biochar surfaces. PFOA adsorbed in WW is 25% less than that in LW. | (Inyang and Dickenson, 2017) |

| A | dsorbate | Adsorbe | nt | Or | ganic matter | | | |
|---|---|---|---|---|---|---|--|---|
| Target PFAS | Level | Туре | Batch dose or EBCT | Source (Water matrix) | Concentration | Experimental setup | Remarks | References |
| PFPeA PFHxA PFOA PFOS | $17.6 \pm 2.4 \text{ ng L}^{-1}$ 9.5 ± 1.4 ng L ⁻¹ 7.3 ± 0.8 ng L ⁻¹ 4.1 ± 5.6 ng L ⁻¹ Real (Mix) | GAC (Norit 830) Anthracite (Leopold) Biochar (HWC) | 8 min | EfOM (Tertiary treated WW effluent) | DOC = 4.9 mg L ⁻¹ | Column Pilot-scale | Faster breakthrough for PFAS tested is observed in anthracite and biochar filters than GAC. The latter shows the best PFAS removal efficiency in comparison with anthracite and HWC. Effect of OM has not been highlighted. | (Inyang and Dickenson, 2017) |
| PFBS PFHpA PFNA PFOA | 32 ng L ⁻¹ 27 ng L ⁻¹ 7 ng L ⁻¹ 26 ng L ⁻¹ | Biofilter (O ₃ + GAC) | 23 min | DOM (water reclamation plant) | DOC = 4.17 mg L ⁻¹ | Column Pilot-scale | In the pre-ozonated regenerated GAC biofilter more active sites are accessible for PFAS, due to the oxidation of competitive organic compounds. However, short-chain PFAS adsorption amount is lower than long-chain ones. | (Sun et al., 2018) |
| $C_4 - C_{13}$ PFCAS (PFBA, PFPeA PFHxA, PFHpA, PFDA, PFDA, PFDA, PFDA, PFDDA, PFTrDA) $C_4 - C_{10}$ PFSAS (PFBS, PFPeS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxS, PFHxA, PFHxA, PFDA, PF | 1 μg L ⁻¹ of each compound Spiking (Mix) | PEI-f-CMC | 25 mg L ⁻¹ | DOM (LW) Isolated NOM (hydrophobic type) Isolated NOM | DOC = 2 mg L^{-1} SUVA ₂₅₄ = $2.0 \text{ L} \text{ mg}^{-1} \text{ m}^{-1}$ DOC = 2.5 mg L^{-1} SUVA ₂₅₄ = $4.9 \text{ L} \text{ mg}^{-1} \text{ m}^{-1}$ | Batch | The longest PFAS (PFDoDA, PFTrDA, PFNS, PFDS) are better removed in lake water than in DI (removal efficiency is ~100% and ~85%, respectively). Whereas, the removal efficiency of short PFCAs is higher in DI (<20%). Removal efficiency of others PFAS is almost equal in both LW and DI. The removal efficiency of short-chain PFAS is higher at the highest SUVA ₂₅₄ (hydrophobic NOM). However, short-chain PFAS removal efficiency is lower than 30%. The difference in NOM composition (different SUVA ₂₅₄) does not influence the adsorption of longer PFAS, whose removal efficiency is higher than 70%. | (Ateia et al., 2018) |
| PFHpS, PFOS, PFNS, PFDS) | | | | Isolated NOM (hydrophilic type) | DOC = 2.5 mg L ⁻¹ SUVA ₂₅₄ = 1.7 L mg ⁻¹ m ⁻¹ | | | |
| EBCT: Emp Surface wat treatment pl wastewater perfluorooct montmorillou fluorographe | ty bed contact time; er; RSSCT: rapid sn ant; TOC: total orga treatment plant; TCE anesulfonyl fluoride nite; HDPE: high-der ene; AFFF: Aqueous | PAC: powdered activat hall-scale column tests; nic carbon; DW: drinkin E: tri- chloroethylene; M washing wastewater; D nsity polyethylene; PS: film-forming foam; CTI | ed carbon; EfC MWCNTs: mu g water; FA: fu B: methylbenz FB-CDP : cros polystyrene; P F: Covalent tria | DM: effluent organio Ilti-walled carbon n Ilvic acids; AE: anio ene; SDS: sodium ss-linked polymer n S-COOH: poly-styr azine-based framev | c matter; DOC: dissolved org anotubes; HA: humic acids; on-exchange; GW: groundwa dodecyl sulphate; ACF: activ etwork where β-CD substitut ene carboxylic acid; RW: riv vork; SWNT: single-walled c | panic carbon; GAC R-CAC: reactivate ater; LW: lake wate vated carbon fiber es decafluorobiph er water; SeaW: s arbon nanotubes; | C: granular activated carbon; DOM: dissolved orga ad coconut shell based GAC; EWTP: electroplating er; NOM: natural organic matter; DI: deionized wat ; BdAC: bamboo-derived AC; PFSOF WWW: henyl; BSA: bovine serum albumin; F-MT: Fluorina eawater; MNPs@FG: magnetic nano-particles atta HWC: hardwood biochar; PWC: pinewood biochar | nic matter; SW: J wastewater ter; WWTP: ted ached into r; PEI-f-CMC: |

Table 4 Experimental studies (both batch and column test) of PFAS adsorption performed in the presence of organic matter (continued).

poly(ethylenimine)-functionalized cellulose microcrystals; SUVA₂₅₄: specific ultra-violet absorbance at 254 nm.

| Table 5 Chemical | regeneration | of PFAS-sa | turated materials | s. |
|------------------|--------------|------------|-------------------|----|
| | regeneration | 0111710 00 | taratoa matoriale | ~ |

| Adsorbate | Adsorbent | Water matrix in adsorption experiments | Ratio mass:solution mixture | Experimental setup | Chemical solution | Regeneration percentage (%) | References |
|---------------|---|--|-----------------------------------|--|---|-----------------------------------|-------------------------|
| PFOS | PAC | | | | 100% C₂H₅OH | 75.41 | |
| | hydrophobic surface | | | | 70% C ₂ H ₅ OH + 30% DI | 87.41 | |
| | $S_{BET} = 980 \text{ m}^2 \text{ g}^{-1}$ | | | | 50% C ₂ H ₅ OH + 50% DI | 94.58 | |
| | pore volume = 276 mm ³ g ⁻¹ | | | | 40% C ₂ H ₅ OH + 60% DI | 81.46 | |
| | | | | | 30% C ₂ H ₅ OH + 70% DI | 80.96 | |
| | | | | | 20% C ₂ H ₅ OH + 80% DI | 55.16 | |
| | | | | | 10% C ₂ H ₅ OH + 90% DI | 45.22 | |
| | HMS | | | | 100% C ₂ H ₅ OH | 101.27 | |
| | hydrophilic surface | | | Batch | 70% C₂H₅OH + 30% DI | 101.14 | |
| | $S_{BET} = 712 \text{ m}^2 \text{ g}^{-1}$ | | | Adsorbed PFOS is extracted | 50% C ₂ H ₅ OH + 50% DI | 100.16 | / 5 |
| | pore volume = $773 \text{ mm}^3 \text{ g}^{-1}$ | DI | 100 mg:50 mL | by varying ethanol and Milli-Q | $40\% C_2 H_5 OH + 60\% DI$ | 74.74 | (Punyapalakul et |
| | | | Ŭ | water ratios | $30\% C_2 H_5 OH + 70\% DI$ | 71.50 | al., 2013) |
| | | | | T=25 °C | 20% C ₂ H ₅ OH + 80% DI | 68.47 | |
| | | | | | 10% C ₂ H ₅ OH + 90% DI | 58.69 | |
| | OD-HMS | | | | 100% C ₂ H ₅ OH | 101.12 | |
| | hydrophobic surface | | | | 70% C ₂ H ₅ OH + 30% DI | 100.72 | |
| | $S_{BET} = 476 \text{ m}^2 \text{ g}^{-1}$ | | | Pro | 50% C ₂ H ₅ OH + 50% DI | 101.34 | |
| | pore volume = $499 \text{ mm}^3 \text{ g}^1$ | | | | 40% C ₂ H ₅ OH + 60% DI | 61.70 | |
| | | | | | 30% C ₂ H₅OH + 70% DI | 66.07 | |
| | | | | | 20% C ₂ H ₅ OH + 80% DI | 60.98 | |
| | | | | | 10% C ₂ H₅OH + 90% DI | 57.90 | |
| | Purosorb PAD 500 | | 5 g:250 mL | Batch, magnetic stirrer at 250 rpm in a thermostatic oven for 80 h | 5% NH₄CI | 0 | (Conte et al., 2015) |
| | Polysyrenic macroporous-type, | | | | 5% NH₄OH | 0 | |
| | nonionic | | | | 3% NH4CI + 3% NH4OH | 0 | |
| | Exchange capacity = n.a. | | | | 30% MeOH | 20 | |
| | | | | | 50% MeOH + 3% NH ₄ OH | 90 | |
| | Macronet MN102 | | | | 5% NH ₄ Cl | 0 | |
| | Polystyrenic crosslinked | DI | | | 5% NH₄OH | 0 | |
| | macroporous-type, tertiary amine | | | | 3% NH ₄ Cl + 3% NH ₄ OH | 0 | |
| | functional groups | | | | 30% MeOH | 20 | |
| | Exchange capacity = $0.2 \text{ meg } L^{-1}$ | | | | 50% MeOH + 3% NH4OH | 90 | |
| PFOA | AE resin | | | | 5% NH₄CI | 20 | |
| | Purolite A600E | | | | 5% NH₄OH | 30 | |
| | Polystyrenic gel-type, quaternary | | | 1=20 °C | 3% NH4CI + 3% NH4OH | 85 | |
| | ammonium with trimethyl group | | | | 30% MeOH | < 20 | |
| | functional groups Exchange capacity = 1.4 meg L^{-1} | | | | 50% MeOH + 3% NH₄OH | 40 | - |
| | AE resin | | | | 5% NH₄Cl | 35 | |
| | Purolite A520E | | | | 5% NH₄OH | 35 | |
| | Polystyrenic macroporous-type, | | | | 3% NH ₄ Cl + 3% NH ₄ OH | 90 | |
| | quaternary ammonium with trimethyl | | | | 30% MeOH | 20 | |
| | group functional groups Exchange capacity $= 0.9 \text{ meg L}^{-1}$ | | | | 50% MeOH + 3% NH4OH | 50 | |
| * After 5 Ads | orption/regeneration cycles. | L | 1 | 1 | 1 | 1 | |

PAC: powdered activated carbon; S_{BET}: BET surface area; DI: deionized water; HMS: hexagonal mesoporous silica; OD-HMS: N-octyldichlorosilane grafted hexagonal mesoporous silica; AE: anionexchange;

| Adsorbate | Adsorbent | Water matrix in adsorption experiments | Ratio mass:solution mixture | Experimental setup | Chemical solution | Regeneration percentage (%) | References |
|-------------------------------|--|--|-----------------------------------|---|--|-----------------------------------|--------------------------|
| | BdAC | • | | Batch. | DI | 19.8 | |
| | $S_{BET} = 2450 \text{ m}^2 \text{ g}^{-1}$ Effective size = 0.6–0.85 mm | | | orbital shaker at 175 rpm for 24 h | 50% CH ₃ OH | 93 | |
| | | | | T = 25 °C | 50% C ₂ H ₅ OH | 98 | |
| | | | | Batch, orbital shaker at 175 rpm for 7 h T = 80 °C | | DI | |
| | | | | Batch, | 0.06% NaCl | . 1 | |
| PFOS | | DI | 10 g:100 mL | orbital shaker at 175 rpm for 24 h | 0.06% NaOH | < 1 | (Deng et al., |
| | | | - | Detel | 40% C₂H₅OH | 89 | 20150) |
| | | | | Batch, | 10% C₂H₅OH | 46 | |
| | | | | orbital snaker at 175 rpm for 23 n | 20% C ₂ H₅OH | 71 | |
| | | | | 1 = 45 °C | 30% C ₂ H₅OH | 80 | |
| | | | | Batch, orbital shaker at 175 rpm for 12 h T = 25 °C | 50% C₂H₅OH | 70 * | |
| PFOA | BdAC | | | Batch, | | 60 * | |
| PFHpA | $S_{BET} = 2450 \text{ m}^2 \text{ g}^{-1}$ | | 25 g:30 ml | spent adsorbents shake at a thermostatic | 50% CH₂OH | < 30 * | |
| PFHxA | Effective size = $0.6-0.85$ mm | | | shaker at 170 rpm for 12 h | | < 10 * | |
| PFOA | AE resin | Actual WW | | Batch, | | < 80 * | (Du et al., 2015) |
| PFHpA | Amberine IRA-67 Acrylic gel-type, tertiary amine | | 10 g:30 mL | spent adsorbents shake at a thermostatic shaker at 170 rpm for 12 h | 1% NaCl/CH₃OH | < 40 * | |
| PFHxA | functional groups Exchange capacity = 1.6 meg mL ⁻¹ | | | T = 25 °C | | < 10 * | |
| | AE resin Purolite A600E | | | • | 5% NaCl 5% KCl | 0 | |
| | Polystyrene-DVB gel-type, trimethyl quaternary amine functional groups Exchange capacity = 1.6 eq L^{-1} | DW | 300 | | 5% NH₄Cl 2% NaOH | 0 - 5 | (Zaggia et al., 2016) |
| | | | | | 2% KOH | | |
| | | | | | 2% NH₄OH | | |
| | | | | | 0.5% NaOH + 0.5% NaCl | | |
| PFBA | | | 1 g:1 L | Batch, | 0.5% KOH + 0.5% KCI | 40 - 60 60 - 80 | |
| PFOA | | | | flash stirred for 18 h and later at | 0.5% NH ₄ OH + 0.5% NH ₄ CI | | |
| PFBS PFOS | | | | controlled temperature for 60 h | 80% CH ₃ OH + 1% NH ₄ Cl | | |
| | | | | 1=20 C | 80% CH ₃ CH ₂ OH + 1% NH ₄ Cl | | |
| | AE resin Burolite 4520E | | | | 5% NaCl 5% KCl | 0 | |
| | Polystyrene-DVB macroporous- | | | | 5% NH4Cl | < 10 | |
| | type, trimethyl quaternary amine functional groups | DW | | | 2% NaOH 2% KOH | 0 - 5 | |
| | Exchange capacity = 0.9 eq L ⁻¹ | | | | 2% NH₄OH | < 10 | 1 |
| * After 5 adso BdAC: bambo | prption/regeneration cycles. | E surface area: AF | anion-exchange: V | | pnized water. | | |

Table 5 Chemical regeneration of PFAS-saturated materials (continued).

| Adsorbate | Adsorbent | Water matrix in <mark>adsorption</mark> experiments | Ratio mass:solution mixture | Experimental setup | Chemical solution | Regeneration percentage (%) | References | | |
|--|---|---|-----------------------------------|--|---|-----------------------------|-------------------------------|--|--|
| PFOS | Chitosan-based MIP | DI | 0.01 g:100 mL | Batch regeneration solution in an orbital shaker for 24 h T = 40 °C | 90% NaOH + 10% C₃H₅O | 60 * | (Yu et al., 2008) | | |
| PEOS | | | | Column | NaCl (320 mM) | 0.0 | (Carter and Farrell, 2010) | | |
| FF03 | AE resin Amberlite IRA-458 | | | Resin loaded with PFOS or PFBS packed in glass column | NaOH (320 mM) | 0.36 | | | |
| PFBS | Acrylic gel-type, quaternary ammonium functional groups Exchange capacity = 1.25 meq mL ⁻¹ | וט | n.a. | (diameter of 1 cm, height of 10 cm) Flow rate 20 mL/min for 12 h T=22 °C | NaOH (320 mM) | 4 | | | |
| | AE resin Amberlite IRA-958 Acrylic macroreticular-type, quaternary ammonium functional groups Exchange capacity = 0.8 eq L ⁻¹ | Chromium - planting WW (inorganic anions) | 20 mg:100 mL | Batch Resin loaded with PFOS and regeneration solution in an orbital shaker for 24 h at 150 | 5% NaCl 5% NaCl + 10% CH ₃ OH 1% NaCl + 10% CH ₃ OH 1% NaCl + 30% CH ₃ OH 100% CH ₃ OH 4% NaOH | < 10 | (Deng et al., 2010) | | |
| | | | | | 1% NaCl + 50% CH₃OH | 70 | | | |
| | AE resin | | | | 1% NaCl + 50% CH₃OH | 90 | | | |
| PFOS | | | | | 100% CH ₃ OH | < 5 | | | |
| | Amberlite IRA-67 | | | rpm | 4% NaOH | < 5 | | | |
| | Acrylic gel-type, tertiary amine | , | | Т = 25 °С | 0.4% NaOH | 45 | | | |
| | functional groups | | | | 0.04% NaOH | 50 | | | |
| | Exchange capacity = 1.6 med mL | | | | 1% NaCl + 30% CH ₃ OH | 20 | | | |
| | | | | | 1% NaCl + 50% CH ₃ OH | 85 | | | |
| | | | | | 1% NaCl + 70% CH ₃ OH | 95 | | | |
| | | | | | 1% NaOH + 30% CH ₃ OH | 95 | | | |
| | | | | | 1% NaOH + 50% CH ₃ OH | 90 | | | |
| * After E colo | | | | 1 | 1% NaOH + 70% CH ₃ OH | 90 | | | |
| MIP: molecularly imprinted: AF: Anion-exchange: WW: wastewater: DW: drinking water: DI: deionized water. | | | | | | | | | |

| AF resin Polysyteme-DVB macroprous-type, timetryl quaternary amine functional groups DW 1 g:1 L 1 g:1 L Batch, flash stirred for 18 h and later 0 h 0.0% RNOH + 0.5% RCI 0.5% RVH - 0.5% RCI 0.5% RVH, 04 + 0.5% RVICI 0.5% RVH, 04 + 0.5% RVH 0.5% RVH, 04 - 0.5% SVH, 04 + 0.5% RVICI 0.5% RVH, 04 - 0.5% SVH, 04 + 0.5% RVH 0.5% RVH, 04 - 0.5% SVH, 04 + 0.5% RVICI 0.5% RVH, 04 - 0.5% SVH, 04 + 0.5% RVH 0.5% RVH 0.5% RVH + 0.5% RVH 0.5% RV | Adsorbate | Adsorbent | Water matrix in <mark>adsorption</mark> experiments | Ratio mass:solution mixture | Experimental setup | Chemical solution | Regeneration percentage (%) | References |
|--|-----------|--|---|-----------------------------------|--|--|-----------------------------|--------------------|
| Proofie 6320E (minetry quaternary amine functional groups Exchange capacity = 0.9 eq L ⁻¹ DW 1 g:L Issue 1 g:L Batch, lash stirred for 18 h and later a controlled temperature for groups Exchange capacity = 0.9 eq L ⁻¹ So - 65 (| | AE resin | | | | 0.5% NaOH + 0.5% NaCl | 10 - 20 | |
| Pros Projection-DVB macroporous-type, intreding quarper sample functional groups DW 1 gr1L I gr1L Desk strend of 13 M and blate at contribution (groups Exchange capacity = 0.9 eq L ⁻¹) OS% NH_QCH + 0.5% NH_QCI 80% CH_QCH + 1% NH_QCI 90% CH_QCH + 1% NH_QCI 80% CH_Q | | Purolite A520E Polystyrene-DVB macroporous-type, trimethyl quaternary amine functional | | | Batch, | 0.5% KOH + 0.5% KCI | 50 - 65 | |
| From R-CAC Stars R-CAC Stars R-CAC Stars Actual WW 10mg20 mL Batch, 10mg20 mL 110mg20 mL Batch, 10mg20 mL 10mg20 mL Batch, 10mg20 mL 10mg20 mL Batch, 10mg20 mL 10mg20 mL Batch, 10mg20 mL 10mg20 mL | | | DW | 4 . 41 | flash stirred for 18 h and later | 0.5% NH₄OH + 0.5% NH₄CI | 70 - 80 | |
| PFBA Pros groups Exchange capacity = 0.9 eq L ⁻¹ 0 ^{on} T = 2 ^{on} C 80% CH ₂ CH ₂ CH +1% NH ₂ CL 5% NGCL 80 - 90 AF resin Pros AF resin Providite AS32E Polystymeic macroproves/pee, blunctional groups Exchange capacity = 0.85 eq L ⁻¹ pw 1 g:1 L Batch, tash stirred for 18 h and later 0 for 0 5% NGCL 0 FFSS R-CAC Sarr = 1750 m ² g ⁻¹ pW 1 g:1 L Batch, tash stirred for 18 h and later 0 for 0 0.5% NH ₂ CL 0 - 5 0.5% NH ₂ CL 0 0 20(6) 20(6) 20(6) 20(6) 0 5 20(6) | | | Dvv | 1 g:1 L | at controlled temperature for | 80% CH ₃ OH + 1% NH ₄ Cl | 80 - 90 | |
| PFBA PFOS R-CAC SHET = 1750 m ² g ⁻¹ DW 1 g-1 L I m 20 C 5% KG1 (2agia et al., 05% KG1) (2agia et al., 2% KG1) | | groups | | | бо n T = 20 °C | 80% CH ₃ CH ₂ OH + 1% NH ₄ Cl | | |
| PFBA PFOS AE resin Prost Matrix Providite AS2E Polystyrenic macroprous-type, bifunctional groups Exchange capacity = 0.85 eq L ⁻¹ DW 1 g:1 L Batch, 1 g:1 L Start, 1 g:1 L Batch, 1 g:1 L Start, 1 g:1 L Batch, 1 g:1 L Batch, 1 g:1 L Batch, 1 g:1 L Start, 1 g:1 L Batch, 1 g:1 L Batc | | Exchange capacity = $0.9 \text{ eq } L^{-1}$ | | | | 5% KCI | | |
| PFOA PFDS PFOS Purclise A532E Polystyretic macroprous-type, bifunctional quaternary amine functional q | | AE resin | | | | 5% NaCl | 0 | |
| PFOS Polystyrenic macroprous-type, bifunctional groups L(2diggle ef al., 2016) Control (2diggle ef a | PFBA | Purolite A532E | | | | 5% KCI | 0 | (Zennie stal |
| PFOS bifunctional quaternary smine functional groups Exchange capacity = 0.85 eq L ⁻¹ DW 1 g:1 L Batch. n = 20 °C Batch. exchange capacity = 0.85 eq L ⁻¹ 0 20% NB(-H) 0 PFOS R-CAC Swer = 1750 m ² g ⁻¹ DW 1 g:1 L Batch. n = 20 °C 0.5% ND(-H) + 0.5% ND(-1) 0 - 5 0.5% ND(-H) + 0.5% ND(-1) PFOS R-CAC Swer = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch. shaking at 170 rpm for 12 h T = 40 °C 70% CH, OH + 0.5% ND(-1) 0 - 5 0.55 NO(-H) + 0.5% ND(-1) PFOS R-CAC Swer = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch. shaking at 170 rpm for 12 h T = 40 °C 70% CH, OH = 88.5 00% CH, OH = 88.5 00% CH, OH = 88.5 F-53B R-CAC Swer = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 40 °C 50% CH, OH = 88.3 000.0 00.4 F-53B R-CAC Swer = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 60 °C 70% CH, OH = 88.3 000.0 000.0 F-53B R-CAC Swer = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 60 °C 70% CH, OH | PFUA | Polystyrenic macroporous-type, | | | | 5% NH₄CI | 0 - 5 | (∠aggia et al., |
| First or functional groups Exchange capacity = 0.85 eq L ⁻¹ DW 1 g:1 L finals stirred for 18 h and later at controlled temperature for 60 h 2% KOH 0 PFOS R-CAC Secr = 1750 m ² g ⁻¹ DW 1 g:1 L finals stirred for 18 h and later at controlled temperature for 60 h 0.5% NH_OH 0 PFOS R-CAC Secr = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C 50% CH_OH 80.5 100% CH_OH 80.5 100% CH_OH 80.5 100% CH_OH 80.5 100% CH_OH 10mg:20 mL F-53B R-CAC Secr = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C 50% CH_OH 80.4 20% CH_OH 90.6 20% CH_OH 90.6 | PEOS | bifunctional quaternary amine | | | Batch, | 2% NaOH | 0 | 2010) |
| Exchange capacity = 0.85 eq L ¹ DW 1 g:1 L at controlled temperature for 0 h T = 20 °C 2% NH_QH 0.5% NACL 0.5% NACL 0.5% NHC1 0 - 5 PFOS R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 PFOS R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 0 - 5 0 - 5 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 mL 50% CH_0H 80.4 - 100% CH_10H 0 - 5 0 - 5 R-CAC Starr = 1750 m ² g ⁻¹ Actual WW 1 0mg:20 mL Batch, 51 + 10 mg:20 + 10 </td <td>103</td> <td>functional groups</td> <td></td> <td></td> <td>flash stirred for 18 h and later</td> <td>2% KOH</td> <td>0</td> <td>1</td> | 103 | functional groups | | | flash stirred for 18 h and later | 2% KOH | 0 | 1 |
| $ \begin{tabular}{ c c c c c c } \hline F-53B & $$ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $ $$ | | Exchange capacity = $0.85 \text{ eq } L^{-1}$ | DW | 1 g:1 L | at controlled temperature for | 2% NH₄OH | | |
| $ \begin{tabular}{ c c c c c c } \hline F-53B \end{tabular} F-53B \end{tabular} \end{tabular} \begin{tabular}{ c c c c c c c } \hline T = 0 \ ^{\circ}C \end{tabular} \en$ | | | | - | 60 h | 0.5% NaOH + 0.5% NaCl | 0 5 | _ |
| PFOS R-CAC Ser = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C 0.5% NH,CL 80% CH,OH = 1% NH,CH 80% CH,OH = 1% NH,CL 80% CH,OH = 1% NH,CL 80% CH,OH = 1% NH,CL 80% CH,OH = 1% NH,CH 80% CH,OH = 1% NH,CH 80% CH,OH = 1% NH,CH 80% CH,OH = 1% NH,CH 90% CH,OH = 89.5 90% CH,OH = 89.5 90% CH,OH = 89.5 90% CH,OH = 90.2 100% CH,OH = 90.2 100% CH,OH = 90.2 90% CH,OH = 90.2 100% CH,OH = 90. | | | | | T = 20 °C | 0.5% KOH + 0.5% KCI | 80 - 90 | |
| R-CAC SBET = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C Batch, shaking at 170 rpm for 12 h T = 50 °C Batch, shaking at 170 rpm for 12 h T = 50 °C Sec H_SOH 90% CH_SOH 50% CH_SOH 100% CH_SOH 80.5 m 85.1 m 83.1 m 90% CH_SOH (Due tal., 2016a) F-53B R-CAC SBET = 1750 m ² g ⁻¹ Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 40 °C 50% CH_SOH 90% CH_SOH 83.5 m 90% CH_SOH 90.2 m 90% CH_SOH 83.6 m 90% CH_SOH 90.2 m 90% CH_SOH 90.2 m 90% CH_SOH 90.2 m 90% CH_SOH 90.2 m 90% CH_SOH 90.2 m 90% CH_SOH 90.2 m 90% CH_SOH 90.4 m 90% CH_SOH 90.2 m 90% CH_SOH 90.4 m 90% CH_SOH 90.4 m 900% CH_SOH< | | | | | | 0.5% NH ₄ OH + 0.5% NH ₄ Cl | | |
| $ \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | | | | | | 80% CH ₃ OH + 1% NH ₄ Cl | | |
| $ \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | | | | | | 80% CH ₃ CH ₂ OH + 1% NH ₄ Cl | | |
| $ \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | | R-CAC S _{BET} = 1750 m ² g ⁻¹ | | | Datah | 50% C₂H₅OH | 76.0 | |
| PFOS Actual WW 10mg:20 mL Shading at 170 rpm for 12 h T = 50 °C 90% C,H_0OH 100% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0OH 90% C,H_0O 90% C,H_0OH 90% C, | | | | | shaking at 170 rpm for 12 h T = 50 °C | 70% C₂H₅OH | 89.5 | |
| PFOS Actual WW 10mg:20 mL $100\% C_{H_0OH}$ 83.1 50% CH _{0OH} 83.1 85% CH _{0OH} 83.1 85% CH _{0OH} 85.5 90% CH _{0OH} 85.1 100% CH _{0OH} 90.2 85.6 90% CH ₀ OH 90% CH ₀ OH 90.2 50% CH ₀ OH 90.2 85.6 90% CH ₀ OH 90.2 85.6 90% CH ₀ OH 90.2 85.6 90% CH ₀ OH 90.2 85.6 90% CH ₀ OH 90.0 85.6 90% CH ₀ OH 90.6 F-53B Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C 50% C ₂ H ₀ OH 88.3 50% CH ₀ OH 88.3 70% CH ₀ OH 88.3 70% CH ₀ OH 88.3 70% CH ₀ OH 88.3 70% CH ₀ OH 88.3 70% CH ₀ OH 90.2 100% CH ₀ OH 93.1 90% CH ₀ OH 93.1 90% CH ₀ OH 92.6 90% CH ₀ OH 92.6 50% C ₂ H ₀ O 97.6 100% CH ₀ OH 92.6 100% CH ₀ OH 92.6 50% C ₂ H ₀ O 97.6 90% CH ₀ O 97.6 90% CH ₀ OH 93.4 00% C ₂ H ₀ O 93.4 00% C ₂ H ₀ O 93.4 | | | | 10mg:20 mL | | 90% C₂H₅OH | 85.1 | |
| $ \begin{tabular}{ c c c c c c } \hline PFOS & Actual WW & Actual WW & 10mg:20 mL \\ \hline & 10m$ | | | | | | 100% C₂H₅OH | 83.1 | |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$ | | | | | Batch, shaking at 170 rpm for 12 h T = 40 °C | 50% CH ₃ OH | 85.3 | |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | PEOS | | Actual W/W | | | 70% CH₃OH | 89.5 | |
| $ \left \begin{array}{c c c c c c c c c c c c c c c c c c c $ | 103 | | | | | 90% CH₃OH | 95.1 | |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$ | | | | | | 100% CH₃OH | 90.2 | |
| $ \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | | | | | | 50% C ₃ H ₆ O | 80.6 | |
| $ \begin{array}{ c c c c c c c } \hline F-53B & \hline R-CAC & & & & & & & & & & & & & & & & & & $ | | | | | | 70% C ₃ H ₆ O | 85.6 | |
| R-CAC S _{BET} = 1750 m ² g ⁻¹ Batch, shaking at 170 rpm for 12 h T = 50 °C 50% C ₂ H ₅ OH 80.4 (Du et al., 2016a) F-53B Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 50 °C 50% C ₂ H ₅ OH 90.2 66.6 90.0 90.4 90.6 90.2 | | | | | | 90% C ₃ H ₆ O | 91.6 | |
| $ \mathbf{F} - \mathbf{53B} \left[\begin{array}{c} \mathbf{R} - \mathbf{CAC} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{F} - \mathbf{53B} \end{array} \right] \\ \mathbf{F} - \mathbf{53B} \left[\begin{array}{c} \mathbf{R} - \mathbf{CAC} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} - \mathbf{C} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} - \mathbf{C} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} - \mathbf{C} \\ \mathbf{R} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{R} \\ R$ | | | | | | 100% C ₃ H ₆ O | 90.0 | (Du et al. 2016a) |
| $\mathbf{F}-\mathbf{53B} = \begin{bmatrix} \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{F}-\mathbf{53B} \end{bmatrix} \begin{bmatrix} \mathbf{S}_{BET} = 1750 \text{ m}^2 \text{ g}^{-1} \\ \mathbf{A}_{Ctual} WW \end{bmatrix} 10 \text{ mg: 20 mL} \end{bmatrix} \begin{bmatrix} \mathbf{D}_{atch}, \\ \mathbf{shaking at 170 \text{ rpm for 12 h}} \\ \mathbf{T} = 50 \text{ °C} \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_2\text{H}_5\text{OH} \\ 90\% \text{ C}_2\text{H}_5\text{OH} \\ 100\% \text{ C}_2\text{H}_5\text{OH} \end{bmatrix} \begin{bmatrix} 96.6 \\ 90\% \text{ C}_2\text{H}_5\text{OH} \\ 90\% \text{ C}_2\text{H}_5\text{OH} \end{bmatrix} \begin{bmatrix} 96.6 \\ 90\% \text{ C}_2\text{H}_5\text{OH} \\ 90\% \text{ C}_3\text{OH} \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{OH} \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{OH} \\ 90\% \text{ C}_3\text{H}_6\text{O} \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_3\text{H}_6\text{O} \\ 90\% \text{ C}_3\text{H}_6\text{O} \\ 90\% \text{ C}_3\text{H}_6\text{O} \\ 90\% \text{ C}_3\text{H}_6\text{O} \\ 90\% \text{ C}_3\text{H}_6\text{O} \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_3\text{H}_6\text{O} \\ 90\% \text{ C}_3\text{H}_6\text{O} \\ 93.4 \end{bmatrix} \begin{bmatrix} 70\% \text{ C}_3\text{ C}_$ | | R-CAC | | | Batch | 50% C ₂ H ₅ OH | 80.4 | (20 01 01., 20100) |
| F-53B Actual WW 10mg:20 mL $T = 50 \degree C$ $90\% C_2H_5OH$ 90.2 Batch, shaking at 170 rpm for 12 h $70\% CH_3OH$ 88.3 90% C_2H_5OH 88.3 50% CH_3OH 88.3 90% C_2H_5OH 88.3 50% CH_3OH 93.1 90% CH_3OH 93.1 90% CH_3OH 92.6 50% CH_3OH 92.6 90% CH_3OH 92.3 90% CH_3OD 92.3 90% CH_3OD 93.4 | | $S_{BET} = 1750 \text{ m}^2 \text{ g}^{-1}$ | | | balch, shaking at 170 rpm for 12 h | 70% C₂H₅OH | 96.6 | - |
| F-53B Actual WW 10mg:20 mL $100\% C_2H_5OH$ 88.3 Batch, 50% CH ₃ OH 88.3 90% CH ₃ OH 93.1 90% CH ₃ OH 93.1 100% C ₂ H ₅ OH 88.3 10mg:20 mL Batch, shaking at 170 rpm for 12 h 100% CH ₃ OH 92.6 50% CJ ₃ H ₆ O 87.4 T = 40 °C 70% C ₃ H ₆ O 92.3 90% C ₃ H ₆ O 97.6 100% C ₃ H ₆ O 93.4 | | | | | T = 50 °C | 90% C₂H₅OH | 90.2 | |
| F-53B Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 40 °C | | | | | 1 - 00 0 | 100% C₂H₅OH | 88.3 | |
| F-53B Actual WW 10mg:20 mL Batch, shaking at 170 rpm for 12 h T = 40 °C $70\% CH_3OH$ 93.1 90% CH ₃ OH 97.7 100% CH ₃ OH 92.6 50% C ₃ H ₆ O 87.4 70% CH ₃ OH 92.6 90% CH ₃ OH 92.3 90% CH ₃ OH 92.3 90% CH ₃ OH 93.4 | | | | | | 50% CH₃OH | 88.3 | |
| $\begin{bmatrix} 90\% CH_3OH & 97.7 \\ 100\% CH_3OH & 92.6 \\ 50\% C_3H_6O & 87.4 \\ 7 = 40 °C & 70\% C_3H_6O & 92.3 \\ 90\% C_3H_6O & 97.6 \\ 100\% C_3H_6O & 93.4 \\ \end{bmatrix}$ | F-53B | | Actual WW | 10mg·20 ml | | 70% CH ₃ OH | 93.1 | |
| $\begin{bmatrix} 100\% CH_3OH & 92.6 \\ 50\% C_3H_6O & 87.4 \\ 7=40 °C & 70\% C_3H_6O & 92.3 \\ 90\% C_3H_6O & 97.6 \\ 100\% C_3H_6O & 93.4 \end{bmatrix}$ | | | | 10111g.20111E | Batch | 90% CH ₃ OH | 97.7 | |
| $T = 40 \degree C$ $T = 40 \degree C$ $\frac{50\% C_3 H_6 O}{90\% C_3 H_6 O}$ $\frac{87.4}{90\% C_3 H_6 O}$ $\frac{92.3}{90\% C_3 H_6 O}$ $\frac{97.6}{100\% C_3 H_6 O}$ $\frac{93.4}{93.4}$ | | | | | shaking at 170 rpm for 12 h | 100% CH ₃ OH | 92.6 | |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | | | | T = 40 °C | 50% C ₃ H ₆ O | 87.4 | |
| $\frac{90\% C_{3}H_{6}O}{100\% C_{3}H_{6}O} \frac{97.6}{93.4}$ | | | | | | 70% C ₃ H ₆ O | 92.3 | |
| | | | | | | 90% C ₃ H ₆ O | 97.6 | |
| | | | | | | $100\% C_3 H_6 O$ | 93.4 | |

Table 5 Chemical regeneration of PFAS-saturated materials (continued).

Table 5 Chemical regeneration of PFAS-saturated materials (continued).

| Adsorbate | Adsorbent | Water matrix in adsorption experiments | Ratio mass:solution mixture | Experimental setup | Chemical solution | Regeneration percentage (%) | References | | |
|--|-----------|--|---|---|---|-----------------------------|------------------------|--|--|
| PFOS PFHxS PFBS | PCMAs | DI | 0.5 g/L of PCMAs with 50 mg/L of each PFAS | Adsorbed PFAS are extracted with methanol. Regenerated PCMAs are reused for subsequent PFAS sorption experiments. | Сн₃ОН | 85 - 88 * | (Wang et al., 2014) | | |
| PFOS | PACFs | DI | 10mg:100 mL | Batch, shaking at 180 rpm for 24 h T = 25 °C | DI 10% C ₂ H ₅ OH 30% C ₂ H ₅ OH 50% C ₂ H ₅ OH 100% C ₂ H ₅ OH | 5 22 65 85 87 | (Chen et al., 2017) | | |
| * After 5 adsorption/regeneration cycles | | | | | | | | | |

DI: deionized water; PCMAs: permanently confined micelle arrays; PACFs: Polyacrylonitrile fiber (PANF)-derived activated carbon fibers

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Figure 1 Box-and-whiskers plot concerning the adsorption capacity of long- and shortchain PFAS on different adsorbent materials (AC: activated carbon; Resin; SM: Synthetized materials).



Figure 2 The main interactions established between OM and PFAS molecules during GAC adsorption. A: pore blockage; B: hydrophobic interaction; C: electrostatic repulsion.



Figure 3 The main interactions established between OM and PFAS molecules during anion-exchange process. B: Hydrophobic interaction; C: Electrostatic repulsion.



Figure 4 Chemical regeneration of PFAS-exhausted adsorbents using a solution of sodium salt and organic alcohol.

Highlights

- Most PFAS adsorption studies were carried out under unrealistic conditions.
- Organic matter often improves long-chain PFAS adsorption by aggregates formation.
- Co-existing OM reduces the short-chain PFAS adsorption efficiency.
- Short-chain PFAS are better removed by anion-exchange mechanism.
- Regeneration of PFAS-saturated adsorbents often needs harmful organic solvents.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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