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Review

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# Physicochemical properties and interactions of perfluoroalkyl substances (PFAS) - Challenges and opportunities in sensing and remediation

Shui Cheung Edgar Leung <sup>a,b</sup>, Dushanthi Wanninayake <sup>a,b</sup>, Dechao Chen <sup>a</sup>, Nam-Trung Nguyen <sup>a</sup>, Qin Li <sup>a,b,\*</sup>

<sup>a</sup> Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia
<sup>b</sup> School of Engineering and Built Environment, Griffith University, Nathan, QLD 4111, Australia

# HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- Challenges in sensing and removal of PFAS have been identified.
- Categorised the physicochemical properties and intermolecular interactions of PFAS.
- Influential factors to the intermolecular interactions have been reported.
- Recommendation for affinity materials design for targeting PFAS have been given.



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# ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) is a class of persistent organic pollutants that presents health and environmental risks. PFAS are ubiquitously present in the environment, but current remediation technologies are ineffective in degrading them into innocuous chemicals, especially high energy degradation processes often generate toxic short chain intermediates. Therefore, the best remediation strategy is to first detect the source of pollution, followed by capturing and mineralising or recycling of the compounds. The main objective of this article is to summarise the unique physicochemical properties and to critically review the intermolecular and intramolecular physicochemical interactions of PFAS, and how these interactions can become obstacles; and at the same time, how they can be applied to the PFAS sensing, capturing, and recycling process. The physicochemical interactions of PFAS chemicals are being reviewed in this paper includes, (1) fluorophilic interactions, (2) hydrophobic interactions, (3) electrostatic interactions and cation bridging, (4) ionic exchange and (5) hydrogen bond. Moreover, all the different influential factors to these interactions have also been reported. Finally, properties of these interactions are compared against one another, and the recommendations for future designs of affinity materials for PFAS have been given.

\* Corresponding author at: Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia. *E-mail address*: qin.li@griffith.edu.au (Q. Li).

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#### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of emerging environmental pollutants that are now ubiquitously present in the environment (Marchiandi et al., 2021). PFAS attributes materials with heatproof, waterproof, and non-stick properties, and therefore, are adopted in various consumer products such as non-stick cooking utensils, cleaning products and furniture (Gardiner, 2014; Savvaides et al., 2022). They are also widely used in industrial and medical applications such as electroplating, biomedical imaging, firefighting, and textile industries etc. (Hamon et al., 2020; Høisæter et al., 2019; Liu et al., 2022; Ma et al., 2022). In 2021, the Organisation for Economic Co-operation and Development (OECD) has revised definition of PFAS as fluorinated substances that contain at least one fully fluorinated alkyl moiety, either methyl (-CF<sub>3</sub>) or methylene carbon atom (-CF<sub>2</sub>-) that already meets the definition by Buck et al. (2011) and with fully fluorinated alkanediyl moieties and or aromatic ring that are under the new OECD definition (Wang et al., 2021). However, they are with a few exceptions, that includes, without any H, Cl, Br or I atom attached to those fully fluorinated alkyl moieties (Wang et al., 2021). According to PubChem Classification, there are over 7 million species of PFAS chemicals found globally and is still growing (Schymanski et al., 2023).

Amongst all PFAS, perfluoroocatanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have had the longest production history and their toxicity have been well-documented (Dean et al., 2020). As a result, now PFOA, its salts and related substances; PFHxS, its salts and related substances, and PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) have been added to the list of new Persistent Organic Pollutants (POPs) under Stockholm Convention (UNEP, 2022). Animal studies showed that chronic exposure of PFAS leads to great health risks in immunotoxicity and carcinogenicity (Antoniou et al., 2022; Temkin et al., 2020). Moreover, PFAS exposure also hinders foetal growth and development, and shows correlation to hormonal dysfunction and other diseases such as ulcerative colitis, hypertension, and high cholesterol (Beale et al., 2022; Ding et al., 2020; Steenland et al., 2020).

In the natural environment, PFAS is extremely mobile and can penetrate various environmental matrices including surface, ground water, soil and even air (Costello and Lee, 2020). PFAS are also prone to bioaccumulation and cannot be removed by typical municipal water and wastewater treatment processes (Costello and Lee, 2020; Gonzalez et al., 2021). Other than the US and some developed countries, the regulations and law enforcements in some less developed countries are relatively lax (Morales-McDevitt et al., 2022). However, as PFAS contamination becomes a global concern, regulations in the less developed areas of the world are expected to tighten.

Even though the major manufacturers of PFOS/PFOA have mostly phased out and stopped their production for years, PFAS do not degrade in ambient environment under normal conditions but can undergo physicochemical changes to form compounds of smaller alkyl chains (Teaf et al., 2019). Moreover, due to their irreplaceable properties, shorter chain alternatives such as perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), GenX, ADONA, and F—53B have been manufactured to replace the heavily regulated ones (Ateia et al., 2019). However, various recent reports have shown that these smaller substitutes have even higher toxicity (Nian et al., 2020). Since most of the regulatory attention has been focused on the phased-out products, the production of these short chain alternatives has been unrestricted and therefore PFAS contamination is an ever-growing global concern.

In broad sense, there are 3 stages of remediation of contaminants. The first step is detection of the contaminant from environment and to locate the source of pollution. Then, it is followed by capturing and then finally destruction of the contaminants. In our previous review literature on degradation technologies of PFAS, it was concluded that with current technology, the drawbacks of degradation of PFAS outweighs its advantages (Leung et al., 2022). Due to recalcitrance of PFAS, degradation often leads to the emission of toxic short chain intermediates. The

current staple sensing method that can reliably detect PFAS in very low concentration is mass-spectrometry based sensors and require long sample preparation time and high equipment cost. As for capturing of PFAS, active carbon and anionic exchange resin are two popular choices. However, they suffer from low selectivity and limited regenerative ability (Park et al., 2020).

Though sensing and capturing of PFAS are two distinctively different operations, they both rely on the same principle of affinity-based physicochemical interactions. Therefore, it is crucial to first understand the specific attractive forces/interactions towards PFAS in order to develop affinity-based molecules for sensing and capturing. Meanwhile, some of the physicochemical properties in PFAS makes remediation a highly challenging task. In this article, we will focus on identifying the challenges brought by the physicochemical properties of PFAS and examine the affinity-based interactions surrounding PFAS. This article also aims to report on the mechanisms of intermolecular interactions in sensing and capturing applications, providing insights for future designs of affinity-based sensors and adsorbents for PFAS remediation.

# 2. Properties of PFAS

To examine the physicochemical interactions of PFAS, the first step is to understand their unique chemical structure. This section describes the differences between PFAS and their hydrocarbon counterparts. All PFAS variants consist of two main components, namely a perfluorinated chain (tail) and a functional group (head), Fig. 1.

A perfluorinated chain ( $R_f$ ) is essentially an alkyl chain with all the hydrogen atoms replaced by fluorine atoms, and the head can be a sulfonate, or carboxylate. The perfluorinated tail attributes PFAS to their unique physical and chemical properties that are drastically different to their hydrogenated counterparts. As the term 'perfluorinated' suggests, the most abundant element in PFAS is fluorine; and the atomic structure of fluorine is a key factor in shaping the chemical and physical characteristics of PFAS. In the following section, the physicochemical properties of PFAS will be introduced from an atomic level up to a molecular level.

# 2.1. Properties of fluorine

The physicochemical characteristics of PFAS are largely influenced by the properties of fluorine and the C—F bonds, which are present in abundance in the compounds. Fluorine is characterised by its high electronegativity, high ionization potential and low polarizability. Fluorine is the most electronegative element in the periodic table, and when bonded to carbon, forms one of the strongest and the most inert single bonds found in organic compounds with its bond dissociation energy up to 531.5 kJ mol<sup>-1</sup> in PFAS (Krafft and Riess, 2015; Zhang et al., 2013; Zhou et al., 2013). Therefore, PFAS, when compared to their



Fig. 1. Structure of a PFAS molecule.

hydrocarbon counterparts, have much higher chemical and physical stability.

#### 2.2. Chemical properties

PFAS benefits from the optimal overlap between the fluorine's 2 s and 2p orbitals with the carbon orbitals in the C—F bonds, forming multiple dipolar resonance structures (Fig. 2) along the perfluoralkyl chain (Kirsch, 2013). The strength of C—F bonds further increases as the number of fluorine atoms bonded to the central carbon atom increases. Fig. 2A depicts the dipolar resonance structures for a perfluorinated compound:  $CF_4$ .

The three lone pairs of fluorine atoms and the negative partial charge create a steric shield and an electrostatic shield. Kinetic stability is achieved through the shielding of the central carbon atom by the fluorine which safeguards PFAS against nucleophilic attack of the central carbon atom (Kirsch, 2013; Krafft, 2001). This configuration is a major contributor to the chemical inertness of PFAS (Chambers, 2004; Kirsch, 2013).

Due to the high electronegativity, C—F bonds in the perfluorinated tail are highly polarised. The shared electrons within the C-F bond are attracted towards F ( $\delta$ -) as sp<sup>3</sup> carbon is highly electropositive ( $\delta$ +). In addition, the low atomic radius of fluorine atoms also leads to very high polarization energy (Lide, 2006; Politzer et al., 2002; Politzer and Murray, 2018). The low polarisability in fluorine is also responsible for the ionic character of PFAS and a higher bond strength when compared to their hydrocarbon analogues. The strong inductive effect of perfluoralkyl chain has strong electron-withdrawing, which can increase the acidity of alcohols and lowers the strength of organic bases (Chambers, 2004; Kirsch, 2013). The increase in acidity is also attributed by hyperconjunctive stabilization in  $\beta$ -fluorination (Fig. 2B). This is indicated by the drop in pKa value when hydrogen atom is replaced by fluorine atom in the alkyl chain. Moreover, the low polarization of the s and p electrons in F also makes it a poor hydrogen bond acceptor despite the high electronegativity or lone pairs (Kirsch, 2013).

# 2.3. Physical properties

Due to the larger van der Waals radius of fluorine (1.47 Å) when compared to hydrogen (1.20 Å), steric congestion happens when all of hydrogen atoms in the  $R_f$  are replaced by fluorine atoms, leading to a dramatic change in the conformation of the molecule, Fig. 3A and B (O'Hagan and Rzepa, 1997; Smart, 2001). Steric repulsion occurs between the fluorine atoms bound to the carbon backbone in the relative 1,3 positions, and when combined with the increased van der Waals radius, the carbon backbone becomes stretched and twisted by an average of 12 degrees, forming a 15/7 helix, with left and right helices in equal proportion which is different to the zigzag configuration in hydrocarbon (Krafft and Riess, 2015; Monde et al., 2006). This makes PFAS a more rigid molecule with lower conformational flexibility when compared to its hydrocarbon counterpart. Conformational flexibility is represented by the trans/gauche interchange entropy in which PFAS are 25 % higher than their hydrocarbon analogue, indicating less conformational freedom of the  $R_f$  as compared to alkyl chain (Krafft and Riess, 2009). The comparison of structure in hydrocarbon chain and perfluoroalkyl chain is illustrated in Fig. 3C.

On the other hand, PFAS show very weak intramolecular and intermolecular interactions due to the low polarizability of fluorine, which is characterised by their much higher volatility and lower boiling points (Fig. 3D) compared to their hydrocarbon counterparts of similar molecular mass (Kirsch, 2013). Moreover, the low intermolecular forces also lead to exceptionally low surface tension of PFAS, which is responsible for their excellent surface wettability. Furthermore, the lack of van der Waals forces leads to oleophobic character (Van Oss et al., 1986). In conjunction with an amphiphilic structure makes PFAS the perfect surfactant; reducing surface tension of water from 72 dyn/cm to 15-20 dyn/cm compared to 25-35 dyn/cm for their hydrocarbon counterparts (Kirsch, 2013). Despite C-F bond being highly polarised, local dipole moments within a PFAS molecule cancel out, giving the molecule its overall nonpolar, hydrophobic character (Kirsch, 2013). The amphiphilic character of PFAS enables them to segregate from both polar and non-polar solvents and forms their own partition (Gladysz et al., 2006). When mixed with water and organic solvent, PFCs form a unique fluorous phase, which sits outside of the aqueous or organic layers (Fig. 4A).

One of the most important parameters in PFAS is their critical micelle concentration (CMC), which not only affects their transport in the natural environment, but such parameter can also be utilised for PFAS removal from aqueous media. Generally, the cancelling of dipole moments in PFAS leads to lower critical micelle concentrations (CMC) of PFAS as compared to their hydrocarbon counterparts, as the energy of micellization of CF2 in a linear fluorocarbon chain is equivalent to 1.5 times of CH<sub>2</sub> (Krafft and Riess, 2015). As surfactants, surface activity is the most important character which makes fluorinated surfactants much more effective than their hydrocarbon counterparts. In fluorinated surfactants, surface activity correlates positively with the chain length of Rf (Fig. 4D), and longer chain length surfactants also displays larger solubilization at low concentration than shorter chain surfactants (Kunieda and Shinoda, 1976). Meanwhile, the counterions also affect surface activity but the effect is insignificant as compared to the Rf chain length (Kunieda and Shinoda, 1976). However, the Krafft point (where the ionic surfactants start to form water-soluble micelles) is escalated with longer Rf chain length (Fig. 4C); therefore, the chain length of fluorinated surfactants are limited to C7-C8 when used at room temperature (Kunieda and Shinoda, 1976).

According to Kancharla et al. (2021), fluorinated surfactants form smaller spherical micelles than their hydrocarbon counterparts (Fig. 4B). On the other hand, the salt concentration in the bulk solution



Fig. 2. A Dipolar resonance structures of C—F bond in CF<sub>4</sub>; red denotes negative and blue positive partial charges (Kirsch, 2013). Fig. B Hyperconjugation in β-fluorination (Smart, 2001).



**Fig. 3.** (A) Comparison of Van der Waals radius of CH<sub>3</sub> and CF<sub>3</sub> (Seebach, 1990). (B) Steric repulsion in perfluoroalkyl chain (Kirsch, 2013). (C) Conformational differences between hydrocarbon chain and perfluoroalkyl chain (Hasegawa, 2017). (D) Comparison of hydrocarbons boiling points versus fluorocarbons boiling points with different numbers of carbon atoms [reproduced from (Smart, 2001)].

will not only affect the size but also the shape of the micelles. At high salt concentration, short chain PFAS form ellipsoidal micelles while long chain PFAS form rod-like micelles. Moreover, CMC of PFAS is lowered when as salt concentration increases due to reduction in repulsive forces from the anionic headgroups (Kancharla et al., 2021).

A great concern of PFAS in the environment arises from their bioaccumulative nature, which is governed by three important physicochemical parameters; namely water solubility, vapour pressure, and CMC. Bhhatarai and Gramatica (2011) have developed a quantitative structure-property relationship (QSPR) model which relates aqueous solubility (Aqs), vapour pressure (VP), and CMC on various PFAS based on predicted and experimental data. It was found that BP is positively related to AqS and CMC and is inversely related to VP (Fig. 4E), which also implies that longer chain PFAS are more bioaccumulative.

# 3. Challenges in environmental remediation of PFAS

There are many challenges surrounding the topic of remediation of PFAS contaminated water due to the extremely stringent regulatory requirements that cannot be easily achieved and the lack of simple analytical techniques and methodologies to meet the requirements.

There is no alternative to replace PFAS compounds for certain applications due to their unique physical and chemical properties including, excellent surface functions as described above. Even though PFOS and PFOA have already been phased out, there is an increasing number of short chain alternatives being produced and used worldwide. While the legacy PFOS and PFOA problems remain unresolved, new short chain alternatives such as GenX and PFBS are being released into the environment and poses new unknowns. Therefore, apart from developing facile sensors to target the source of pollution, it is also equally important to develop effective and selective capturing methods to remove PFAS chemicals and reuse them or eliminate them from the environment using effective PFAS destruction method/s.

# 3.1. Challenges in sensing

Due to the physicochemical properties and low concentration, PFAS are very difficult to detect in the environment. Current available standard analytical methods for PFAS testing could only quantitatively measure very limited number of PFAS compounds (e.g. 18 PFAS using USEPA and 21 PFAS using ASTM standard methods). First, they have no intrinsic optical properties, therefore colorimetric or direct opticalbased sensors are not viable. Secondly, the highly inert nature of PFAS suggests limited possibility to develop sensors based on chemical reactions hence, conventional analytical methods using derivatization in detecting POPs is also limited (Guelfo and Higgins, 2013). Therefore, only advanced chromatographic methods such as gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS) and high-performance liquid chromatography (HPLC) techniques are used as standard analytical processes (Gremmel et al., 2017; Trojanowicz and Koc, 2013; Fiedler and Sadia, 2021).

A comprehensive review carried out by Zarębska and Bajkacz (2023), considered advancement of PFAS analytical methodologies over the last ten years. The paper outlined various advanced analytical methodologies. For instance, LC-ESI-MS/MS in negative ion mode using target analysis was the commonly used method for anionic PFAS, while less



**Fig. 4.** A Schematic diagram of fluorous phase formation with aqueous phase and lipophilic phase. Fig. B Changes in CMC and micelle size as a function of chain length ( $n_c$ ) and added salt (Kancharla et al., 2021). Fig. C The relationship between the number of carbon atoms in Rf chain and the Krafft point of perfluoroalkane carboxylates (Kunieda and Shinoda, 1976). Fig. D Plots of surface tensions against concentration for F(CF<sub>2</sub>)<sub>n</sub>COONa at 25 °C, where n = A:1; B:2; C:3; D:4; E:5; F:6 (Tamaki et al., 1989). Fig. E PCA plot on water solubility, vapour pressure, and CMC of 174 PFCs within the structural applicability domain of all these models; red line represents the increasing trend of BCFs based on available experimental values (Bhhatarai and Gramatica, 2011).

common positive ion mode is used to determine cationic and zwitterionic PFAS. However, there is no standard methods available for positive ion mode. Due to the lack of authentic standards for majority of PFAS, they all remain unidentified. The review suggests that calibration using surrogate may be an alternative strategy (Zarębska and Bajkacz, 2023). Although HRMS is a great advancement in identifying emerging PFAS in the environment, it is highly labour intensive and time consuming, and requires highly skilled specialists and advanced software, suggesting artificial intelligence may be a solution in future. The paper concludes that suspected screening analysis (SSA) and nontargeted analysis (NTA) have limitations in quantitative estimation, but they are the most promising strategies to measure PFAS in the environment and to understand human exposure to them (Zarębska and Bajkacz, 2023).

Moreover, owing to the low polarizability of fluorine, intermolecular interactions are very weak, together with the hydrophilic functional groups, PFAS are highly mobile in the environment. Therefore, sensors need to have extremely low limit of detection (LOD) and real-time detection is highly preferable. Despite the aforementioned laboratory analytical methods provide excellent selectivity and impressive LOD, they involve very complex pre-concentration step with polystyrenedivinylbenzene (SDVB) solid-phase extraction (SPE) to the samples (Shoemaker and Tettenhorst, 2018; Shoemaker et al., 2018). These analytical methods lack rapid analytical result, real-time monitoring, cost-effectiveness and require trained personnel (Bell et al., 2021). They also increase the risk of sample contamination and the time and cost for transport. This calls for the development of real-time and in-situ sensors free from pre-treatment. Although there are many examples of affinity-based optical and electrochemical sensors for PFAS being reported, none of those methods are close to commercialisation because of low selectivity and sensitivity due to interferences from co-existing contaminants.

In terms of challenges in selectivity, although PFOS and PFOA are both usually known in their anionic forms due to their prevalence in the environment, they can also exist in cationic and zwitterionic forms under different pH values (Nakayama et al., 2019). Moreover, PFAS is a class of chemicals with hundreds of variants of different chain lengths and functional head groups, and many PFAS within their own class share very similar chemical and physicochemical properties, making it extremely difficult to develop sensors that can differentiate them individually. To make matters worse, new variants of PFAS found in the environment is constantly expanding due to the emergence of new shortchain PFAS alternatives, adding to the total amount of PFAS in the environment.

# 3.2. Challenges in capturing

Capturing is the next vital step in PFAS remediation after sensing and detecting the pollution source. However, conventional separation processes such as air stripping, soil vapour extraction and conventional municipal water and wastewater treatment methods are ineffective in removing PFAS (Kucharzyk et al., 2017). Similar to many organic contaminants, PFAS are mainly removed from aqueous matrices via adsorption or ionic exchange methods. Granular activated carbon (GAC) is by far the most cost-effective widely used method for long chain PFAS removal, however, less effective for shorter chain ones (Ross et al., 2018). Due to the phasing out of PFOS/PFOA and the introduction of short chain alternatives, GAC will be insufficient as a full-range adsorbent for PFAS. On the other hand, there are also commercially available ionic exchange resin specifically designed for PFAS, but the high cost is often an issue, and more importantly, regeneration of the resin often requires toxic chemicals (Gagliano et al., 2020; Xie et al., 2022). Furthermore, adsorption or ionic exchange methods follow the captureand- regeneration pathway or disposal, which involves transfer of the exhausted adsorbents offsite. As a result, the extra cost, and risks in handling and transportation of these spent adsorbents concentrated with toxic pollutants are undesirable. Lastly, fouling and interference from co-existing organic matter in the waste stream is a fundamental drawback of adsorption and ionic-exchange-based methods, therefore requiring complex pre-treatment steps, which greatly raises the overall cost of the treatment system. Mechanism of the interference will be explained later in this article.

#### 4. Physicochemical interactions of PFAS

There are many different physicochemical interactions reported between PFAS chemicals and other co-contaminants as well as various other surfaces, including fluorophilic interactions, electrostatic interactions, ion-bridging interactions with divalent cations, hydrophobic interactions, $\pi$ - $\pi$  bonds, hydrogen bonds, ionic exchange and van der Waal forces (Du et al., 2014; Hayama et al., 2014). These attractive forces can facilitate the adsorption of PFAS, which can be applied to capturing or sensing. In the following section, the mechanisms of the various physicochemical interactions related to PFAS will be explained categorically.

# 4.1. Fluorophilc interactions

Fluorophilic interactions are driven by fluorophilicity, which refers to the unique partition and sorption properties often shown by highly fluorinated organic compounds rich in sp3 carbon-fluorine bonds (Hayama et al., 2014). Although the term 'fluorophilicity' has always been referred to as a major driving force for PFAS interactions with adsorbents or sensors, the exact mechanisms of these interactions have never been reported in detail. Materials having high fluorophilicity are often preferred to bind to PFAS over other coexisting contaminants. However, the mechanisms and favourable conditions for fluorophilicity of substances containing perfluoralkyl (Rf) group have long been unclear up to date and the material designs have mostly been carried out based on experiences (Hasegawa, 2017). As mentioned earlier, when mixed in aqueous and organic phase, fluorous compounds will segregate themselves to form a unique immiscible fluorous phase. This partitioning action is driven by the disparity in the cohesive energy densities between the three immiscible layers (Goss and Bronner, 2006; Krafft and Riess, 2009). The partitioning action is driven by non-covalent molecular forces, according to Hasegawa (2017), miscibility of different molecules can be found by matching the Hildebrand parameters ( $\delta$ ), which is a parameter used to quantify intermolecular forces.  $\delta$  is the square root the cohesive energy density of the solvent, which correlates to the polarity of the molecules.

# 4.1.1. Partitioning of fluorous material

The partition procedure of fluorous material has been described by (Goss and Bronner, 2006) and it resembles the typical biphasic separation process in Fig. 5. The partition is driven by the free energy of intermolecular interactions of the solute in the different phases. There are two steps in phase partitioning, with the first being the creation of a cavity. Free energy is first consumed to separate PFAS from each other to form a cavity (Fig. 5B); and the free energy required for cavity formation depends on the interaction free energy (or cohesive free energy) between the like molecules (PFAS) in the condensed phase and the size of the required cavity (volume of PFAS molecule). In the second step after cavity formation, the cavity molecules can establish interactions with its new neighbours (Fig. 5C). These interactions include non-specific van der Waals forces and other specific interactions such as H-bonds given that solute and the phase molecules have complementary properties. Note that cavity formation is less likely to happen when cohesive energy reaches a certain low point (Kiss et al., 2001).

Most  $R_f$ -specific spontaneous aggregation/partition is often referred to as 'fluorous' or 'fluorophilic' effect (Hasegawa, 2017). This is also equivalent to other terms such as fluorine-fluorine (F—F) attraction or Fchemistry (Krafft and Riess, 2009). The chemical mechanism inducing the fluorous effect is essential to explaining the material properties of  $R_f$ compounds, and their affinity to PFAS.

Non-covalent inter/intramolecular interaction (London Dispersion) in a condensed matter is driven by the Coulomb ( $\sim$ 250 kJ mol<sup>-1</sup>), hydrogen-bonding (HB;  $\sim$ 25 kJ mol<sup>-1</sup>) and van der Waals ( $\sim$ 2 kJ mol<sup>-1</sup>) interactions in a decreasing order (Atkins and De Paula, 2011; Israelachvili, 2011). However, as mentioned earlier, the tail part of PFAS is non-polar and lacks the ability to form hydrogen bonds due to cancelling of dipole moments, weak van der Waals interaction is the main driving force for molecule aggregation. There are three factors of van der Waals forces on quantum mechanics proposed by London, namely orientation, induction, and dispersion forces (Atkins and De Paula, 2011; Israelachvili, 2011).

$$\bar{\mathbf{u}}_{orientation} = -\frac{1}{3R^6} \frac{\mu^4}{K_B T} \left(1 + 3\cos^2\Theta\right) \tag{1}$$

$$\bar{\mathbf{u}}_{induction} = -\frac{2}{R^6} \mu^2 \tag{2}$$

$$\bar{\mathbf{u}}_{dispersion} = -\frac{3}{4R^6} \mathbf{h} \nu_0 \alpha^2 \tag{3}$$

Negative sign in the equation suggests the forces are attractive. *R* refers to the distance between two molecules, while  $\mu$  and  $\alpha$  are the



Fig. 5. A thermodynamic cycle of micelles formation of anionic PFAS, blue background denotes bulk aqueous phase, yellow sphere denotes hydrophilic head of PFAS and grey spheres denote perfluoroalkyl tail of PFAS.

dipole moment and molecular polarizability, respectively.  $\bar{u}_{\text{orientation}}$  is the interactive force between two molecules having permanent dipole moments depending on the relative orientation angle.  $\bar{u}_{\text{induction}}$  is the induction force, which is the interaction between a molecule having a permanent dipole moment and another molecule having none. This refers to an induced dipole moment (p in Eq. (4)) in which the dipole moment of the first molecule will change the charge distribution of the second molecule. *p* is induced by external electric field, *E*, via molecular polarizability,  $\alpha$ , the induction force involves both  $\alpha$  and  $\mu$  in Eq. (2).

$$p = \alpha E$$
 (4)

Finally,  $\bar{u}_{dispersion}$  is the dispersion force that does not involve permanent dipole as it is a quantum-mechanic-driven force and only involves  $\alpha$  (Hasegawa, 2017).  $h\nu_0$  in Eq. (3) is the absorption energy which is replaceable by the ionization energy (Hasegawa, 2017). Despite London theory is not applicable to the intermolecular interactions in the presence of solvent due to having more than one absorption energy, the equation is still a powerful tool to denote the differences between the molecular interactions of R<sub>f</sub> compounds and their hydrocarbon counterparts (Kiss et al., 2001). The calculated interactive forces are summarised in Table 1.

The results show that  $R_f$  compounds are mainly held together by orientation forces, which means the intermolecular forces between PFAS are dominated by dipole-dipole attraction, matching the finding in the Density-function theory (DFT) study by Omorodion et al. (2015).

On the other hand, interactions between  $R_{\rm f}$  based fragments (hydrophobic interactions) are attracted to each other mainly by dispersion force. Note that this model is just a rough estimate and cannot be used to show the intermolecular forces between  $R_{\rm f}$  - based material and any other materials.

# 4.1.2. Factors affecting fluorophilicity

There are a few computational simulation models of fluoropilicity proposed to estimate the strength of attraction under different conditions. Kiss et al. (2001) produced a computational model comparing 59 fluorinated organic molecules using a combination of eight descriptors, including properties such as electrostatic potential, HOMO and LUMO energies, and weighted holistic invariant molecular (WHIM) descriptors. Kiss et al. (2001) points out that a simple relationship between the total number of fluorine atoms in the molecule and the phase preference of the molecules holding the  $R_f$  tail simply does not exist. Kiss et al. (2001) listed five important rules in flurophilicity:

- 1. The fluorine content: there should be at least 60 wt% fluorine in the compound. This is easily achievable by inserting  $R_f$  group in the compound until it reaches the structural limit.
- 2. The lengths of the fluorinated tail: longer fluorous chains lead to increased partition coefficient and decrease in absolute solubilities in both phases. Conversely, by increasing the anti-fluorous domain (e. g., hydrophobic) will increase the absolute solubility in organic phase, leading to reduced fluorophilicity.
- 3. The number of fluorinated tails: same rationale as rule number 2.
- 4. The molecular structure: various parameters such as the number of functional groups involved in other active intermolecular interactions such as orientation forces, hydrogen bonds should be limited.
- Structure of the fluorinated tail: several factors such as branching, heteroatoms as part of -CF<sub>2</sub>OCF<sub>2</sub>-, CF<sub>2</sub>SCF<sub>2</sub>-, or -CF<sub>2</sub>N(R<sub>f</sub>)<sub>2</sub> segments or conformational rigidity versus flexibility, will affect the fluorophilicity of the compound.

# 4.1.3. Computational prediction of fluorophilicity

The model of Kiss et al. (2001) concluded that the distribution of fluorine is an insignificant factor, as mentioned above, as they did not have molecule with low fluorine content to make comparison. However, the surface area of the fluorous molecule and the distribution of fluorine throughout the molecule plays a significant role on affecting fluorophilicity, especially when fluorine atoms are placed on the outer domain of the molecule, will increase contact with the fluorous phase.

Huque et al. (2002) made a similar model with addition of a linear free energy relationship (LFER). The descriptors include excess molar refraction term (E), a dipolarity/polarizability (S), hydrogen bond acidity and basicity terms (A) and (B) and McGowan's characteristic molecular volume (V) and an additional sixth descriptor F, the percentage fluorine content of the solute. It was found that the most

Table 1	
The three van der Waals forces between two C—H or C—F fragments (Hasegawa	, 2017).

	$\mu/D$	$lpha /  imes 10^{-30} m^3$	IE/eV	$\textit{Orientation}/  imes 10^{-79}\textit{Jm}^3$	$\textit{Induction}/\times 10^{-79}\textit{Jm}^3$	$Dispersion/10^{-79} Jm^3$
С-Н	0.40	0.652	10.64	0.422 (6.96 %)	0.209 (3.44 %)	5.43 (89.6 %)
C-F	1.39	0.555	9.11	61.5 (91.8 %)	2.14 (3.20 %)	3.37 (5.03 %)

significant descriptor was the fluorine content percentage. On the other hand, hydrogen bond basicity was deemed insignificant and taken out of the model. Duchowicz et al. (2004) proposed a computational model based on multivariate regression of topological molecular descriptors with same pool of organic molecules as Huque et al. (2002) but included 17 more descriptors. de Wolf et al. (2004) adopted a universal lipophilicity model based on the mobile order/disorder (MOD) solution theory which showed that by extending the R<sub>f</sub> tail does not necessarily result in higher partition coefficients. Finally, Daniels et al. (2004) developed a model with the same set of organic and fluorous molecules in Huque et al. (2002)'s model but expanded further by taking into account of 8 transition metal complexes.

All these models presented are well-designed and have taken into account of a wide range of environmental parameters, and in most cases, should produce similar prediction results. Kiss et al. (2001) model laid the foundation of the newer models but the remark on the distribution of fluorine is an insignificant factor is a bit contradictive and was later repudiated by Huque et al. (2002). On the other hand, the model developed by Daniels et al. (2004) is the only one that accounts for transition metal complexes, which is very common in the sensing and adsorption application such as metal organic framework (MOF).

# 4.2. Hydrophobic interaction

'Hydrophobic interaction' is often cited as one of the main driving forces for PFAS attraction. The term itself is somehow misleading. As the R<sub>f</sub> chains mostly display hydrophobic tendencies, the molecular interactions between the R<sub>f</sub> chain and other hydrophobic species such as alkyl chain in hydrocarbons are often conveniently addressed as 'hydrophobic interaction' (Hasegawa, 2017). In fact, these 'hydrophobic' interactions are just London's dispersion force, which is driven by the disparity of cohesive energy density of the different molecules to segregate into different phases, albeit the differences in the intermolecular forces involved as explained previously.

Simultaneous hydrophobicity and oleophobicity is a unique feature only found in R<sub>f</sub> compounds. Normally in a 2-phase situation (aqueous and organic), the two properties oppose each other. Adsorbents especially carbon-based ones, have amphiphilic properties, but can still adsorb the oleophobic PFAS. Chen et al. (2009) reported that PFOS was absorbed on the surface of diesel oil in an aqueous environment. This phenomenon, in a sense, means that PFOS is more hydrophobic than oleophobic, so when placed in a 2-phase situation, will be forced to settle in the organic phase. Such attraction is strong enough to overcome the negative charges on the negatively charged organic molecules as explained above. In the measurement of hydrophobicity, octanol-water partition coefficient (Kow) is often used. However, Kow value for PFAS cannot be obtained by experimental methods due to the low solubility of PFAS in octanol and creating a new method to determine this is highly challenging due to the amphiphobicity of PFAS (Franco and Trapp, 2008).

# 4.2.1. Factors affecting hydrophobic interactions

PFAS have lower CMC than their hydrocarbon counterparts and are prone to form micelles or hemimicelles due to C—F chain aggregation. Moreover, hydrophobicity or chain length of PFAS has a negative correlation to its critical micelle concentration (Campbell et al., 2009). In terms of application, this feature is advantageous to PFAS capturing as multilayer sorption can occur where hemimicelles and micelles can form in the narrow spaces within the porous structures of adsorbents at high PFAS concentration (Zhang et al., 2011). This phenomenon is reported in porous carbon-based adsorbents such as maize-derived ash and crosslinked chitosan beads (Chen et al., 2011; Zhang et al., 2011). However, the formation of micelles in the outer region of the adsorbent can also block the access to the active sites in the core region of the adsorbent. Same applies to sensing, in which micelles and hemimicelles can form at the interfaces between water and the sensor, blocking access to the active sites for binding (Guelfo and Higgins, 2013; Yu et al., 2009). However, due to the drastic increase in CMC with regards to chain length as mentioned before, short chain PFAS like GenX are unable to form micelles in bulk water (Choudhary and Bedrov, 2022). Lastly, due to the positive correlation of hydrophobicity and  $R_f$  chain length, the long chain PFAS should be more competitive at establishing interaction with the affinity molecule than short chain PFAS until micelles start to form (McCleaf et al., 2017; Rahman et al., 2014). According to Gagliano et al. (2020), the adsorption capacity of short-chain PFAS is always lower than that of long-chain PFAS regardless of the adsorbent used.

As mentioned before, naturally occurring organic matter is usually negatively charged on the surface, despite attraction can still be established via hydrophobic interactions, the repulsive force generated by the negative charges still reduces the adsorption capacity and sorption rate. Also, as mentioned in the Rule 2 in the model of Kiss et al. (2001), an increase in the fluorous domain will decrease the solubility of organic phase and vice versa.

A study by Cai et al. (2022) suggests that enhanced sorption in the presence of cations as it decreases PFAS solubility due to increased hydrophobicity at high ionic strength and salting-out effect.

# 4.3. Electrostatic interactions

There are 2 sources of electrostatic interactions in PFAS. First, due to the low pKa in neutral solution, PFAS are anionic surfactants with negatively charged functional groups such as  $CO_2^-$  and  $SO_3^-$ . PFAS are described as having a positively charged core and a negatively charged shell and electrostatic attraction is often cited as the main driving force for PFAS attraction (Xiao et al., 2011). PFAS can establish electrostatic attraction with materials that are positively charged at the same pH. On the other hand, the fluorine atoms on the R<sub>f</sub> chain are highly electronegative, drawing electrons towards themselves, leaving behind 3 lone pairs of electrons. Therefore, these F atoms can act as Lewis base to attract positively charged molecules. However, the strength of Rf chaininduced electrostatic interaction is weak (Xiao et al., 2011). In fact, the hydrophobic effect of the Rf chain may often overcome the electrostatic effect, while the functional head is still the primary source of electrostatic attraction. Both positively charged adsorbents such as carbon nanotube (CNT) and negatively charged adsorbents such as chitosan and anion-exchange are linked with electrostatic interactions (He et al., 2020; Zhang et al., 2011; Zhang et al., 2009). The positively charged surface functional groups on the adsorbent surfaces can attract the anionic functional groups in the PFAS via electrostatic attraction. On the contrary, the negatively charged adsorbents will repel the anionic PFAS. Other than the direct electrostatic transfer, dipole attraction is also found in materials such as silica with -NH2 and -OH surface functional groups, which can create weak ion-dipole to the anionic PFAS molecules (Karoyo and Wilson, 2013; Punyapalakul et al., 2013).

#### 4.3.1. Factors affecting electrostatic attraction

Electrostatic interactions are heavily affected by the effect of the solution pH due to protonation and deprotonation (Deng et al., 2012). As pH increases, the surface charges of the affinity molecule will become more negatively charged or less positively charged. This leads to repulsion or drop in attraction towards the negatively charged functional head of the PFAS. Ionic strength also affects electrostatic attraction; increase in such can lead to compression of electrical double layers of the sorbents, which weakens the overall electrostatic interactions between the sorbent and the PFAS, while increasing electrostatic repulsion between the PFAS anionic heads (Tang et al., 2010; Zhou et al., 2013). Therefore, at high ionic strength, the effect of pH change can be offset by the electrical double layer compression (Tang et al., 2010). On the other hand, the presence of divalent cations such as  $Mg^{2+}$ and Ca<sup>2+</sup> can neutralise negative charges present in the bulk solution, displaying salt bridging effect which shifts negative sites of the adsorbent surfaces to positive to increase electrostatic attraction towards

# PFAS (Tang et al., 2010; Zhou et al., 2013).

Interference from organic matter found in clay and natural sediments has been reported (Chen et al., 2012; Pan et al., 2009; Xiao et al., 2011; Yu et al., 2012). This occurs when the negatively charged organic matter was first attracted to the adsorbent via hydrophobic interactions, inducing negative charge to the surface of the adsorbent. As a result, repulsive forces are established between the negatively charged adsorbent and the other anionic PFAS, leading to reduction in adsorption capacities and sorption rates (Yu et al., 2012). This effect will be indicated by a drop of the pH of zero point of charge.

With regards to focusing on the differences in electrostatic interactions in the functional head, take the difference between perfluorinated sulfonic-acid (PFSA) and perfluorinated carboxylic acid (PFCA) as an example, PFSA contains a sulfonic group whereas PFCA contains a carboxylic head. According to the Pearson's hard-soft acidbase (HSAB) principle, 'hard acids and bases have high charge (positive for acid and negative for bases) to ionic radius ratio with higher oxidative states' and vice versa for soft acids and bases (Ho, 1975). Sulfonate in PFSA, such as PFOS, is a soft base while carboxylate in PFCA, such as PFOA, is a hard base. A hard–hard interaction, or a soft–soft one is stronger than others, indicating the difference in affinity of different functional heads towards different ionic species (Li et al., 2015).

# 4.3.2. Cation bridging interactions

A study conducted by (Cai et al., 2022), using per-fluorinated and poly-fluorinated PFAS compounds, that includes short and long chain PFCAs and PFSAs, suggest that increased cations concentration enhance PFAS sorption due to the formation of cation bridges between PFAS with anionic head groups and negatively charged surfaces, and alter the tendency to orient PFAS on the sorbent surface. The study revealed that the contribution to enhance sorption with increased cation concentration is little, but the effects are stronger with long chain PAFS than shorter chain once with the increased valency of the cations in the solution. In other words, effects are greater with polyvalent cations, as they bind more strongly to the PFAS head groups than single valent cations. This property has an ability to structural rearrangement and better packing of PFAS at the PFAS-adsorbent interface. This phenomenon makes greater benefits to contaminated site remediators to make decisions on PFAS mobility in the environment depending on soil chemistry.

The pH plays a major role in adsorption behaviour and mechanism. Generally, increasing solution pH decrease adsorption of PFAS onto adsorbent surface. In contrast, a review by (Du et al., 2014) reported that the increasing pH, increase PFAS adsorption when divalent cations present in the solution. This is attributed to the available basic sites on the surface of the adsorbent to bind divalent cations. As a result, increased PFCA adsorption to the adsorbent through cation bridge interactions. Apart from bridging interaction between PFAS molecule and adsorbent surface through divalent cations, it can also create bridge interactions between two PFAS molecules. The review discussed that  $Mg^{2+}$  could only form bridges between carboxyl groups, while  $Ca^{2+}$  is able to form bridges for both carboxyl and sulfonate groups due to its lower covalent nature. Furthermore, not only inorganic cations but also inorganic anions have relatively complicated effects on PFC adsorption. The review briefly discussed such effects including electrical doublelayer compression, surface-charge neutralization, salting-out effects and competitive adsorption in addition to divalent cation bridging effects.

#### 4.4. Electrostatic interactions in ionic exchange

Although there are many ionic exchange resins reported for PFAS, their exact chemical composition and mechanisms have rarely been reported as many are commercialised products with undisclosed chemical formulations. Fig. 3B is a graphical illustration by Gagliano

et al. (2020) that summarises the whole anionic exchange resin process. Anionic exchange (AEX) resins are essentially cross-linked polymeric materials having fixed positively charged exchange sites throughout its entire structure which are originally bonded with negatively charged mobile exchangeable ions. When PFAS passes through the column which contains these resins, first a diffusion process is initiated due to a concentration gradient between the solid phase (resins) and the liquid phase (influent stream with PFAS), the exchangeable ions diffuse out from the exchange resin while anionic PFAS diffuse into the exchange resins (Inglezakis, 2005). At this point, the electroneutrality is disrupted. If the ions carried no electric charges, these concentration differences would be levelled out solely by diffusion. But in this case, since these positively charged exchange sites have higher affinity towards PFAS than the mobile exchangeable ions, the negatively charged PFAS anions will be attracted towards the stationary exchange sites (positively charged) and when the mobile exchangeable anions are drawn to the liquid phase, which will leave the column with the liquid flow. Eventually, an ionic exchange equilibrium is established when the tendency of the ions to level out the concentration differences is balanced by the resins' electric field (Inglezakis, 2005).

GAC and AEX resins are both column-based treatment methods for PFAS. However, their working mechanism are entirely different. The main attractive force in AEX is ionic interaction, and there is also hydrophobic interaction between the crosslinked polymer and the  $R_f$  chain of PFAS (Fig. 6B), whereas in GAC, hydrophobic interaction is the dominant attractive force (Fig. 6A). Moreover, both GAC and AEX resins suffer from competition from organic matter due to their hydrophobicity. And often because of the negative charges on the surface of the organic matter bound on the adsorbent's surface, electrostatic repulsion with PFAS occurs.

# 4.4.1. Factors affecting ionic exchange

Pohl et al. (1997) listed a number of factors that are related to the effectiveness of the ionic exchange process, including (a) the charge on the solute ion, (b) the solvated size of the solution ion, (c) the polarizability of the solute ion, (d) the degree of cross-linking of the resin, (e) the ion-exchange capacity of the resin, (f) the functional group on the ion-exchanger, and (g) the nature and concentration of the eluent ion. The most important factor on the solid phase (resin) is the ionic-exchange capacity, which is simply its active charge (Inglezakis, 2005). As the pH of the liquid phase increases, the exchange capacity decreases. The presence of co-existing anions can also compete with PFAS binding. On the other hand, the level of cross-linking will also affect the hydrophobicity of the resin. Due to the knowledge gap in the chemical structure and other parameters in the AEX resins, the discussion of ionic exchange will not be continued further.

# 4.5. Hydrogen bond

Hydrogen bond does not form on the  $R_f$  tail of PFAS due to the low polarization of its s and p electrons, making fluorine on the  $R_f$  chain a poor acceptor of hydrogen bond (Kirsch, 2013). Nonetheless, oxygen atoms in the functional groups of PFCs are good acceptors in hydrogen bond (Gao and Chorover, 2012; Takayose et al., 2012). Therefore, hydrogen bond can be established on the functional head of the PFAS and shows good stability, as seen in the SAM study by (Omorodion et al., 2015). The effect of hydrogen bonding is also confirmed in several adsorbents on PFAS (Deng et al., 2012; Li et al., 2011; Zhang et al., 2009). However, in carbon nanotube (CNT) studies, it was often found that CNT with extra carboxyl and hydroxyl surface groups performs worse than pristine CNTs. It was postulated that these functional groups on the CNT can form hydrogen bond with the water molecules, which leads to competitive sorption thus lowering the effectiveness of PFAS attraction (Deng et al., 2012; Li et al., 2011; Zhang et al., 2009).



Fig. 6. A) The main interactions between PFAS, OM molecules and GAC; B) The main interactions between PFAS, OM molecules and AEX resin (Gagliano et al., 2020).

# 4.6. Comparison of various interactions

Despite not having any study that directly compares all binding strengths of the different intermolecular interactions with PFAS, it is important to understand how these binding forces can affect one another, as well as how they can individually affect the binding of PFAS to the affinity molecules. Having a stronger binding strength between PFAS and the affinity molecule implies less competition from foreign materials, which is beneficial to both sensing and capturing applications, and on a contrary, it will hinder desorption. This section will list out some discrete findings from literature comparing the strengths for an indirect comparison. Fig. 7 summarises the different interactions between PFAS and the affinity material surfaces.

When looking at electrostatic interaction versus the rest of the other interactions, one example is shown by the overpowering of electrostatic repulsion of negatively charged surfaces of adsorbents via hydrophobic interactions as reported by (Chen et al., 2012; Pan et al., 2009; Xiao et al., 2011; Yu et al., 2012). Electrostatic interaction has stronger attractive force than all other intermolecular forces in the context of PFAS which is shown in the Density-function theory (DFT) computational study by Omorodion et al. (2015). However, when the  $R_f$  is long enough, the high hydrophobicity generated by dispersion forces could overpower the electrostatic interactions. Moreover, the effectiveness of electrostatic attraction is also heavily affected by the effect of pH and the presence of other charged co-contaminants. Outside of electrostatic interactions, hydrogen bond alone should be the strongest. However, there are only limited sites for hydrogen bond to establish in a PFAS molecule.

The strength of F—F interactions has been a very debatable topic but there is not much information on it. From the London Theory, we know that it is almost solely governed by dipole-dipole interactions, which is not a strong intermolecular force. DFT shows that  $C-F\cdots F-C$  interaction is present in  $R_f$ -based material and is weakly energetically stabilizing on its own, especially when compared to the hydrogen bonds formed in the functional head (Omorodion et al., 2015). However, when measured collectively within the whole molecule, the overall binding can reach a high energy level. Therefore, when considering the strength of the interactions, it is also worth looking at the coverage of the interactions.

Moreover, Fang et al. (2018) synthesised a self-assembled monolayer (SAM) of fluoro-carbon chain and hydrocarbon chain and made a comparison of their interactions with different perfluoro surfactants (PFOA and PFOS) and with some hydrocarbon surfactants. It was found that the interaction between C-F\_SAM and R<sub>f</sub> chain domain is much stronger than that of the alkyl chain domain. This study shows that the C-F...F-C interaction is indeed stronger than hydrophobic interactions which involves C-F...C-H interactions, which is found in most carbon-based adsorbents.

In terms of how the structure of PFAS affects the overall attractive force to the affinity molecules, a longer the chain length of  $R_f$  yields higher hydrophobicity(Meegoda et al., 2020). It is shown in various cases that adsorbents with hydrophobicity outperform those with lower hydrophobicity (Deng et al., 2012; Senevirathna, 2010; Zhou et al., 2010). However, the case for increase in fluorophilicity with increase in  $R_f$  chain length has been debated as the model proposed by Huque et al. (2002) did not stand with others.

#### 5. Affinity molecules design considerations

In the context of this article, affinity molecule refers to a molecule that has affinity towards PFAS but requires to be incorporated into functional materials to carry out their functions. In this section, we will discuss some important points to consider in the design of such molecule on a molecular standpoint, as well as in a structural standpoint of the material.

#### 5.1. Molecular level design

The common goal in sensing and capturing is to maximise the selectivity between the functional molecule (sensor or adsorbent) and the target molecule (PFAS). In sensing, good selectivity means limited interference from other co-existing contaminants for less false signal and



Fig. 7. Various interactions between PFAS and the affinity material surfaces.

noise. In capturing of PFAS, the presence of highly selective adsorbents leads to low competition for active sites for effective adsorption of the target molecules.

A significant factor that determines the selectivity is how the functional molecule is prone to competition from co-existing contaminants in the working environment. In this area, fluorophilic interaction is outstanding. As explained earlier, fluorophilicity is at a high level whenever there is a single perfluorinated domain in a compound. Moreover, according to rule No. 1 in the model proposed by Kiss et al. (2001), a compound must have at least 60 wt% of fluorine to be considered fluorophilic. Rarely will there be any naturally occurring contaminant that can match the fluorophilicity of PFAS. Therefore, having a R<sub>f</sub> domain is a rational choice for being the foundation of an affinity molecule for PFAS due to the high expected selectivity in the natural environment. Moreover, in GenX adsorption, it has been shown that under the same condition, a polycationic gel with fluorinated backbone outperforms that of a hydrocarbon backbone (Choudhary and Bedrov, 2022). This implies the lower effectiveness of hydrophobicity versus fluorophilicity in terms of short chain PFAS attraction. Although adding R<sub>f</sub> moieties offers high potential in selectivity towards PFAS, the stability of the synthesised molecule raises concerns in environmental risks if not properly immobilised.

There are also a few points to note when employing electrostatic interactions in the design of functional molecules. First, as PFAS can exist in anionic, zwitterion or cationic form in different pH environment, it is very important to consider the working condition of the material. Moreover, in the design of the affinity molecules, a hard acid domain can be incorporated for better affinity towards PFCA and a soft acid domain can be used for PFSA.

Despite having computational models to predict fluorophilicity of different fluorinated compounds, it is extremely difficult to differentiate PFAS within the same class, especially when there is little difference in chain lengths. Selectivity can potentially be improved by incorporating multiple complementary interactions to the material, for example synthesizing affinity molecules with an R<sub>f</sub> tail that matches the fluorophilicity, and a cationic head that matches the anionic head of the target PFAS (Fig. 8). Moreover, introducing fluorination to AEX resin can also be another solution, this has been recently done by Xie et al. (2022) and it was found to be selective towards PFOA amongst a range of PFAS. However, regeneration buffer used contained 90 % acetonitrile (MeCN) and 10 % methanesulfonic acid (MSA) which are both extremely toxic. Moreover, in the design of adsorbents, having both flurophilic and cationic moieties in the structure can increase both the removal efficiency and adsorption capacity as electrostatic attraction is responsible for efficient capturing of the anionic PFAS molecules while the fluorinated segment in the adsorbent provides selective recognition of PFAS via fluorous attractions (Tan et al., 2022). Tan et al. (2022) has synthesised an adsorbent that contains a novel amphiphilic poly (ethylene glycol)-perfluoropolyether (PFPE) block polymer. This adsorbent has impressively removed 99 % of GenX (initial concentration



Fig. 8. Interactions of the surface of a typical affinity material and it's intermolecular interactions with PFAS.

100 ppb) with an estimated sorption capacity of 219 mg g<sup>-1</sup> in just 3 min. Another highlight of this hybrid material is that it also contains a magnetic moiety while allows rapid recovery of the adsorbents in a bulk solution. With magnetic properties, adsorbents do not have to be immobilised in surfaces, and when they are dispersed as fine particles in bulk solution, the surface area of contact between the adsorbents and PFAS is improved. Magnetic moieties have also been engineered into ionic exchange resin, covalent organic framework (COF), biochar, carbon nanotube composite, and natural clay and clay minerals for the same purpose of PFAS removal (Hassan et al., 2022; Mukhopadhyay et al., 2021; Park et al., 2020; Song et al., 2023; Wang et al., 2022).

# 5.2. Structural level design

The structure of the material that carries the affinity molecules is also very important as it relates to the access of the interactive sites of the affinity molecules by PFAS, affecting the interactions between PFAS and the affinity molecules. Having a good surface area to volume ratio is an important feature; this is proven by the increased adsorption of both PFOS and PFOA as switching from GAC to powder active carbon (PAC) (Yu et al., 2009). Moreover, the large particle size of adsorbents also causes steric hindrance, limiting the intermolecular interactions (Du et al., 2014). However, when the size of the particles becomes too small,



Fig. 9. Adsorption of PFAS micelles and PFAS molecules on a mesoporous structure.

containing and recovering the adsorbent may become an issue on a practical standpoint. This problem can be solved by incorporating a magnetic domain to the structure (Park et al., 2020; Tan et al., 2022). Many PFAS capturing materials have porous structures for the same reason: to increase surface area. As mentioned earlier, micelles of long chain PFAS can form at high concentrations, which can further aid adsorption. When the pore size is too small, micelles formation will be hindered, or the micelles formed will easily block the pores, limiting access to the material's inner structures. Du et al. (2014) suggested that mesoporous or macroporous structures are favourable for diffusion or adsorption of PFOS and PFOA (Fig. 9).

# 6. Desorption

Desorption of PFAS is a very important but rarely discussed topic. Due to PFAS's irreplaceable surface properties, the most ideal action is to recycle them after the end of use. The efficiency of regenerating solution depends on the properties of the affinity molecule and the interactions established between its functional groups and PFAS (Deng et al., 2010). There are two approaches in sorbent regeneration, namely chemical and thermal regeneration. Gagliano et al. (2020) published a review article that summarises the various adsorbent generation techniques. Some of the highlights of this review article will be reported here.

- 6.1. Chemical regeneration
- Anionic head in PFAS could be desorbed with salts while organic solvent is required to desorb the hydrophobic and fluorophilic R<sub>f</sub> chain (Deng et al., 2015; Du et al., 2015; Yu et al., 2008; Yu et al., 2009; Zaggia et al., 2016).
- Regeneration performed at high temperature (80 °C) and at higher ethanol concentration (Chen et al., 2017; Du et al., 2014; Du et al., 2015; Punyapalakul et al., 2013; Wang et al., 2014). However, the use of alcohol is not applicable to drinking water treatment.
- Presence of organic matter (OM) co-adsorbed on the materials may affect desorption efficiency and non-desorbed OM on the materials leads to decrease in efficiency after each regeneration cycle (Buttress et al., 2016; Deng et al., 2015; Du et al., 2015; Zaggia et al., 2016).

# 6.2. Thermal regeneration

- 600 °C in N<sub>2</sub> stream was effective in the complete regeneration of GAC, which is higher than the decomposition temperature of PFOS and PFDA (480 °C and 200 °C respectively); with adsorption of GAC remained constant after various regeneration cycles (Feng et al., 2016).
- Addition of calcium hydroxide can limit formation of short-chain fluorinated gas (Feng et al., 2016).
- Microwave (MW) irradiation can be an alternative to conventional thermal regeneration process for active carbon (AC) and has



**Fig. 10.** A Graphical description of a typical chemical adsorbent regeneration process (Gagliano et al., 2020). Fig. B schematic diagram of in situ MW plant for soil remediation, 1 = Power supply; 2 = MW generator; 3 = antenna; 4 = VOC extraction well; 5 = water/vapour phase separation system; 6 = water/vapour treatment plant (Falciglia et al., 2018). Fig. C schematic diagram of the antenna for MW propagation (Falciglia et al., 2018). Fig. D Schematic diagram of a pilot scale ex-situ continuous MW treatment system (Buttress et al., 2016).

advantages of quicker reaction time and selective heating (Falciglia et al., 2017; Falciglia et al., 2018). Regeneration occurs via interactions between delocalised  $\pi$ -electrons of AC and MW (Falciglia et al., 2017).

Chemical regeneration of PFAS saturated adsorbents requires the use of organic solvents, which are harmful and unsuitable for drinking water. Moreover, thermal regeneration at high temperature of exhausted activated carbon causes a drop in adsorption capacity due to changes in morphology. It also raises concerns in short chain fluorinated gases emission. Overall, both in-situ chemical or thermal regeneration of adsorbents are infeasible (Fig. 10). Lastly, the desorption of PFAS from perfluorinated materials have been rarely reported. Recently, Xie et al. (2022) reported a dual grafted fluorinated hydrocarbon amine weak anionic exchange resin polymer for PFOA adsorption. Adsorption capacity remained stable after 5 runs but highly toxic 90 % MeCN and 10 % MSA was applied as desorption buffer. Xie et al. (2022) also noted the similar Hildebrand values between MeCN and ethanol and ethanol can be used as an alternative. However, the experimental results were only shown in the MeCN/MSA buffer.

# 7. Conclusion and future perspective

In this review, the unique physiochemical properties of PFAS have been highlighted, which relate to the difficulty in tackling the PFAS contamination problem. A single PFAS molecule consists of a per or polyfluorinated hydrophobic tail and a hydrophilic functional head, which makes it amphiphilic and oleophobic. This unique configuration makes PFAS an excellent surfactant; and on the flip side, makes them not only persistent but also extremely pervasive in the environment. Due to the stability of the compounds and emission of toxic gases during degradation, the best remediation strategy is to first detect, then capture and recycle the end-of-life PFAS. Both sensing and capturing of PFAS rely on affinity-based physicochemical interactions, which include (1) fluorophilic interactions, (2) hydrophobic interactions, (3) electrostatic interactions, (4) ionic exchange and (5) hydrogen bond. Other than ionic exchange, all other interactions are weak intermolecular forces. Amongst the intermolecular forces, fluorophilic and hydrophobic interactions are both driven by entropy, meaning that materials with the similar cohesive energy level will be attracted to each other via weak intermolecular forces to form their own phase. These intermolecular forces are weak individually but can be a lot stronger when they exist collectively. Fluorophilic interactions have been identified as a main driving force in PFAS interactions, supported by computational studies.

The common goal in the design of sensors and adsorbent is to maximise selectivity. To target the R<sub>f</sub> tail, fluorophilic moiety has the advantage over hydrophobic moiety as highly fluorophillic substances are rarely found in the environment, therefore materials with fluorinated moieties have the advantage over hydrophobic moieties. It has also been proven that fluorocarbon moiety is more effective than hydrocarbon moiety in the adsorption for short chain PFAS. To target the anionic head, pair a soft base for a PFAS with a soft base head, and vice versa. AEX could also be a good option with stronger attraction towards PFAS than electrostatic-based materials, but regeneration of resins could be an issue. On the structural level of the affinity material, having a high surface area to volume ratio and a mesoporous structure are very important. Lastly, so far the commonly considered desorption methods, namely chemical and thermal methods are deemed infeasible for in-situ applications. In the design of affinity materials for PFAS, it has been relied heavily on experiences rather than solid formulation (Hasegawa, 2017). It should also be noted that to develop a commercially viable PFAS affinity material, the cost and life cycle analysis must be carefully considered to make it feasible and environmentally friendly.

Finally, one of the most glaring knowledge gaps in PFAS study is the lack of information on short chain PFAS like GenX and PFBS. As short chain PFAS become more prominent in the future, further research must be conducted to address the variations in the interactions and their adsorption mechanisms with affinity materials, which is vital to improving both sensing and adsorption materials.

# CRediT authorship contribution statement

Shui Cheung Edgar Leung: Conceptualization; Literature collection; Data analysis; Writing - original draft.

Dushanthi Wanninayake: Literature collection; Writing review & editing.

Dechao Chen: Writing - graphics; review & editing.

Nam-Trung Nguyen: Writing - review & editing.

Qin Li: Funding acquisition; Writing - original draft; Writing - review & editing.

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# Declaration of competing interest

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.

# Data availability

Data will be made available on request.

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